structures on the reactions of both solids have been suggested by an experimentalist[35]. These are currently under progress in our group and will be reported elsewhere soon.

Acknowledgement. This work was supported in part by Korea Science and Engineering Foundation (KOSEF-873-0303-002-2) and by the ETRI. Numerical calculations were performed on the CYBER 170-720D system at Kangweon National University.

References

1. S. C. Park, C. H. Cho, and C. H. Rhee, *Bull. Kor. Chem. Soc.*, **11**, 1 (1990).
2. R. A. Stansfield, K. Broomfield, and D. C. Clary, *Phys. Rev. B.* **39**, 7680 (1989).
3. S. C. Park, R. A. Stansfield, and D. C. Clary, *J. Phys. D.* **20**, 880 (1987).
4. S. C. Park and D. C. Clary, *J. Appl. Phys.*, **60**, 1183 (1986).
5. R. A. Gibbs, S. P. Holland, K. E. Foley, B. J. Garrison, and N. Winograd, *J. Chem. Phys.*, **76**, 684 (1982).
6. M. C. Chuang and J. W. Coburn, *J. Appl. Phys.*, **67**, 4372 (1990).
7. J. W. Coburn and H. F. Winters, *J. Appl. Phys.*, **50**, 3189 (1979).
8. V. M. Donnelly, D. L. Flamm, W. C. Dautremont-Smith, and D. J. Werder, *J. Appl. Phys.*, **55**, 242 (1984).
9. A. W. Kolfschoten, R. A. Haring, A. Haring, and A. E. de Vries, *J. Appl. Phys.*, **55**, 3813 (1984).
10. D. J. Oostra, A. Haring, R. P. van Ingen, and A. E. de Vries, *J. Appl. Phys.* **64**, 315 (1988).
11. S. M. Sze, *in VLSI Technology*, edited by S. M. Sze, pp.1-7 (M'Graw-Hill, New York, 1983).
12. C. J. Mogab, *in VLSI Technology*, edited by S. M. Sze, pp. 303-346 (M'Graw-Hill, New York, 1983).
13. B. N. Chapman, *Glow Discharge Process* (Wiley, New York, 1980).
14. J. W. Coburn and H. F. Winters, *Ann. Rev. Mater. Sci.*, **13**, 91 (1983).
15. K. E. Foley and B. J. Garrison, *J. Chem. Phys.*, **72**, 1018 (1980).
16. B. J. Garrison, N. Winograd, and D. E. Harrison, Jr., *Surf. Sci.*, **87**, 101 (1970).
17. M. H. Shaipro, P. K. Haff, T. A. Tombrello, D. E. Harrison, Jr., and R. P. Webb, *Rad. Effects* **80**, 234 (1985).
18. D. P. Jackson, *Can. J. Phys.*, **53**, 1513 (1975).
19. N. Winograd, B. J. Garrison, and D. E. Harrison, Jr., *Phys. Rev. Lett.*, **41**, 1120 (1978).
20. B. J. Garrison, N. Winograd, and D. E. Harrison, Jr., *Phys. Rev. B.* **18**, 6000 (1978).
21. S. P. Holland, B. J. Garrison, and N. Winograd, *Phys. Rev. Lett.*, **44**, 756 (1980).
22. D. W. Moon, N. Winograd, and B. J. Garrison, *Chem. Phys. Lett.*, **114**, 237 (1985).
23. P. Sigmund, *Phys. Rev.*, **184**, 383 (1969).
24. P. Sigmund, *in Topics in Applied Physics*, edited by R. Behrisch, Vol. 47, pp.10-71 (Springer-Verlag, Heidelberg, 1981).
25. W. Y. Lee and J. M. Eldridge, *J. Appl. Phys.*, **55**, 3813 (1984).
26. J. M. Bowman and S. C. Park, *J. Chem. Phys.*, **77**, 5441 (1982).
27. S. C. Park and J. M. Bowman, *J. Chem. Phys.*, **81**, 6277 (1984).
28. R. R. Lucchese and J. C. Tully, *Surf. Sci.*, **137**, 570 (1983).
29. J. W. Coburn, E.-A. Knabbe, and E. Kay, *J. Vac. Sci. Technol.*, **20**, 480 (1982).
30. S. Tachi, K. Miyake, and T. Tokuyama, *Jap. J. Appl. Phys.*, **20**, L411 (1981).
31. M. W. Thompson, *Phil. Mag.*, **18**, 377 (1968).
32. M. W. Thompson, *Phys. Rep.*, **80**, 336 (1981).
33. B. M. Farmery and M. W. Thompson, *Phil. Mag.*, **18**, 415 (1968).
34. D. E. Harrison, Jr., W. L. Moore, Jr., and H. T. Holcombe, *Rad. Effects* **17**, 167 (1973).
35. A. E. De Vries, (Private communications).

A Shapiro Reaction with N,N-Diethylaminosulfonylhydrazones

Jahyo Kang*, Ji Han Kim, and Gil-Seong Jang

Department of Chemistry, Sogang University, Seoul 121-742, Korea

Received December 23, 1991

A modified Shapiro reaction was developed using N,N-diethylaminosulfonylhydrazones.

Introduction

The formation of alkenes from the reaction of arylsulfonylhydrazones with strong bases such as alkyllithiums (Shapiro reaction), has proved to be a useful reaction and has been subject of numerous studies[1,2]. Following the initial deprotonation at the amide nitrogen of arylsulfonylhydrazones, the second proton abstraction occurs at the α-carbon *syn* to the sulfonylamide group[3,4], which has been attributed to the chelation effect[5,6] and a 6π-electron non-bonded through-space interaction[7]. Since a strong steric bias exists in the stereochemistry of tosylhydrazones prepared from unsymmetrical

Table 1. Preparation of Diethylaminosulfonylhydrazones in Refluxing Solvents

Carbonyl Cpd	Rxn solvent	Recrystaln solvent	Hydrazones	Yield (%)	mp. (℃)
Cyclohexanone	Ether	Cyclohexane	**3**	94	38-40
Acetone	MC	20% ether/*n*-pentane	**4**	87	48-50
2-Butanone	MC	*n*-Pentane	**5**	88	33-35
2-Methyl-4-pentanone	THF	Pet. ether	**6**	72	53-55
Acetophenone	MC	Ethanol	**7**	85	100-102
Propanal	MC		**8**	94	Oily
Hexanal	MC		**9**	89	Oily
Crotonaldehyde	MC		**10**	81	Oily

Table 2. NMR Spectral Data of Diethylaminosulfonylhydrazones

Entry	Hydrazones	*syn/anti* Ratio (α-Me)	^{1}H-NMR absorption (δ)	
		(E/Z Isomer ratio)	*syn* α-Me	*anti* α-Me
1	Acetone **4**		1.73	1.88
2	2-Butanone **5**	78/22	1.70	1.85
3	4-Methyl-2-pentanone **6**	83/17	1.80	1.85
4	Acetophenone **7**	100/0	2.20	

ketones, the regioselective formation of hydrazone dianion (and thus of the resulting alkene) toward the less hindered side of the iminocarbon has been found to be general[8]. Also, it is possible to extend the scope of the reaction further by allowing the vinyllithium intermediate to be trapped by added electrophiles under mild conditions. In this reaction, excess base beyond the 2 equiv is needed for stoichiometric dianion formation because of metalation[9] at the ortho position of the aryl group. Otherwise, the vinyllithium species metalates the remaining dianion, giving directly alkenes without further reaction. Thus, excess *n*-butyllithium base (typically, 3.5-4.5 equiv) must therefore be used with tosylhydrazones, and this in turn necessitates the use of excess electrophile and the separation of side products which result from attack of the *n*-butyllithium on the electrophile.

These problems can be overcome by the use of 2,4,6-triisopropylbenzenesulfonylhydrazones (trisylhydrazones)[9]. And there is another important advantage with this bulky hydrazone in that dianion decomposition to vinyllithium is accelerated relative to the tosylhydrazones. The latter requires 1-8 h at room temperature, whereas the trisylhydrazone dianion forms the corresponding vinyllithium species rapidly at 0℃[10]. However, the starting material, trisylhydrazine itself[10a] and also its hydrazone derivatives[10b] are thermally unstable, which limits the use of this valuable methodology.

This study is concerned with a modification of the valuable and widely used Shapiro reaction. In order to avoid the limitations mentioned above, 1) the hydrazine and also the resulting hydrazones to be used in this study should be readily available, 2) the hydrazones should not be metallated at the sulfonyl residue, and 3) they should undergo efficient Shapiro reactions under a variety of circumstances. One such possibility would be the use of dialkylaminosulfonylhydrazones instead of the more traditional arylsulfonylhydrazone derivatives. The corresponding hydrazones may serve such as precursors of diazo compounds and carbenes[11,12], activating groups for regiospecific alkylation[13] and a tool for carbonyl group modification[14], *etc.* Thus, efforts were made to examine the possibility of utilizing the aminosulfonylhydrazone in the Shapiro technology, which is the subject of the present paper. Future development will feature the obvious extension to generation of alkenyllithium.

Results and Discussion

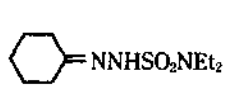
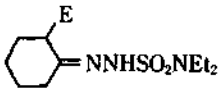
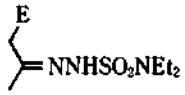
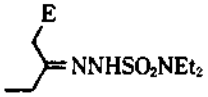
The reaction of N,N-diethylaminosulfonyl chloride **1**, prepared in 73% yield by careful addition of diethylamine to a large excess of sulfuryl chloride followed by gentle refluxing for 24 h in neat condition[14], with hydrazine in an aqueous solvent gave the N,N-diethylaminosulfonylhydrazine **2** as a white crystals in a good yield (88%)[5]. This compound was stable for extended period.

$$\underset{\mathbf{1}}{Et_2NSO_2Cl} + NH_2NH_2 \xrightarrow[H_2O]{\text{ovenight}} \underset{\mathbf{2}}{Et_2NSO_2NHNH_2}$$

For preparation of the N,N-diethylaminosulfonylhydrazones from the hydrazine **2** and carbonyl compounds, an equimolar mixture of diethylaminosulfonylhydrazine and an aldehyde or a ketone was allowed to react in an organic solvent. After refluxing the reaction mixture for about an hour, the solvent was evaporated to yield a solid ketone hydrazones, which were recrystallized for purification. For aldehyde hydrazones, the reaction was carried out at 23℃, and the product was chromatographically and spectroscopically homogeneous oil and thus could not be induced to crystallize. As can be seen in Table 1, the yields of hydrazones are excellent, including aldehyde hydrazones.

The NMR spectra of these unsymmetrical diethylaminosulfonylhydrazones ($CDCl_3$) showed the methyl signals separated by *ca.* 0.15 ppm. The ratio of these *syn/anti* α-methyl signals, which is indicative of the ratio of the E/Z isomers,

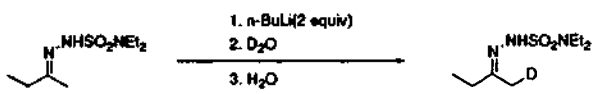
Table 3. α-Substituted Diethylaminosulfonylhydrazones by Alkylation

Hydrazones	Electrophile (E^+)	Product		Yield (%)	Mp.(℃)
					
3	MeCOMe	E = $Me_2C(OH)$-,	**12**	73	128-130
	PhCHO	E = PhCH(OH)-		78	
		(**13**/**14** = 50 : 50)[a],			
			13[b]		107-109
			14[c]		117-120
	$PhCH_2CHO$	E = $PhCH_2CH(OH)$-		82	
		(**15**/**16** = 51 : 49)[a]			
			15[d]		118-120
			16[d]		104-107
	$PhCH_2Br$	E = $PhCH_2$-,	**17**	72	89-92
	n-BuBr	E = *n*-Bu-,	**18**	63	
	MeI	E = Me-,	**19**	55	79-82
					
4	MeCOMe	E = $Me_2C(OH)$-,	**20**	80	115-118
	PhCHO	E = PhCH(OH)	**21**	84	104-106
	$PhCH_2Br$	E = $PhCH_2$-,	**22**	78	64-67
					
5	MeCOMe	E = $Me_2C(OH)$-,	**23**	72	105-108
	PhCHO	E = PhCH(OH)-,	**24**	65	
	$PhCH_2Br$	E = $PhCH_2$-,	**25**	71	
	MeI	E = Me-,	**26**	48	

[a]The ratio was determined by products separated by column chromatography. [b]E product. [c]Z isomer. [d]The stereochemical identity of these products has not been clearly established. See text.

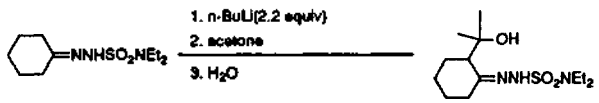
are summarized in Table 2.

The assignment of stereochemistry and *syn* regiospecificity of dianion formation in diethylaminosulfonylhydrazones could be confirmed by deuteration of an E/Z mixture (78 : 22) of 2-butanone diethylaminosulfonylhydrazone **5**. Conversion to the dianion (2.0 equiv of *n*-butyllithium, THF, −78℃) followed by D_2O quenching provided the corresponding deuterated diethylaminosulfonylhydrazone **11** in 79% yield.



5 **11**

Having established the preparative method for the hydrazones, it was set out to develop the alkylation of the hydrazones. For instance, the diethylaminosulfonylhydrazone of cyclohexanone **3** in THF was treated with *n*-butyllithium (2.2 equiv) at −78℃ to get the corresponding dianion, which could be trapped with acetone to give the hydrazone of 2-(1-hydroxy-1-methylethyl)cyclohexanone **12** after acidic quench.

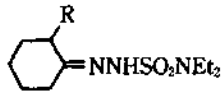
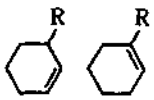
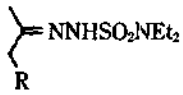
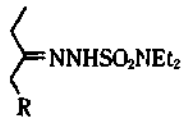


3 **12 (73%)**

Likewise, various diethylaminosulfonylhydrazone dianions formed under the similar conditions afforded α-substituted diethylaminosulfonylhydrazones in good yields when trapped with electrophiles such as ketones, aldehydes and alkyl halides. It is to be noted, however, that aldehyde hydrazones could not be alkylated cleanly to any extent for some unknown reasons. The results are summarized in the Table 3.

Especially, the reaction of cyclohexanone diethylaminosulfonylhydrazone with benzaldehyde and phenylacetaldehyde produced an approximately 1 : 1 mixture of two chromatographically separable (silica gel; 25% methylene chloride, 25% ether in *n*-hexane) isomers in each case- **13** and **14**, and **15** and **16**, respectively. Spectral data of these compounds were very similar pairwise, indicating that these may be the E/Z isomers and/or diastereomeric pair. However, NMR spectral data (NOESY) of **13** and **14** clearly showed that

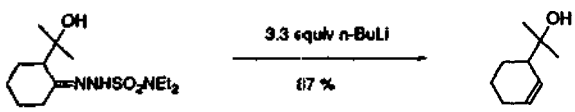
Table 4. Decomposition of Substituted N,N-Diethylaminosulfonylhydrazones

Hydrazones		*n*-BuLi (equiv)	Temp. (℃)	Time (h)	Product	Yield (%)
						
R=MeC(OH)-	(12)	3.3	rt	20	**27**	87
PhCH(OH)-	(13)[a]	3.3	20	4	**28**	80
	(14)[b]	5.0	rt	24	**28** and **29**	75
$PhCH_2CH(OH)$-	(15)[c]	3.3	20	3.5	**30**	81
	(16)[c]	5.0	rt	21	**30** and **31**	86
$PhCH_2$-	(17)	3.5	rt	4	**32**	81
						
$R=Me_2C(OH)$-	(20)	5.5	20	3	**33**	70[d]
PhCH(OH)-	(21)	5.5	20	3	**34**	64
$PhCH_2$	(22)	2.5	20	3	Complex mixture	
						
$R=Me_2C(OH)$-	(23)	5.5	rt	23	**35**	44
PhCH(OH)-	(24)	5.5	25	1	**36**	81
$PhCH_2$	(25)	2.5	20	3	Complex mixture	

[a]E product. [b]Z isomer. [c]The stereochemistry uncertain. See text. [d]Crude yield.

the more polar compound **13** was an E isomer, while it was not possible at all to ascertain the relative stereochemistry of the two chiral centers. On the other hand, the spectral assignment on the phenylacetaldehyde adducts, **15** and **16**, could not be made with certainty.

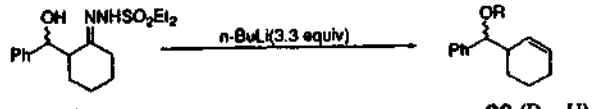
Treatment of these α-substituted diethylaminosulfonylhydrazones with excess *n*-butyllithium (3-5 equiv) followed by warming up to room temperature to induce decomposition lead to the corresponding alkenes in good yields. For instance, diethylaminosulfonylhydrazone of 2-(1-hydroxy-1-methylethyl)cylohexanone **12** could be decomposed with excess *n*-butyllithium at room temperature to produce 3-(1-hydroxy-1-methylethyl)cylohexene **27** in 87% yield.



12 **27**

Various attempts to reduce the amount of *n*-butyllithium to the theoretical quantity lead to the decrease in yields of the products. Also, it is to be noted that the metalation at the ethyl groups of the diethylaminosulfonyl moiety did not occur even with such a large amount of *n*-butyllithium, as judged by D_2O quenching experiment. Thus, it is not clear the exact role of the excess amount of *n*-butyllithium. The optimal reaction temperature was 0℃ initially, which was raised slowly to room temperature. The yields of this step were respectable except for the cases of acyclic benzylated hydrazones **22** and **25**. The results are summarized in Table 4.

In order to study the isomerization of α-substituted diethylaminosulfonylhydrazones and allylic substituted alkene, it was necessary to analyze the reactions in detail. *syn*-Elimination of E-2-(1-hydroxybenzyl)cyclohexanone diethylaminosulfonylhydrazone **13**, lead to fast conversion (requiring only 4 h at 23℃; *vide infra*), cleanly to 3-(1-hydroxybenzyl)-cyclohexene **28** in 80% yield at room temperature, which was then acetylated to the corresponding acetate **37** in 79% yield. The ^1H NMR spectra of cyclohexenes, **28** and **37**, showed the vinyl signal as broad singlets at 5.86 and 5.76 ppm, each representing 2 protons. The acetoxy signal of the acetate **37** was a sharp singlet at 2.09 ppm, even though the compound was considered to be a mixture of diastereomers.

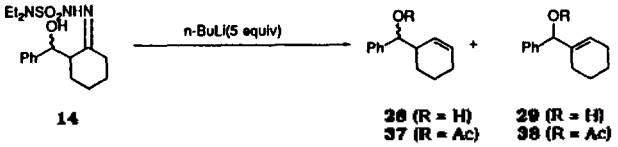


13

28 (R = H)
37 (R = Ac)

But the same kind of decomposition of the Z-hydrazone **14** was slow (requiring 24 h at 23℃), leading to a non-separable mixture of homoallylic alcohol **28** and allylic alcohol **29** in 75% yield. Subsequent acetylation of the mixture gave a mixture of homoallylic acetate **37** and allylic acetate **38**

in 71% yield. The NMR spectrum of the allylic alcohol **29**, separated by HPLC, showed a singlet at 5.10 ppm (sp^3 methine) and a broad singlet at 5.72 ppm (sp^2 methine). The acetoxy signal of the acetate **38** was separated as two singlets at 2.05 and 2.09 ppm, presumably due to the nearby asymmetry in the molecule.



14 **28** (R = H) **29** (R = H)
37 (R = Ac) **38** (R = Ac)

Thus, the aforementioned spectral assignment on the stereochemistry of the hydrazone **13** as an E isomer (that is, the sulfonylamide functional group is *anti* to the hydroxybenzyl group.), and that of **14** being a Z isomer was confirmed by kinetic evidence. The deprotonation at the sterically less hindered carbon in (E)-2-(1-hydroxybenzyl)cyclohexanone diethylaminosulfonylhydrazone **13** should be aided by internal coordination of alkyllithium to hydrazine nitrogen. But deprotonation of the hydrazone **14** from the side of hydrazone nitrogen must be more difficult since it has to occur at the sterically congested methine carbon and the resulting dianion should be destabilized by electronic repulsion between the two adjacent anionic centers. Since the negatively charged oxygen atom of the compound **14** would decrease the acidity of the *syn* α-proton by the inductive effect, the alternative *anti* deprotonation could occur to some extent, eventually producing a mixture of compounds **28** and **29**.

The same kinetic trend was observed in the cases of the phenylacetaldehyde adducts, **15** and **16**. In view of these facts, although nothing could be ascertained about the stereochemistry by spectral analysis, it is tempting to say that slow-moving component, **15**, was an E product, while the less polar **16** was a Z adduct. Also, it might be appropriate to mention that various attempts to isomerize the isomeric pair of the hydrazones (**13-14** and **15-16**) under a number of conditions have failed so far.

Experimental

General. All reactions involving organometallic reagents were carried out under an inert atomosphere of nitrogen or argon. Tetrahydrofuran (THF) and dietyl ether were freshly distilled from sodium benzophenone ketyl, and methylene chloride, DMF, DMSO and HMPA from calcium hydride prior to use and solvents and liquid reagents were transferred using hypodermic syringes. Alkyllithium solution (Aldrich) were assayed for active alkyl by titration with 2-butanol in THF using 1,10-phenanthroline as indicator. All other reagents and solvents were reagent grade. Small -and medium- scale purifications (20 mg-2 g) were performed by radial chromatographyl by using a Harrison Research Chromatotron on plates of 1-, 2-, or 4-mm thickness made with Merck silica 60 PF_{254} containing gypsium. Flash chromatography was performed on a Tokyo Rikagikai EF-10 with Merck 230-400 mesh silica gel and HPLC on a Waters analytical HPLC system (analytical) and Waters DeltaPrep 4000 (preparative). Melting points were determined on a Thomas-Hoover capillary melting point apparatus. All boiling and melting points are uncorrected.

^1H NMR spectra were obtained on a Varian EM-360A (60 MHz), a Hitach R-24B spectrometer (60 MHz) or a Varian Gemini 300 (300 MHz) instruments and ^{13}C spectra on the Varian Gemini 300 (75 MHz) spectrometer. NMR spectra were recorded in ppm (δ) relative to Me_4Si (δ=0.00) as an internal standard unless stated otherwise and are reported as follows: chemical shift, multiplicity (br=broad, s=singlet, d=doublet, t=triplet, q=quartet), coupling constant and integration. Other internal standards (if specified in the text) used were either CH_2Cl_2 (δ 5.35) or $CHCl_3$ (δ 7.25). Infrared spectra were obtained on a Shimadzu IR-400, a Perkin-Elmer 1430 Infrared Spectrophotometer (IR-440) or Mattson Galaxy 2000 spectrophotometers. Mass spectra were taken on a VG Trio 2000 (low resolution) spectrometers with an electron beam energy of 70 eV for EI spectra and methane gas for CI spectra and elemental analysis by Carlo Erba EA 1108 elemental analyzer.

Diethylaminosulfonyl chloride 1[14]. To sulfuryl chloride (36 m*l*, 0.45 mol) was added dropwise diethylamine (16.7 m*l*, 0.15 mol) at 0-5℃. The mixture was warmed to rt, and refluxed for 24 h. After cooling to rt, 100 m*l* of ice water and 100 m*l* of diethyl ether were added. The ethereal solution was separated, washed with brine, dried over Na_2SO_4, filtered, evaporated to give 22.8 g of crude oil. The fractional distillation produced the corresponding product (19.6 g, 73%). bp 65-66℃/5 mmHg (lit[14]. 69℃/5 mmHg); NMR ($CDCl_3$) δ 1.35 (t, J=7.2 Hz, 6H), 3.25 (q, J=7.2 Hz, 4H).

Diethylaminosulfonylhydrazine 2. To a suspension of 80% hydrazine solution (37.3 g, 0.60 mol) in 70 m*l* of THF was dropwise added diethylaminosulfonyl chloride **1** (48.2 g, 0.27 mol) for 2h at rt. After the reaction mixture stirred overnight at rt, THF layer was separated and the aqueous layer was extracted with 150 m*l* of methylene chloride. The combined organic layer was dried over $MgSO_4$, filtered, and evaporated to produce 42 g of crude oil. The oil was solidified with pet. ether to give the corresponding product (39.8 g, 88%). mp. 38-40℃; TLC R_f 0.28 (Ether); NMR ($CDCl_3$) δ 1.20 (t, J=7.2 Hz, 6H), 3.20 (q, J=7.2 Hz, 4H), 4.20 (br. s, 3H); IR (KBr) 3360, 3280 cm^{-1}. Anal. Calcd. for $C_4H_{13}N_3O_2S$: C, 28.73; H, 7.84; N, 25.13. Found: C, 28.00; H, 8.10; N, 24.17.

Cyclohexanone Diethylaminosulfonylhydrazone 3. Cyclohexanone (28.6 g, 0.29 mol) was dropwise added to a solution of diethylaminosulfonylhydrazine **2** (39.8 g, 0.24 mol) in 110 m*l* of the ether for 10 min at rt. The mixture was refluxed for 3 h and evaporated to give 62 g of white solid. The solid was recrystallized to give the hydrazone **3** (55.0 g, 94%). mp. 38-40℃; TLC R_f 0.50 (50% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.20 (t, J=7.2 Hz, 6H), 1.60 (br. s, 6H), 2.20 (br. s, 4H), 3.20 (q, J=7.2 Hz, 4H), 7.70 (br. s, 1H); IR (KBr) 3220 cm^{-1}. Anal. Calcd. for $C_{10}H_{21}N_3O_2S$: C, 40.56; H, 8.56; N, 16.99. Found: C, 40.78; H, 8.99; N, 16.56.

In a similar manner, the following compounds were prepared.

Acetone Diethylaminosulfonylhydrazone 4. After recrystallization with 20% ether/*n*-pentane, 87% yield. mp. 48-50℃; TLC R_f 0.20 (50% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.20 (t, J=7.2 Hz, 6H), 1.75 (s, 3H), 1.88 (s, 3H), 3.20 (q, J=7.2 Hz, 4H), 7.20 (br. s, 1H); IR (KBr) 3220 cm^{-1}.

2-Butanone Diethylaminosulfonylhydrazone 5. Af-

ter recrystallization with *n*-pentane, 88% yield. mp. 33-5℃; TLC R_f 0.23 (50% ether in *n*-hexane): NMR ($CDCl_3$) δ 1.08 (q, J=7.2 Hz, 9H), 1.70 (s, 2.35H), 1.85 (s, 0.65H), 1.18 (q, J=7.2 Hz, 2H), 3.23 (q, J=7.2 Hz, 4H), 7.14 (br. s, 1H); IR (KBr) 3240 cm^{-1}.

Diethylaminosulfonylhydrazone of 4-Methyl-2-pentanone 6. After recrystallization with pet. ether, 72% yield. mp. 53-5℃; TLC R_f 0.43 (25% MC, 25% ether in *n*-hexane); NMR ($CDCl_3$) δ 0.90 (d, J=6.6 Hz, 7H), 1.20 (t, J=7.2 Hz, 6H), 1.78 (s, 2.85H), 1.94 (s, 0.15H), 2.10 (br. s, 2H), 3.36 (q, J=7.2 Hz, 4H), 7.44 (br. s, 1H); IR (neat) 3230 cm^{-1}.

Acetophenone Diethylaminosulfonylhydrazone 7. After recrystallization with ethanol, 85% yield. mp. 100-2℃; TLC R_f 0.29 (25% MC, 25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.25 (t, J=7.2 Hz, 6H), 2.21 (s, 3H), 3.46 (q, J=7.2 Hz, 4H), 7.40 (m, 3H), 7.76 (m, 3H); IR (KBr) 3200 cm^{-1}.

Propionaldehyde Diethylaminosulfonylhydrazone 8. After column chromatography, 94% yield TLC R_f 0.25 (50% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.10 (q, J=7.2 Hz, 9H), 2.12 (m, 2H), 3.24 (q, J=7.2 Hz, 4H), 6.95 (t, J=4.8 Hz, 1H), 7.30 (br. s, 1H); IR (neat) 3560, 3220 cm^{-1}.

Hexanal Diethylaminosulfonylhydrazone, 9. Yield 89%; TLC R_f 0.28 (50% ether in *n*-hexane); NMR ($CDCl_3$) δ 0.80-1.45 (m, 15H), 2.10 (t, J=5.4 Hz, 2H), 4.20 (q, J=7.2 Hz, 4H), 6.90 (t, J=4.8 Hz, 1H), 7.40 (br. s, 1H); IR (neat) 3560, 3220 cm^{-1}. Anal. Calcd. for $C_{10}H_{23}N_3O_2S$: C, 48.16; H, 9.30; N, 16.85. Found: C, 48.43; H, 9.15; N, 15.84.

Crotonaldehyde Diethylaminosulfonylhydrazone, 10. Yield 81%; TLC R_f 0.25 (60% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.15 (t, J=7.2 Hz, 6H), 1.80 (d, J=4.8 Hz, 3H), 3.30 (q, J=7.2 Hz, 4H), 5.90 (d, J=4.8 Hz, 2H), 7.10 (m, 1H), 7.80 (br. s, 1H); IR (neat) 3550, 3210 cm^{-1}.

Deuterium Incorporation in 2-Butanone Diethylaminosulfonylhydrazone 5. To a solution of hydrazone **5** (0.14 g, 0.63 mmol) in 5 m*l* of ether was dropwise added 1.20 M of *n*-butyllithium (2.2 m*l*, 2.64 mmol) at −78℃. The mixture was stirred for 1 h at the temperature, and then warmed to −15℃. The reaction mixture was quenched with 0.50 m*l* of D_2O, added 1.0 m*l* of DCl at 0℃. The ethereal layer was separated, the aqueous layer was extracted with ether. The organic layer was washed with 2 m*l* of brine, dried over $MgSO_4$, filtered, and evaporated to obtain the deuterium-incorporated product. The product was recrystallized in *n*-pentane to obtain the pure product (0.11 g, 79%). TLC R_f 0.23 (50% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.15 (q, J=7.2 Hz, 9H), 1.80 (m, 2H), 2.28 (q, J=7.2 Hz, 2H), 3.40 (q, J=7.2 Hz, 4H), 7.40 (br. s, 1H).

2-(1-Hydroxy-1-methylethyl)cyclohexanone Diethylaminosulfonylhydrazone, 12. To a solution of cyclohexanone diethylminosulfonylhydrazone **3** (0.62 g, 2.5 mmol) in 4 m*l* of THF was added dropwise 1.20 M of *n*-butyllithium (4.6 m*l*, 5.5 mmol) at −78℃, and the mixture was stirred for 1 h at −78℃, after which acetone (0.18 m*l*, 2.5 mmol) was added. The resulting mixture was stirred for 1 h, and warmed to 0℃. Subsequently, 4 m*l* of 1 N HCl was added and THF layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with 5 m*l* of brine, dried over MgSO4, and evaporated to produce crude **12**. Crystallization with pentane gave 0.56 g (73%) of the pure product **12**. mp. 128-130℃; TLC R_f 0.16 (60% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.11 (t, J=7.2 Hz, 6H), 1.26 (d, J=3.0 Hz, 6H), 1.55 (br. s, 6H), 2.10-2.80 (m, 4H), 3.15 (q, J=7.2 Hz, 4H), 9.30 (br. s, 1H); IR (neat) 3460, 3100 cm^{-1}. Anal. Calcd for $C_{13}H_{27}N_3O_3S$: C, 51.12; H, 8.91; N, 13.76. Found: C, 51.61; H, 9.15; N, 13.52.

Similarly, the following products were prepared.

2-(1-Hydroxybenzyl)cyclohexanone Diethylaminosulfonylhydrazones 13 and 14. Recrystallization with diisopropyl ether gave 1.37 g (78%) of a 1 : 1 mixture of **13** and **14**, which was separated by column chromatography. **E Isomer (13)**: mp. 117-119℃; TLC R_f 0.12 (25% MC, 25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.18 (t, J=7.2 Hz, 6H), 1.55 (br. s, 7H), 1.72 (br. s, 2H), 2.45 (m, 2H), 3.30 (q, J=7.2 Hz, 4H), 5.20 (d, J=2.4 Hz, 1H), 7.05 (s, 5H), 7.35 (s, 1H); IR (KBr) 3500, 3240 cm^{-1}. **Z Isomer (14)**: mp. 107-109℃; TLC R_f 0.25 (25% MC, 25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.18 (t, J=7.2 Hz, 6H), 1.43 (br. s, 6H), 2.46 (br. s, 2H), 3.40 (q, J=7.2 Hz, 5H), 4.90 (d, J=10.8 Hz, 1H), 7.40 (s, 5H); IR (KBr) 3440, 3195 cm^{-1}. Anal. Calcd for $C_{17}H_{27}N_3O_3S$: C, 57.76; H, 7.70; N, 11.89. Found: C, 57.40; H, 8.04; N, 12.24.

2-(1-Hydroxy-2-phenylethyl)cyclohexanone Diethylaminosulfonylhydrazone 15 and 16. Yield 82% (for **15** and **16**): **Z Isomer 15**: mp. 118-120℃; TLC R_f 0.19 (25% MC, 25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.25 (t, J=7.2 Hz, 6H), 1.62 (m, 6H), 1.96 (br. s, 2H), 2.40 (m, 2H), 3.10 (m, 1H), 3.30 (q, J=7.2 Hz, 4H), 4.05 (m, 1H), 7.30 (s, 5H), 8.10 (br. s, 1H); IR (KBr) 3410, 3260 cm^{-1}: **Z Isomer 16**: mp. 104-107℃; TLC R_f 0.13 (25% MC, 25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.20 (t, J=7.2 Hz, 6H), 1.10-2.60 (m, 9H), 2.8 (m, 2H), 3.40 (q, J=7.2 Hz, 4H), 4.00 (m, 1H), 7.30 (s, 5H), 8.54 (s, 1H).

2-Benzylcyclohexanone Diethylaminosulfonylhydrazone (17). Yield 72%; mp. 89-92℃; TLC R_f 0.18 (50% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.15 (m, 6H), 1.65 (m, 6H), 2.45 (m, 4H), 3.10 (m, 5H), 6.90 (d, 5H), 7.20 (m, 1H); IR (KBr) 3230 cm^{-1}.

2-*n*-Butylcyclohexanone Diethylaminosulfonylhydrazone (18). Yield 63%; TLC R_f 0.57 (50% ether in *n*-hexane); NMR ($CDCl_3$) δ 0.80-1.40 (m, 15H), 1.60 (m, 6H), 2.20 (m, 3H), 3.22 (q, J=7.2 Hz, 4H), 7.30 (br. s, 1H); IR (KBr) 3180 cm^{-1}.

2-Methylcyclohexanone Diethylaminosulfonylhydrazone (19). Yield 55%; mp. 79-82℃; TLC R_f 0.40 (50% ether in *n*-hexane); NMR ($CDCl_3$) d 1.00 (d, J=6.0 Hz, 3H), 1.15 (t, J=7.2 Hz, 6H), 1.65 (m, 6H), 2.20 (m, 3H), 3.24 (q, J=7.2 Hz, 4H), 7.20 (br. s, 1H); IR (KBr) 3230 cm^{-1}.

Diethylaminosulfonylhydrazone of 4-Hydroxy-4-methyl-2-pentanone 20. After recrystallization with diisopropyl ether, 80% yield of white crystals. mp. 115-118℃; TLC R_f 0.14 (60% ether/*n*-hexane); NMR ($CDCl_3$) δ 1.15 (t, J=7.2 Hz, 6H), 1.30 (s, 6H), 1.94 (s, 3H), 2.30 (s, 2H), 2.80 (br. s, 1H), 3.20 (q, J=7.2 Hz, 4H), 9.40 (br. s, 1H); IR (KBr) 3460, 3090 cm^{-1}.

4-Hydroxy-4-phenyl-2-butanone Diethylaminosulfonylhydrazone (21). Yield 84%; mp. 104-106℃; TLC R_f 0.17 (50% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.13 (t, J=7.2 Hz, 6H), 2.23 (s, 3H), 2.50 (m, 2H), 3.16 (q, J=7.2 Hz, 4H), 4.85 (m, 1H), 7.01 (s, 5H), 8.66 (s, 1H); IR (KBr) 3460, 3220 cm^{-1}.

4-Phenyl-2-butanone Diethylaminosulfonylhydrazone (22). Yield 78%; mp. 64-67℃; TLC R_f 0.51 (33% ethyl ace-

tate in *n*-hexane); NMR ($CDCl_3$) δ 1.15 (t, J=7.2 Hz, 6H), 1.80 (s, 3H), 2.70 (m, 2H), 2.90 (s, 2H), 3.30 (q, J=7.2 Hz, 4H), 7.30 (s, 6H); IR (neat) 3220 cm^{-1}.

Diethylaminosulfonylhydrazone of 5-Hydroxy-5-methyl-3-hexanone 23. 72% yield. mp. 105-108℃; TLC R_f 0.20 (60% ether/*n*-hexane); NMR ($CDCl_3$) δ 1.15 (q, J=7.2 Hz, 9H), 1.30 (s, 6H), 2.30 (q, J=7.2 Hz, 2H), 2.40 (s, 2H), 2.80 (br. s, 1H), 3.30 (q, J=7.2 Hz, 4H), 9.60 (br. s, 1H); IR (KBr) 3480, 3120 cm^{-1}.

1-Hydroxy-1-phenyl-3-pentanone Diethylaminosulfonylhydrazone (24). Yield 65%; TLC R_f 0.41 (30% ethyl acetate in *n*-hexane); NMR ($CDCl_3$) δ 1.20 (t, J=7.2 Hz, 9H), 1.15-2.38 (m, 3H), 2.43-2.95 (m, 2H), 3.38 (q, J=7.2 Hz, 4H), 5.05 (m, 1H), 5.40 (s, 5H); IR (KBr) 3480, 3230 cm^{-1}.

1-Phenyl-3-pentanone Diethylaminosulfonylhydrazone (25). Yield 71%; TLC R_f 0.40 (50% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.16 (t, J=7.2 Hz, 1.92-2.31 (m, 2H), 2.35-2.95 (m, 4H), 3.35 (q, J=7.2 Hz, 4H), 7.28 (s, 5H), 7.85 (br. s, 1H); IR (neat) 3140 cm^{-1}.

3-Pentanone Diethylaminosulfonylhydrazone (26). Yield 48%; TLC R_f 0.45 (50% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.15 (q, J=7.2 Hz, 12H), 2.15 (m, 4H), 3.25 (q, J=7.2 Hz, 4H), 7.00 (br. s, 1H); IR (KBr) 3210 cm^{-1}.

3-(1-Hydroxy-1-methylethyl)cyclohexene (27). To a solution of E-diethylaminosulfonylhydrazone of 2-(1-hydroxy-1-methylethyl)cyclohexanone **12** (0.15 g, 0.50 mmol) in 7 m*l* of THF was added dropwise 1.35 M of *n*-butyllithium (1.67 m*l*, 2.25 mmol) at 0℃. The mixture was stirred at 20℃ for 24 h. Subsequently, 5 m*l* of water was added dropwise. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with 5 m*l* of brine, dried over $MgSO_4$, evaporated to give yellowsh oil, which was purified by chromatography on silica gel to obtain 0.061 g (87%) of colorless oil. TLC R_f 0.44 (50% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.17 (s, 3H), 1.21 (s, 3H), 1.47-2.32 (m, 7H), 5.82 (s, 2H); IR (neat) 3620, 3490 cm^{-1}.

3-(1-Hydroxybenzyl)cyclohexane 28. To a solution of E-diethylaminosulfonylhydrazone of 2-(1-hydroxybenzyl)cyclohexanone **13** (0.46 g, 1.25 mmol) in 7 m*l* of THF was added dropwise 1.20 M of *n*-butyllithium (3.40 m*l*, 4.13 mmol) at 0℃. The mixture was stirred at 20℃ for 4 h. Subsequently, 5 m*l* of water was added dropwise. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with 5 m*l* of brine, dried over $MgSO_4$, evaporated to give 0.39 g of yellowish oil, which was purfied by chromatography on silica gel to obtain 0.16 g (80%) of colorless oil. TLC R_f 0.25 (25% MC, 25% ether/*n*-hexane) 0.43 (25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.10-1.80 (m, 6H), 2.00 (br. s, -OH), 2.50 (m, 1H), 4.45 (d, J=7.2 Hz, 1H), 5.86 (s, 2H), 7.35 (s, 5H); IR (neat) 3590, 3420 cm^{-1}.

3- and 1-(1-Hydroxybenzyl)cyclohexene, 28 and 29. To a solution of the Z isomer of diethylaminosulfonylhydrazone of 2-(1-hydroxybenzyl)cyclohexanone **13** (0.46 g, 1.25 mmol) was in 7 m*l* of THF at 0℃ was added dropwise 5.20 m*l* of 1.20 M *n*-butyllithium (6.26 mmol). The mixture was stirred for 24 h at room temperature, after which 4 m*l* of 1 N HCl was added, the orgainc layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic solution was washed brine, dried over $MgSO_4$ and evaporated to obtain yellowish oil. The crude product was purified by column chromatography to give a non-separable mixture of the two alkenes **28** and **29**. (0.15 g, 75%). TLC R_f 0.12 (25% MC, 25% ether in *n*-hexane) 0.43 (25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.40-2.20 (m, 7H), 2.5 (br. s, 1H), 4.52 (d, J=6.6 Hz, 0.7H), 5.02 (s, 0.7H), 5.31 (m, 0.7H), 5.82 (m, 1H), 7.31 (s, 5H); IR (neat) 3580, 3410 cm^{-1}.

The following alkenes were prepared in the same fashion:

3-(1-Hydroxy-2-phenylylethyl)cyclohexene 30. Yield 81%, TLC R_f 0.34 (25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.10-2.40 (br. m, 8H), 2.75 (m, 2H), 3.65 (m, 1H), 5.83 (s, 2H), 7.30 (s, 5H); IR (neat) 3580, 3440 cm^{-1}.

3- and 1-(1-Hydroxy-2-phenylylethyl)cyclohexene (a mixture of 30 and 31). Yield 86%; TLC R_f 0.44 (25% MC, 25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.10-2.30 (m, 8H), 2.70 (m, 2H), 3.70 (m, 1H), 5.70 (m, 2H), 7.25 (s, 5H); IR (neat) 3640, 3500 cm^{-1}.

3-Benzylcyclohexene (32). Yield 81%; TLC R_f 0.83 (25 % ether in *n*-hexane). NMR ($CDCl_3$) δ 1.10-2.00 (m, 7H), 2.40 (s, 2H), 5.35 (s, 2H), 6.85 (s, 5H).

4- Hydroxy-4-methyl-1-pentene 33. Yield 70%. TLC R_f 0.33 (33.3% ether in *n*-pentane); NMR ($CDCl_3$) δ 2.10 (m, 1H), 2.50 (t, J=6.6 Hz, 2H), 4.72 (t, J=6.0 Hz, 1H), 5.24 (d, J=3.0 Hz, 1H), 5.70-6.10 (m, 1H), 7.38 (s, 5H); IR (neat) 3580, 3440 cm^{-1}.

(E and Z)-5-Hydroxy-5-methyl-2-hexene 35. Yield 44% of colorless product. TLC R_f 0.32 (33.3% ether in *n*-pentane); NMR ($CDCl_3$) δ 1.25 (d, J=1.8 Hz, 6H), 1.65 (m, 3H), 2.20 (m, 2H), 5.50 (m, 2H); IR (neat) 3600, 3460 cm^{-1}.

(E and Z)-1-phenyl-3-penten-1-ol 36. Yield 81%. TLC R_f 0.32 (25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.15 (t, J=5.4 Hz, 3H), 2.20 (br. s, H), 2.50 (q, J=6.0 HZ, 2H), 4.70 (td, J=7.2, 3.0 Hz, 1H), 5.40-5.80 (m, 2H), 7.35 (s, 5H); IR (neat) 3600, 3430 cm^{-1}.

3-(1-Acetoxybenzyl)cyclohexene 37. To a solution of 3-(1-hydroxybenzyl)cyclohexene **28** (0.10 g, 0.64 mmol) and acetyl chloride (0.060 m*l*, 0.84 mmol) in 5 m*l* of methylene chloride was added dropwise pyridine (0.070 m*l*, 1.0 mmol) at 0℃. The reaction mixture was stirred for 3 h at rt, and then 5 m*l* of water was added. The organic layer was separated, the aqueous layer was extracted with methylene chloride. The combined organic layer was washed with 2 m*l* of 5% $NaHCO_3$, 5% H_3PO_4, and 2 m*l* of brine. The organic layer was dried over $MgSO_4$, filtrated, and evaporated. The resulting oily residue was purified by column chromatography to provide the pure acetate (0.10 g, 79%). TLC R_f 0.55 (25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.25-2.15 (m, 6H), 2.10 (s, 3H), 2.64 (br. s, 1H), 5.50 (d, J=9.0 Hz), 5.78 (s, 2H), 5.78 (s, 2H), 7.35 (s, 1H); IR (neat) 1720 cm^{-1}.

1- and 3-(1-acetoxybenzyl)cyclohexene 37 and 38 (as a mixture). Yield 71%; TLC R_f 0.55 (25% ether in *n*-hexane); NMR ($CDCl_3$) δ 1.36-2.20 (m, 11H), 2.17 (d, J=3.6 Hz, 3H), 2.70 (m, 0.55H), 5.10-6.25 (m, 3H), 7.22 (s, 5H); IR (neat) 1720 cm^{-1}.

Acknowledgement. The authors are grateful for the support of this work from the Organic Chemistry Research Center.

References

1. R. H. Shapiro, *Org. React.*, **23**, 405 (1976).
2. (a) P. L. Fuchs, *J. Org. Chem.*, **41**, 2937 (1976); (b) S. D. Yound and W. T. Burden, *Tetrahedron Lett.*, 4019

(1976); (c) R. H. Shapiro, M. F. Lipton, K. J. Kolonko, R. A. Buswell, and L. A. Capuano, *Tetrahedron Lett.*, 1811 (1975); (d) J. E. Stemke and F. T. Bond, *Tetrahedron Lett.*, 1815 (1975); (e) R. H. Shapiro, *Tetrahedron Lett.*, 345 (1968); (f) K. J. Kolonko and R. H. Shapiro, *J. Org. Chem.*, **43**, 1404 (1976).
3. W. G. Kofron and M. K. Yeh, *J. Org. Chem.*, **41**, 439 (1976).
4. M. E. Jung, P. A. Blair, and J. A. Lowe, *Tetrahedron Lett.*, 1439 (1976).
5. F. E. Henoch, K. G. Hampton, and C. R. Hauser, *J. Am. Chem. Soc.*, **91**, 676 (1969).
6. F. N. Jones, C. R. Hauser, *J. Org. Chem.*, **27**, 701 (1962).
7. N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 3087 (1973).
8. M. F. Lipton and R. H. Shapiro, *J. Org. Chem.*, **43**, 1409 (1978).
9. (a) A. R. Chamberlin, J. E. Stemke, and F. T. Bond, *J. Org. Chem.*, **43**, 147 (1978); (b) A. R. Chamberlin and F. T. Bond, *Synthesis*, **44**, (1979).
10. (a) N. J. Cusack, C. B. Reese, A. C. Risius, and B. Roozpeikar, *Tetrahedron Lett.*, **32**, 2157 (1976); (b) S. H. Bertz and G. Dabbagh, *J. Org. Chem.*, **48**, 116 (1983).
11. W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).
12. (a) A. R. Chamberlin and F. T. Bond, *J. Org. Chem.*, **43**, 154 (1978); (b) G. M. Kaufman, J. A. Smith, G. G. Vand der Stouw, and H. Shechter, *J. Am. Chem. Soc.*, **87**, 935 (1965).
13. (a) D. M. Orere and C. B. Reese, *Chem. Commun.*, 280 (1977); (b) S. H. Bertz and G. Dabbagh, *J. Chem. Soc.*, **103**, 5932 (1981).
14. W. W. Binkley and E. F. Degering, *J. Am. Chem. Soc.*, **61**, 3250 (1939).
15. L. F. Audrieth and M. Von Brauchitsch, *J. Org. Chem.*, **21**, 426 (1956).

Reaction of Sodium Diethyldihydroaluminate with Selected Organic Compounds Containing Representative Functional Groups†

Nung Min Yoon*, Young Seok Shon, and Jin Hee Ahn

Department of Chemistry, Sogang University, Seoul 121-742

Received January 6, 1992

The approximate rates and stoichiometry of the reaction of excess sodium diethyldihydroaluminate (SDDA) with 68 selected organic compounds containing representative functional groups were examined under standard conditions (THF-toluene, 0℃) in order to compare its reducing characteristics with lithium aluminum hydride (LAH), aluminum hydride, and diisobutylaluminum hydride (DIBAH) previously examined, and enlarge the scope of its applicability as a reducing agent. Alcohols, phenol, thiols and amines evolve hydrogen rapidly and quantitatively. Aldehydes and ketones of diverse structure are reduced rapidly to the corresponding alcohols. Reduction of norcamphor gives 11% *exo*-and 89% *endo*-norborneol. Conjugated aldehydes such as cinnamaldehyde are rapidly and cleanly reduced to the corresponding allylic alcohols. *p*-Benzoquinone is mainly reduced to hydroquinone. Hexanoic acid and benzoic acid liberate hydrogen rapidly and quantitatively, however reduction proceeds very slowly. Acid chlorides and esters tested are all reduced rapidly to the corresponding alcohols. However cyclic acid anhydrides such as succinic anhydride are reduced to the lactone stage rapidly, but very slowly thereafter. Although alkyl chlorides are reduced very slowly alkyl bromides, alkyl iodides and epoxides are reduced rapidly with an uptake of 1 equiv of hydride. Styrene oxide is reduced to give 1-phenylethanol quantitatively. Primary amides are reduced very slowly; however, tertiary amides take up 1 equiv of hydride rapidly. Tertiary amides could be reduced to the corresponding aldehydes in very good yield (>90%) by reacting with equimolar SDDA at room temperature. Hexanenitrile is reduced moderately accompanying 0.6 equiv of hydrogen evolution, however the reduction of benzonitrile proceeds rapidly to the imine stage and very slowly thereafter. Benzonitrile was reduced to give 90% yield of benzaldehyde by reaction with 1.1 equiv of hydride. Nitro compounds, azobenzene and azoxybenzene are reduced moderately at 0℃, but nitrobenzene is rapidly reduced to hydrazobenzene stage at room temperature. Cyclohexanone oxime is reduced to the hydroxylamine stage in 12 h and no further reaction is apparent. Pyridine is reduced sluggishly at 0℃, but moderately at room temperature to 1,2-dihydropyridine stage in 6 h; however further reaction is very slow. Disulfides and sulfoxides are reduced rapidly, whereas sulfide, sulfone, sulfonic acid and sulfonate are inert under these reaction conditions.

Introduction

Sodium diethyldihydroaluminate[1] (SDDA) has two available hydrides for reduction in a molecule and can be regarded as an aluminum counterpart of alkylborohydrides. Therefore it was of interest to examine the reducing characteristics of this dialkyl aluminohydride and compare with those of lithium aluminum hydride[2] (LAH), aluminum hydride[3] and diisobutylaluminum hydride[4] (DIBAH), previously studied.

†Dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday.