n-hexane: ether = 7:3, SiO_2; IR (NaCl, neat) 2950, 2850, 2750, 1700, 1690, 1620 cm^{-1}; ^1H-NMR (80MHz, $CDCl_3$) 0.90-1.40 (m, 17H), 2.70 (t, 2H), 6.78 (dd, 1H), 6,88 (dd, 1H), 9.80 (d, 1H). 4-oxotridecan-1-ol; TLC; Rf = 0.25, n-hexane: ether = 7:3, SiO_2; IR (NaCl, neat) 3100-3400, 2955, 2850, 1720 cm^{-1}; ^1H-NMR (80MHz, $CDCl_3$) 0.88-1.80 (m, 17H), 2.50-3.00 (m, 6H), 3.80 (t, 4H). (Z)-13-eicosen-10-one (**1**); IR (NaCl, neat) 2960, 1715, 1620, 1450 cm^{-1}; ^1H-NMR (80MHz, $CDCl_3$) 0.90 (t, 6H), 1.15-1.50 (m, 22H), 1.80-2.50 (m, 8H), 5.30 (m, 2H).

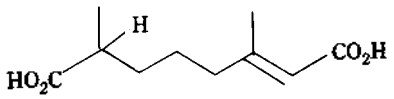
13. G. Piancatelli, A. Scettri, and M. D'Auria, *Tetrahedron*, **36**, 661 (1980).

A Short Synthesis of (±)-Callosobruchusic Acid, the Copulation Release Pheromone(Erectin) of the Azuki Bean Weevil

Suk-Ku Kang* and Dong-Ha Lee

Department of Chemistry, Sung Kyun Kwan University, National Science Campus, Suwon, 170.
Received September 14, 1987

In 1981, Yamamoto *et al.*[1] isolated and identified the copulation release pheromone of the azuki bean weevil, *Callosobruchus chinensis* L., as (E)-3,7-dimethyl-2-octene-1,8-dioic acid(1) (Callosobruchusic acid) (Figure 1). In 1983, Mori *et al.*[2] synthesized two enantiomers. Both were biologically active[2] as the copulation release pheromone of *Callosobruchus chinensis* L.. This pheromone induces the male to extrude his genital organ and to attempt copulation.



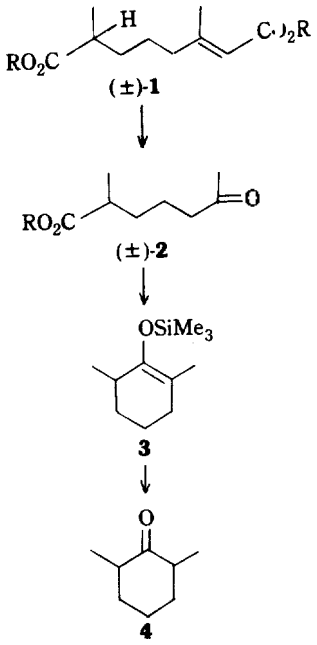
(±)-1

Figure 1

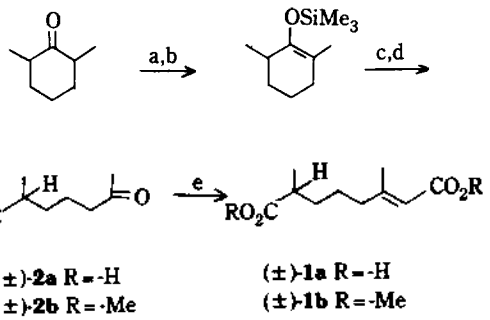
The azuki bean weevil is a persistent pest insect of the azuki bean, cowpea and other important beans. The Institute of Agricultural Sciences in Suwon Korea needed a fair amount of this pheromone to conduct field test experiments, therefore we undertook to synthesize (±)-callosobruchusic acid, (±)-1, (±)-(2E)-3,7-dimethyl-2-octene-1,8-dioic acid.

It has been well known that the Emmons olefination reaction of the ketone **2** with the anion of dimethylmethoxycarbonylmethylphosphonate gives predominantly (E)-olefin ester stereoselectively[3]. A simple retrosynthetic analysis(Scheme 1) reveals that methyl 2-methyl-6-oxo-heptanoate **2** is the key intermediate. The ketone **2** can be easily prepared from silyloxyalkene **3** by ozonization reaction[4]. Silyloxyalkene **3** can be obtained by silylation[5] of the enolate of commercially available 2,6-dimethylcyclohexanone, **4**.

2,6-Dimethylcyclohexanone(4) was silylated by treating with LDA followed by addition of Me_3SiCl to give silyloxyalkene **3**[7] in 95% yield. Ozonolysis of **3** in methanol followed by Me_2S work up afforded (±)-2-methyl-6-oxo-heptanoic acid **2a** in 60% yield. Esterification of the acid **2a** with diazomethane[6] gave the methyl ester **2b**[7] in 95% yield. Emmons olefination reaction of the ketone **2b**[7] with the anion of dimethylmethoxycarbonylmethylphosphonate furnished the unsaturated ester (±)-**1b**[7] in 80% yield. The diester **1b** was treat-



Scheme 1



(±)-**2a** R = -H (±)-**1a** R = -H
(±)-**2b** R = -Me (±)-**1b** R = -Me

Scheme 2. Synthesis of (±)-**1a**[a]

[a](a) LDA, THF, -78°C (b) Me_3SiCl (c) O_3, MeOH, -78°C (d) Me_2S, -78°C→rt (e) $(MeO)_2POCH_2CO_2Me$, NaH, DME, 50—60°C.

ed with 1N HCl to afford the diacid **1a**[7] in 85% yield(Scheme 2). The compound synthesized was identical in all respects (TLC, IR, NMR) with the compound reported in the literature.

References

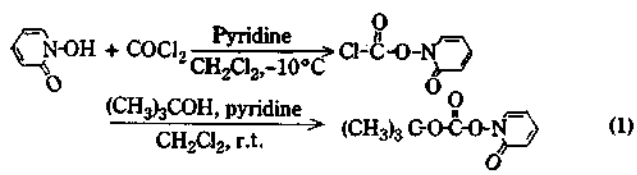
1. K. Tanaka, K. Ohsawa, H. Honda and I. Yamamoto, *J. Pesticide Sci.*, **6**, 75 (1981).
2. K. Mori *et al.*, *Tetrahedron*, **39**, 2303 (1983).
3. K. H. Dahm, B. M. Trost and H. Roller, *J. Amr. Chem. Soc.*, **89**, 5292 (1967).
4. R. D. Clark and C. H. Heathcock, *J. Org. Chem.*, **41**, 1396 (1976).
5. G. Stork and P. F. Hudrlik, *J. Amr. Chem. Soc.*, **90**, 4462 (1968).
6. F. Arndt, Org. Syn. Coll, II, 461 (1943).
7. Satisfactory physical properties and spectroscopic data (^{1}H-NMR, IR) were obtained for the compounds: Siloxyalkene (3): TLC; R_f=0.74, hexane:CH_2Cl_2=5:5, SiO_2; IR(NaCl, neat) 2900, 1670 cm^{-1}; ^{1}H-NMR (80MHz, $CDCl_3$) 0.15(9H, s, $3CH_3$), 1.05(3H, d, CH_3), 1.32(4H, m, CH_2CH_2), 1.55(3H, s, CH_3), 1.95(3H, m, HCH_2); bp 40°C/15 mmHg. 2-Methyl-6-oxo-heptanoic acid(2b): TLC; R_f=0.47, CH_2Cl_2, SiO_2; IR (NaCl, neat) 2950, 1720 cm^{-1}; ^{1}H-NMR(80MHz, $CDCl_3$) 1.17(3H, d, CH_3), 1.56(4H, m, CH_2CH_2), 2.14(3H, s, CH_3), 2.43(3H, m, HCH_2), 3.68(3H, s, CH_3). 3,7-Dimethyl-2-octene-1,8-dioate(1b): TLC; R_f=0.82, CH_2Cl_2, SiO_2; IR(NaCl, neat) 2930, 1715, 1640 cm^{-1}; ^{1}H-NMR(80MHz, $CDCl_3$) 1.16(3H, d, CH_3), 1.55(4H, m, CH_2CH_2), 2.14(3H, s, CH_3), 2.43(3H, m, HCH_2), 3,68(6H, s, CH_3CH_3), 5.67(1H, s, H). 3,7-Dimethyl-2-octene-1,8-dioic acid(1a): TLC; R_f=0.14, CH_2CH_2, SiO_2; IR(NaCl, neat) 3600, 3000, 2950, 1700, 1650 cm^{-1}; ^{1}H-NMR(80MHz, $CDCl_3$) 1.20(3H, d, CH_3), 1.62(4H, m, CH_2CH_2), 2.16(3H, s, CH_3), 2.46(3H, m, HCH_2), 5.79(3H, brs, HC=, CO_2H, CO_2H).

t-Butyl 2-Pyridon-1-yl Carbonate and Benzyl 2-Pyridon-1-yl Carbonate. New Amino Protective Reagents foı t-Butoxycarbonylation and Benzyloxycarbonylation of Amines and Amino Acids

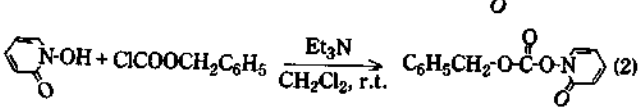
Sunggak Kim*, Jou Hyeon Park, and Sung Soo Kim

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131
Received September 21, 1987

The t-butoxycarbonyl (Boc) group is one of the most important amino protective groups along with benzyloxycarbonyl (Cbz) group because of the resistance to racemization during peptide synthesis and facile cleavage of Boc group.[1]. The Boc group was originally introduced with t-butyl chloroformate but its use has been limited due to its instability.[2] In the case of benzyloxycarbonylation of amino acids, benzyl chloroformate has been widely used, but it is thermally unstable and decomposes to yield carbon dioxide and benzyl chloride when it is stored over a long period of time. Thus, considerable efforts have been devoted to the development of a variety of useful and reliable reagents for the protection of amino acids during last 30 years.[1,3] Recently, we have introduced several efficient amino protective reagents for t-butoxycarbonylation and benzyloxycarbonylation of amino acids.[4,5] We now wish to report that new amino protective reagents, t-butyl 2-pyridon-1-yl carbonate and benzyl 2-pyridon-1-yl carbonate, are very effective for t-butoxycarbonylation and benzyloxycarbonylation of amines and amino acids.



(1)



(2)

t-Bytyl 2-pyridon-1-yl carbonate was conveniently prepared in 70% yield by the reaction of 2-pyridon-1-yl chloroformate, generated from phosgene and 1-hydroxy-2(1H)-pyridone[6] in the presence of pyridine, with equimolar amounts of t-butyl alcohol in methylene chloride at room temperature (Eq. 1).[7] Benzyl 2-pyridon-1-yl carbonate was easily prepared in 90% yield by treatment of benzyl chloroformate with equimolar amounts of 1-hydroxy-2(1H)-pyridone and triethylamine in methylene chloride at room temperature (Eq. 2).[8] t-Butyl 2-pyridon-1-yl carbonate and benzyl 2-pyridon-1-yl carbonate were obtained as stable crystalline compounds, showing no sign of decomposition when kept at room temperature for one month.

As shown in Table 1, simple amines were cleanly t-butoxycarbonylated to give the corresponding t-butyl carbamates within 10 min at room temperature and sterically hindered amines such as 2,6-dimethylpiperidine and diisopropylamine worked well, although they required longer reaction times. Similarly, benzyloxycarbonylation of amines proceeded well with benzyl 2-pyridon-1-yl carbonate. When t-butoxycarbonylation of amino acids were carried out in aqueous N,N′-dimethylformamide, the N-Boc amino acids were obtained in relatively low yields because t-butyl 2-pyridon-1-yl carbonate was decomposed to some extent in aqueous N,N′-dimethylformamide. It was found that t-butoxycarbonylation of amino acids proceeded cleanly in p-dioxane, even