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LETTERS

A Short Synthesis of (Z)-7-Eicosen-11-one, the Pheromone of Peach Fruit Moth

Suck-Ku Kang[†] and Hyun-Sung Cho

Department of Chemistry, Sung Kyun Kwan Universrity, Natural Scienec Campus, Suwon 170, Korea

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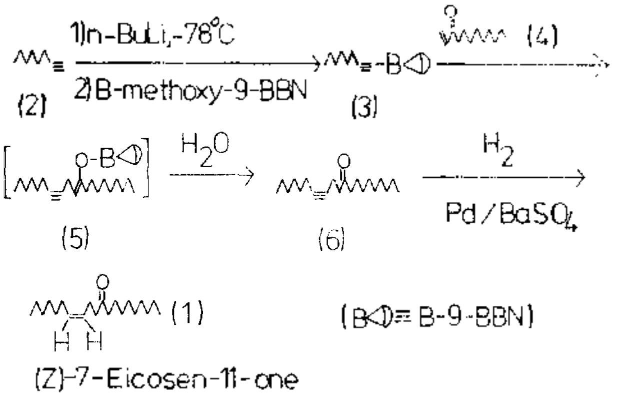
(Z)-7-Eicosen-11-one, an active component of the famale sex pheromone of the peach fruit moth, *Carposina niponenesis* Walsingham, a major economic pest of apple, peach and other fruits, was isolated by Tamaki[1] in 1977. Several syntheses of (Z)-7-eicosen-11-one have been reported[2].

To our knowledge, the direct conjugate addition of alkali- or alkaline earthacetylides[3,4] to enone system has not previously been observed in the literature, but a few examples of conjugate addition of alkynyl organoboranes[5] and alkyl organolanes[6] to α,β-unsaturated ketones have been known. We wish to report a short synthesis of the title compound (1) based on conjugate addition of organoborane to α,β-unsaturated ketone system.

Lithium 1-octynide was obtained from 1-octyne (2) using n-BuLi (1.0 mol equiv.) in dry THF at −78°C. This acetylide was treated *in. situ.* with B-methoxy-9-BBN (1.0 mol equiv.) and the reaction mixture was strirred for 2 hr at −78 °C. Then boron trifluoride diethyl etherate (1.3 mol equiv.) was added and the mixture was stirred for 1 h at −78 °C and allowed to warm to room temperature. From the reaction mixture, the volatiles were distilled off to yield a yellow solid which was supposed to be B-1-octynyl-9-BBN (3). This solid was dissolved in dry pentane and 1-dodecen-3-one[7] (4) was added and stood overnight at room temperature. After work-up, 7-eicosyn-11-one was obtained by Kugelrohr distillation (b. p.) 109-118°C/10^{-3} mm) in 46 % overall yield from 1-octyne (2), IR (neat) 2260, 1720, 1450, 1370 cm^{-1}; NMR ($CDCl_3$) δ_{TMS} 0.90 (6H), 1.05-1.75 (22H), 1.90-2.60 (8H). Catalytic hydrogenation with palladium on barium sulfate afforded the desired (Z)-7-eicosen-11-one[8] (1), IR (neat) 2940, 1720, 1460, 1375 cm^{-1}; NMR ($CDCl_3$) δ TMS 0.90 (6H), 1.10-1.70 (22H), 1.80-2.75 (8H), 5.35 (2H); MS, m/e 295 (M^+).



Scheme 1

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(7) 1-Dodecen-3-one was prepared from decylaldehyde

in two steps (61%):(1) vinylmagnesium bromide addition (2) pyridinium chlorochromate oxidation; J. H. Babler, B. J. Invergo and S. J. Sarussi, *J. Org. Chem.*, **45**, 4241 (1980).

(8) (Z)-7-Eicosen-11-one prepared by this method was proved biologically active by its field tests in South Korea.

PMO Theory of π^*-π^* Interaction

Ikchoon Lee[+] **and Kiyull Yang**

Department of Chemistry, Inha University, Incheon 160, Korea *(Received February 11, 1984)*

Recently chemical as well as physical concequences of π^*-π^* orbital interaction have been demonstrated[1]. Direct experimental examination of such orbital interaction has been practicable using electron transmission spectroscopy (ETS)[1b,2]. Two important, yet unaccounted-for, features of the experimental results on π^*-π^* orbital interactions through 2 and 4 C-C σ bonds (N=2 and 4) of the connecting σ frawework[2] were: (i) level splitting (ΔE) of the symmetry adapted orbitals (SAO), π^*_+ and π^*_-, is considerably greater than that for the corresponding π-π interactions, and (ii) the average level (ε_{av}) of the two SAO is above the basis level (ε_0), the π^* level for monoene.

In this work we will show that these features are the results of enhanced effect of through-space interaction (TSI) in the π^*-π^* interaction compared with that in the π-π interaction.

To second-order in overlap S, the levels ε_+ and ε_- of the SAO, π_+ and π_-, (or n_+ and n_-) had the expressions (1a) and (1b) for N=odd and even systems respectively[3].

$$\left.\begin{aligned}\varepsilon_+&\cong e'-\delta e_l+2y(1+\alpha+\beta)\\ \varepsilon_-&\cong e'+\delta e_h-2x(1+\alpha-\beta)\end{aligned}\right\}\quad(1a)$$

$$\left.\begin{aligned}\varepsilon_+&\cong e'-\delta e_l-2x(1+\alpha-\beta)\\ \varepsilon_-&\cong e'+\delta e_h+2y(1+\alpha+\beta)\end{aligned}\right\}\quad(1b)$$

where e', which is negative, is the environment adjusted level of the basis level, δe_l and δe_h are depression and elevation of e' due to TSI, and x, y, α and β are positive quantities difined as:

$$x=\frac{<\pi|H'|\Psi^0_{\mathrm{LU}}>^2}{\Delta e},\quad y=\frac{<\pi|H'|\Psi^0_{\mathrm{HO}}>^2}{\Delta e},$$

$$\alpha=\left|\frac{e''}{\Delta e}\right|^2+\left|\frac{e''}{\Delta e}\right|^4+\cdots,\ \text{and}$$

$$\beta=\left|\frac{e''}{\Delta e}\right|+\left|\frac{e''}{\Delta e}\right|^3+\cdots^{3,4}.$$

Equations (1a) and (1b) clearly indicate that the effects of second-order perturbation (through-bond interaction (TBI)) is to elevate one of the SAO (π_+ and π_- for N=odd and even cases respectively) substantially but to depress the other by a small amount. These are natural consequences of narrow (wide) energy gaps involved in the interactions of $\pi_\pm$ with the framework HO-σ (LU-σ^*) orbitals. The depression effect on a SAO has been shown to be small but by no means negligible[5], as expected from eq(1), since $(\beta-\alpha)<1.0$[3].

In π^*-π^* orbital interactions, the environment adjusted level of the basis orbital, e^*, should be approximately equal to the π^* level of ethylene since there will be no first-order (electrostatic) interaction between an empty π^* orbital and a neutral molecule. The basis level is therefore given as

$$\varepsilon_0\cong e^*-x(1+\alpha+\beta)+y(1+\alpha-\beta)\quad(2)$$

where $e^*\cong e_{\pi^*}$ (ethylene)>0 and x, y, α and β are positive quantities similarly defined as above. It is evident from eq (2) that the basis level is somewhat depressed relative to the ethylenic π^* level since the second-order effect is to depress (by an amount x $(1+\alpha+\beta)$) more than to elevate (by an amount $y(1+\alpha-\beta)$) the level e^*. This is in accord with the experimental results[2] (see Table).

The environment adjusted levels e_+ and e_- for the SAO, π^*_+ and π^*_-, are obtained using the usual approximation, $H_{mn}\cong -kS_{mn}$[3], where k is a positive constant.

$$\left.\begin{aligned}e_+&\cong e^*+<\pi^*_+|H'|\pi^*_+>\cong e^*-\delta e_l\\ e_-&\cong e^*+<\pi^*_-|H'|\pi^*_->\cong e^*+\delta e_h\end{aligned}\right\}\quad(3)$$

where $\delta e_l\cong kS(1-S)$ and $\delta e_h\cong kS(1+S)$. The level splitting, ΔE_S, and energy destabilization, $\delta\varepsilon_S$, as a result of TSI are thus given as,

$$\Delta E_S=e_--e_+=\delta e_l+\delta e_h\cong 2kS\quad(4)$$

$$\delta\varepsilon_S=\delta e_h-\delta e_l\cong 2kS^2\quad(5)$$

The corresponding ones for π-π TSI are[3]: $\Delta E_S(\pi)\cong 2S(k+e_1)$ and $\delta\varepsilon_S\cong 2(k+e_1)S^2$ where e_1 is the first-order level depression of π orbital, $e_1<0$. Hence $\Delta E_S(\pi^*)$ and $\delta\varepsilon_S(\pi^*)$ should be larger (positive quantities) than $\Delta E_S(\pi)$ and $\delta\varepsilon_S(\pi)$ respectively.

Inclusion of second-order (TBI) terms gives the final expressions (6a) and (6b) for N=odd and even cases respectively.

$$\left.\begin{aligned}\varepsilon_+&\cong e^*-\delta e_l+2y(1+\alpha-\beta))\\ \varepsilon_-&\cong e^*+\delta e_h-2x(1+\alpha+\beta))\end{aligned}\right\}\quad(6a)$$

$$\left.\begin{aligned}\varepsilon_+&\cong e^*-\delta e_l-2x(1+\alpha+\beta))\\ \varepsilon_-&\cong e^*+\delta e_h+2y(1+\alpha-\beta))\end{aligned}\right\}\quad(6b)$$

Thus in π^*-π^* TBI, one of the SAO (π^*_+ and π^*_- for N