COMMUNICATIONS

LETTERS

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

Suck-Ku Kang† and Hyun-Sung Cho

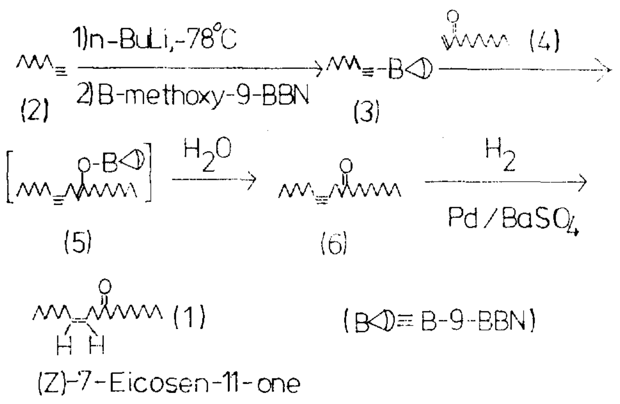
Department of Chemistry, Sung Kyun Kwan Universrity, Natural Scienec Campus, Suwon 170, Korea

(Received November 28, 1983)

(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

Acknowledgement. We thank the Korea Science and Engineering Foundation for financial support.

References

(1) Y. Tamaki, K. K. Honma and K. Kawasaki, *Appl. Entmol. Zool.*, **12,** 60 (1977).

(2) (a) Y. Naoshima, M. Kawakubo, S. Wadayabashi and S. H. Hayashi, *Agric. Biol. Chem.*, **45,** 439 (1981): (b) K. Mori, S. Tamada and M. Matsui, *Agric. Biol. Chem.*, **42,** 191 (1978); (c) Sagami Chemical Research Center Japan Kokai Tokkyo Koho JP 81, 118 036 (Chemical Abstract 96 68339e).

(3) G. H. Posner, Cu-acetylides do not add to enones, *Org. React.* **19,** 1 (1972); E. J. Corey and D. J. Beams, *J. Amer. Soc.*, **94,** 7210 (1972).

(4) R. Locher and D. Seebach, *Angew. Chem. Int. Ed. Engl.*, **20,** 569 (1981).

(5) (a) M. Bruhn, C. H. Brown, P. W. Collins, J. R. Palmer, E. Z. Dajani and R. Pappo, *Tetrahedron Lett.*, **32,** 235 (1976); (b) P. Jacob, III and H. C. Brown, *J. Amer. Chem. Soc.*, **98,** 7832 (1976); (c) J. A. Sinclair and H. C. Brown, *J. Org. Chem.*, **41,** 1078 (1976); (d) J. A. Sinclair, G. A. Molander and H. C. Brown, *J. Amer. Chem. Soc.*, **99,** 954 (1977).

(6) (a) R. Pappo and P. W. Collins ,Tetrahedron Lett., **28,** 2626 (1972); (b) R. T. Hansen, D. B. Carr and J. Schwartz, *J. Amer. Chem. Soc.*, **100,** 2244 (1978).

(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].

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

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

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:

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

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

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

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

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

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, $H_{\mathrm{mn}} \cong -kS_{\mathrm{mn}}$[3], where k is a positive constant.

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

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,

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

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

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.

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

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

Thus in π^*-π^* TBI, one of the SAO ($\pi_\pm^*$ and $\pi_\pm^*$ for N