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Photoreaction of Pseudoionone

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The great majority of works on the photoreaction of conjugated dienone has been dealt extensively with cyclic compounds.[1–4] Only a few examples involving acyclic dienone have been known, *e. g.*, the photodimerization of cinnamylidene acetone[5,6] and the photoisomerization of crotonylidene acetone.[3] Büchi and Yang[3] obtained a polymeric material by the photoreaction of pseudoionone (I), an acyclic dienone. This is the only report on the photoreaction of I. As part of photochemical studies on enone systems the photoreaction of I has been studied.

First, it was confirmed that I had a structure of conjugated dienone (all trans type in diene[7]) with

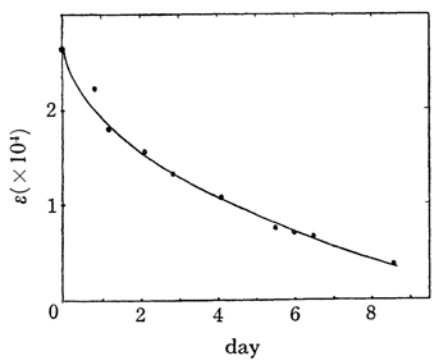


Fig. 1. The change of ε at 293 mn of pseudoionone with irradiation time.

1) W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., "Advances in Photochemistry," Vol. 4, Interscience, New York (1966), p. 81, 195.

2) P. de Mayo and S. T. Reid, *Quat. Rev.* (London), **15**, 393 (1961).

3) G. Büchi and N. C. Yang, *J. Am. Chem. Soc.*, **79**, 2318 (1957).

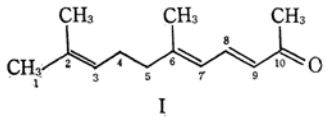
4) P. de Mayo, J. B. Stothers and R. W. Yip, *Can. J. Chem.*, **39**, 2135 (1961).

5) H. Stobbe and W. Simon, *J. Prakt. Chem.*, **110**, 129 (1925).

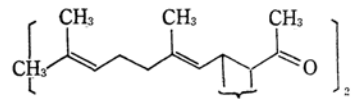
6) H. Stobbe and C. Rücker, *Ber.*, **44**, 861 (1911).

7) C. H. Chen and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1965**, 5528.

one isolated double bond by UV, IR and NMR spectra as shown in experimental part. When the solution of I in *n*-hexane was irradiated with a high pressure mercury lamp, UV absorption at 293 nm gradually decreased indicating the disappearance of the conjugated double bond. (Fig. 1) The reaction mixture showed four spots of R_f values of 0.45, 0.43, 0.40 and 0.0 on a silica gel thin layer chromatogram with benzene - ethyl acetate (9 : 1). The substance of R_f 0.45 was identified with I. The substances which show the R_f values of 0.43, 0.40 and 0.0 were designated as II, III and IV, respectively. Both II and III were isolated by a silica gel chromatography. When left at room temperature, I readily, and II or III gradually polymerized. So the viscous IV would be a mixture of polymers from I, II and III.



I



II and III

The ozonolysis of II and III, followed by decomposition with hydrogen peroxide and then by esterification with diazomethane, gave methyl levulinate as a main product. However, II and III were presumed to be cyclobutane derivatives from the following spectra and other reactions.

The UV spectra indicate that no conjugated system is contained in II and III. It is also supported by the shift of IR band at 1665 cm^{-1} of I to 1705 cm^{-1}. The NMR spectra of II and III show signals at τ 8.35 due to isopropylidene methyls. This shows that 2,3-double bond remains. The signals at τ 4.9 of II and III are assigned to 3- and 7-protons. The molecular peaks of mass spectra of (V) and (VI) (*m/e* 394 and 392 respectively), which were obtained by the catalytic reduction of II and III respectively, are consistent with the experimental facts that II absorbed five moles of hydrogen over platinum oxide and III absorbed four moles over palladium black. The above facts and A_2B_2 like multiplets at τ 7.6—6.9 of II and τ 7.1—6.3 of III also support the cyclobutane structure. The chemical shifts of 6-methyl protons and acetyl methyl protons of II and III move to a higher magnetic field, compared with I. Especially acetyl methyl protons of III show two singlets, indicating that the surrounding of two acetyl groups are slightly different. The IR spectrum of V shows strong absorption at 3450 cm^{-1} (OH) and 1700 cm^{-1} (CO). A doublet at τ 8.84 in NMR of V is due to methyl of CH_3-CH-OH and a singlet at τ 7.86 comes from acetyl methyl group. This indicates that four C=C bonds and one C=O bond were reduced in V. On the other hand, the IR spectrum of VI shows a strong absorption at 1710 cm^{-1} (CO) and no hydroxy absorption, indicating that only C=C bond were reduced in VI. Consequently it can be concluded that II and III are dimers of I, which contain cyclobutane ring at 8,9-positions.

Experimental

Pseudoionone was purified by fractional distillation *in vacuo* and column chromatography. UV: λ_{max}^{EtOH} 293 nm (ε 26000); IR: $\nu_{max}^{liq.\ film}$ cm^{-1}, 1665 (CO), 1630, 1590, 973 (diene), 825(C=C); NMR: (τ, in CCl_4), 8.36 (d, J=4.5 cps, isopropylidene methyls), 8.09 (s, 6-methyl), 7.80 (m, 4- and 5-methylenes), 7.80 (s, acetyl), 4.90 (m, 3-proton), 3.98 (d, J=12.5 cps, 7-proton), 3.93 (d, J=15.5 cps, 9-proton) and 2.58 (q, J=12.5 and 15.5 cps, 8-proton). A Taika H-type 125W high pressure mercury lamp was used as light source. IR, UV, NMR and Mass spectra were measured by Hitachi ESI-S2 type spectrometer, Hitachi EPS-3T type spectrophotometer, Hitachi H-60 type spectrometer and Hitachi Mass spectrometer, respectively. Hitachi KGL-2A type gas chromatography apparatus (polydiethylene glycol succinate) was used for analysis.

Irradiation of Pseudoionone (I). A *n*-hexane solution of I (7.5 g/70 m*l*) was irradiated with a high pressure mercury lamp for 8 days at room temperature. The reaction was followed by UV spectra of aliquots (Fig. 1). From the reaction mixture the solvent was evaporated under reduced pressure and the residual pale yellow liquid was fractionated by column chromatography using silica gel eluted with benzene - ethyl acetate. Unreacted I (0.75 g) was recovered from the benzene elute. From the benzene - ethyl acetate (9 : 1) elute, the mixture of II and III (1.8—1.9 g), was obtained. Ratio of II by III was found to be 1 : 1 by measuring the intensity of methine proton signals in NMR spectra. Pure II and III were separated by repeating column chromatography. Photodimer II, a pale yellow liquid, Found: C, 81.49; H, 10.31%. Calcd for $C_{26}H_{40}O_2$: C, 81.20; H, 10.48%.

UV: λ_{max}^{EtOH} nm(ε), 283 (sh, 190).

IR: (cm^{-1}, liq. film) 1705, 1675, 1445, 1358, 832.

NMR: (τ, in CCl_4) 8.35 (d, J=4.5 cps, 12H), 8.34 (d, J=1.0 cps, 6H), 8.00 (s, 6H), 7.6—6.9 (m, 4H), 4.9 (m, 4H).

Photodimer III, a pale yellow liquid. Found: C, 81.79; H, 9.99%. Calcd for $C_{26}H_{40}O_2$: C, 81.20; H, 10.48%.

UV: λ_{max}^{EtOH} nm (ε), 283 (sh, 200).

IR: (cm^{-1}, liq. film) 1705, 1670, 1440, 1355, 820.

NMR: (τ, in CCl_4) 8.35 (d, J=4.5 cps, 12H), 8.36 (d, J=1.0 cps, 6H), 7.96 (s, 3H), 7.93 (s, 3H), 7.1—6.3 (m, 4H), 4.9 (m, 4H).

Catalytic Reduction of Photodimer II. In the presence of 28 mg of platinum oxide as catalyst, 205 mg of II was hydrogenated in ethanol (7.5 m*l*). The sample absorbed 59 m*l* of hydrogen. After the solvent was evaporated, 210 mg of a colorless liquid (V) was obtained.

Found: C, 79.89; H, 12.50%. Calcd for $C_{26}H_{50}O_2$: C, 79.12; H, 12.77%.

UV: λ_{max}^{EtOH} nm (ε), 282 (48).

IR: (cm^{-1}, liq. film), 3450, 1700, 1460, 1360, 1070.

NMR: (τ, in CCl_4), 9.11 (d, J=6.0 cps, 18H), 8.80 (m, 20H), 8.84 (d, J=8.0 cps, 3H), 7.86 (s, 3H), 7.8—7.3 (m, 4H), 6.4 (m, 1H), 4.7 (broad s, 1H).

Mass: (*m/e*) 394 (mol. peak), 376, 198, 197, 196, 195, 127, 113, 111, 109 (base peak), 97, 96, 85, 83, 71, 57, 43.

Catalytic Reduction of Photodimer III. In the presence of palladium black (51 mg) as catalyst, 54 mg of III was hydrogenated in ethanol (10 m*l*). The sample absorbed 12 m*l* of hydrogen. Removal of the solvent gave 55 mg of a colorless liquid (VI).

Found: C, 79.67; H, 11.86%. Calcd for $C_{26}H_{48}O_2$: C, 79.53; H, 12.32%.

UV: λ_{max}^{EtOH} nm (ε), 283 (sh, 78).

IR: (cm^{-1}, liq. film), 1710, 1460, 1360.

NMR: (τ, in CCl_4), 9.10 (d, J=6.0 cps, 18H), 8.77 (m, 20H), 7.98 (s, 3H), 7.92 (s, 3H), 7.7—6.6 (m, 4H).

Mass: (*m/e*), 392 (mol. peak), 196, 195, 127, 113, 109 (base peak), 97, 95, 85, 83, 71, 57, 43.

Ozone Oxidation of II. Ozonolysis and decomposition with hydrogen peroxide of 980 mg of II gave neutral material (260 mg) and acidic material (280 mg). Esterification of acidic material by diazomethane gave 62 mg of methyl levulinate as main product, identified with the authentic sample by NMR and gas chromatography.

Ozone Oxidation of III. By a similar procedure as described above, 800 mg of III gave 200 mg of neutral material, 220 mg of acidic material and 55 mg of methyl levulinate.