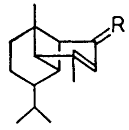
The Photocyclization of an Acyclic Bis-unsaturated Carbonyl System

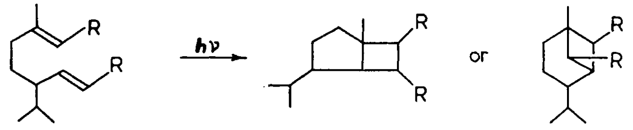
By MORRIS BROWN

(*Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California*)

WHILE investigating synthetic routes to copaene[1,2] (I;R = H) the preparation and photolysis of the bis-unsaturated compound (II) have been investigated. This photocyclization which could yield either the 5–4 fused system (III) (head-to-head cyclization) or the 6–4 bicyclic ring system (IV) (head-to-tail cyclization) appears to afford only the head-to-head products (III).



(I)



(II) (III) (IV)

Isovaleraldehyde piperidine eneamine (V) was condensed with methyl vinyl ketone at 0° and the adduct immediately hydrolyzed with aqueous oxalic acid to the keto-aldehyde(VI)[3] (60% overall yield) Condensation of (VI) with two equivalents of triethyl phosphonoacetate[4] afforded the bis-unsaturated diester (VIIa)* in 50% yield, b.p. 128—145° (0·1 mm), λ_{max} (95% EtOH) 216 mμ (23,800); λ_{max} 5·82 μ, 6·08.

Confirmation of the assigned structure is obtained from the n.m.r. spectrum,[5] which in addition to the expected absorptions for the isopropyl and ethyl ester protons, showed absorption for three protons as a doublet (J = 1 c./sec.) at δ = 2·1 p.p.m. (vinyl methyl), and three vinyl protons at 5·6 (singlet), 5·7 (doublet, J = 15 c./sec.) and 6·7 (quartet, J = 15, 8 c./sec.).

Irradiation of a 5% solution of the diester (VIIa) in cyclohexane (pyrex vessel) with acetophenone as a sensitizer or direct irradiation in a silica apparatus afforded the same mixture (v.p.c. 220°, silicone oil column) of saturated esters (VIIIa) (λ_{max} 5·78 μ). Saponification of the ester mixture with sodium hydroxide led to the isolation in 55% yield of a crystalline diacid (VIIIb),* m.p. 148—150°.

The assignment of structure (VIIIb) to the diacid was obtained as follows. Admixture of the diacid (VIIIb) with phosphorus pentoxide followed by evaporative distillation [140° (0·05 mm.)] affords the oily anhydride (IX)* in 90% yield, λ_{max} (film) 5·38 μ, 5.61. This infrared spectrum is clearly only consistent with the five-membered anhydride arising from a 1,2-disubstituted cyclobutane. The n.m.r. spectrum of the anhydride showed an ABX type spectrum at δ = 3·0 (J_{AB} = 6·5 c./sec.; J_{BX} = 3; J_{AX} = 0), and is therefore also only consistent with structure (IX).

---

* Satisfactory elemental analyses were obtained for the compounds indicated with an asterisk.

[1] G. Büchi, S. H. Feairheller, P. de Mayo and R. E. Williams, *Proc. Chem. Soc.*, 1963, 214.

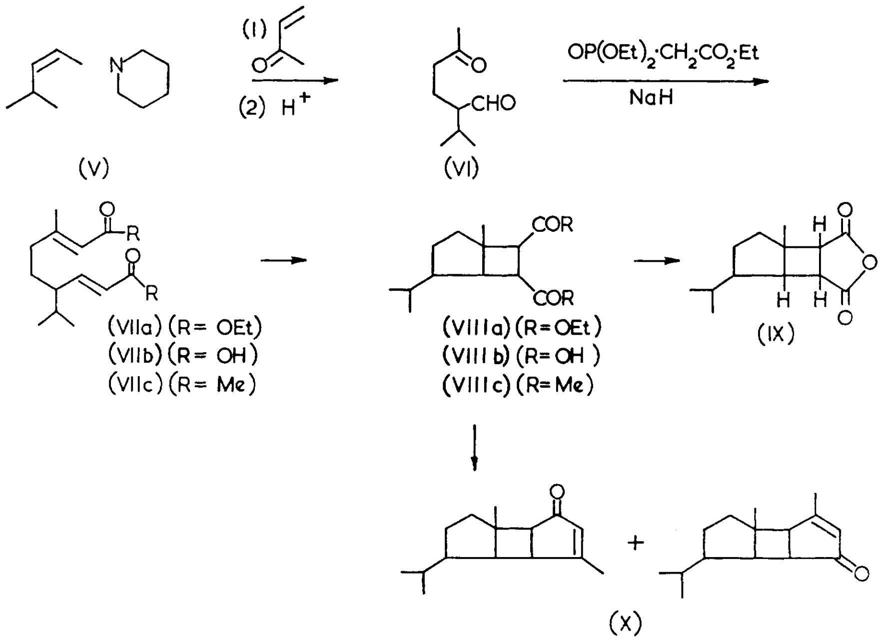
[2] V. H. Kapadia, B. A. Nagasampagi, V. G. Naik, and S. Dev, *Tetrahedron*, 1965, **21**, 607.

[3] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, 1963, **85**, 207. The keto-aldehyde (VI) was not isolated in this case.

[4] W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, 1961, **83**, 1733.

[5] N.m.r. spectra were determined at 60 megacycles. Carbon tetrachloride was employed as solvent and tetramethylsilane as an internal standard.

The diketone (VIIIc)* was prepared in 77% yield from the diacid (VIIIa) by the multistep procedure of Stork,[6] and purified by chromatography and evaporative distillation [100° (0·1 mm.)] $\lambda_{\max}$ 5·85 μ. Cyclization of (VIIIc) with potassium t-butoxide in t-butyl alcohol afforded after distillation, b.p. 100° (1 mm.), the unsaturated ketone mixture (X) (75% yield), $\lambda_{\max}$ (EtOH) 239 mμ (14,200); $\lambda_{\max}$ ($CHCl_3$) 5.90 μ, 6·2.



An investigation of the mother liquors from the crystallization of the diacid (VIIIb) has shown that only head-to-head products are formed in the photocyclization. Thus on treatment of the mother liquors with P_2O_5 followed by evaporative distillation, an oily anhydride was obtained in good yield, which again exhibited absorption at 5·38 μ and 5·61 μ in the infrared. The non-crystalline diacids present in the mother liquors must therefore be diastereoisomers of the crystalline diacid (VIIIb).

Photocyclization of diacid (VIIb),* m.p. 126—127°; and the corresponding diketone (VIIc),* b.p. 110° (0·05 mm), prepared in 25% yield from the diacid (VIIb) and methyl-lithium, $\lambda_{\max}$ (EtOH) 232 mμ (18,600), $\lambda_{\max}$ 5·95 μ, 6·18; were also carried out and shown to afford only head-to-head products.

Since other unsaturated carbonyl compounds are known to dimerize in both the head-to-head and head-to-tail manner[7] it is not clear why the photocyclization of (VII) leads exclusively to head-to-head products. This is one of the very few acyclic systems studied thus far which affords a cyclization product on irradiation in solution. The cyclic systems, which yield both types of dimerization products, may differ in geometry in the excited state from the acyclic systems. This possible difference in the geometry of the excited state may account for the difference in products observed. The difference in products might also be due to a favoured conformation in the ground state of (VII) which may, of course, not be present in other systems or in intermolecular dimerizations. The fact that both the sensitized and direct irradiation of the diesters (VIIa) yield the same mixture of products strongly implies this reaction is proceeding *via* the triplet state.

(*Received, June 23rd,* 1965; *Com.* 389.)

---

[6] G. Stork and F. H. Clarke, Jr., *J. Amer. Chem. Soc.*, 1961, **83**, 3114.

[7] See, for example, the dimerization of cyclopentenone, P. E. Eaton, *J. Amer. Chem. Soc.*, 1962, **84**, 2344. The dimerization of cyclohexenone is similar, G. S. Hammond and D. H. Valentine, unpublished results.