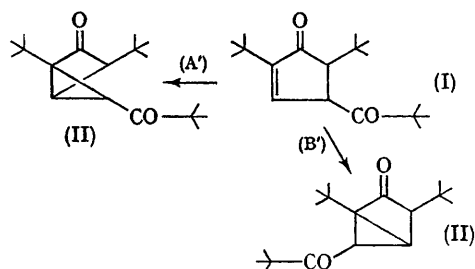


The Mechanism of the Photochemical Formation of Bicyclo[2,1,0]pentan-2-ones

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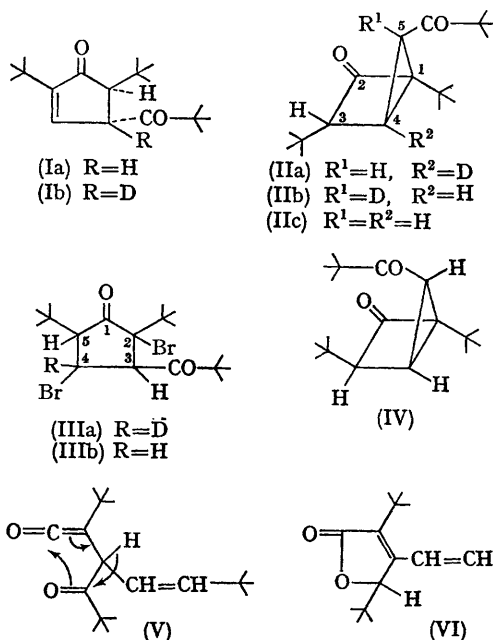
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PREVIOUSLY we have reported¹ the photochemical rearrangement of 2,5-di-*t*-butyl-4-pivaloylcyclopent-2-enones (I) to 1,3-di-*t*-butyl-5-pivaloylbicyclo[2,1,0]pentan-2-ones (II). For this novel photo-reaction, we have suggested two possible mechanisms: (A') process involving a switching of the 4,5 bond and (B') process involving bond formation between the positions 2 and 4 with migration of the pivaloyl group. We now report confirmation for the latter mechanism.



When *trans*-2,5-di-*t*-butyl-4-pivaloylcyclopent-2-enone (Ia)¹ was treated with anhydrous potassium carbonate in MeOD at room temperature overnight and then the mixture was diluted with D₂O, *trans*-4-deuterio-compound (Ib) was obtained. The structure was confirmed by its n.m.r. spectrum in which both 3- (τ 3.35) and 5- (τ 7.66) protons appear as a singlet. Irradiation[†] of this compound yielded a bicyclo[2,1,0]pentan-3-one (IIa) bearing an *exo*-pivaloyl group. Its n.m.r. spectrum shows two singlets at τ 6.85 and 7.88, which appeared to

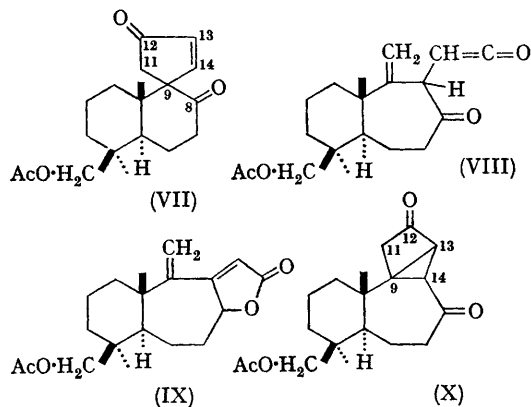
be assigned as the protons at 3- and 5-positions. Since one of these protons of the non-deuteriated compound (IIc) does not couple with an adjacent proton,¹ we could not determine the position of the deuterium atom of (IIa). Therefore, (IIa) was converted into its bromine adduct (IIIa)¹ by treatment with bromine in CDCl₃. The adduct (IIIa)[‡] shows two singlets at τ 6.06 and 6.65, whereas the



[†] Irradiation was carried out in a benzene solution with a 100 w high-pressure mercury lamp (Pyrex filter).

[‡] Compounds (Ia), (IIa), and (IIIa) were obtained as crystals and their m.p.s did not depress on admixture with an authentic sample of corresponding non-deuteriated compounds reported previously (ref. 1).

non-deuteriated adduct (IIIb) shows a quartet (τ 5.46, $J = 6.5$ and 7.5 c./sec., 4-proton) and two doublet (τ 6.06, $J = 7.5$ c./sec. and 6.65 , $J = 6.5$ c./sec.; 3- and 5-protons). This establishes that a deuterium atom is located at 4-position in (IIIa) and accordingly at 4-position in (IIa). These results led us to conclude that the photochemical rearrangement of (Ia) to (IIa) proceeds by the



pivaloyl migration mechanism of type (B'), since (Ia) should form (IIb) by type (A') mechanism.

Recently Burkinshaw and his co-workers² have reported that a spiro-diketone (VII) photochemically rearranges to a butenolide (IX), and they have suggested a keten intermediate (VIII), which can be visualised as proceeding by homolysis of the bonds 11,12 and 8,9 of (VII). We have reported that thermolysis of a stereoisomer (IV) of (IIc) gives a butenolide (VI) which may be formed *via* a keten intermediate (V).¹ If our reaction scheme is applied to the conversion of (VII) into (IX), it can be clearly rationalised as follows. The spiro-diketone (VII) rearranges photochemically to an intermediate (X) by the (B') process with migration of the 8,9-bond. Homolysis of the bonds 9,13 and 11,12 of (X) gives the keten intermediate (VIII), from which (IX) is formed by rearrangement accompanying a hydrogen migration. Other related photo-reactions reported by Burkinshaw and his co-workers² can also be explained by a similar mechanism involving type (B') process.

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¹ T. Matsuura and K. Ogura, *J. Amer. Chem. Soc.*, 1967, **89**, 3850.

² G. F. Burkinshaw, B. R. Davis, and P. D. Woodgate, *Chem. Comm.*, 1967, 607.