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PHOTOCHEMICAL TRANSFORMATION OF ACYLCYCLOPROPENE DERIVATIVES*

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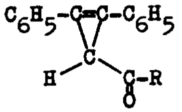
We wish to report the photochemical transformation of some 3-acylcyclopropene derivatives(1) by ultra-violet light.



Ia : $R = C_6H_5$
Ib : $R = CH_3$

Because of its unique structure, there will be several reaction paths in the photo-reaction of cyclopropenylketone (I) in addition to hydrogen abstraction by the keto-group from the solvent(2) and intra or intermolecular oxetane formation(3). First, carbon-carbon bond on one side of a carbonyl group may be cleaved(α-cleavage)(4) and produce a cyclopropenyl radical. Secondly, destruction of the cyclopropene skeleton may take place and produce an acylcarbene and diphenylacetylene, as is observed in the case of

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* Part III of " Cyclopropene Derivatives "
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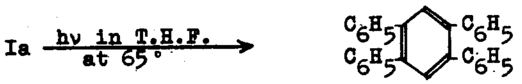
the cyclopropane derivatives(5). In addition, cyclopropene may expand or be opened and give rearranged products(4,6). Finally, cyclopropene may dimerize as an isolated olefin(7) and form a cyclobutane derivative.

It is reported that under the influence of ultra-violet light(8) and also visible light(9), 2,3-diphenylcyclopropenone undergoes α-cleavage to form diphenylacetylene and carbon monoxide in very high yield. No dimeric material has been detected, so far. On the other hand, ultra-violet irradiation of 1,3,3-trimethylcyclopropene-1 in acetone in the presence of benzophenone results in the formation of two isomeric dimers, tricyclo[3,1,0,$0^{2,4}$]hexane derivatives (10). In connection with these observations, the photochemical behavior of the cyclopropenylketone, Ia and Ib was investigated.

Irradiation of Ia by high pressure mercury lamp in tetrahydrofuran produced 1,2,4,5-tetraphenylbenzene(II) in 25.3% yield. The remaining glassy material has not yet been characterized. The structure of II was firmly established by comparison with an authentic sample prepared through a known route(11).



(II)

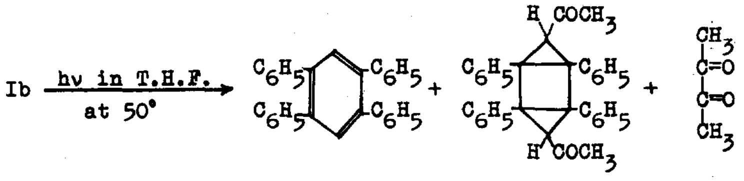
Under the same conditions, Ib gave a new compound III in addition to tetraphenylbenzene(II) and biacetyl(IV). Compound III melted at 285-287° with decomposition. The analytical results were in good agreement with an isomer or dimer of the starting 3-acetyl-1,2-diphenylcyclopropene (Ib). The molecular weight determination of III by the vapor pressure osmometer gave a value of 451(chloroform). Since the molecular weight for Ib is calculated to be 234, compound III must be a dimeric material with a molecular weight of 468.

<u>Anal</u>.Calcd. for $C_{34}H_{28}O_2$: C, 87. 15 ; H, 6.02.
Found : C, 87.13 ; H, 6.10.

In the infra-red region, III exhibited the characteristic absorptions at 1700 cm^{-1} and at 1020 cm^{-1}. The carbonyl stretching frequency observed corresponds to that expected for cyclopropylketone (12). The 1020 cm^{-1} absorption is due to the cyclopropane skeleton(12). Two characteristic peaks at 1840 cm^{-1} and 1685 cm^{-1} observed in the starting ketone(1) disappeared in the product. Therefore, it is clear that no diphenylcyclopropene skeleton is present in compound (III)(13). The ultra-violet absorption spectrum of III showed a broad maximum at 226 mμ(log ϵ 4.21) and a shoulder at 275 mμ(log ϵ 3.74). Again, the characteristic pattern for cyclopropene derivatives(13) disappeared. The proton magnetic resonance spectrum of III exhibited a multiplet (10 hydrogens) at 2.85 τ, a singlet(1 hydrogen) at 4.80 τ and a singlet(3 hydrogens) at 8.25 τ.

Chemically, III did not discolor a solution of potassium permanganate in acetone at room temperature after one hour, whereas <u>cis</u>-stilbene did. Consequently, the structure of III was considered to be 1,2,4,5-tetraphenyl-3,6-diacetyl-tricyclo[3,1,0,0 ^{2,4}]hexane, and not to be the isomeric

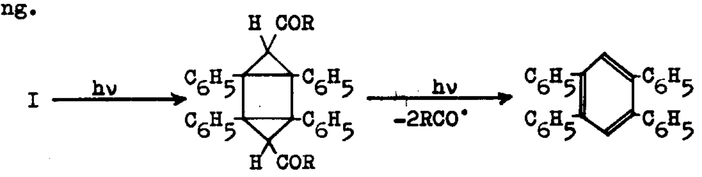
1,2,4,5-tetraphenyl-3,6-diacetylcyclohexa-1,4-diene. The stereochemistry of this compound is not yet known. The yield of II and III were 20.6% and 6.7%, respectively. Later fractions on alumina column chromatography eluted by benzene or ether gave yellow glassy materials and they have not yet been characterized.



(II) (III) (IV)

When III itself was irradiated further under the same conditions, II was obtained in 43.4% yield. In this case glassy materials were also formed. Consequently, compound III is actually the intermediate in the transformation of Ib to II. In other words, the cyclopropenylketone Ib dimerized preferentially to the cyclobutane derivative III. Further irradiation caused α-cleavage and produced a biradical of a tricyclohexane derivative, which then rearranged to benzene derivative.

Breslow reported(14) that an attempt to produce cyclopropenyl radical resulted in the formation of a dimer, biscyclopropenyl. This dimer rearranged to a benzene derivative on heating, by irradiation, or by treatment with potassium amide. In the present case, however, the dimerization occured not through the formation of a cyclopropenyl radical, but through the cycloaddition of the double bond in the cyclopropene. It appears, therefore, that the double bond in a cyclopropene skeleton might be more easily excited than the carbonyl group and formed cyclobutane ring.



(II)

Tricyclo[3,1,0,0^{2,4}]hexanes could be intermediates for the formation of benzene derivatives.

Another interesting possibility for this transformation is that the carbonyl group is absorbing most of the light, but the double bond is doing most of the reaction(15). In the present experiment, however, no evidence is available to decide whether most of the light was absorbed by the carbonyl or by the double bond, because the diphenylcyclopropene system absorbed the light at appreciably longer wave length with the high intensity. More precise consideration of the mechanism will be a subject of further investigation.

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