PHOTOCHEMICAL SYNTHESES

9. THE CONVERSION OF DIBENZOYLMETHANE TO TRIBENZOYLETHANE

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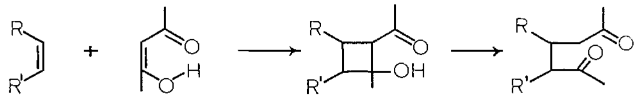
Received July 13, 1964

ABSTRACT

Irradiation of dibenzoylmethane in benzene gives tribenzoylethane. In more concentrated solution a solid dimer (II) separates which, on solution, is converted by dealdolization into an isomer. This isomer (I, R = H) on irradiation, gives tribenzoylethane in a photolytic reaction which has been shown to have some generality. The overall conversion of dibenzoylmethane to tribenzoylethane therefore involves two photochemical and one chemical reactions.

Some time ago, as part of our studies on photochemical cyclo-addition, we reported the reaction between acetylacetone and a number of alkenes and cycloalkenes (1). The main products derived from the process are indicated below.



To ascertain whether the process was general for all enolized β-diketones, we studied the reaction between dibenzoylmethane and cyclohexene. This diketone is largely enolized in hydrocarbon solvents and the reaction could be conveniently followed by observing the formation of the non-enolized benzoyl grouping in the carbonyl region.

The products proved difficult to crystallize and the first substance obtained in crystalline form, from a study of its spectra, evidently did not contain a cyclohexyl residue. This conclusion was confirmed when it was found that the yield was greatly increased (to 37%) by irradiation of dibenzoylmethane in benzene solution.*

The substance showed only benzoyl carbonyl in the infrared spectrum, and the ultraviolet absorption was typical of acetophenones. The nuclear magnetic resonance (n.m.r.) spectrum showed the presence of only three protons other than aromatic hydrogen. These were a doublet (two protons) at τ 6.23 and a triplet (one hydrogen) at τ 3.85. These protons were coupled with $J = 7$ c.p.s. The two protons of the doublet were evidently identical. This required the part structure $\mathrm{{-}CH_2{-}CH}\!<$.

Alkaline hydrolysis of the substance under mild condition gave diphenacyl and benzoic acid (1 mole) as the only isolable products. The substance was therefore identified as tribenzoylethane. The remarkably low-field position of the methine proton is noteworthy.

The mode of genesis of the tribenzoylethane was not immediately obvious, but since two molecules of dibenzoylmethane, at least, were required to participate in its formation the possibility of dimerization at some stage appeared reasonable. Accordingly, the irradiation was performed with a higher concentration of dibenzoylmethane.

Under these conditions the reaction proceeded differently. Although the infrared spectrum of the *solution* appeared to be showing the expected changes, a white crystalline solid separated during the irradiation. This material was separated by filtration and

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**We are indebted to Mr. R. W. Yip for this observation.*

although it initially appeared insoluble in chloroform, it dissolved in a large volume of this solvent from which, after considerable concentration, it could be crystallized on the addition of light petroleum.

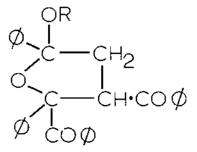
This substance was not tribenzoylethane, but a new substance. Again, the ultraviolet spectrum indicated essentially acetophenone-type absorption. The infrared spectrum showed absorption at 3 400 (hydroxyl), 1 680, and 1 645 cm^{-1}. From this it seemed probable that the absorption at 1 645 cm^{-1} was due to benzoyl carbonyl lowered by hydrogen bonding with the hydroxyl group. The n.m.r. spectrum showed the presence of three protons attached to carbon. These were present as three quartets centered at τ 6.29, 6.17, and 4.57. All three protons were therefore coupled together. This again suggested the $—\mathrm{CH_2}—\mathrm{CH}\!<$ system, where now the methylene protons were not identical.

The n.m.r. spectrum further indicated that the ratio of the ortho hydrogens to meta and para hydrogens (near τ 2.0 and 2.5 respectively) was not that (2:3) expected of benzoyl groups. It appeared to be rather greater than 1:2 which suggested that an isolated phenyl group might be present. Combination of these facts led to the consideration of (I, R = H) as a structure for this new substance.

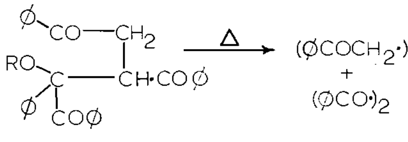
Chemical attempts to confirm this by dealdolization to benzil and diphenacyl were unsuccessful. The desired object was achieved by heating at 195°, when both these substances sublimed away and were obtained in high yield.

In an earlier attempt to dehydrate (I) or to induce dealdolization, the substance was allowed to stand at room temperature in methanol in the presence of a small amount of sulfuric acid. A crystalline product separated which now lacked the hydroxyl group in the infrared spectrum, but which still showed only acetophenone absorption in the ultraviolet.

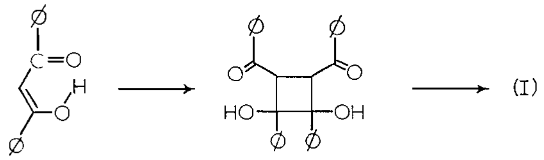
Six protons attached to carbon, other than aromatic protons, were visible in the n.m.r. spectrum. Of these one appeared near τ 4.0 as an apparent triplet and two in the τ 7.0–6.3 region as two quartets centered at τ 7.20 and 7.29. In addition a singlet (three protons) appeared at τ 7.62. No acetyl group or vinyl methyl was possible, and a methoxyl group, despite the impressively high position, seemed inevitable. This was confirmed by the analysis which revealed the presence of one methoxyl group. The structure (I, R = Me) or an alternative, cyclic, structure (IA, R = Me) is possible (and the equivalent IA, R = H may contribute to I) for this molecule; the latter formulation is supported by the ultraviolet extinction.*



(IA)



(I)



(II)

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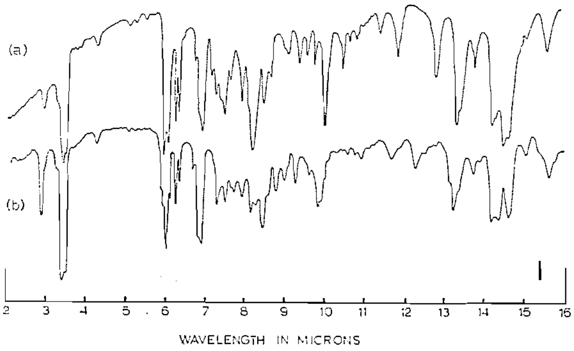
*We are grateful to Dr. R. E. Lutz for informing us of his own relevant observations in similar systems and stressing the likelihood of the cyclic structure.

The structure (I, R = H) could be reasonably derived from a dimer (II) by dealdolization accelerated by relief of strain from the opening cyclobutane ring. At this point the original crystalline precipitate from the irradiation was subjected to closer scrutiny.

As originally obtained it was completely different from (I) in solubility in all solvents. However, once having been dissolved only (I) could be recovered. Hence the wish to examine its properties appeared necessarily subject to a degree of frustration. Its infrared spectrum in Nujol was significantly different from that of (I, R = H) (Fig. 1) and is at least compatible with the formulation (II).

The final step in the sequence was the required conversion of (I, R = H) into tribenzoylethane. In fact, irradiation of (I, R = H) in benzene gave the triketone in 48% yield. The formation of tribenzoylethane from dibenzoylmethane can thus be rationalized.

The photolysis of (I, R = H) was of general interest and was investigated briefly. Since the dibenzoylethyl group attached to the carbon bearing the hydroxyl group should be without special significance, similar cleavage could be expected when this grouping was replaced by some other function.



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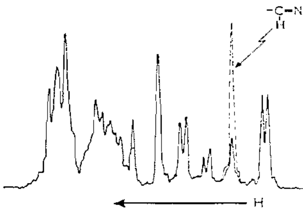

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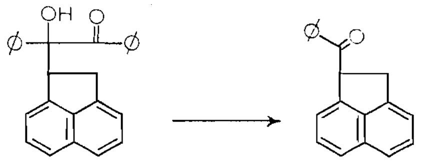
FIG. 1. Infrared spectrum (Nujol mull) of (*a*) alcohol (I) and (*b*) diol (II).

FIG. 2. Nuclear magnetic resonance spectrum of aromatic protons and azomethine proton in benzaldehyde 2,4-dinitrophenylhydrazone and the partially deuterated derivative. Solvent: dimethyl sulfoxide at 103°.

The substituted benzoin (III), itself having been prepared photochemically, was available in these laboratories from other studies (2). Irradiation of this in benzene solution gave benzoylacenaphthene (IV) (2), though in poor yield, and no benzaldehyde. Similar irradiation of benzoin (V, R = H) itself gave benzaldehyde. Irradiation of deuteriobenzoin (V, R = D) gave a mixture of benzaldehyde and (VI) deuteriobenzaldehyde. The location of the aldehydic deuteron was accomplished by a determination of the n.m.r. spectrum (in dimethylsulfoxide at 103°) of the 2,4-dinitrophenylhydrazone when, in the deuterated compound, the azomethine proton (see Fig. 2) was reduced by about 50%. This was confirmed by deuterium analysis. That the deuterium was not lost by exchange through hydrogen abstraction prior to photolysis was shown by brief irradiation, with partial conversion of the deuteriobenzoin. No methine proton was detected in the recovered benzoin.

The presence of the hydroxyl proton is necessary for benzaldehyde formation, but its absence, as in the phenyl ether (3), does not significantly affect the rate of destruction of the benzoin as measured by the disappearance of the methine proton. Hence, assuming the photolytic step is the same in both cases, it is not preceded by hydrogen abstraction

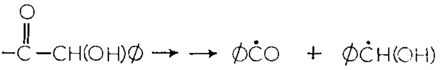


(III) (IV)

(V) (VI)

of the hydroxyl proton. Abstraction of the methine proton is unlikely since this proton is not present in the substituted benzoins already discussed. Furthermore the methine proton, as indicated by deuteration, appears in the same position in the resultant benzaldehyde.

No benzaldehyde in appreciable amount is produced in the substituted benzoins, so it seems likely that after photolysis, the benzyl radicals, by hydrogen transfer, act as



$$\phi\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-CH(OH)}\phi \rightarrow \rightarrow \phi\dot{C}O + \phi\dot{C}H(OH)$$

the only source of benzaldehyde. Such exchange as does occur probably occurs after the initial photolysis.

EXPERIMENTAL

Melting points were determined on the Kofler hot stage and are uncorrected. The term 'petrol' refers to petroleum ether of b.p. 60–80°. The benzene used (thiophene free) was percolated through a column of alumina before use. Infrared spectra were determined in chloroform solution and n.m.r. spectra in deuteriochloroform, unless otherwise stated.

Irradiations were conducted in a water-cooled vycor immersion apparatus of capacity ca. 250 ml under oxygen-free nitrogen, and with magnetic stirring. The light source was a Hanovia 450 W mercury arc and was encased in a pyrex cylinder.

Irradiation of Dibenzoylmethane

(a) A solution of dibenzoylmethane (5 g) in benzene (250 ml) was irradiated for 75 h (until the carbonyl absorption near 6 μ did not appear to be increasing). After evaporation of the solvent the residue was extracted with petrol until the extract was colorless. Evaporation of the petrol extract gave an oil which was dissolved in ethanol, and a solution (0.25 *M*) of 2,4-dinitrophenylhydrazine added until no more precipitate formed. Crystallization from ethyl acetate – petrol gave the 2,4-dinitrophenylhydrazone of benzaldehyde (36 mg, 11%) identical in every respect with an authentic specimen.

The residue remaining after petrol extraction was crystallized from ethyl alcohol to give tribenzoylethane (1.4 g, 37%), m.p. 153–155°, raised to 154–156° on recrystallization. (Lit. (4) 156–157°.) λ_{max} 248 mμ (log ε 4.7).

Anal. Calcd. for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.81; H, 5.72.

A solution of tribenzoylethane (0.21 g) in aqueous sodium hydroxide (0.1 *N*, 50 ml) and ethanol (100 ml) was allowed to stand at room temperature for 17 h. Concentration of the solution gave a precipitate of diphenacyl which on crystallization from methanol (0.11 g, 76%) had m.p. 145–146°. (Lit. (5) 145°, λ_{max} 244 mμ (log ε 4.42).)

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 6.92. Found: C, 80.59; H, 5.78.

Acidification of the aqueous filtrate gave, after isolation with ether and crystallization from water, benzoic acid, m.p. 120–122°, identical in every respect with an authentic specimen.

In a separate experiment titration of the hydrolyzed tribenzoylethane showed the generation of 1 equivalent of acid.

(b) A solution of dibenzoylmethane (30 g) in benzene (250 ml) was irradiated. After 45 h a heavy precipitate (6.3 g) was collected. Irradiation for 24 h more gave a further 4.9 g and prolonged irradiation (67 h) produced 0.9 g. The combined precipitates were washed with petrol and dried *in vacuo* to give a total of 12.1 g (40%), of (II), m.p. 140–141°.

Anal. Calcd. for $C_{30}H_{24}O_4$: C, 80.33; H, 5.39. Found: C, 79.57; H, 5.44.

1-Phenyl-1,2,3-tribenzoylpropan-1-ol (I, R = H)

A solution of (II) (12.1 g) in chloroform (500 ml) was heated under reflux for 1 h. Evaporation to dryness and crystallization from petrol gave the alcohol (I, R = H) (3.6 g), m.p. 138–140°. Admixture with (II) gave a depression of 20°. λ_{max} 250 mμ (log ε 4.46).

Anal. Calcd. for $C_{30}H_{24}O_4$: C, 80.33; H, 5.39. Found: C, 80.64; H, 5.10.

A solution of the alcohol (I, R = H) (45 mg) in acetone (5 ml) and 0.1 *N* sodium hydroxide (20 ml) was heated under reflux for 30 min. Concentration, collection of the precipitate, and crystallization from methanol gave diphenacyl (13 mg, 55%) identical in every respect with the material described above.

Sublimation of the alcohol (I, R = H) (40 mg) at 195° and 1.5 mm gave a yellow oil. Separation by thin-layer chromatography using silicic acid and eluting with chloroform gave diphenacyl (20 mg, 95%), m.p. 145–146°, and benzil (17 mg, 90%), melting point and mixed melting point 93–95°.

1-Methoxy-1-phenyl-1,2,3-tribenzoylpropane (I, R = Me or IA, R = Me)

To a solution of the alcohol (I, R = H) (0.1 g) in methanol (10 ml) concentrated sulfuric acid (2 drops) was added and the mixture allowed to stand. Crystallization occurred within 5 min, but the solution was left for 14 h. Collection of the crystalline precipitate and recrystallization from methanol gave the ether (I, R = Me) (48 mg, 47%), m.p. 189–191°, λ_{max} 252 mμ (log ε 4.32).

Anal. Calcd. for $C_{31}H_{26}O_4$: C, 80.56; H, 5.67; OMe (1), 6.7. Found: C, 80.88; H, 5.84; OMe, 6.21.

Irradiation of 1-Phenyl-1,2,3-tribenzoylpropan-1-ol (I, R = H)

The alcohol (0.114 g) in benzene (250 ml) was irradiated for 12 min. Evaporation of the solution and crystallization from ethanol gave tribenzoylethane (42 mg, 48%), m.p. 153–155°.

Irradiation of α-1-Acenaphthenylbenzoin (III)

A solution of (III) (0.2 g) in benzene (250 ml) was irradiated for 1 h. After evaporation of the solvent the brown residual oil was crystallized twice from methanol (charcoal) to give 1-benzoylacenaphthene (IV) (20 mg, 14%), m.p. 133–135°, identical in every respect with an authentic specimen.

Irradiation of Benzoin

A solution of benzoin (0.5 g) in benzene (250 ml) was irradiated for 70 min. The solvent was evaporated and the residue extracted with petrol. Conversion of the material extracted by the petrol to the 2,4-dinitrophenylhydrazone in the usual way gave the derivative of benzaldehyde (0.13 g, 20%) identical with an authentic specimen in every respect. The residue from the extraction contained material with the same retention time as benzyl alcohol on a 20% Carbowax 20M 6 ft × ¼ in. column at 150°. Calibration of response indicated that it was present to the extent of 4%.

Similar irradiation of α-deuteriobenzoin (0.53 g) gave the 2,4-dinitrophenylhydrazone containing 5.94% excess deuterium.

α-Deuteriobenzoin

Sodium (0.1 g) was added to a mixture of D_2O (99.6%, 3 ml) and dioxan (50 ml), followed by benzoin (2.2 g). The mixture was heated under reflux for 1 h under nitrogen, the solvent evaporated, and the residue redissolved in dioxan (50 ml) and D_2O (3 ml) and again refluxed for 1 h. The cycle of operation was repeated twice more, the mixture being protected from outside moisture throughout. After the final evaporation D_2O (8 ml) was added and the mixture acidified with *N* hydrochloric acid. The benzoin was collected and crystallized from benzene–petrol, m.p. 134–136°. No methine proton could be detected in the n.m.r. spectrum.

Irradiation of α-Deuteriobenzoin

The deuterated benzoin (0.13 g) was irradiated in benzene (250 ml) for 5 min. Evaporation of the solvent and crystallization from petrol gave recovered deuteriobenzoin (0.05 g, 39%). Irradiation of benzoin phenyl ether and benzoin in comparable concentrations (100 mg, 250 ml) in benzene showed approximately the same rate of disappearance of the methine hydrogen, as followed by n.m.r. Disappearance was complete in about 30 min.

ACKNOWLEDGMENTS

The authors are indebted to the A.F.O.S.R. for support of this research under grant AF-AFOSR-61-6. They thank Mr. R. E. Klinck and Mr. D. Ross for the n.m.r. spectra.

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