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PHOTOINDUCED REACTIONS—XX

THE PHOTOPINACOLIZATION OF CERTAIN 1,4-DIKETONES.[1] †

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Abstract—UV irradiation (> 280 mμ) of acetonylacetophenone (I) in isopropyl alcohol yielded two products, ketone A $C_{22}H_{24}O_3$ and a neutral compound $C_{28}H_{38}O_4$, for which the structures II and III were assigned, respectively. These compounds are the secondary products from two stereoisomeric pinacols. Acid hydrolysis of III gave ketone B (IV), a stereoisomer of II. The stereochemical structures of these compounds were assigned as IIa, IIIa, and IVa. IIa has *meso*-configuration in the pinacol moiety of the molecule, whereas both IIIa and IVa have DL-configuration. Irradiation of I in n-hexane or benzene yielded a mixture of IIa and IIIa. Photolysis of 1,2-dibenzoylethane in isopropyl alcohol gave a more complex result yielding a mixture of oligomeric products.

ALTHOUGH the photochemical reactions of several types of 1,4-diketones, for example 1,2-dibenzoyl olefins,[2–6] 1,2-dibenzoylcyclopropane,[7] dibenzoylstilbene episulfide,[4] and *o*-dibenzoylbenzene,[8] have been reported, little attention has been drawn to photochemical reactions of 1,4-diketones of the type —CO—CH_2—CH_2—CO— in which two C atoms between CO groups are fully saturated. Acetonylacetophenone (I) and 1,2-dibenzoylethane (VIII) were chosen as the starting materials for the present photochemical study. In the beginning of our investigation, three possible courses which might occur in the photolysis of such 1,4-diketones were taken into consideration; (i) formation of a 1,3,5,7-tetrahydroxycyclooctane by double photopinacolization, (ii) formation of a cyclopropanol by intramolecular hydrogen abstraction, and (iii) formation of a 3-hydroxycyclopentanone by intramolecular hydrogen abstraction from the Me group in the case of I. However, photoproducts isolated from I were found to be secondary products resulting from simple photopinacols.

When a solution of acetonylacetophenone (I) in isopropyl alcohol was irradiated with a high-pressure mercury lamp (Pyrex filter) under nitrogen atmosphere, two crystalline products, ketone A $C_{22}H_{24}O_3$ in 56% yield and a neutral compound $C_{28}H_{38}O_4$, designated as compound C, in 8% yield, were obtained. The molecular formula of ketone A was confirmed by the appearance of the parent peak at *m/e* 336 in its mass spectrum. The IR spectrum showed a saturated CO band at 1710 cm^{-1} but no OH band. Bands at 1200–1000 cm^{-1} regions suggest that ketone A may possess ether linkages. The presence of a ketone group was confirmed by its transformation to a monosemicarbazone and a monoxime. The NMR spectrum of ketone A consists of two singlets at τ 8·30 and 8·13, a multiplet centered at τ 2·70, and complex signals centered at τ 8·17, with peak area ratio 6:10:8, corresponding to two Me groups,

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either $-\mathrm{COCH_3}$ or $-\mathrm{O}-\overset{|}{\mathrm{C}}(\mathrm{CH_3})-\mathrm{O}-$, two Ph groups, and eight aliphatic protons, respectively. Thus, structure II was assigned for ketone A.

Of the two CO groups in acetonylacetophenone (I), the benzoyl CO is considered to be more reactive than the acetyl CO under irradiation conditions employed. Although the n,π^*-absorption maximum of the CO groups of I could not be detected because of overlapping with a strong π,π^*-absorption of the benzoyl group, an n,π^*-maximum should be around 320 mμ for a benzoyl CO and below 280 mμ for an acetyl CO. Therefore, the photopinacolization of I with the light through a Pyrex filter should lead to a pinacol V which then cyclizes to its intramolecular ketal II.

Compound C is very sensitive to acids. On treatment with dilute hydrochloric acid or even with silica gel, it gave ketone B (IV) isomeric to ketone A (II) by the loss of six C atoms. The NMR spectrum of ketone B is very similar to that of II and consists of two singlets at τ 8·14 and 8·03, a multiplet centered at τ 3·1, and complex signals centered at τ 7·6. The fragmentation pattern in its mass spectrum was virtually identical to that of II. These results indicate that ketone B is diastereomeric to ketone A (II), and that the structure of ketone B should be represented as a 2-dimensional formula IV (= II).

In general, the photopinacolization of unsymmetrical ketones gives a diastereomic mixture of pinacols, DL and *meso*.[†] Thus, stereostructure IIa (*meso*) or IVa (DL) is possible for ketone A or B.

Ketone A exhibits a distinct shoulder around 225 mμ in its UV spectrum, while ketone B does not (Fig. 1). Since it is known that an interaction between π-orbitals of two non-conjugated benzene rings in a molecule causes an extra UV band at 220–250 mμ in addition to normal benzenoid absorption,[9] ketone A should be represented by formula IIa with *meso*-configuration and therefore ketone B by formula IVa with DL-configuration. In fact, inspection of Dreiding stereomodels demonstrates that the dihedral angle of two Ph—C bonds is about 30° in IIa and about 60° in IVa, showing that π-orbitals of these two Ph groups are enough close to interact each other in IIa but not in IVa. As will be discussed below, stereochemistry of compound C, which can be converted to ketone B under mild acidic conditions, also supports the above assignments.

Compound C shows neither OH or CO band in its IR spectrum. The NMR spectrum exhibits a singlet (6 protons, two Me's) at τ 8·90, two doublets (12 protons) at τ 9·65 (J = 6 c/s) and τ 9·05 (J = 6 c/s), and a diffused septet (2 protons) at τ 6·15 (J = 6 c/s), in addition to multiplet peaks of ten aromatic protons and eight aliphatic protons. The doublets and the septet indicate the presence of two non-equivalent i-Pr groups, one of which is highly shielded probably by a benzene ring in the molecule. The instability of compound C under acidic conditions leading to ketone B suggests that it has isopropyl ketal moieties. In fact, recrystallization of III from ethanol gave a mixture of ketone B and a diethyl ketal VIa. Acid hydrolysis of this mixture yielded ketone B as a sole product. The NMR spectrum of the mixture shows, in addition to peaks attributed to ketone B, two triplets at τ 9·35 (J = 7 c/s) and 8·79 (J = 7 c/s) and two quartets at τ 6·28 (J = 7 c/s) and 6·38 (J = 7 c/s). These signals indicate the

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[†] See a previous paper (Part XIX)[1] and Refs cited therein.

[‡] One enantiomeric structure is given for each formula.

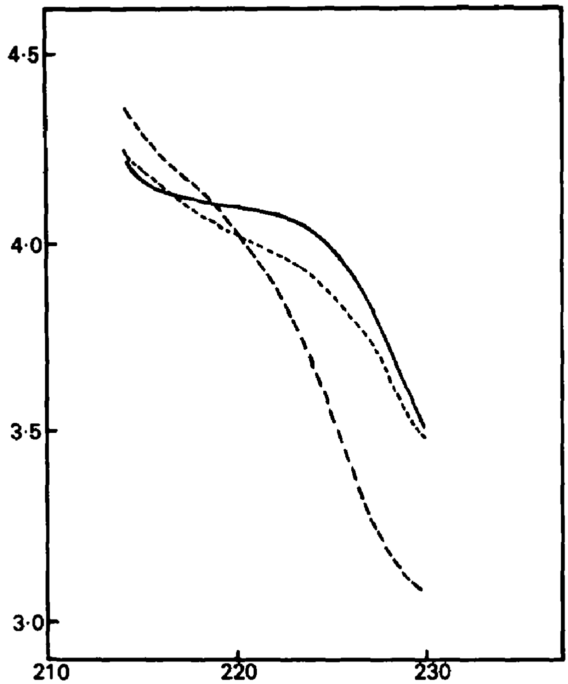
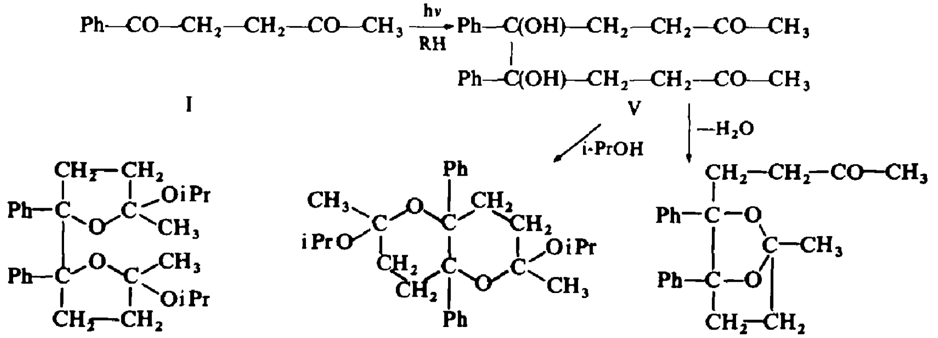


FIG. 1 UV spectra of ketone A (———), ketone B (– – – –), and compound C (··········) in EtOH.

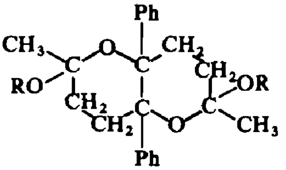
presence of two OEt groups, one of which is again highly shielded. In the case of VIa, the signals of two Me groups appear as two singlets at τ 8·80 and 8·65 in contrast to compound C which possesses two equivalent methyls.

In a similar way, compound C was converted to a mixture of ketone B and a dimethyl ketal VIb. The NMR spectrum of the mixture exhibits, in addition to peaks attributed to ketone B, a singlet at τ 6·92 corresponding to two methoxyls and a singlet at τ 8·80 corresponding to two equivalent methyls. The transformation of compound C into VIa and VIb can be easily rationalized by replacement of the i-OPr groups of compound C with OEt and OMe groups, respectively. The above results led us to assign a 2-dimensional structure III for compound C. An alternative structure VII for compound C is difficult to explain facts that compound C and its ethoxy analogue (VIa) possess two non-equivalent i-Pr and Et groups, respectively.

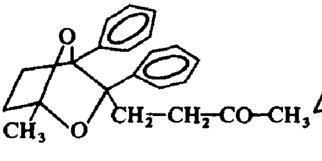
Stereochemistry of compound C was deduced from its UV and NMR spectral data. The UV spectrum of compound C shows a shoulder around 225 mμ with a lower extinction coefficient than that of ketone A (Fig. 1). As been discussed above, the shoulder indicates that π-orbitals of two Ph groups of compound C overlap each other. Thus a 3-dimensional structure with a *cis* ring fusion, in which two Ph groups have equatorial and axial conformations with respect to one of the pyrane rings, respectively, is assigned, as formula IIIa or its conformer IIIb. There are several reports[10] which demonstrate that in the NMR spectrum of certain compounds two methyls of a i-Pr group appear non-equivalent. However, since the NMR spectrum of the diethyl ketal VIa also exhibits two non-equivalent methyls of OEt groups, it is more reasonable to consider that, as shown in formula IIIa, two alkoxy and also the diethyl ketal groups in compound C have different configurations; namely one is axial and the other is equatorial. In summary, it can be concluded that ketone A might be formed from the *meso*-pinacol of I and ketone B and compound C from the DL-pinacol.



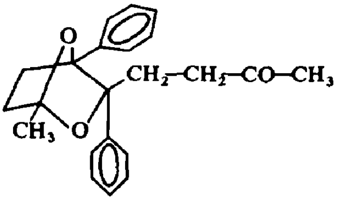
I V VII III II, IV



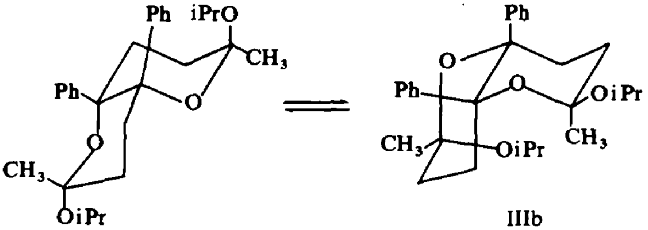
VIa: R = Et
VIb: R = Me



IIa (*meso*)



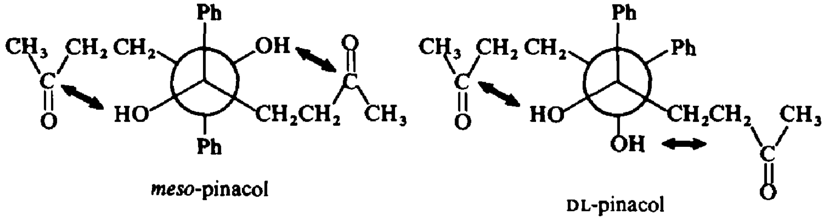
IVa (DL)



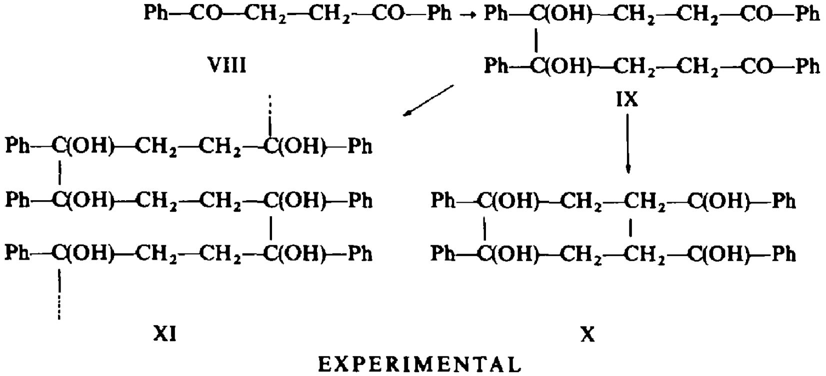
IIIa IIIb

When acetonylacetophenone (I) was irradiated in n-hexane which is considered to be a poor hydrogen donor in photoreduction of CO compounds, ketone A (IIa) and ketone B (IVa) were obtained in 15·5 and 4·5% yields, respectively, in addition to some polymerized products. On the other hand, on irradiation of I in benzene, which is inert as a hydrogen donor, I reacted very slowly to afford IIa (14·6%), IVa (7·3%), and biphenyl (48%) in addition to the unreacted I. In the latter case, the starting material itself probably acts as a hydrogen donor for the photopinacolization of I leading to IIa and IVa. The formation of biphenyl is better rationalized by a photochemical cleavage of Ph—CO bond of I rather than by a hydrogen abstraction by the triplet state of I from benzene.

It is clearly demonstrated that the DL:*meso* ratio of pinacols, which are formed as the primary products and lead to the secondary products, IIa, IIIa, and IVa, is dependent upon the solvent employed. The ratios are 1:7 in isopropyl alcohol, 1:3·5 in n-hexane, and 1:2 in benzene. As been discussed in a previous paper,[1] the DL:*meso* ratio of pinacols in the photopinacolization of simple unsymmetric aromatic ketones has been found to be nearly 1:1. Therefore, in the case of I the acetyl groups on the side chain may play an important role for the preferred formation of a *meso*-isomer, and the solvent effect is also important. In the photopinacolization of I, intermolecular interactions between the CO and the OH groups might be of importance in deciding the preferred orientation of the intermediate radicals just prior to dimerization.† In such cases, the *meso*-pinacol is expected to be predominant over the DL-pinacol which is more crowded by a gauche conformation of two Ph groups as shown below.



Finally, the photopinacolization of 1,2-dibenzoylethane (VIII), which possesses two equivalent CO groups in the molecule, was also investigated. Irradiation of VIII in a 1:1 mixture of isopropyl alcohol and benzene resulted in a complex mixture of products from which a crystalline compound was isolated in a low yield. The major part of the products consisted of a mixture of oligomers. The crystalline compound is supposed to be a dimeric product which might be formed by dehydration of a cyclooctanetetraol X. The major pathway would be the formation of oligomers XI and their dehydration products, which could be formed by subsequent intermolecular pinacolizations of the primary pinacols IX.



EXPERIMENTAL

Irradiation was made with a 450-W high-pressure mercury vapor lamp (Ushio Type UM 450) surrounded by a Pyrex cooling jacket under bubbling N_2.

Acetonylacetophenone (I). This compound was prepared according to the procedure described by Helberger,[12] except that levulinic acid chloride was purified by vacuum-distillation at 85–90°/35 mm.

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† Similar arguments have been recently discussed in the case of the photopinacolization of *p*-substituted acetophenones in which intermolecular hydrogen bonding between the OH groups of two ketyl radicals is considered to play an important role.[11]

Photolysis of acetonylacetophenone (I) *in isopropyl alcohol*

A soln of 5·10 g of I in 450 ml i-PrOH was irradiated under cooling with water, until the starting material was not detected by VPC (5 hr). The reaction mixture was concentrated to about 150 ml and allowed to stand in a refrigerator overnight. Crystals separated were collected by filtration (532 mg; 8%) and recrystallized from i-PrOH to give compound C (III) as fine leaflets, m.p. 160–170° (dec). (Found: C, 75·92; H, 8·80. Calc. for $C_{28}H_{38}O_4$: C, 76·67; H, 8·73%). The compound was so unstable under air atmosphere that it easily changed to a mixture of III and II.

The filtrate was concentrated to deposit ketone A (II) as crystals (0·78 g) which were collected by filtration. Evaporation of the filtrate gave 3·80 g of a brown liquid which was dissolved in $CHCl_3$ and passed through a column containing silica gel. Elution with $CHCl_3$ yielded crystals of ketone A (II). The total yield of II was 2·73 g (56%). Recrystallization from n-hexane gave colorless prisms, m.p. 117°. (Found: C, 78·51; H, 7·43. Calc. for $C_{22}H_{24}O_3$: C, 78·34; H, 7·19%). On recrystallization from methanol, II did not change.

Oxime of ketone A (II). To a soln of 100 mg of II in 30 ml MeOH was added a soln of 70 mg hydroxylamine hydrochloride and 100 mg NaOAc in 10 ml water. The mixture was heated at reflux for a few min, then allowed to stand overnight. Concentration of the mixture deposited crystals which were recrystallized from aqueous MeOH to give 85 mg of the oxime. Several recrystallizations gave 23 mg of prisms, m.p. 124°; IR spectrum: 3250 cm^{-1} (N—OH) and no CO band. (Found: C, 74·84; H, 7·68; N, 3·81. Calc. for $C_{22}H_{25}NO_3$: C, 75·18; H, 7·17; N, 3·99%).

Semicarbazone of ketone A (II). The semicarbazone was prepared in a similar manner to the preparation of the oxime. Recrystallization of the product from aqueous MeOH gave fine crystals, m.p. 122°. (Found: C, 70·18; H, 7·66; N, 10·39. Calc. for $C_{23}H_{27}N_3O_3$: C, 69·49; H, 7·86; N, 10·57%).

Hydrolysis of compound C (III) *to ketone B* (IV)

A soln of 100 mg of III in 30 ml benzene was mixed with 1 g silica gel powder and allowed to stand at room temp overnight. The silica gel was filtered off and washed with MeOH, and the filtrate was evaporated to give 90 mg of crystals. Recrystallization from pet. ether gave 56 mg of IV as needles, m.p. 100–100·5°. (Found: C, 78·74; H, 7·04. Calc. for $C_{22}H_{24}O_3$: C, 78·34; H, 7·19%).

This compound was also obtained by mild acid treatment of III. To a soln of III in benzene was added a few drops of dil HCl and the mixture was allowed to stand overnight. The mixture was washed with $NaHCO_3$ aq, then with water, and evaporated to give a residue, the IR spectrum of which was identical with that of IV obtained above. On recrystallization from MeOH IV was recovered unchanged.

Alcoholysis of compound C (III)

(a) *With ethanol.* Recrystallization of 450 mg of III from EtOH gave 230 mg of needles, m.p. 160° (dec). The NMR spectrum indicated that the product is a mixture of VIa and IV in about 1:1 ratio.

(b) *With methanol.* Recrystallization of 100 mg III from MeOH gave 44 mg of plates, m.p. 120° (dec). The NMR spectrum showed that the product is a mixture VIb and IV in about 8:3 ratio.

Photolysis of acetonylacetophenone (I) *in n-hexane*

A soln of 5·39 g acetonylacetone in 500 ml n-hexane was irradiated as described above. During irradiation a ppt deposited on the walls of the reaction vessel. After 53 hr the starting material was not detected by VPC. The reaction mixture was filtered from a light brown ppt (0·41 g) which were polymerized material. The filtrate was concentrated under red press at room temp. The distillate was found to be almost n-hexane by VPC analysis. The VPC analysis of the residual liquid (4·80 g) showed more than 10 peaks. The residual liquid was distilled *in vaccuo* (10^{-3} mm) to give 3 fractions; (i) b.p. 32–100°, 2·01 g, (ii) b.p. 110°, and (iii) brown residue, 1·03 g. The fraction (ii) was agitated in pet. ether, and colorless crystals (0·55 g) separated were collected by filtration, which were identified as IIa by IR. The filtrate and the fraction (i) were combined and passed through a column containing 20 g of neutralized alumina. Elution with benzene–pet. ether (1:1) yielded 0·43 g of crystals, which by NMR analysis were estimated to consist of a 1:1 mixture of the ketones II and IV. The total yields of II and IV were 15·5% and 4·5% respectively.

Photolysis of acetonylactophenone (I) *in benzene*

A soln of 1·03 g of I in 450 ml benzene was irradiated as described above. After 132 hr about half amount of the starting material remained unreacted. The mixture was evaporated to give 1·13 g of a reddish brown oil, which was dissolved in benzene and passed through a column containing 35 g silica gel. Elution with benzene yielded 103 mg of crystals, which were identified as biphenyl (by IR). Elution with benzene-chloroform yielded 117 mg of crystals, which by NMR analysis were esitmated as a 2:1 mixture of II and IV. Further elution with the same solvent mixture yielded 470 mg of the starting material. The yields of biphenyl, II and IV were calculated as 48, 14·6, and 7·3% on the basis of the reacted I.

Photolysis of 1,2-*dibenzoylethane* (VIII) *in* 1:1 *benzene–isopropyl alcohol*

A soln of 4 g of VIII in a mixture of 200 ml benzene and 200 ml i-PrOH was irradiated for 10 hr, until no CO band was detected by IR analysis of the reaction mixture. Insoluble crystals (56 mg) deposited during irradiation were collected by filtration. The crystals did not melt at 280°; IR spectrum: ca. 3400 cm^{-1} (OH) and no CO band. (Found: C, 83·65; H, 6·44. Calc. for $C_{32}H_{30}O_3$: C, 83·09; H, 6·35%). Concentration of the filtrate deposited the same substance as crystals (70 mg).

The filtrate from the crystals was evaporated and the residue was chromatographed on 140 g silica gel. Elution with benzene–$CHCl_3$ and $CHCl_3$ gave two fractions, (i) 1·15 g of a viscous liquid and (ii) 1·8 g of a solid. Rechromatography of the fraction (i) yielded 658 mg of a crystalline material which did not show a clear m.p. Mol. wt (Rast method: crystals from fraction (i) 513; fraction (ii) 857) and TLC analyses showed that both fractions are a complex mixture of oligomeric products.

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