*Tetrahedron.* Vol. 24, pp 6149 to 6156. Pergamon Press 1968 Printed in Great Britain

# PHOTO-INDUCED REACTIONS—XVI

## PHOTOPINACOLIZATION OF TRIKETOINDANE DERIVATIVES[1,2]

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(*Received in Japan* 19 *March* 1968; *Received in the UK for publication* 21 *May* 1968)

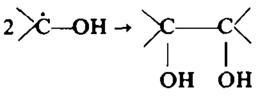
**Abstract**—The photochemical reaction of triketoindane and its derivatives in various solvents has been investigated. It was found that hydrindantin is the major product from the photochemical reactions of, (i) triketoindane hydrate (ninhydrin) in water, (ii) the isopropyl alcohol adduct of triketoindane in isopropyl alcohol or in benzene, and (iii) the t-butyl alcohol adduct of triketoindane in t-butyl alcohol. Irradiation of an aqueous solution of alloxan hydrate also affords a corresponding pinacol, alloxanthin. During the course of the reactions (ii) and (iii), the formation of acetone was observed. The above results indicate that the photopinacolization of triketoindane does not involve photoreduction processes but proceeds by a homolytic cleavage of C—O single bond in its hydrate (ninhydrin) and hemiketal (alcohol adducts) at the C-2 position.

TRIKETOINDANE (I) undergoes photopinacolization in isopropyl alcohol to yield hydrindantin (II).[3] This reaction has been classified[4] as photoreduction of carbonyl compounds which lead to pinacols as represented generally in Eqs. 1–4.[5] In this paper, however, we present evidence supporting that the photopinacolization of triketoindane in isopropyl alcohol is a photocleavage reaction of an α-substituted ketone (Eq. 5) as elaborated by the Swiss investigators.[6]

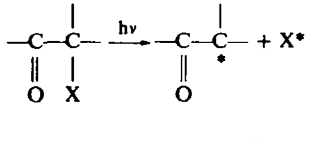
$$>C{=}O \xrightarrow[n,\pi^*]{h\nu} >\dot{C}{-}\dot{O} \tag{1}$$

$$>\dot{C}{-}\dot{O} + Me_2CHOH \rightarrow >\dot{C}{-}OH + Me_2\dot{C}{-}OH \tag{2}$$

$$>C{=}O + Me_2\dot{C}{-}OH \rightarrow >\dot{C}{-}OH + Me_2C{=}O \tag{3}$$



$$2>\dot{C}{-}OH \rightarrow >\underset{OH}{C}{-}\underset{OH}{C}< \tag{4}$$



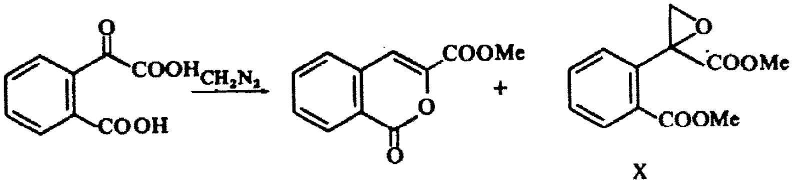
$$-\underset{O}{\overset{\|}{C}}-\underset{X}{C}- \xrightarrow{h\nu} -\underset{O}{\overset{\|}{C}}-\overset{|}{\underset{*}{C}}- + X^* \tag{5}$$

X = OH, —OR etc * = · or +/−

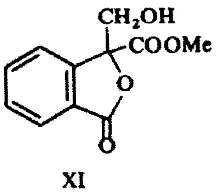
Triketoindane (I) is easily hydrated to give a monohydrate, ninhydrin (III), which possesses a partial structure —CO—C(OH)$_2$— similar to Eq. 5. Therefore, the photolysis of ninhydrin may cause a cleavage at the C—OH bond to give the hydroxyl radical and 2-(2-hydroxy-1,3-diketo)indanyl radical (IV) which will couple with another molecule of IV to form hydrindantin (II).

When an aqueous solution of ninhydrin (III) was irradiated with a high-pressure mercury lamp (Pyrex filter) under nitrogen, hydrindantin (II) was deposited as crystals (58%) in the course of the reaction. The mother liquor from hydrindantin contained a mixture of acidic products from which o-phthalaldehydic acid (V), phthalic acid (VI), phthalonic acid (VII), and phthalide-3-carboxylic acid (VIII) were isolated by column chromatography in 2·5%, 3·1%, 4·9%, and 2·4% yields, respectively. Methylation of the mixture of acidic products with diazomethane followed by the separation of the reaction mixture yielded two esters, $C_{11}H_{10}O_4$ (IX, 3%) and $C_{12}H_{12}O_5$ (X, 17·8%) in addition to dimethyl phthalate (9·3%). The structure of the first ester was assigned as methyl isocoumarin-3-carboxylate (IX) from its spectral properties and was established by an independent synthesis.[7]

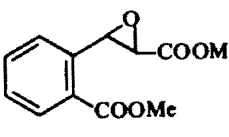
The molecular formula $C_{12}H_{12}O_5$ for the second ester was confirmed by the molecular peak (*m/e* 236) of its mass spectrum. IR bands at 1745 and 1710 cm$^{-1}$ and an UV maximum at 229 mμ (ε 14,800) suggest the presence of two ester groups, conjugated and and non-conjugated. Its NMR spectrum shows a multiplet, of four aromatic protons at τ 1·8–2·7, two singlets of two methoxycarbonyl groups at τ 6·12 and 6·30, and an AB quartet at τ 6·28 and 7·10 ($J$ = 6 c/s). Two possible structures X and Xa can be deduced from the above spectral data and from the fact that it gives a positive epoxide test.[8] Acid-hydrolysis of the ester followed by methylation of the resulting acid gave a hydroxy ester $C_{11}H_{10}O_5$ which shows IR bands at 3500, 1770, and 1750 cm$^{-1}$ assigned for an OH group, a γ-lactone, and a saturated ester, respectively. The NMR spectrum of the hydroxy ester shows signals of four aromatic protons, a methoxycarbonyl group, and a primary.alcohol group, $>\!C\!<\!—CH_2OH$;[9] a broad OH signal at τ *ca.* 7·1 and an AB quartet at τ 5·62 and 5·99 ($J$ = 12 c/s) in chloroform and a triplet at 4·38 ($J$ = 6·5 c/s) and two quartets at τ 5·75 and 5·99 ($J$ = 6·5 and 12 c/s) in DMSO. The results eliminate structure Xa for the ester $C_{12}H_{12}O_5$ which should give a hydroxy ester having a secondary alcohol group. Thus, structures X and XI were assigned for the second ester and the hydroxy ester respectively. It should be noted that ester XI can be obtained by the methylation of phthalide-3-carboxylic acid (VIII) with diazomethane.*



VII IX X



XI



Xa

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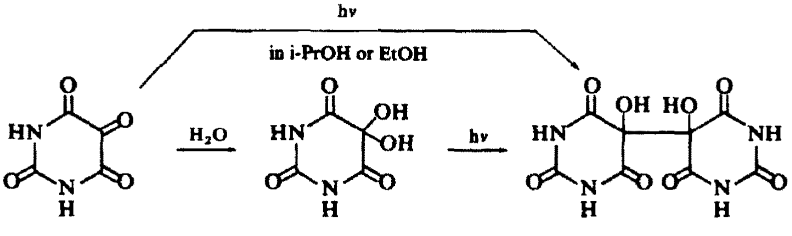
* This unusual reaction was found independently by Inoue *et al.*[11]

Reaction of phthalonic acid (VII) with diazomethane gave a mixture of esters IX and X with various product ratios depending upon conditions employed. The formation of these two esters IX and X from VII can be rationalized as the insertion of methylene into the C—O bond of the ketone group and C—C bond of the benzoyl group in VII, respectively.

The above results are summarized as follows: the photolysis of ninhydrin (III) gave hydrindantin (II, 58%), *o*-phthaladehydric acid (V) 2·5%), phthalic acid (VI, 9%), phthalonic acid (VII, 21%), and phthalide-3-carboxylic acid (VIII, 2·4%), and the material balance is good as 93%.

Although it is known that alloxan (XII), a 1,2,3-triketone, on irradiation in isopropyl alcohol or in ethanol gives a corresponding pinacol, alloxanthin (XIII),[10] we also found that irradiation of an aqueous solution of alloxan hydrate (XIV) afforded alloxanthin (XIII) in 76% yield. The photochemical pinacol formation from ninhydrin and alloxan hydrate in water has been found independently by Otsuji *et al.* who have given some detailed accounts on the latter case.[12]



XII XIV XIII

These observations can be rationalized by a homolytic cleavage of C—OH bond in the hydrate form of both 1,2,3-triketones, as shown in Eq. 5.* The outline of our proposed mechanism for the photochemical reaction of ninhydrin is shown in Chart I. The homolytic cleavage of C—OH bond (path a) in the excited ninhydrin molecule, probably via n, π* transition,[6] results in fragmentation into the hydroxyl radical† and a ketyl radical IV. Two molecules of IV then couple to form hydrindantin (II). On the other hand, the Norrish type I cleavage of α-bond of the excited carbonyl group leads to a biradical XV which may be the precursor of the minor reaction products (path b).‡ Phthalide-3-carboxylic acid (VIII) is formed by the recyclization of XV in its oxygen radical form (XVa). Quite similar reactions have been observed in the photochemical rearrangement of various non-enolizable 1,3-diketones.[14] The attack of two molecules of the hydroxyl radical to the biradical XV leads to phthalonic acid (VII). Further cleavage of α-bond of another carbonyl group in XV followed by the rearrangement of the resulting biradical (XVI) gives a diketene intermediate XVII. The diketene XVII is hydrated to form *o*-phthaladehydic acid which is finally oxidized to phthalic acid (VI).

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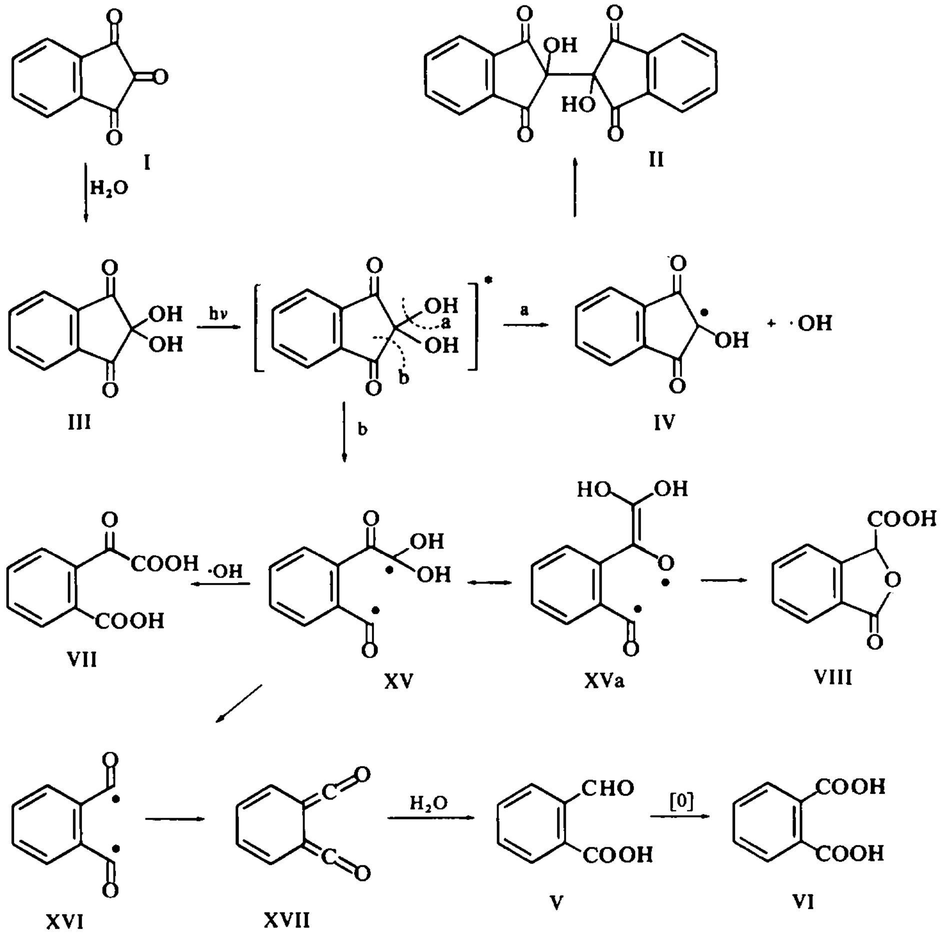
* The same conclusion has been given by Otsuji and his collaborators.[12]

† Otsuji *et al.* have reported that the hydroxyl radical produced during the photolysis of alloxan hydrate can be trapped with benzoic acid which is transformed to salicylic acid.[11]

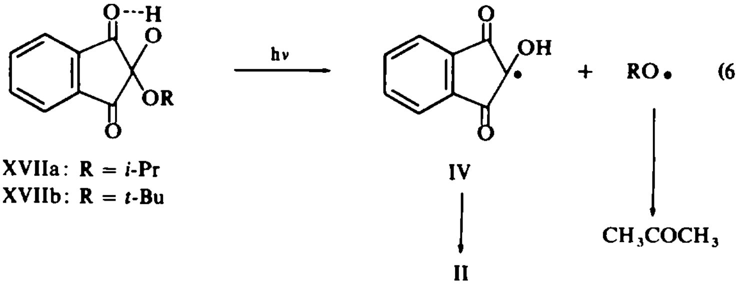
‡ A similar α-cleavage in the photolysis of acyclic vicinal triones has been reported.[13]

Chart 1



We now describe the photopinacolization of triketoindane in hydrogen-donating protic solvents. Although Schönberg and Moubasher reported that red crystals of triketoindane dissolve in isopropyl alcohol under the influence of light to give a pale yellow solution, we have found that triketoindane dissolves in the same solvent in the dark to yield a crystalline isopropyl alcohol adduct. The adduct shows UV absorption bands at 227·5 mμ (ε 13,400) and 248 mμ (shoulder), which indicate the presence of the 1,3-indanedione structure.[15] The IR spectrum shows bands at 3400 (OH), 1760 (non-bonded 5-membered ketone), and 1730 cm$^{-1}$ (bonded 5-membered ketone). It exhibits NMR signals of four aromatic protons at τ 1·9–2·2 (multiplet), a hydroxyl proton at 5·25 (s), and an isopropoxy group at 5·18 (septet, $J$ = 6 c/s) and 8·82 (d, $J$ = 6 c/s). The adduct gradually loses isopropyl alcohol in a dry atmosphere to revert to triketoindane. From the above results, a hemiketal structure XVIIa was given for the isopropyl alcohol adduct.

Irradiation of the adduct XVIIa in isopropyl alcohol gave hydrindantin (II) in 72·6% yield and the simultaneous formation of acetone was observed. When the adduct XVIIa was irradiated in benzene, hydrindantin (II, 18·6%) and acetone were also obtained together with several other products. The results can be explained by a homolytic cleavage of C—O*i*-Pr bond in XVIIa leading to the 2-(2-hydroxy-1,3-diketo)indanyl radical (IV) and the isopropoxyl radical as shown in Eq. 6.



(6)

XVIIa: R = *i*-Pr
XVIIb: R = *t*-Bu

Another possible, but unlikely explanation for this photopinacolization is an actual photoreduction process (as Eq. 1–4) of triketoindane (I), which is produced from an equilibrium, XVIIa ⇌ I + i-PrOH. This alternative process was eliminated by the following experiment. Treatment of triketoindane in boiling t-butyl alcohol resulted in gradual dissolution giving a pale yellow solution. Concentration of the resulting solution deposited a crystalline adduct which was unstable under dry conditions to lose t-butyl alcohol. Although the adduct could not be isolated in a pure form, there is no doubt that its structure is represented by formula XVIIb. Irradiation of a solution of the t-butyl alcohol adduct XVIIb in t-butyl alcohol gave again hydrindantin in 31% yield, and acetone was detected from the reaction mixture.

It is also possible that hydrindantin was formed by the photoreduction of triketoindane (I) which was produced from an equilibrium, XVIIb ⇌ I + t-BuOH. However, t-butyl alcohol is generally considered to be inert as a hydrogen donor in photoreduction, and even in cases when it can donate hydrogen it does so inefficiently.[16] Since hydrogen is abstracted from methyl groups in t-butyl alcohol when it acts as a hydrogen donor, 2,5-dimethyl-2,5-hexanediol must be formed in photoreduction.[17, 18] In our case, we could not detect 2,5-dimethyl-2,5-hexanediol by careful gas chromatography of the photolyzed mixture, but acetone was detected.

Therefore, it should be concluded that the photochemical formation of hydrindantin (II) from triketoindane and its alcohol adducts in alcoholic solvents is initiated by the homolytic cleavage of C—OR bond in the alcohol adducts as shown in Eq. 6. This type of reaction provides the photochemical cleavage of O—H bond in alcohols, although indirectly.

## EXPERIMENTAL

M.ps are uncorrected. Irradiations were made using a 100 w or a 450 w high-pressure mercury lamp (Ushio UM 100 or UM 450) with a water-cooled Pyrex jacket under $N_2$, unless otherwise indicated. NMR spectra were taken with a Japan Electronic Co. spectrometer, Model 3H-60 (60 Mc). UV spectra were taken with a Shimazu recording spectrometer, Model SU-50. IR spectra were taken with JASCO recording spectrometer, Model DS-402G.

*Irradiation of ninhydrin* (III) *in water.* Ninhydrin (5 g) in water (1 l.) was irradiated (450 w lamp) for 5 hr. Solids deposited were collected by filtration and recrystallized from acetone to give fine crystals, m.p. 243°, which were identified as II[3] by IR. The yield amounted to 2·62 g (58%). The filtrate was evaporated *in vacuo* to leave a semicrystalline solid which was dissolved in ether, then was separated into the acidic part and the neutral part by extracting with a $NaHCO_3$aq. The acidic part was chromatographed on silica gel (35 g). Elution with $CHCl_3$ followed by recrystallization from ether and pet. ether (2:7) yielded 128 mg (2·5%) of needles, m.p. 65·5–66·5°, which were identified as V[19] by IR. (Found: C, 67·03; H, 5·78. $C_{10}H_{10}O_3$ requires: C, 67·40; H, 5·66%). The ester was probably formed by esterification of the parent acid with EtOH in ether or chloroform.

Elution with $CHCl_3$–acetone (99:1) followed by recrystallization from $CHCl_3$ yielded 153 mg (3·1%) of crystals, m.p. 151°, which were identified as VIII[20] by IR and mixed m.p.

Elution with $CHCl_3$–acetone (97:3) followed by recrystallization from $CHCl_3$ and benzene (8:2) yielded 268 mg (4·9%) of plates, m.p. 146–148°, which were identified as VII[21] by IR and mixed m.p.

Further elution with $CHCl_3$–MeOH (100:2) followed by recrystallization from $CHCl_3$ yielded 111 mg (2·4%) of plates, m.p. 230°, which were identified as phthalic acid by IR.

*Methylation of the acidic part from irradiation of ninhydrin.* The acidic part obtained from ninhydrin (35 g) as described above was dissolved in ether and the soln was treated overnight with excess diazomethane in ether. The mixture was evaporated to leave a semi-crystalline liquid which was digested with ether and filtered. Crystals obtained (475 mg) was recrystallized from MeOH to give IX as needles, m.p. 173°, which were identical with an authentic sample[*] by IR and mixed m.p. IR: 1735, 1725, 1645, and 1567 cm$^{-1}$. $\lambda_{max}^{EtOH}$ 231 (ε 21,800), 242 (14,500), 252 (12,500), 781 (13,300), 291 (12,500), and 315 mμ (5700). (Found: C, 64·53; H, 4·07. $C_{11}H_{10}O_4$ requires: C, 64·70; H, 3·95%).

The filtrate from IX was evaporated to leave a liquid which was distilled *in vacuo* to give three fractions (b.p. 70–170°/0·01 mm) and a residue (8·51 g). Fraction 1 (2·00 g) was found by VPC to consist of 1·8 g of dimethyl phthalate and 0·20 g of ester X. The former was isolated and identified with an authentic sample (by IR and TLC). Recrystallization of fraction 2 (5·40 g) from MeOH yielded 3·90 g of X as plates, m.p. 77–78°. IR: 1745, 1710, and 1275 cm$^{-1}$; $\lambda_{max}^{EtOH}$ 229 (ε 1470) and 277 mμ (3561); saponification equivalent: 124 ($C_8H_6O(COOCH_3)_2$ requires 118). (Found: C, 60·98; H, 5·02. $C_{12}H_{12}O_5$ requires: 61·01; H, 5·02%).

Recrystallization of fraction 3 (1·25 g) gave 124 mg of methyl isocoumarin-3-carboxylate. The yields of the products isolated amounted to 9·3% for dimethyl phthalate, 17·8% for X, and 3% for IX.

*Acid-hydrolysis of ester* X. Epoxy-ester (200 mg) obtained above was heated under reflux in 5% $H_2SO_4$ (20 ml) for 1·5 hr. Ether extraction of the hydrolyzate followed by evaporation yielded 144 mg of a hydroxy acid, which was recrystallized from $CHCl_3$–EtOH to give plates, m.p. 181–183°. IR: 3300, 1775, and 1700 cm$^{-1}$. The acid was methylated with ethereal diazomethane. Recrystallization from MeOH gave XI as plates, m.p. 112–113°; IR: 3500, 1775, and 1735 cm$^{-1}$; $\lambda_{max}^{EtOH}$ 203 (ε 12,800), 223 (11,600), 272 (2240), and 279 mμ (2120). (Found: C, 58·89; H, 4·48. $C_{11}H_{10}O_5$ requires: C, 59·46; H, 4·54%).

This hydroxy ester XI was also obtained from VIII. Treatment of the acid (500 mg) with ethereal diazomethane overnight followed by recrystallization of the product from $CHCl_3$ gave XI (273 mg) as plates, m.p. 112°, identical with a sample obtained above (by IR) and also with a sample obtained by Inoue *et al.*[†] (by IR in chloroform and NMR).

*Methylation of phthalonic acid* (VII) *with diazomethane.* Phthalonic acid (500 mg) was treated overnight with with a dilute diazomethane soln in ether, 30 mg of IX deposited were collected by filtration (IR) Recrystallization of the product from MeOH gave dimethyl phthalonate (343 mg) as needles, m.p. 66°, which were identical with an authentic sample. On the other hand, treatment of phthalonic acid (500 mg) with a concentrated diazomethane soln in ether overnight followed by recrystallization from MeOH gave 263 mg of X.

*Irradiation of alloxan hydrate* (XIV) *in water.* An aqueous soln (6 ml) of alloxan hydrate (200 mg) was externally irradiated (450 W lamp) under $N_2$ in a Pyrex tube for 36 hr. Crystals (155 mg; 75%) deposited were collected by filtration, m.p 253–254° (dec), which were identical with an authentic sample of alloxanthin dihydrate (by IR).

*Isopropyl alcohol adduct* (XVIIa) *of triketoindane.* Triketoindane (10 g) was dissolved in isopropyl alcohol (50 ml) by heating on a water-bath. On standing in a refrigerator, the pale yellow soln deposited

[*] The methyl ester, m.p. 173°, was prepared by the Fischer's esterification of isocoumarin-3-carboxylic acid.[7]

[†] We are indebted to Professor H. Inoue, Faculty of Pharmaceutical Science, Kyoto University, for a geneous supply of an authentic sample.

XVIIa as almost colorless crystals (11·2 g), which were collected by filtration and washed with pet. ether. The adduct was unstable and gradually changed in a vacuum dessicator and even in an atmosphere of dry air to give triketohydrindane. Therefore, measurements of its physical constants listed below was done immediately after isolation. The adduct, however, is stable in an atmosphere saturated with isopropyl alcohol vapor; IR: 3400, 1760 (sh), and 1725 $cm^{-1}$; $\lambda_{max}^{i\text{-}PrOH}$ 225 mμ (ε 13,400) with shoulder at 243 mμ.

*Irradiation of isopropyl alcohol adduct* XVIIa *in isopropyl alcohol.* A soln of the adduct (10 g) obtained above in absolute isopropyl alcohol (100 ml) was irradiated (100 W lamp) for 6 hr. Hydrindantin (2·15 g) deposited was collected by filtration and the filtrate was evaporated to dryness. Recrystallization of the crystalline residue from acetone yielded further hydrindantin (3·25 g), m.p. 243°. The total yield of hydrindantin amounted to 72·6%. The distillate, which had been collected into a container cooled with a freezing mixture, was mixed with excess of 2,4-dinitrophenylhydrazine in alcoholic $H_2SO_4$ and the mixture was allowed to stand overnight. 2,4-Dinitrophenylhydrazone (1·18 g; 10·9%), which was isolated by extracting with $CHCl_3$ after evaporation of the reaction mixture, was identified as that of acetone (by IR). As a control experiment, acetone (2·64 g) in isopropyl alcohol (100 ml) was treated with 2,4-dinitrophenylhydrazine in a similar manner to give 4·30 g (39·8%) of acetone 2,4-dinitrophenylhydrazone. This indicates that the yield of acetone formed in the photo-reaction may be much more than 10·9%.

*Irradiation of isopropyl alcohol adduct* XVIIa *in benzene.* A soln of the adduct (10 g) in dry benzene (150 ml) was irradiated (100 W lamp) for 15 hr After 3 hr irradiation crystals began to deposit After the reaction crystals were collected by filtration and were recrystallized from acetone to give hydrindantin (1·35 g; 18·6%), identified by IR. The filtrate was evaporated to dryness. Recrystallization of the crystalline residue from acetone–pet. ether gave plates (1·28 g), m.p. 190° (dec); IR: 3450, 1780, 1710, and 1250 $cm^{-1}$; $\lambda_{max}^{EtOH}$ 227 (ε 34,750) and 247 mμ (7620; sh). Acetylation of this substance with $Ac_2O$ and pyridine followed by recrystallization of the product from acetone gave crystals, m.p. 242–243° (dec).

From the mother liquor of the above crystals, phthalic acid (0·32 g) was obtained after fractional recrystallization and was identified by IR.

The above distillate was treated overnight with an excess of 2,4-dinitrophenylhydrazine in alcoholic $H_2SO_4$. 2,4-Dinitrophenylhydrazone (0·36 g; 3·4%), which was isolated as described in the preceding experiment, was identified as that of acetone (by IR). Acetone (2·64 g) in benzene (150 ml) was treated with 2,4-dinitrophenylhydrazine in a similar manner. Acetone 2,4-dinitrophenylhydrazone (3·56 g; 33%) was obtained. This indicates that the yield of acetone formed in the photo-reaction may be more than 3·4%.

*Irradiation of triketohydrindane in t-butyl alcohol.* A suspension of triketohydrindane (6 g) in t-butyl alcohol (200 ml) was heated under reflux for a few days. Triketohydrindane gradually dissolved to give finally a pale yellow soln. An attempt to isolate XVIIb, which crystallized from the reaction mixture, was unsuccessful because of its instability. In the atmosphere of air, the adduct easily reverts to the starting material. The soln was irradiated (100 W lamp) for 16 hr. Hydrindantin (1·85 g; 31 %) deposited during irradiation was collected by filtration and was identified by IR. The filtrate was evaporated and the distillate was treated with excess 2,4-dinitrophenylhydrazine in alcoholic $H_2SO_4$ overnight. The mixture was evaporated *in vacuo* to dryness and the residue was extracted with chloroform. Evaporation of the extract followed by silica gel chromatography of the residue yielded 0·54 g (6·2%) of acetone 2.4-dinitrophenylhydrazone, identified by IR. Careful VPC analysis of the original reaction mixture did not show the presence of 2 5-dimethyl-2,5-hexanediol.

## REFERENCES

[1] This work was presented at the *20th Annual Meeting of the Chemical Society of Japan.* Tokyo. March (1967); cf. *Abstracts of Papers*, III, p. 175.

[2] Part XV: T. Matsuura and I. Saito, *Tetrahedron Letters*, 3273 (1968).

[3] A. Schöberg and R. Moubasher, *J. Chem. Soc* 366 (1944); 213 (1949).

[4] [a] A. Schöberg, *Präparative Organische Photochemie* p. 114. Springer-Verlag, Berlin (1958);
[b] P. de Mayo, *Advances in Organic Chemistry* Vol. 2; p. 367. Interscience, New York (1960).

[5] [a] J. N. Pitts, R. N. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.* **81**, 1068 (1959);
[b] G. S. Hammond and W. M. Moore, *Ibid.* **81**, 6334 (1961),
[c] H. L. J. Bäckstrom and K. Sandros, *Acta Chem. Scand.* **14**, 48 (1960).

[6] [a] O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.* **9**, 555 (1964);
[b] K. Schaffner, *Fortschr. Chem. Org. Naturstoffe* **22**, 1 (1964); H. Hüppi, G. Eggert, S. Iwasaki, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta* **49**, 1986 (1966).

[7] H. W. Johnston, C. E. Kaslow, A. Langsjoen, and R. L. Shriner, *J. Org. Chem.* **13**, 477 (1948).

[8] G. G. Freeman, J. E. Gill, and W. S. Waring, *J. Chem. Soc.* 1105 (1959).

[9] O. L. Chapman and R. W. King, *J. Am. Chem. Soc.* **86**, 1256 (1964).

[10] [a] G. Ciamician and P. Silber, *Ber. Dtsch. Chem. Ges.* **36**, 1575 (1903);
[b] R. Moubasher and A. M. Othman, *J. Am. Chem. Soc.* **72**, 2667 (1950).

[11] H. Inoue, T. Okuda, N. Nagakura, and M. Okigawa, *Tetrahedron Letters* 4713 (1967).

[12] [a] Y. Otsuji, S. Waki, and E. Imoto, *20th Annual Meeting of the Chemical Society of Japan.* Tokyo, March (1967); cf. *Abstracts of Papers,* III, p. 169;
[b] Y. Otsuji, S. Waki, and E. Imoto, *Symposium on Photochemistry.* Tokyo, November (1967); cf. *Abstracts of Papers*, p. 23.

[13] W. H. Urry, M.-S. H. Pai, and C. Y. Chen, *J. Am. Chem. Soc.* **86**, 5342 (1964).

[14] [a] H. Nozaki, Z. Yamaguchi, and R. Noyori, *Tetrahedron Letters* 37 (1965);
[b] H. Nozaki, Z. Yamaguchi, T. Okada, R. Noyori, and M. Kawanishi, *Tetrahedron* **23**, 3393 (1967) and Refs. cited therein

[15] A. Mangini and R. Passerini, *Gazz. Chim. Ital.* **85**, 840 (1955).

[16] cf. D. S. Kendall and P. A. Leermakers, *J. Am. Chem. Soc.* **88**, 2766 (1966).

[17] S. G. Cohen and S. Aktipis, *Tetrahedron Letters* 579 (1965); *J. Am. Chem. Soc.* **88**, 3587 (1966).

[18] M. S. Newman, *Organic Synthesis* **40**, 90 (1961).

[19] H. Meyer, *Mh. Chem.* **25**, 498 (1904).

[20] S. Ruhemann, *J. Chem. Soc.* **97**, 2025 (1910).

[21] R. C. Fuson, *J. Am. Chem. Soc.* **48**, 1093 (1926).