The photodimerization of 3-(*p*-anisyl)-2-cyclohexenone and 3-(*p*-nitrophenyl)-2-cyclohexenone

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Ultraviolet irradiation of 3-(*p*-anisyl)-2-cyclohexenone and 3-(*p*-nitrophenyl)-2-cyclohexenone has been found to give a single photodimer in each case, the structures of which have been established as the *cis–anti–cis* head-to-head cyclobutane derivatives XI and XIII, respectively.

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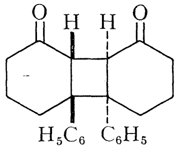
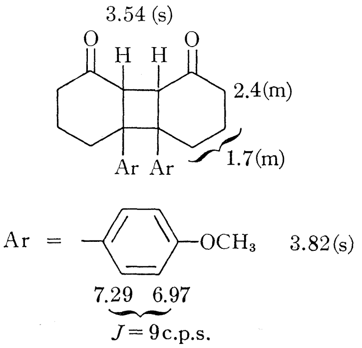
As part of an investigation into the influence of structure on the course of the photodimerization of α,β-unsaturated carbonyl compounds, we have studied the photodimerization of 3-phenyl-2-cyclohexenone, 3-(*p*-anisyl)-2-cyclohexenone, and 3-(*p*-nitrophenyl)-2-cyclohexenone. Evidence establishing I as the structure of the photodimer of 3-phenyl-2-cyclohexenone was discussed in the preceding paper (1). In this paper we present the data for the other 3-arylcyclohexenones.



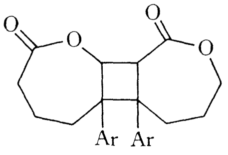
I

Irradiation of 3-(*p*-anisyl)-2-cyclohexenone in benzene solution in a Pyrex vessel with a medium-pressure Hanovia lamp gave a good yield of a single crystalline photodimer, which is assigned structure II on the basis of its spectra and degradation. Its infrared spectrum (λ_{max} ($CHCl_3$) 5.87 μ) indicated the presence of unconjugated carbonyl groups, and its ultraviolet spectrum (λ_{max} (EtOH) 231 (ϵ 14 700) and 276 mμ (ϵ 5 030)) suggested the presence of two isolated *p*-anisyl groups. The assignment of the signals in its nuclear magnetic resonance (n.m.r.) spectrum is shown in structure II (the chemical shift values are recorded on the δ scale). The retention of the skeletons of the monomer units in the dimer was indicated by the ready reversion of the latter to monomer in weakly acidic solutions.



II

The degradation of the photodimer is shown in Scheme 1. Oxidation with *m*-chloroperbenzoic acid gave the crystalline dilactone III (λ_{max} 5.77 μ) in a good yield, together with a small quantity of an amorphous solid which separated from the mother liquors from the crystallization of III. The n.m.r. spectrum of this solid, which was not purified further, showed doublets at δ 4.20 and 5.94 p.p.m. (J = 4 c.p.s.), in addition to all of the signals present in the spectrum of dilactone III. The singlet at δ 5.55 p.p.m. assigned to the tertiary, cyclobutyl protons of III appeared



Ar = $C_6H_4OCH_3$-*p*

IV

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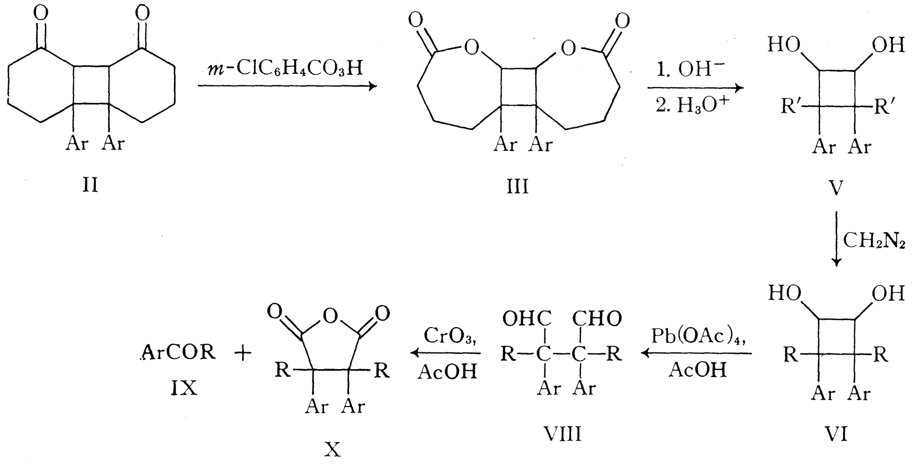
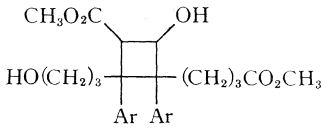


SCHEME 1. Ar = $C_6H_4OCH_3$-*p*, R = $(CH_2)_3CO_2CH_3$, R′ = $(CH_2)_3CO_2H$.

as only a very weak signal in this spectrum. This evidence suggests that the amorphous solid is a mixture of a small amount of III and the unsymmetrical dilactone IV arising from migration of a secondary carbon atom in the Baeyer–Villiger oxidation.

Hydrolysis of dilactone III with aqueous base gave the dicarboxylic acid V, which was converted by treatment with diazomethane into its dimethyl ester VI. The bands at 2.90 and 5.80 μ in the infrared spectrum of VI confirmed the presence of hydroxyl and ester groups. The n.m.r. spectrum of the diester VI showed doublets at δ 4.05 and 4.75 p.p.m. ($J = 9$ c.p.s.). Deuterium exchange led to the disappearance of the former band and the collapse of the latter to a singlet. These signals can therefore be assigned to the hydroxyl and cyclobutyl protons of VI, respectively.

When crude fractions of the Baeyer–Villiger oxidation product were hydrolyzed, and the material that collected in the mother liquors from the purification of the dicarboxylic acid V was esterified with diazomethane, the presence of a second hydroxy ester was observed. The crude product showed hydroxyl and ester carbonyl absorption in its infrared spectrum. Its n.m.r. spectrum showed two distinct signals at δ 3.58 and 3.72 p.p.m. attributable to methyl ester protons, as well as multiplets at δ 3.2 and 5.2 p.p.m., which are not present in the spectrum of the diester VI. These multiplets appeared as a triplet and doublet, respectively, after the sample was shaken with D_2O. This hydroxy ester is considered to have the structure VII and to arise from the unsymmetrical lactone IV observed in the crude oxidation mixture.



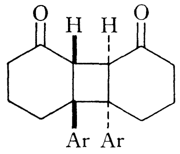
Ar = $C_6H_4OCH_3$-*p*

VII

The reaction of both esters with lead tetraacetate was investigated. The unsymmetrical hydroxy ester VII was recovered unchanged after treatment with lead tetraacetate in glacial acetic acid at room temperature for 48 h. The hydroxy ester VI, however, after oxidation with this reagent, gave the dialdehyde VIII, the infrared spectrum of which showed the characteristic carbon–hydrogen stretching band of an aldehyde at 3.62 μ, as well as a broad carbonyl stretching band at 5.80 μ. The n.m.r. spectrum of VIII showed the expected singlet at δ 10.00 p.p.m. Surprisingly, this dialdehyde did not form a cyclic hydrate, although such a hydrate was formed very readily with the corresponding dialdehyde in the phenyl series (1).

Oxidation of the dialdehyde VIII with chromic acid in hot glacial acetic acid gave a mixture of methyl γ-anisoylbutyrate IX, whose identity was confirmed by its hydrolysis to γ-anisoylbutyric acid, and the anhydride X. The latter product could be obtained in a better yield by oxidation of VIII with chromic acid at room temperature, although the further oxidation product IX always accompanied it. The infrared spectrum of X showed bands at 5.40, 5.61, and 5.78 μ, indicating the presence of a five-membered anhydride ring. This evidence establishes the presence of a cyclobutane ring in the photodimer II and confirms that the hydroxy groups in the diester VI are adjacent. Thus, the photodimer must have a head-to-head orientation. This assignment is corroborated by the magnitude of the coupling constant (4 c.p.s.) observed for the two tertiary, cyclobutyl protons in the n.m.r. spectrum of the unsymmetrical dilactone IV. A value of this magnitude corresponds to a 1,2, but not a 1,3, relationship of protons on simple or fused cyclobutane rings (2).

Photodimer II was recovered unchanged from refluxing methanolic sodium methoxide, showing that each of the six-membered rings is *cis* fused to the cyclobutane ring, since it has been demonstrated that the corresponding *trans*-fused systems, which have been observed in other photochemical reactions (3), are converted into their *cis*-fused isomers by treatment under even mildly basic conditions (3*b*). The stereochemical relationship between the two six-membered rings in the hydroxy ester VI was established as *anti* by its slow rate of oxidation with lead tetraacetate; the second-order rate constant at 25° was found to be 0.25 ± 0.04 l mole^{-1} min^{-1} (cf. ref. 4), indicating that the two hydroxyl groups are *trans* to one another. This assignment is compatible with the magnitude of the coupling constant for the cyclobutyl protons of the dilactone IV (see above), but not required by it (2*b*). Since Baeyer–Villiger oxidation is known to take place with retention of configuration (5), the tertiary, cyclobutyl protons in the photodimer must also be *trans* to one another. The full structure of the dimer is thus established as XI, the *cis–anti–cis* isomer of the head-to-head structure II.

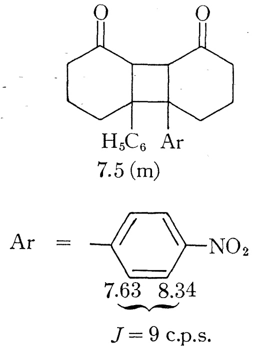


Ar = $C_6H_4OCH_3$-*p*

XI

The orientational and stereochemical identity of the photodimers of 3-phenyl-2-cyclohexenone (I) and 3-(*p*-anisyl)-2-cyclohexenone (XI) was confirmed by the introduction of *p*-methoxyl groups into the phenyl rings of the photodimer I, as shown in Scheme 2.

Nitration of I with nitric acid – sulfuric acid mixtures led to extensive oxidation of the cyclohexanone rings. When cupric nitrate in acetic anhydride was used as the nitrating agent, a mononitro compound (XII) was obtained. Its n.m.r. spectrum showed in the aryl proton region a multiplet at δ 7.5 assigned to the monosubstituted benzene ring protons, and an A_2B_2 signal pattern with δ 7.63 and 8.34 p.p.m. assigned to the protons of a *p*-disubstituted benzene ring.[2]



XII

When nitric acid in cold nitromethane – acetic anhydride was used for the nitration (7), the dinitro derivative XIII was formed in a 57% yield. Its infrared spectrum

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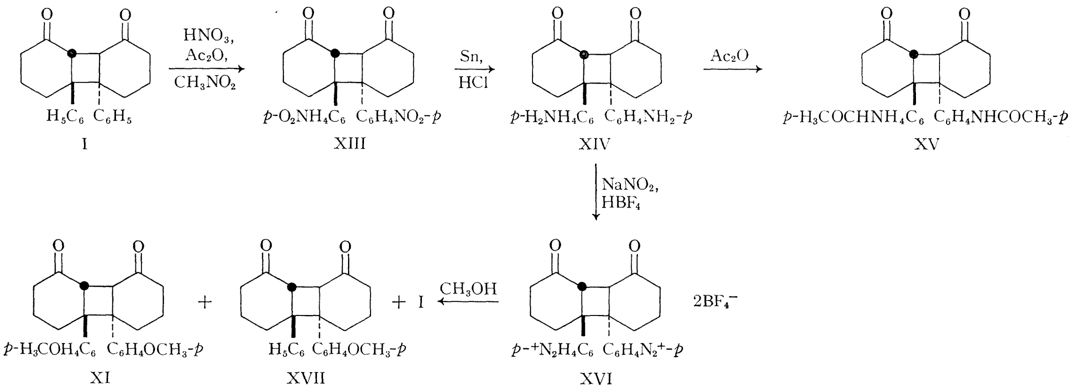
[2] The pattern is that characteristic of the proton signals of a *p*- rather than an *o*-disubstituted benzene ring (6) (see also footnote 3).



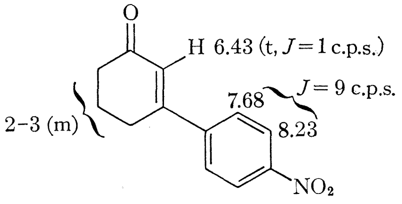
SCHEME 2.

(KBr) had bands at 5.89 (ketonic C=O), 6.60 (NO_2), and 7.40 (NO_2) μ, and its n.m.r. spectrum (in trifluoroacetic acid) showed a single A_2B_2 signal pattern for the aryl protons with δ 7.77 and 8.46 p.p.m., confirming the structural assignment.

Compound XIII was converted into the corresponding diamino compound XIV by reduction with tin and hydrochloric acid. The amine, which was isolated as colorless crystals, deteriorated rapidly on exposure to air. Its infrared spectrum had bands at 2.89 and 2.95 (NH_2 stretch), 5.88 (ketonic C=O), and 6.17 (NH_2 bend) μ. It was characterized as the more stable diacetyl derivative XV.

Compound XIV gave a crystalline fluoborate on treatment with 30% fluoboric acid. An aqueous solution of the fluoborate was diazotized to give the orange bis-diazonium fluoborate XVI, which was decomposed immediately in methanol. The products obtained from the decomposition of XVI in methanol were highly dependent upon the conditions of the reaction. DeTar (8) has investigated the decomposition of benzenediazonium salts in methanol under a variety of conditions and has reported that the reaction of benzenediazonium fluoborate with methanol gave 93% anisole. When buffers were used, the chief product was benzene; the yield of the ether was decreased if a nitrogen atmosphere was used, and was highest under oxygen. The diazonium salt XV decomposed in refluxing methanol to give chiefly the reduction product, the photodimer I. When acid catalysts were added, the spectra of the products indicated the formation of the monomethoxy compound XVII and mixtures of the photodimers I and XI; however, only small amounts of impure XI could be isolated from the mixtures. Decomposition of the bis-diazonium salt at room temperature in methanol which had been treated with gaseous hydrogen chloride and saturated with oxygen yielded a crude product, the n.m.r. spectrum of which showed singlets at δ 3.00 and 3.12 p.p.m., suggesting dimethyl ketal formation. Acid hydrolysis and chromatography of the crude product gave a compound that was identical with the photodimer XI obtained by the irradiation of 3-(p-anisyl)-2-cyclohexenone.

When it was found that the change in the electronic character of the substituent at the β carbon of an α,β-unsaturated carbonyl system associated with replacement of a phenyl by a p-anisyl group did not affect the course of photodimerization, it became of particular interest to determine whether p-nitro substitution on the phenyl ring would have any effect. 3-Phenyl-2-cyclohexenone was nitrated under the same conditions as used for the nitration of its photodimer (see above) to give 3-(p-nitrophenyl)-2-cyclohexenone (XVIII). The structure of the nitration product was established by bands at 6.00 (conjugated C=O), 6.60 (conjugated NO_2), and 7.41 (NO_2) μ in its infrared spectrum, and signals in its n.m.r. spectrum



XVIII

which can be assigned as shown in structure XVIII.

The insolubility of XVIII in most solvents and the still greater insolubility of its photodimer defeated all attempts to irradiate the compound under the same conditions as used for the phenyl and *p*-anisyl monomers. In most experiments an amorphous brown solid coated the walls of the irradiation tube in a short time and stopped the reaction. From a saturated solution of XVIII in methanol, a small amount of photodimer precipitated on irradiation. This compound was shown to be identical with compound XIII obtained by dinitration of the dimer I. Thus the photodimers of each of the three 3-aryl-2-cyclohexenones examined are all of the *cis–anti–cis* head-to-head type.

The photodimer XIII did not revert to monomer when left in concentrated sulfuric acid, but was recovered unchanged. This may be compared with the very facile reversion of the photodimer (XI) of 3-(*p*-anisyl)-2-cyclohexenone to the monomer in weak acid, and the similar reversion of photodimer I to monomer in concentrated sulfuric acid (1). These differences suggest that ring opening occurs by the type of route shown in Scheme 3.

The evidence clearly shows that a *p*-methoxy substituent on the phenyl ring of 3-phenyl-2-cyclohexenone fails to affect the mode of photodimerization. In the case of a *p*-nitro substituent, however, the evidence is less compelling because of the very low yield of the photodimer. Nevertheless, no indication was obtained with the *p*-nitro compound that a dimer other than the *cis–anti–cis* head-to-head isomer was formed, and it appears probable that in all three cases this type of photodimer is formed exclusively. The results of the present investigation therefore suggest that the mode of photodimerization of 3-aryl-2-cyclohexenones is insensitive to polar effects. As in the case of 3-phenyl-2-cyclohexenone (1), both 3-(*p*-anisyl)-2-cyclohexenone and 3-(*p*-nitrophenyl)-2-cyclohexenone have high-intensity ultraviolet maxima at >280 mμ, and it is conceivable that $\pi \rightarrow \pi^*$ singlet excitation is involved and thus that these cases differ fundamentally from those of 2-cyclohexenone and the alkyl-2-cyclohexenones.

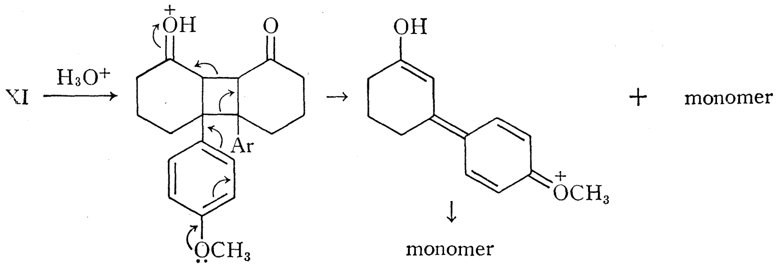
The photodimer of 3-(*p*-anisyl)-2-cyclohexenone, like that of 3-phenyl-2-cyclohexenone (1), undergoes extensive reversion to monomer on irradiation in dilute solution in benzene in a Pyrex vessel. With the photodimer of 3-(*p*-nitrophenyl)-2-cyclohexenone, photodecomposition occurred but no monomer could be isolated from the amorphous, brown product. Since the major part of the product obtained on irradiation of the monomer is a similar material, it is possible that photoreversion of the dimer to monomer takes place with the *p*-nitro compound also. The occurrence of photoreversion to monomer in at least two of the cases studied suggests the possibility that the orientation and stereochemistry of the photodimers may be controlled by photoequilibration processes. However, it appears unlikely that photoequilibration would result in the production of the *cis–anti–cis* head-to-head isomers alone. Resolution of this question must await the synthesis of other isomers and the study of their photochemistry.

EXPERIMENTAL

Melting points were determined on a Fisher–Johns hot stage, and are uncorrected unless otherwise stated. Infrared spectra were recorded on Beckman IR-5 and IR-8 spectrophotometers and were calibrated with the 6.24 μ band of polystyrene. Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 505 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer; tetramethysilane was used as an internal standard. Irradiations were carried out with a Hanovia 450 W medium-pressure mercury arc lamp.

3-(p-Anisyl)-2-cyclohexenone

3-(*p*-Anisyl)-2-cyclohexenone was prepared from



SCHEME 3. (Ar = $C_6H_4OCH_3$-*p*)

ethyl *p*-anisoylacetate (K and K Laboratories, 33.4 g, 0.15 mole), *t*-butyl alcohol (32.5 ml), methyl vinyl ketone (Matheson, Coleman, and Bell, 10.4 g, 0.15 mole), and benzyltrimethylammonium hydroxide (British Drug Houses, 40% in water, 27 ml) according to the general directions of Walker (9). The product, after two recrystallizations from ether, was obtained as pale-yellow prisms (6.36 g, 21%), m.p. 84–85° (lit. m.p. 80–82° (10) and 86.2–87.2° (11)), $\lambda_{\max}$ (CCl_4) 6.00 and 6.24 μ, $\lambda_{\max}$ (EtOH) 229 (ϵ 11 800) and 315 mμ (ϵ 20 600); δ (CCl_4) 2.2 (m), 2.7 (m), 3.80 (s), 6.22 (t, J = 1 c.p.s.), and 6.85 and 7.43 (A_2B_2 system, J = 9 c.p.s.)[3] p.p.m.[4]

Photodimer of 3-(p-Anisyl)-2-cyclohexenone (II)

Solutions of 3-(*p*-anisyl)-2-cyclohexenone (1 g) in benzene (30 ml) in Pyrex vessels were irradiated with the Hanovia lamp during about 40 h. The originally pale-yellow benzene solutions became colorless, and sometimes photodimer crystallized. Removal of the solvent gave a solid, from which pure photodimer II could be obtained in a 50–60% yield after two recrystallizations from ethyl acetate. The mother liquors yielded more of the compound. Chromatography of the residues from the mother liquors and infrared and n.m.r. spectral examination of the crude fractions failed to give any evidence of the presence of another photodimer.

The photodimer II crystallized from methanol as large needles, and from ethyl acetate as very small needles, m.p. 234–236° (decomp.), $\lambda_{\max}$ ($CHCl_3$) 5.87 and 6.20 μ, $\lambda_{\max}$ (EtOH) 231 (ϵ 14 700) and 276 mμ (ϵ 5 030); δ ($CDCl_3$) 1.7 (m), 2.4 (m), 3.54 (s), 3.82 (s), and 6.97 and 7.29 (A_2B_2 system, J = 9 c.p.s.)[3] p.p.m.

Anal. Calcd. for $C_{26}H_{28}O_4$: C, 77.20; H, 6.98. Found: C, 77.11; H, 7.08.

The *bis-2,4-dinitrophenylhydrazone* of II was prepared by the method of Fieser (13); it crystallized from ethanol – ethyl acetate as fine, orange needles, m.p. 236–238°; $\lambda_{\max}$ ($CHCl_3$) 6.16, 6.25, and 7.45 μ.

Anal. Calcd. for $C_{38}H_{36}N_8O_{10}$: C, 59.68; H, 4.75; N, 14.65. Found: C, 59.68; H, 4.84; N, 14.49.

Acid-Catalyzed and Photochemical Reversion of Dimer II to Monomer

The photodimer II reverted to the monomer on irradiation and in acid.

The monomer was isolated by chromatography of the mixture that resulted when II was left for 1 week in a solution of perbenzoic acid in chloroform. It was identified by its infrared spectrum.

Irradiation of II (46 mg) in benzene (20 ml) in a Pyrex tube with the Hanovia lamp for 24 h gave a viscous oil, from which the monomer I (30 mg) was extracted with carbon tetrachloride. The rest of the material was unchanged II. The monomer was identified by its infrared and n.m.r. spectra.

Baeyer-Villiger Oxidation of the Photodimer II; Formation of the Dilactones III and IV

The pure photodimer II (10.00 g, 0.025 mole) was oxidized with *m*-chloroperbenzoic acid (FMC Corporation, 85% peracid, 17.00 g, 0.084 mole) in refluxing methylene chloride (700 ml) for 10 h. After the solution had stood overnight, it was washed twice with aqueous 5% sodium hydroxide and twice with water, and dried over magnesium sulfate. Removal of the solvent gave a quantitative yield of a semicrystalline material, from which crystalline dilactone III (8.4 g, 77%) could be obtained by stirring with carbon tetrachloride. These crystals, and those obtained after recrystallization from carbon tetrachloride, were very fine and very difficult to remove by filtration. An analytical sample was prepared by repeated crystallization from benzene, from which large prisms containing benzene of crystallization were obtained. A final heating with carbon tetrachloride without complete solution of the crystals removed the benzene of crystallization and gave small prisms, m.p. 234–235°; $\lambda_{\max}$ ($CHCl_3$) 5.77, 6.20, and 8.80 μ; δ ($CDCl_3$) 1.4 (m), 2.1 (m), 3.87 (s), 5.55 (s), and 7.1 (m) p.p.m.

Anal. Calcd. for $C_{26}H_{28}O_6$: C, 71.54; H, 6.47. Found: C, 71.49; H, 6.49.

The portion of the oxidation product which did not crystallize gave an amorphous, beige solid when left for a long time in the cold in benzene–hexane. An n.m.r. spectrum ($CDCl_3$) of this solid showed, in addition to the signals present in the spectrum of the dilactone III, doublets at 4.20 and 5.94 p.p.m. (J = 4 c.p.s.) attributed to the unsymmetrical lactone IV; the signal at 5.55 p.p.m. was

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[3] Signal systems here designated as A_2B_2 are more exactly described as $AA'BB'$ systems. They were analyzed by the method of Richards and Schaefer (12) for such systems with $J_{AA'} = J_{BB'}$ and $J_{AB'} = 0$; J denotes J_{AB}.

[4] Abbreviations used: s, singlet; d, doublet; t, triplet; and m, multiplet.

much less intense than that in the spectrum of pure III.

Hydrolysis of Dilactone III; Formation of Dicarboxylic Acid V

Dilactone III (2.00 g) was hydrolyzed by heating it for 3 h with a mixture of saturated aqueous sodium bicarbonate (250 ml) and aqueous 5% sodium hydroxide (40 ml) under reflux. The dicarboxylic acid V was isolated by acidification and filtration. Recrystallization from acetone–benzene gave V (1.50 g, 69%) as fine needles, m.p. 201–203°.

Anal. Calcd. for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 66.05; H, 7.05.

Dimethyl Ester (VI) of the Dicarboxylic Acid V and Ester VII

Esterification of V with ethereal diazomethane gave the dihydroxy dimethyl ester VI, which crystallized from methanol as prisms, m.p. 135–137°; λ_{max} ($CHCl_3$) 2.90, 5.80, 9.19, and 10.20 μ; δ ($CDCl_3$) 1.3 (m), 2.0 (m), 3.58 (s), 3.83 (s), 4.05 (d, $J = 9$ c.p.s., absent after D_2O treatment), 4.75 (d, $J = 9$ c.p.s., singlet after D_2O treatment), and 6.97 and 7.39 (A_2B_2 system, $J = 9$ c.p.s.)[3] p.p.m.

Anal. Calcd. for $C_{28}H_{36}O_8$: C, 67.10; H, 7.21. Found: C, 67.18; H, 7.25.

Esterification of the residues from the mother liquors from the recrystallization of the dicarboxylic acid V obtained by the hydrolysis of the crude lactone samples yielded another hydroxy ester (VII), which crystallized from benzene–hexane or carbon tetrachloride as a gelatinous solid, m.p. 95–105°, λ_{max} ($CHCl_3$) 2.90 and 5.80 μ; δ ($CDCl_3$) 1.4 (m), 2.1 (m), 3.2 (m, t with $J = 6$ c.p.s. after D_2O treatment), 3.58 (s), 3.72 (s), 3.82 (s), 5.2 (m, d with $J = 9$ c.p.s. after D_2O treatment), and 6.94 and 7.37 (A_2B_2 system, $J = 9$ c.p.s.)[3] p.p.m. This ester could not be induced to crystallize satisfactorily.

Rate of Oxidation of the Diester VI with Lead Tetraacetate

The rate of oxidation of the diester VI with lead tetraacetate was determined according to the directions of Criegee *et al.* (4*b*). The second-order rate constant at 25° was found to be 0.25 ± 0.04 $l\ mole^{-1}\ min^{-1}$.

Oxidation of the Diester VI with Lead Tetraacetate; Formation of the Dialdehyde VIII

A solution of VI (1.60 g, 0.0032 mole) in glacial acetic acid (110 ml) which had been saturated with lead tetraacetate was left in the dark for 20 h, after which titration indicated that slightly more than 1 equivalent of the oxidizing agent had been consumed. The reaction mixture was poured into a solution of potassium iodide (5 g) and crystalline sodium acetate (120 g) in water (250 ml), and solid sodium thiosulfate was added to destroy the iodine that formed. The aqueous solution was extracted with ether and chloroform. The organic layer was washed three times with water, twice with aqueous 5% sodium hydroxide, and again with water, and was dried over anhydrous magnesium sulfate. Removal of the solvent gave the dialdehyde VIII as a pale-yellow oil (1.5 g, 95%), which crystallized when stirred with carbon tetrachloride. Recrystallization from carbon tetrachloride gave prisms, m.p. 90–92°, λ_{max} ($CHCl_3$) 3.62 and 5.80 μ; δ ($CDCl_3$) 1.4 (m), 2.2 (m), 3.59 (s), 3.80 (s), 6.82 (s), and 10.00 (s) p.p.m.

Anal. Calcd. for $C_{28}H_{34}O_8$: C, 67.45; H, 6.87. Found: C, 67.22; H, 6.81.

Attempts to induce VIII to crystallize as a hydrate by adding water and traces of acid to its solution in carbon tetrachloride failed.

The hydroxy ester VII was recovered unchanged after it was left in a glacial acetic acid solution of lead tetraacetate at room temperature for 48 h.

Oxidation of Dialdehyde VIII; Formation of Anhydride X and Methyl γ-Anisoylbutyrate (IX)

Oxidation of samples of crude VIII with solutions of chromium trioxide in glacial acetic acid (using varying proportions of reagents for different lengths of time at different temperatures) gave mixtures showing carbonyl absorption at 5.40, 5.60, 5.78, and 5.98 μ. Chromatography of 400 mg of such a mixture on silica (50 g) separated it into three major components.

First to be eluted from the column with 5% ether in benzene was methyl γ-anisoylbutyrate (IX, 98 mg), which crystallized from petroleum ether (b.p. 60–70°) as white plates, m.p. 52° (lit. m.p. 49–51° (14) and 52–54° (15)); λ_{max} ($CHCl_3$) 5.79, 5.98, and 6.24 μ; δ (CCl_4) 2.0 (m), 2.3 (m), 2.88 (t, $J = 7$ c.p.s.), 3.60 (s), 3.80 (s), and 6.85 and 7.85 (A_2B_2 system, $J = 9$ c.p.s.)[3] p.p.m. Ester IX was hydrolyzed to γ-anisoylbutyric acid, which was recrystallized from water as white needles, m.p. 141–142° (lit. m.p. 138.5–141° (16)); λ_{max} ($CHCl_3$) 2.85–3.40, 5.57 (shoulder), 5.85, 5.98, and 6.24 μ; δ ($CDCl_3$) 2.1 (m), 2.5 (m), 3.02 (t, $J = 7$ c.p.s.), 3.87 (s), and 6.94 and 7.94 (A_2B_2 system, $J = 9$ c.p.s.)[3] p.p.m.

Other fractions eluted from the column with 10% ether and 50% ether in benzene appeared from their infrared and n.m.r. spectra to be the anhydride X (see below) and unoxidized VIII, which underwent changes on the column which were not further investigated.

A cold solution of chromium trioxide in glacial acetic acid was added slowly to a solution of crude VIII in glacial acetic acid at room temperature until there was no further change in the color. This solution was then left at room temperature for 45 min. The reaction mixture was diluted with water and extracted with ether. The ethereal layer was washed with water, with aqueous 5% sodium hydroxide, and again with water, and was dried over magnesium sulfate. Removal of the solvent gave a pale-yellow oil, which, when stirred with ether, separated into the crystalline anhydride X and a yellow oil (shown by infrared spectroscopy to be a mixture of IX and X).

Anhydride X was recrystallized from carbon tetrachloride as prisms, m.p. 145–147°; λ_{max} ($CHCl_3$) 5.40, 5.61, and 5.78 μ; δ ($CDCl_3$) 1.5 (m), 2.1 (m), 3.54 (s), 3.85 (s), and 6.94 and 7.05 (A_2B_2 system, $J = 9$ c.p.s.)[3] p.p.m.

Anal. Calcd. for $C_{28}H_{32}O_9{\cdot}\frac{1}{2}H_2O$: C, 64.50; H, 6.38. Found: C, 64.51, 64.44; H, 6.21, 6.18.

Treatment of Photodimer II with Base

The photodimer II (200 mg) was heated for 2 h with methanolic 1% sodium methoxide (50 ml) at reflux. The solution was cooled, acidified with dilute acetic acid, and further diluted with water. The precipitate, after recrystallization from ethyl acetate, melted at 230–235° before and after admixture with II. The infrared spectrum of the crude precipitate corresponded to that of II.

Nitration of the Photodimer of 3-Phenyl-2-cyclohexenone (I); Formation of the Mononitration Product XII and the Dinitration Product XIII

The photodimer of 3-phenyl-2-cyclohexenone (I, 300 mg) (1) was dissolved, with warming, in a mixture of cupric nitrate trihydrate (250 mg) and acetic anhydride (5 ml). The reaction mixture was left at room temperature for 7 h. It was then diluted with water, and the water-insoluble oil was extracted with ether – ethyl acetate. The extract was washed thoroughly with aqueous 5% sodium hydroxide and water and dried over magnesium sulfate. Removal of the solvent gave an oil, from which the mononitro compound XII was isolated as a yellow solid (112 mg, 33%) by stirring with ether. Compound XII crystallized from benzene (with benzene of crystallization) as pale-yellow prisms, m.p. 282–285° (decomp.), λ_{max} ($CHCl_3$) 5.85 and 7.04 μ; δ ($CDCl_3$) 1.7 (m), 2.5 (m), 3.67 (s), 7.5 (m), and 7.63 and 8.34 (A_2B_2 system, J = 9 c.p.s.)[3] p.p.m.

Anal. Calcd. for $C_{24}H_{23}NO_4$: C, 74.02; H, 5.95; N, 3.60. Found: C, 73.52; H, 5.90; N, 3.65.

When photodimer I was nitrated by the general procedure of Tanida and Ishitobi (7), the dinitration product XIII was formed. In a typical run, I (4.62 g) was dissolved in a mixture of nitromethane (60 ml) and acetic anhydride (70 ml). The solution was cooled in an ice bath and stirred while concentrated nitric acid (25 ml) was added at such a rate that the temperature of the solution was kept at 8–10°. The solution turned greyish green, and a white precipitate started to form when the last of the acid was added. The reaction mixture was stirred in the ice bath for an additional hour. The crystalline solid (3.47 g, 57%) was removed by filtration and washed successively with cold nitromethane, water, cold ethanol, and ether. Compound XIII was recrystallized from benzene–nitromethane as pale-yellow prisms, m.p. 295° (decomp.) (capillary); λ_{max} (KBr) 5.89, 6.60, and 7.40 μ; δ (CF_3-COOH) 2.0 (m), 2.7 (m), 4.15 (s), and 7.77 and 8.46 (A_2B_2 system, J = 9 c.p.s.)[3] p.p.m.

Anal. Calcd. for $C_{24}H_{22}N_2O_6$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.07; H, 5.12; N, 6.44.

Reduction of Dinitro Compound XIII; Formation of Diamine XIV and Diamide XV

Compound XIII (754 mg) was suspended in 95% ethanol (15 ml), and mossy tin (3 g) was added. While the mixture was stirred and heated under reflux, concentrated hydrochloric acid (15 ml) was added in portions over 1 h. The liquid cleared in about 1.5 h, and was stirred at reflux for an additional hour. The liquid was decanted from the unconsumed tin, diluted with water, and made basic with aqueous 10% sodium hydroxide (500 ml). The amine was extracted from the mixture with three 300 ml portions of ether. The combined ethereal extracts were washed with water until neutral, and dried over anhydrous magnesium sulfate. Evaporation of the ether at room temperature gave yellow, crystalline diamine XIV (480 mg, 74%). The amine could be purified by stirring it with a small quantity of anhydrous ether; the colorless crystals were removed by filtration. Attempts to recrystallize the amine or to make a hydrochloride failed; polymeric materials seemed to be formed. The crude amine had λ_{max} ($CHCl_3$) 2.89, 2.95, 5.88, and 6.17 μ.

The diacetyl derivative was prepared by a standard procedure (17) from freshly prepared XIV and acetic anhydride. The diamide crystallized from 95% ethanol as small, white prisms, m.p. 283–285° (decomp.).

Anal. Calcd. for $C_{28}H_{30}N_2O_4{\cdot}\frac{1}{2}H_2O$: C, 71.95; H, 6.68; N, 5.99. Found: C, 71.97; 71.80, H, 6.60, 6.91; N, 6.35, 5.85.

Diazotization of Diamine XIV; Formation of Bis-diazonium Fluoborate XVI

The crystalline fluoborate salt of the diamine XIV was formed when 30% fluoboric acid (6 ml, made by dilution of Matheson, Coleman, and Bell 48% fluoboric acid) was added to freshly prepared crude XIV (480 mg) and the solution was cooled and stirred in an ice bath. The cream-colored cystals were removed by filtration and dissolved in the minimum amount of water. The solution was filtered to remove a small amount of insoluble material, and one drop of 48% fluoboric acid was added to the filtrate, which was chilled in an ice bath. A solution of sodium nitrite was added dropwise until an excess of nitrous acid was present (as shown by starch – potassium iodide paper). The orange bis-diazonium fluoborate XVI began to precipitate instantly, and the mixture was left in the ice bath for 30 min. The crystals were separated by filtration and washed with cold 5% fluoboric acid, cold methanol, and anhydrous ether. The dry crystals weighed 400 mg (54%).

Decomposition of Bis-diazonium Fluoborate XVI in Methanol

Attempts to decompose the bis-diazonium fluoborate XVI in refluxing anhydrous methanol alone or with varying amounts of concentrated sulfuric acid or hydrogen chloride according to the general directions of DeTar (8) gave dark-colored mixtures. The infrared and n.m.r. spectra of these mixtures showed them to be composed chiefly of varying proportions of photodimer I, the monomethoxy compound XVII, and the photodimer XI. In the absence of acid, I was the main product; addition of acid increased the proportion of methyl ether formation, but the mixtures could only be separated by thin-layer chromatography to give very small amounts of impure XI.

The decomposition reaction was best carried out by dissolving the bis-diazonium fluoborate XVI (400 mg) in methanol (140 ml) which had been treated with gaseous hydrogen chloride and thoroughly flushed with oxygen (cf. ref. 8*b*), and allowing the solution to stand for 1 week at room temperature. The reaction mixture was diluted with water and the resulting solid was extracted with ether. The ethereal solution was washed with aqueous 5% sodium hydroxide and water, and dried over magnesium sulfate. The solvent was removed to give an orange solid, whose infrared and n.m.r. spectra indicated it to be crude XI containing dimethyl ketal (singlets at δ (CCl_4) 3.00 and 3.12 p.p.m.).

The mixture was boiled at reflux for 2 h with 5% hydrochloric acid. The resulting brown solid was extracted with ether, ethyl acetate, and chloroform, and the combined organic extracts were washed with water and dried. Removal of the solvent gave a hard brown solid (150 mg), which was chromatographed on Woelm neutral alumina (grade I, 15 g). The product (99 mg, 35% from XVI) was eluted with 50% ether in benzene. Recrystallization of the product successively from ethyl acetate and methanol gave needles, m.p. 230–235°, mixture m.p. with XI obtained by irradiation 232–235°. The infrared and n.m.r. spectra of the two samples were essentially identical.

3-(p-Nitrophenyl)-2-cyclohexenone (XVIII)

A solution of 3-phenyl-2-cyclohexenone (1.06 g) (1) in nitromethane (6 ml) and acetic anhydride (12 ml) was stirred in an ice bath and treated with concentrated nitric acid (3.6 ml added dropwise during 20 min). After being stirred for a few more minutes in the cold, the reaction mixture was diluted with water and the oil was dissolved in ether. The ethereal solution was washed twice with water, six times with aqueous 5% sodium hydroxide, and another three times with water. It was dried over magnesium sulfate and evaporated to give a yellow oil, which crystallized when stirred with ether. Two crops of crystals (130 mg, 10%) were obtained; these were recrystallized from methanol to give XVIII as yellow prisms, m.p. 143–144°; $\lambda_{\max}$ ($CHCl_3$) 6.00, 6.60, and 7.41 μ; $\lambda_{\max}$ (EtOH) 299 mμ (ϵ 3 320); δ ($CDCl_3$) 2.0–3.0 (m), 6.43 (t, $J = 1$ c.p.s.), and 7.68 and 8.23 (A_2B_2 system, $J = 9$ c.p.s.)[3] p.p.m.

Anal. Calcd. for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.32; H, 5.10; N, 6.45.

Photodimer of 3-(p-Nitrophenyl)-2-cyclohexenone (XIII)

The insolubility of XVIII in most solvents defeated attempts to irradiate the compound under the same conditions as used for 3-phenyl-2-cyclohexenone (1) and 3-(*p*-anisyl)-2-cyclohexenone. In benzene and methylene chloride a brown amorphous solid coated the walls of the tube and no crystalline photodimer could be isolated. The photodimer was obtained in a very low yield when solutions prepared by warming XVIII (100 mg) in methanol (100 ml) were irradiated in Pyrex vessels under nitrogen with the Hanovia lamp for 40 h. The photodimer (5 mg) separated from the solution as yellow prisms. Evaporation of the methanol gave a dark-colored solid which, based on its infrared spectrum, was chiefly monomer XVIII, and from which XVIII could be recovered by recrystallization.

The photodimer, on recrystallization from benzene–nitromethane, gave yellow prisms, m.p. 295° (decomp.) (capillary) before and after admixture with XIII obtained by the nitration of the photodimer of 3-phenyl-2-cyclohexenone; the infrared and n.m.r. spectra of the two samples were identical. Irradiation of a suspension of XIII in benzene in a Pyrex vessel with the Hanovia lamp for 25 h gave a brown amorphous solid, from which none of the monomer XVIII could be obtained. Treatment of XIII with concentrated sulfuric acid for 24 h at room temperature led to the recovery of unchanged XIII.

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