PHOTOCHEMICAL SYNTHESES

2. THE IRRADIATION OF ACENAPHTHENE WITH BENZIL

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ABSTRACT

The irradiation product of acenaphthene and benzil described by Oliveri-Mandalà, Giacalone, and Deleo has been shown to have the structure (III) and not that of the cyclobutane derivative (II, R = H) originally proposed. The main product obtained by the action of acetic anhydride and sulphuric acid on (III) is not the result of an acetylation process, but is the sultone (IV).

The irradiation of hydrocarbons, which are capable of giving stable radicals by hydrogen abstraction, in the presence of carbonyl compounds has been shown to give carbinols (2, 3). Cyclohexene and acetone, for instance, give cyclohexenyldimethylcarbinol (I). The reported irradiation (1), in sunlight, of such a hydrocarbon, acenaphthene, in the presence of a diketone was, therefore, of some interest. The product isolated had an analysis corresponding to 1:1 addition, and structure (II, R = H) was proposed on the basis of diacetate (II, R = Ac) formation on acetylation with acetic anhydride and sulphuric acid. Acetic anhydride and pyridine had no action. If correct, this scheme could well provide a new route to syntheses in the cyclobutane series.

The formation of (II, R = H) was a priori not unreasonable since the expected initial product (III) might well cyclize, such an intramolecular reaction being unexceptional (4). However, the formation of a simple diacetate seemed surprising under conditions of such acidity. Such a strained molecule should provide ample opportunity for acid-catalyzed rearrangement and a number of mechanistically credible routes can be envisaged. Furthermore, the main product of the acetylation process was a substance for which no empirical formula was proposed and which was orange-red in color. Since no simple transformation product of (II, R = H) should be so colored the preparation of the irradiation product was repeated.

Irradiation of benzil and acenaphthene in benzene solution using, however, an ultraviolet lamp, gave the desired product with properties as previously described (1). The structure (II, R = H) was shown to be untenable since the infrared spectrum revealed bands in the carbonyl and hydroxyl region at 1669 and 3460 cm⁻¹ compatible with those expected for a benzoin. The alternative structure (III) seemed, therefore, very probable and its correctness was established by the following experiments.

Reduction of (III) with sodium borohydride gave the corresponding diol showing no carbonyl absorption in the infrared. This was further characterized as a monoacetate. Cleavage of the diol with periodic acid then gave benzaldehyde (characterized as the 2,4-dinitrophenylhydrazone) and benzoylacenaphthene. The latter substance had the expected absorption in the infrared and ultraviolet. In addition the n.m.r. spectrum showed a typical ABX pattern for the three non-aromatic hydrogen atoms. (J_{AB} 17.2, J_{AX} 4.7, J_{BX} 7.9 c.p.s.; τ , 6.46, 6.12, and 4.62). However, since the literature (5) records a substance purporting to be 1-benzoylacenaphthene with a melting point differing from

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that of the degradation product by 60°, the ketone was converted to 1-benzylidineacenaphthene identical with a specimen prepared by a Grignard synthesis from acenaphthenone. The structure of the hydrocarbon was confirmed by ozonolysis to benzaldehyde (isolated as the 2,4-dinitrophenylhydrazone) and by quantitative hydrogenation to the oily 1-benzylacenaphthene, which had the expected spectroscopic properties and yielded a crystalline picrate. In addition, heating the benzoylacenaphthene with sodium ethoxide at 180° in the presence of hydrazine resulted in bond cleavage and the formation, by dealdolization, of acenaphthene, together with benzoic acid presumably derived by a Canizzaro reaction from the first-formed benzaldehyde. The nature of the earlier substance, prepared by the irradiation of benzaldehyde and acenaphthene, remains in doubt. No analysis or properties other than the melting point were recorded.



Treatment of (III) with acetic anhydride and sulphuric acid gave the orange-red main product as described by the Italian workers (1). We were unable, however, to isolate any substance corresponding to the supposed "diacetate" even by chromatography. The original isolation involved hand picking of crystals and the recorded analysis for this substance (only carbon and hydrogen reported) lies midway between the starting material and the main product, as does, indeed, the melting point. It is therefore possible that it was a mixture.

The original carbon and hydrogen analysis for the orange-red substance was confirmed. No band attributable to a carbonyl group was visible in the infrared spectrum. The low value for hydrogen immediately suggested that some element other than carbon, hydrogen, or oxygen might be present. In fact, analysis for sulphur established the empirical formula $C_{26}H_{16}O_3S$. The condition of genesis of the substance suggested unsaturated sultone formation (6) and on mechanistic grounds the structure (IV) seemed probable. Its correctness was established in the following way.

Hydrolysis of (IV) with aqueous alcoholic sodium hydroxide gave 1 molecule equivalent of benzoic acid together with the sodium salt of a yellow sulphonic acid formulated as (V). Its formation may be rationalized as a δ -addition of water to the unsaturated sultone followed by either cleavage of the δ -keto, α - β unsaturated acid, or dealdolization to the mixed anhydride followed by hydrolysis. Ozonolysis of (V) followed by treatment with base gave, by condensation of the intermediate 1,5-diketone (VI), the known hydroxyperinaphthenone (VII), which was identified by comparison with an authentic specimen (7) and by ozonolysis to naphthalic anhydride (VIII).

EXPERIMENTAL

Melting points were taken on the Kofler hot stage. Ultraviolet spectra were determined in 95% ethanol and infrared spectra as Nujol mulls.

Irradiation of Benzil and Acenaphthene

Benzil (15 g) and acenaphthene (11 g) in benzene (50 ml) were irradiated in a pyrex flask under nitrogen with an 85 w HC3 (Hanovia) lamp. After 2 days the precipitate was collected (1.28 g) and crystallized from ethyl acetate to give the adduct, m.p. 237–239° (lit. 234°). Calc. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53%. Found: C, 85.33; H, 5.35%. The substance showed λ_{max} 228 m μ (ϵ , 64,000) in the ultraviolet.

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Reduction of the Adduct to the Diol

The adduct (102 mg) in dioxan (5 ml) was treated with a solution of sodium borohydride (21 mg) in methanol (5 ml) at 10°. After 1 hour, the mixture was poured onto ice water and the product isolated with chloroform containing methanol. The combined extracts were washed with water and dried (Na₂SO₄) and the solvent removed to give, after crystallization from methanol, the diol, m.p. 222-224°. Calc. for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05%. Found: C, 85.12; H, 6.32%. The substance showed λ_{max} 230 mµ (ϵ , 64,000).

Acetylation (acetic anhydride – pyridine at 55° for 20 hours) of the diol (29 mg) gave the monoacetate, m.p. (from ethyl acetate) 264–266°. Calc. for $C_{23}H_{24}O_3$: C, 82.33; H, 5.92%. Found: C, 81.96; H, 6.13%.

Periodate Oxidation of the Diol

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To the diol (25.4 mg) in ethyl acetate (3 ml) and methanol (6 ml) was added aqueous periodic acid (0.4 N; 2 ml) and the mixture allowed to stand overnight. The mixture was then steam distilled (after reduction of excess periodic acid with arsenite) and the distillate treated with 2,4-dinitrophenylhydrazine in hydrochloric acid. The precipitate (81% yield) was identified as benzaldehyde 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. 236-240°) by comparison with an authentic specimen.

In a similar experiment on a larger scale (120 mg) the oxidizing mixture was allowed to stand 64 hours. After dilution with water the mixture was extracted with benzene and the isolated benzoyl acenaphthene crystallized from methanol and from ethyl acetate (charcoal), with m.p. 137–138.5°. Calc. for $C_{19}H_{14}O$: C, 88.34; H, 5.46%. Found: C, 88.56; H, 6.00%. The ketone (36 mg) when heated in a scaled tube at 180° in ethanol (1.25 ml) containing sodium (85 mg) and hydrazine (1 ml) (Wolff-Kishner conditions) gave, by isolation with benzene and sublimation, acenaphthene (12 mg), identified by melting point and mixed melting point, with an authentic specimen. Acidification of the aqueous phase and steam distillation gave, after extraction and crystallization from water, benzoic acid (7 mg), identified by m.p. and mixed m.p.

1-Benzylidine-acenaphthene

(a) From 1-Benzoylacenaphthene

The ketone (49 mg) was reduced with sodium borohydride as described above. The syrupy product was transferred to a Dean and Stark apparatus and refluxed overnight in toluene (100 ml) containing *p*-toluene-sulphonic acid (200 mg). After it was washed with sodium hydroxide solution and water, the solution was evaporated under reduced pressure and the residue chromatographed on alumina (Brockmann Grade 1, 5 g). Light petroleum eluted a gummy fraction (15 mg) which, on hydrogenation, afforded 1-benzylace-naphthene (see below) identified by infrared spectrum and by m.p., mixed m.p., and infrared spectrum of picrate. Further elution of the column with benzene in light petroleum (1:9) furnished a crystalline compound (25 mg) which, after repeated recrystallization from acetone, was identical in all respects with a synthetic specimen of 1-benzylidineacenaphthene.

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(b) From Acenaphthenone

Benzyl Grignard reagent was prepared from Mg (360 mg) essentially as described by Adkins and Zartmann (8). To the cooled ethereal solution was added acenaphthenone (9) (2.1 g) in cold dry benzene (18 ml) and the mixture was stirred at ice-temperature (10) for 2 hours, and for a further 1.5 hours while it was allowed to reach room temperature. The complex was decomposed with ice-cold hydrochloric acid (6 N; 100 ml) and the product isolated in the usual way as a syrup. A portion (950 mg) was intimately mixed with boric acid (925 mg) and heated at 160° for 30 minutes (11). The mixture was extracted with light petroleum and the extracts chromatographed on alumina (50 g).

Elution with light petroleum gave a yellow oil (473 mg) which was retained (fraction I). Elution with benzene – light petroleum (1:4) then gave an orange oil (fraction II) (92 mg) which crystallized slowly from ethyl acetate. Repeated crystallization from acetone gave a product having a melting point of 98.0–98.5°. In a similar experiment fraction II was sublimed *in vacuo* at 110° to give material which, on crystallization from acetone, was identical with that obtained by chromatography. Found: C, 93.66; H, 5.77%. Calc. for: C₁₉H₁₄: C, 94.18; H, 5.82%. The substance showed λ_{max} 246 m μ (ϵ , 27,000) in the ultraviolet.

1-Benzylacenaphthene

(a) 1-Benzylideneacenaphthene (m.p. $98-98.5^{\circ}$) (15.5 mg) in ethyl acetate (5 ml) was hydrogenated in the presence of palladized charcoal (5%; 15 mg) with the uptake of 0.94 molecule equivalent of hydrogen. The resultant oil was identical in every respect with that described under (b) below, and gave an identical picrate.

(b) Fraction I (473 mg) obtained from the boric acid treatment described above was hydrogenated in the presence of palladized charcoal with the uptake of 1 molecule equivalent of hydrogen. The oily product was converted, in ethanolic solution, to the picrate (618 mg) m.p. $81-82^{\circ}$ unchanged by further crystallization from alcohol. Found: C, 63.42; H, 4.31; N, 8.90%. Calc. for C₂₅H₁₉O₇N₃: C, 63.42; H, 4.04; N, 8.88%. The picrate (320 mg) was filtered through a column of alumina (8 g) and the column washed with benzene. Isolation of the eluted hydrocarbon and sublimation gave benzylacenaphthene as an oil, $\lambda_{max} 228 \text{ m}\mu$ (ϵ , 78,500), n_D^{25} 1.6409. Found: C, 93.20; H, 6.45%. Calc. for C₁₉H₁₆: C, 93.42; H, 6.60%.

Ozonolysis of 1-benzylideneacenaphthene

The crystalline hydrocarbon (20 mg) in ethyl acetate (2 ml) was treated with a stream of ozone at -10° for 10 minutes and the residue distilled from water containing a few drops of dilute sulphuric acid and a little Zn dust. The distillate was treated with 2,4-dinitrophenylhydrazine in dilute sulphuric acid and the precipitate (10 mg), purified by chromatography on bentonite-celite (1:1 by volume) and crystallization from benzene, was identified as the benzaldehyde derivative by melting point and mixed melting point.

Treatment of the Adduct (III) with Acetic Anhydride

The adduct (0.49 g) was suspended in acetic anhydride (3 ml) and sulphuric acid added dropwise with shaking until the solid had dissolved (about 10 drops). After 24 hours the precipitate (240 mg; m.p. 184–190°) was collected and crystallized from ethyl acetate to give the sultone, m.p. 190–191.5°. (Oliveri-Mandalà *et al.* (1) give 187–188°.) Calc. for C₂₆H₁₆O₃S: C, 76.45; H, 3.95; O, 11.75; S, 7.85%. Found: C, 75.87, 76.26; H, 3.72; 4.16; O, 12.30; S, 7.97%. The substance showed λ_{max} 450, 384, 366, 346, 289, 238 (inf) (ϵ , 6,200, 14,600, 15,100, 12,900, 11,700, and 14,000 respectively) in the ultraviolet.

Careful examination of the mother liquor in the manner previously described (1), and by chromatography failed to reveal any trace of the substance, m.p. 195-196°, reported by Oliveri-Mandalà *et al.* (1).

Hydrolysis of the Sultone (IV)

The sultone (999 mg) was refluxed in aqueous ethanol (80%; 800 ml) containing sodium hydroxide (32 g) until solution was complete (1 hour) and 1 hour further. After acidification the product was isolated by extraction with ethyl acetate. This was washed with saturated sodium sulphate solution and concentrated to 70 ml. The lower aqueous layer which separated was then further extracted with ethyl acetate and the organic phases dried over sodium sulphate,² evaporated to dryness, and added to a silica column (50 g) in benzene. Elution with chloroform gave benzoic acid (317 mg, 1.06 molecule equivalent) identified by melting point and mixed melting point and infrared spectrum with an authentic specimen.

Elution of the column with ethanol-chloroform (1:4) gave a crystalline mixture. This was extracted with boiling ethyl acetate and the residue crystallized from ethanol to give the sulphonic acid sodium salt (V), m.p. 280° (decomp.). Calc. for $C_{19}H_{13}O_3SNa_2H_2O$, C, 64.56; H, 3.99; S, 9.07; Na₂SO₄, 20.11%. Found: C, 64.16; H, 3.93; S, 8.92; ash (sulphated), 20.12%. The substance showed λ_{max} 350, 343, 328, 314, 264, 251, 233 mµ (ϵ 6,700, 6,700, 13,900, 9,200, 3,600, 2,800, 39,600 respectively) in the ultraviolet.

Ozonolysis of the Sulphonic Acid, Sodium Salt (V)

The sodium salt (49.5 mg) in ethanol (5 ml) was treated with a stream of ozone at -20° until the yellow color was discharged (about 10 minutes). Hydrogen peroxide (30%; 0.25 ml) was added, followed by sodium hydroxide solution (10%; 1 ml) and the mixture refluxed 30 minutes. After acidification the orange-yellow precipitate (18.4 mg, m.p. 218–221°) was recrystallized from ethyl acetate to give 3-hydroxy-2-phenylperinaphthenone, m.p. 219–221°, undepressed on admixture with an authentic specimen. The infrared spectra were superposable.

²The sulphonic acid, being a strong acid, exchanged with the sodium sulphate, probably on drying.

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Ozonolysis of 3-Hydroxy-2-phenylperinaphthenone

The perinaphthenone, 18.4 mg, in alcohol (10 ml) was treated with ozonized oxygen at ca. -25° until just colorless. Water (100 ml) containing sodium hydroxide (80 mg) and hydrogen peroxide (30%; 0.2 ml) was added and the solution was concentrated on the steam bath to ca. 5 ml, cooled, and acidified. The precipitate was collected and crystallized from acetic acid containing a drop of acetic anhydride to furnish naphthalic anhydride (9.0 mg), m.p. and mixed m.p. 270-271°, further identified by the infrared spectrum.

The aqueous filtrate from which the naphthalic anhydride had separated was extracted with ether $(3 \times 10 \text{ ml})$. Evaporation of the extracts and sublimation of the residue followed by recrystallization from water gave benzoic acid (3.5 mg), m.p. and mixed m.p. 120-122°.

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