

Photochemical Transformations of the [4+2] Dimeric Adduct of 2-Benzoylnorborna-2,5-diene and its Derivatives

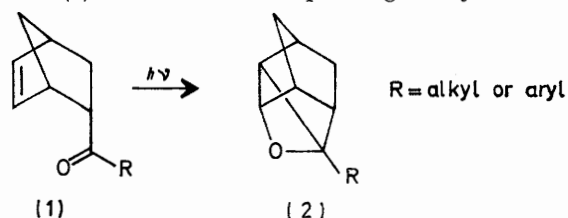
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Irradiation of the [4 + 2] dimeric adduct (7) of 2-benzoylnorborna-2,5-diene yields the [2 + 2] dimeric adduct (9). The head-head combination in structure (9) has been established by its conversion into the known 3,3'-dibenzyl-2,2'-binorborn-5-ene (12). Irradiation of tetrahydro-derivative (8) of the adduct (7), however, gives the retro-diene product, 2-benzoylnorborn-2-ene (16), identified by comparison with synthetic material. The intermediacy of a cyclobutane (19) in the formation of compound (16) was ruled out by the isolation of the cyclobutanol (20) as the major product from irradiation of (19). Mechanistic pathways for these transformations are discussed.

GROWING interest in the solution photochemistry of alkanones has motivated several studies from a mechanistic as well as a synthetic point of view.¹ The most extensively studied transformations are the Paterno-Buchi reaction² and other related reactions of electronically excited ketones with olefins,³ and photoelimination and cyclisation of aryl alkyl ketones having a γ -hydrogen atom.⁴ Both these classes of reaction are known to proceed through the intermediacy of 1,4-diradicals. Cyclic olefins having geometrically accessible acyl functions undergo intramolecular cyclisation to form oxetans on irradiation. For example, *endo*-5-acylnorborn-2-enes (1) photocyclise readily to give the oxetans (2) whereas the corresponding *exo*-derivatives are photochemically inactive.⁵

Substituents in the α - or β -position have a pronounced effect on the fate of intermediate diradical in Type II elimination and cyclisation reactions. α -Substituents increase the percentage of cyclisation products whereas β -substituents have the opposite effect.⁶ For example,

endo-2-benzoylnorbornane (3) gives the elimination product (4) whereas the corresponding α -alkyl derivative



(5) gives exclusively the cyclobutanol (6).⁷ The effect of substituents on the behaviour of the 1,4-diradical intermediates has been explained in terms of the transition states for diradical cyclisation and elimination.^{4,6,7}

Recently we described the formation of the dimer (7) during the thermal 1,4-cycloaddition of ethynyl phenyl ketone to cyclopentadiene.⁸ The dimeric adduct (7) and its tetrahydro-derivative (8) have an *endo*-oriented benzoylnorbornene or benzoylnorbornane structural unit, re-

¹ N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, N. Niemczyk, and N. Schore, *Accounts Chem. Res.*, 1972, **5**, 92.

² E. Paterno and G. Chieffi, *Gazzetta*, 1909, **39**, 341; G. Buchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, 1954, **76**, 4327.

³ I. E. Kochevar and P. J. Wagner, *J. Amer. Chem. Soc.*, 1972, **94**, 3859, and references cited therein.

⁴ P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.

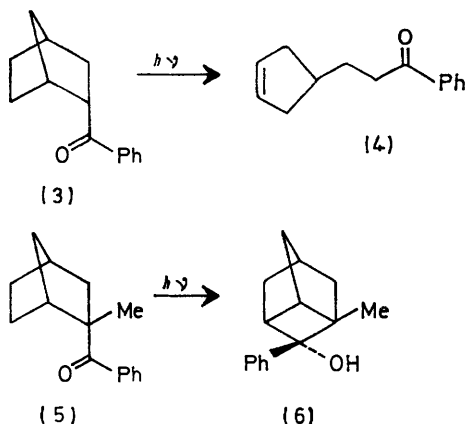
⁵ R. R. Sauer, W. Schinski, and M. M. Mason, *Tetrahedron Letters*, 1969, 79.

⁶ F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, 1972, **94**, 3852.

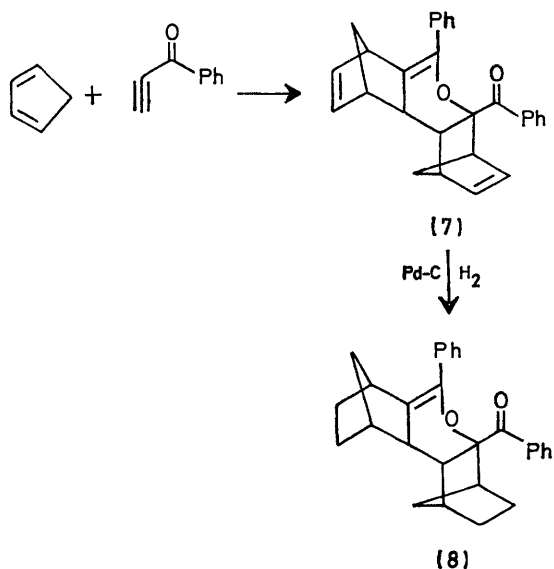
⁷ F. D. Lewis and R. A. Ruden, *Tetrahedron Letters*, 1971, 715.

⁸ P. S. Venkataramani, S. Chandrasekaran, and S. Swaminathan, *Tetrahedron*, 1972, **28**, 1249.

spectively, with an adjoining dihydropyran ring. These structural features prompted us to study the photochemistry of these compounds with the hope of providing



further information of stereochemical and structural relevance to the major photoprocesses described earlier. We also thought that the results might confirm our stereochemical assignment for the dimer (7). We now

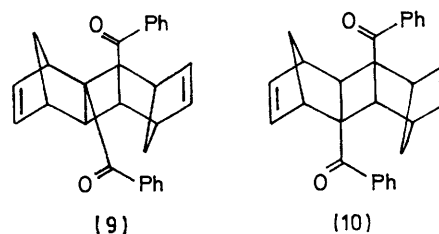


describe some photochemical transformations of the dimer (7) and its tetrahydro-derivative (8).

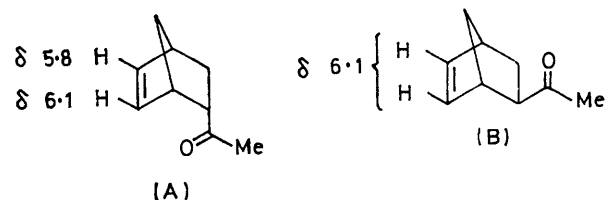
Irradiation of a solution of the dimer (7) in benzene at 300 nm in a nitrogen atmosphere for 22 h gave a single crystalline product isolated by preparative layer chromatography (p.l.c.) in 27% yield. The compound was isomeric with the starting material and its spectral data can be interpreted in favour of a cyclobutane structure (9) or (10). The mass spectrum showed the molecular ion peak at m/e 392 with major fragments at m/e 326, 211, 105 (base peak), and 77. The compound had i.r. absorptions at 6.05, 6.25, and 6.35 μm and a u.v. maximum at 247 nm (ϵ 16,390). The n.m.r. spectrum showed two sets of aromatic proton signals at

δ 7.7—8.0 (4H) and 7.2—7.5 (6H), suggesting the presence of two benzoyl groups. The olefinic region showed absorptions [δ 6.3 (2H) and 5.7 (2H)] characteristic of an *endo*-5-acylnorborn-2-ene structural unit. Absorptions in the methylene region at δ 3.1—3.3 (2H), 2.8—3.0 (2H), and 2.4 (2H) can be assigned to the two allylic bridgehead protons adjacent to the benzoyl groups, the other two allylic bridgehead protons, and the two cyclobutyl protons, respectively. It is pertinent at this stage to elaborate further on the olefinic absorptions of *endo*-5-acylnorbornenes.

The two olefinic protons of *endo*-5-acetylnorbornene absorb at δ 5.8 and 6.1, respectively. Dinwiddie and McManus, who observed this initially, attributed the non-equivalence to the proximity of one of these protons to the carbonyl of the *endo*-acetyl group.⁹ In the *exo*-isomer the acetyl group is too far removed from the



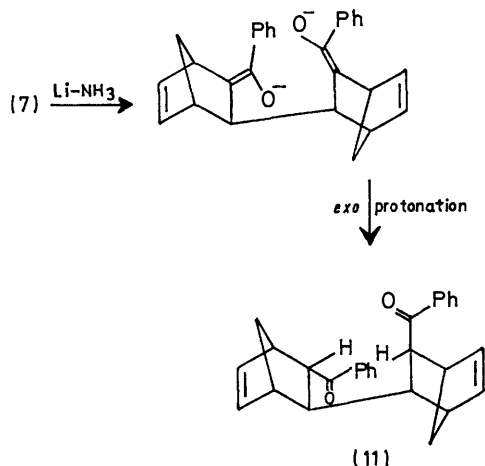
olefinic protons to exert any influence and the two olefinic protons appear equivalent, showing a single absorption at δ 6.1. The assignments made arbitrarily by Dinwiddie and McManus for the olefinic protons of *endo*-5-acetylnorbornene are illustrated [see (A)]. The olefinic protons of *endo*-5-benzoylnorbornene, prepared according to a scheme briefly outlined without experimental details by Sauer,⁵ also show this non-equivalence (δ 5.75 and 6.1). Obviously one of the olefinic protons is shielded by the carbonyl of the *endo*-acyl group. However, it is not apparent from models which proton this is, and further work needs to be done for definitive assignment. Nevertheless such non-equivalence of olefinic protons in an *endo*-acylnorbornene is established and can be used as evidence of *endo* geometry for the acyl function in compounds containing similar structural units. We have previously reported that the dimer (7)



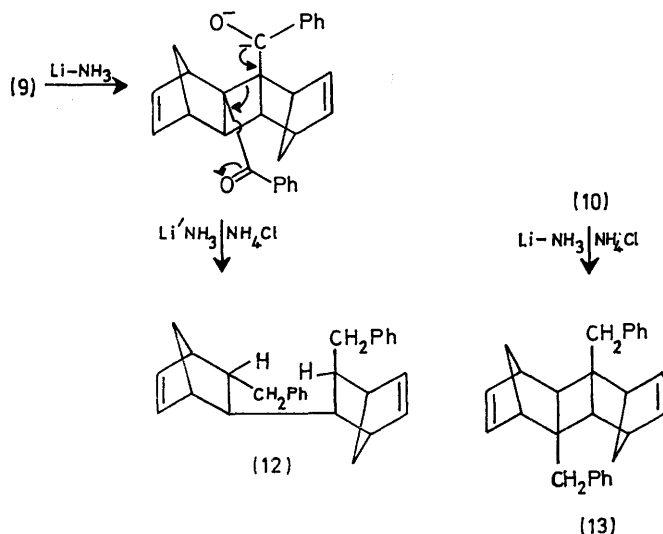
itself, which has an *endo*-oriented benzoylnorbornene system, shows a 3 : 1 ratio of absorptions at δ 6.2 and 5.5 in the olefinic region.⁸ The *endo*-benzoylnorbornene

⁹ J. G. Dinwiddie and S. P. McManus, *J. Org. Chem.*, 1965, **30**, 766.

dimer (11)* shows a 2:2 ratio of olefinic absorptions centred at δ 6.35 and 5.65.



Reduction of the photoproduct [(9) or (10)] with lithium-ammonia provided confirmatory evidence in favour of structure (9) with the head-to-head disposition of the two benzoyl groups. The product (12) was previously obtained by us from similar reduction of the dimer (7).⁸ Compound (9), being a 1,4-diketone can undergo bond cleavage with opening of the cyclobutane ring to give (12), whereas structure (10) could only give rise to the hydrocarbon (13), with the cyclobutane ring intact.

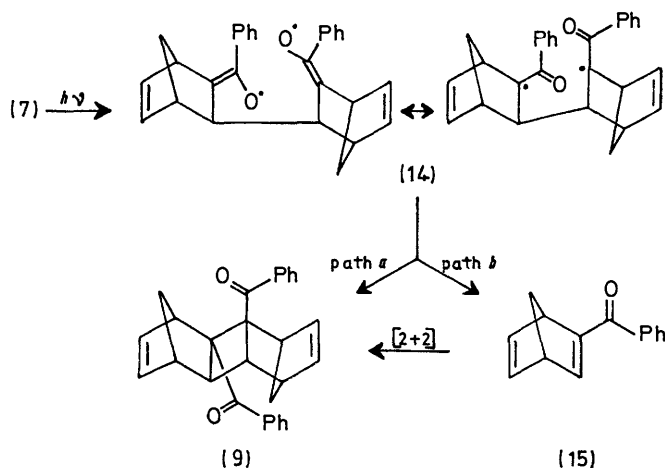


The formation of the photoproduct (9) can be explained by a radical dissociation-recombination mechanism similar to that suggested for the photochemical rearrangement of enol ethers such as 2,3-dihydrofurans.¹²

* Compound (11) results from reduction of dimer (7) with lithium-ammonia followed by quenching with sodium benzoate and ammonium chloride.¹⁰ The *endo*-configuration of the benzoyl groups is expected from the known selectivity of protonation and electrophilic attack on the *exo* (less hindered) side in norbornyl systems.^{8,11}

Thus rupture of the α -alkoxide bond of the carbonyl $n-\pi^*$ excited state of the dimer would give the intermediate enolate diradical (14), which could recombine to form the cyclobutane (9) (path *a*). Alternatively the diradical (14) could dissociate to the retro-diene product (15), which could subsequently undergo a photochemical [2 + 2] dimerisation (path *b*) (Scheme 1).

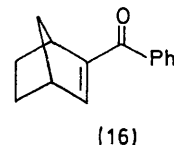
In the absence of additional data a preference for one or other mechanistic pathway cannot be stated. The dienone (15) itself was never isolated from the photo-reaction. This, however, is not unexpected in view of the high reactivity of 2-benzoylnorbornadiene (15) observed earlier.⁸ The dimer (7) could be recovered to the extent of 25%. There was no evidence of formation



SCHEME 1

of oxetans derived either from the dimer (7) or its photoproduct (9). The photochemical transformation of (7) to (9) constitutes a ready one-step conversion of a [4 + 2] dimer of 2-benzoylnorbornadiene into a [2 + 2] dimer.

Irradiation of a solution of the tetrahydro-dimer (8) in benzene at 300 nm in a nitrogen atmosphere for 3 h, followed by p.l.c., furnished a crystalline product, $\text{C}_{14}\text{H}_{14}\text{O}$, in 64% yield; m/e 198 (M^+) with major fragments at 170, 105 (base peak), and 77; λ_{max} 6.17, 6.3, and 6.4 μm ; λ_{max} 245 nm (ϵ 17,120); δ 7.6–7.9 (2H) and 7.2–7.5 (3H) (PhCO), 6.6 (d, β -olefinic proton of an



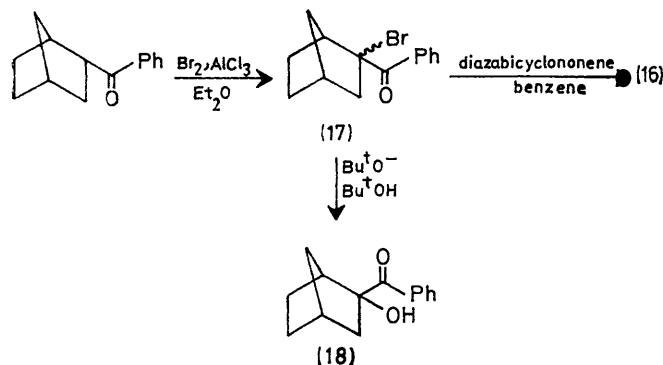
$\alpha\beta$ -unsaturated ketone), and 3.5 and 3.15 (two bridge-head protons). These data can be interpreted in favour of structure (16), which was confirmed by an independent

¹⁰ S. Chandrasekaran, Ph.D. Thesis, University of Madras, 1972.

¹¹ H. Kwart and T. Takeshita, *J. Org. Chem.*, 1963, **28**, 670; H. C. Brown and W. J. Hammer, *J. Amer. Chem. Soc.*, 1967, **89**, 1524.

¹² D. W. Boykin, jun., and R. E. Lutz, *J. Amer. Chem. Soc.*, 1964, **86**, 5046.

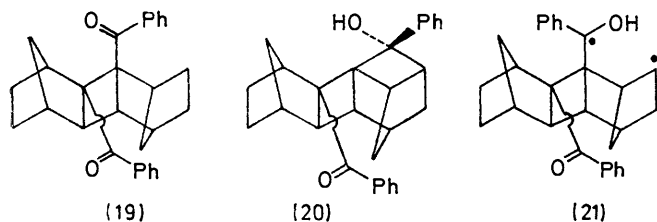
synthesis* (Scheme 2). When the dehydrobromination of the intermediate (17) was effected with *t*-butoxide,¹⁴ compound (18) was isolated in 43% yield. The stereochemistry at C-2 was not rigorously established by us; however, subsequent to the completion of this work



SCHEME 2

Stevens and his co-workers have reported the synthesis of the hydroxy-ketone (18) and its epimer by stereocontrolled transformations.¹⁵ A comparison with the reported m.p.s indicated that our compound (18) was predominantly the *exo*-benzoyl epimer.

The formation of the photoproduct (16) from the tetrahydro-dimer (8) can be rationalised by invoking diradical intermediates as before (*cf.* Scheme 1). The diradical formed can either dissociate as in path *b* to give the retro-diene product (16) directly or recombine to form the cyclobutane (19), which can undergo a [2 + 2] cycloreversion to give (16) (path *a*). The latter possibility, however, was ruled out by the isolation of a different compound (20) as the major product from irradiation of (19) obtained by hydrogenation of the cyclobutane (9). The cyclobutanol (20) showed *m/e*



396 (M^+) with major fragments at 291 and 105; λ_{\max} 2.9, 6.12, 6.3, and 6.4 μm ; δ 7.1–7.4, 7.4–7.6, and 7.7–8.1 (10H) (Ph and PhCO), 2.9–3.1 (bridgehead protons), 2.5–2.8 (OH), and 2.0–2.4 (cyclobutyl H). The stereochemistry at the carbinol centre was based

* The enone (16) was synthesised previously¹³ by Diels–Alder addition of β -chlorovinyl phenyl ketone to cyclopentadiene, followed by hydrogenation and dehydrohalogenation (m.p. 80–81°). A higher melting compound (m.p. 131°; 20%) was also isolated from the dehydrohalogenation step. The structure of the higher-melting compound was not elucidated, and we believe that this might be the Diels–Alder dimer (8) of enone (16). The ready availability of *endo*-2-benzoylnorbornane obtained by the hydrogenation of *endo*-5-benzoylnorbornene prompted us to synthesise (16) by the route outlined in Scheme 2.

on analogy.⁷ Compound (16) was obtained as a minor product from this reaction.

The formation of compound (20) is readily rationalised in terms of cyclisation of the 1,4-diradical intermediate (21) formed by γ -hydrogen abstraction from the carbonyl $n-\pi^*$ excited state of (19). The total absence of any Type II cleavage product from the diradical (21) is in accord with currently accepted views on the factors governing relative rates of cyclisation *vs.* elimination.^{4,6,7} The most favourable transition state for elimination would require overlap of both radical orbitals with the bond undergoing cleavage. Such a transition state may be destabilised in the 1,4-diradical (21) owing to unfavourable 1,2-eclipsing interactions between the α -substituent (the *exo*-cyclobutyl bond) and the Ph and OH groups. The absence of such an interaction in the transition state for cyclisation results in the exclusive formation of the cyclobutanol (20). The reason for the non-participation of the other benzoyl group in cyclobutanol formation is perhaps the amount of strain involved in the formation of a further cyclobutane ring. The formation of the enone (16) can be assumed to arise from a [2 + 2] ring opening of (19) with or without the intervention of the diradical (21).

The formation of the enone (16) by a stepwise photo-retro-diene reaction of the tetrahydro-dimer (8) suggests that perhaps the cyclobutane (9) is also formed through path *b* (Scheme 1) by a similar photo-retro-diene reaction of (7) followed by a [2 + 2] dimerisation.

The action of heat on the dimer (7) did not yield any useful products, whereas the tetrahydro-dimer (8) underwent a smooth retro-diene reaction to give (16) in 73% yield.

EXPERIMENTAL

Petrol refers to the fraction of b.p. 60–80°. Irradiations were carried out in a Rayonet Preparative Photochemical Reactor. N.m.r. spectra were recorded with a Varian A-60 instrument.

Irradiation of the Dimer (7).—A solution of the dimer (7) (600 mg) in dry benzene (400 ml) was purged with nitrogen for 1 h, then irradiated at 300 nm for 22 h. Nitrogen was bubbled through the solution throughout the reaction. Benzene was removed under reduced pressure and the residue was filtered through a short column of silica gel to remove any polymeric material. The resulting pale yellow liquid (500 mg), purified by p.l.c. (silica gel; benzene) gave 2,3-dibenzoylpentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene (9) as a solid (170 mg, 27%), m.p. 149–150° (from petrol) (Found: C, 85.5; H, 6.1. $C_{28}H_{24}O_2$ requires C, 85.7; H, 6.2%) (for spectral data see Discussion section). Starting material (150 mg) was recovered.

Reduction of the Photoproduct (9) with Lithium–Ammonia.—To a stirred solution of lithium (50 mg) in liquid ammonia (250 ml) containing ammonium chloride (10–15 mg) was

¹³ N. K. Kochetkov and A. Ya. Khorlin, *Zhur. obshchei Khim.*, 1957, **27**, 3182 (*Chem. Abs.*, 1958, **52**, 8984g).

¹⁴ H. Kwart and J. L. Nyle, *J. Amer. Chem. Soc.*, 1964, **86**, 2601.

¹⁵ C. L. Stevens, T. A. Treat, and P. M. Pillai, *J. Org. Chem.*, 1972, **37**, 2091.

added a solution of compound (9) (220 mg) in dry ether (20 ml). The solution was stirred for 1 h and decomposed with solid ammonium chloride. The mixture was evaporated and water was added to the residue which was then extracted with ether. The extract was washed with water, dried (MgSO_4), and evaporated. The solid obtained was crystallised from ethanol to give the dibenzylbionbornene (12) (120 mg), m.p. 100–100.5°, identical (m.p. and mixed m.p., i.r. spectrum, t.l.c.) with that obtained previously by us by reduction of the dimer (7).⁸

Irradiation of the Tetrahydro-dimer (8).—Irradiation of compound (8) (400 mg) in dry benzene (400 ml) at 300 nm in a dry nitrogen atmosphere for 3 h gave a liquid which after p.l.c. (silica gel; benzene) and sublimation (115–125° at 2 mmHg) afforded 2-benzoylnorborn-2-ene (16) as a solid, m.p. 77–78° (205 mg, 64%) (Found: C, 84.7; H, 7.3. Calc. for $\text{C}_{14}\text{H}_{14}\text{O}$: C, 84.8; H, 7.1%) (for spectral data see Discussion section).

endo-2-Benzoylnorbornane.—A solution of *endo*-5-benzoylnorborn-2-ene⁵ (2 g) in ethyl acetate (15 ml) containing 10% palladium-charcoal (200 mg) was hydrogenated at 50 lb in⁻² for 30 min. Filtration and distillation left a pale yellow viscous liquid (1.9 g). Distillation *in vacuo* (bath temperature 155–165°; 5 mmHg) gave pure *endo*-2-benzoylnorbornane, λ_{max} (CHCl_3) 6.0 and 6.2 μm ; δ (CDCl_3) 7.8–8.1 (2H, m, *ortho*-protons of CPh), 7.2–7.5 (3H, m, *meta*- and *para*-protons of CPh), 3.4–3.8 (1H, q, CH·CO), 2.4–2.7 (1H, s), and 2.1–2.3 (1H, s) (bridgehead CH), 1.8–2.0 (1H, CH), and 1.0–1.8 (7H, m, methylenes).

2-Benzoyl-2-bromonorbornane (17).—To a solution of 2-benzoylnorbornane (2 g) in dry ether (25 ml) containing anhydrous aluminium chloride (10 mg), cooled in ice, bromine (1.7 g) was added dropwise. The mixture was stirred for 45 min, quenched with water, and, after the usual work-up, gave 2-bromo-2-benzoylnorbornane (17) (2.2 g) as a pale brown liquid, homogeneous on t.l.c., λ_{max} (CHCl_3) 6.0 and 6.25 μm .

2-Benzoylnorborn-2-ene (16).—A mixture of the crude bromo-ketone (17) (900 mg), 1,5-diazabicyclo[3.4.0]non-5-ene (430 mg), and benzene (20 ml) was refluxed on a water-bath for 2 h. The solution was washed with dilute hydrochloric acid and water, dried (MgSO_4), and distilled to leave a pale yellow viscous liquid, which, after p.l.c. (silica gel; benzene) gave 2-benzoylnorborn-2-ene (110 mg), m.p. 77–78° (lit.,¹³ 80–81°), identical (m.p. and mixed m.p., i.r. spectrum, t.l.c.) with compound (16) obtained in the irradiation of the tetrahydro-dimer (8).

2-Benzoylnorborn-2-ol (18).—The crude bromo-ketone (17) (420 mg) in *t*-butyl alcohol (5 ml) was added to potassium *t*-butoxide [from potassium (100 mg)] in *t*-butyl alcohol (10 ml), and the mixture was refluxed for 10 min over a water-bath. The usual work-up gave a yellow liquid (300 mg) which after p.l.c. (silica gel; benzene)

gave a *solid* (140 mg) (43%), m.p. 53–54° (from petrol), M^+ 216, λ_{max} (CHCl_3) 2.85, 5.9, and 6.4 μm ; δ (CDCl_3) 7.2–7.7 (5H, m, aromatic), 3.9–4.1 (1H, m, OH), 3.0–3.2 (1H, s, CH), 2.4–2.6 (3H, s, CH), and 1.2–2.0 (6H, m, methylenes) (Found: C, 77.6; H, 7.8. $\text{C}_{14}\text{H}_{16}\text{O}_2$ requires C, 77.8; H, 7.5%).

The *exo*-benzoyl epimer (18) is reported to melt at 59–60°;¹⁵ our sample was probably contaminated with the *endo*-epimer. Further purification by t.l.c. was not successful probably because both epimers have the same R_F value.

Catalytic Hydrogenation of the Photoproduct (9).—A solution of the photoproduct (9) (300 mg) in ethyl acetate (100 ml) was hydrogenated over 10% palladium-charcoal (100 mg) at 40 lb in⁻² for 45 min. Filtration and removal of solvent left 2,3-dibenzoylpentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]-tetradecane (19) (280 mg), m.p. 147–148° (from petrol); λ_{max} (CHCl_3) 6.075, 6.27, and 6.35 μm ; δ (CDCl_3) 7.0–7.7 (10H, m, aromatic), 2.5–2.7 (4H, s, bridgehead protons), 2.3–2.4 (2H, s, cyclobutyl protons), 2.0–2.2 (2H, s, bridge CH), and 1.0–1.6 (10H, m, methylenes) (Found: C, 84.5; H, 7.3. $\text{C}_{28}\text{H}_{28}\text{O}_2$ requires C, 84.8; H, 7.1%).

Irradiation of the Cyclobutane (19).—A solution of the cyclobutane (19) (300 mg) in benzene (200 ml) was irradiated at 300 nm for 6 h. Removal of solvent left a liquid which showed three spots on t.l.c. (silica gel), R_F 0.6, 0.7, and 0.8 in 30% petrol-benzene. The three components were separated by p.l.c. to give 2-benzoyl-14-phenylhexacyclo[8.2.1.1^{2,12}.1^{4,7}.0^{2,9}.0^{3,8}]-pentadecan-14-ol (20) (100 mg, 33%), R_F 0.6, m.p. 188–189° (from petrol-ethyl acetate) (Found: C, 84.5; H, 7.4. $\text{C}_{28}\text{H}_{28}\text{O}_2$ requires C, 84.8; H, 7.1%) (for spectral data see Discussion section); 2-benzoylnorborn-2-ene, R_F 0.7 (26 mg, 9%), m.p. 76–78°, identical with authentic (16) (m.p. and mixed m.p., i.r. spectrum, t.l.c.); and starting material, R_F 0.8 (90 mg, 30%), m.p. 145–147°.

Action of Heat on the Tetrahydro-dimer (8).—The tetrahydro-dimer (8) (150 mg) was heated to 190–200° at 55 mmHg for 0.5 h. The product that sublimed (110 mg), m.p. 77–78°, was identical with compound (16) (m.p. and mixed m.p., i.r. spectrum, t.l.c.).

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