# Photocyclizations of 5-Acylbicyclo[2.2.2]octenes

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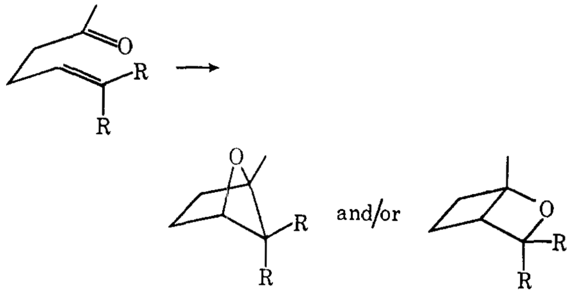
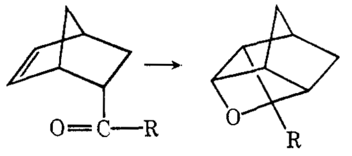
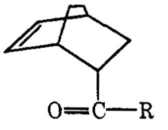
Tetracyclic oxetanes were produced on irradiation of 5-acylbicyclo[2.2.2]octenes. The carbon skeleton of these compounds is believed to be that of twist-brendane (**9**) as shown by conversion of **5** into **9**. Other transformations of synthetic interest are reported.

As a part of a program designed to survey the synthetic potentialities of the intramolecular Paterno–Büchi reaction (eq 1),[1] it was of interest to examine the behavior of some polycyclic unsaturated ketones. It had been shown earlier[2] that 5-acylnorbornenes (**1**) photocyclize cleanly with the formation of synthetically useful oxetanes of general type **2**. It was of interest to extend these studies to the homologous bicyclo[2.2.2]octenes (**3**) with the hope of providing useful intermediates for the synthesis of nine-carbon polycyclic systems. It was also of interest to determine the effect, if any, of the more flexible ring system on the product distribution between the two possible isomeric oxetanes.[1]



(1)

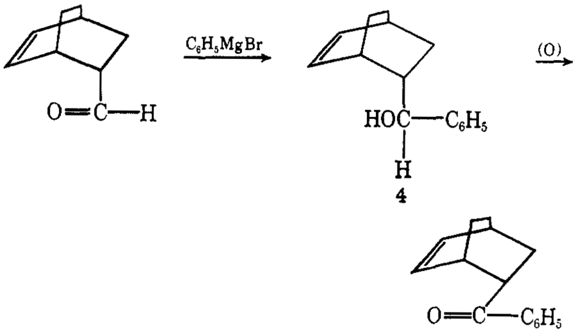




**1** **2** **3**

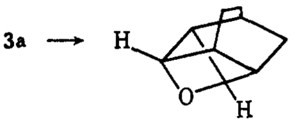
## Results and Discussion

Three representative carbonyl derivatives of bicyclo[2.2.2]octene were chosen for this study: the aldehyde (**3a**, R = H), the methyl ketone (**3b**, R = $CH_3$), and the phenyl ketone (**3c**, R = $C_6H_5$). The aldehyde and methyl ketone were prepared in the usual way from 1,3-cyclohexadiene and the appropriate dienophile. The phenyl ketone **3c** was prepared by oxidation of the alcohols (**4**) produced by addition of phenylmagnesium bromide to aldehyde **3a** (eq 2).

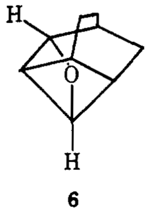


(2)

Irradiations were carried out on *exo–endo* mixtures of the carbonyl compounds in dilute benzene or ether solutions through which nitrogen was bubbled to remove dissolved oxygen. Corex filters (λ >260 mμ) were used with a medium-pressure mercury immersion lamp. The aldehyde **3a** was rapidly consumed under these conditions and a photoproduct was produced which displayed a complex two-proton multiplet at δ 4.42 as the only low field absorption. On the assumption that the product was either oxetane **5** or **6**, a structure proof was designed to reveal the basic carbon skeleton of the compound in question.



**5**



**6**

Reductive cleavage of the oxetane with lithium aluminum hydride proceeded smoothly only in N-methylmorpholine. A secondary alcohol was obtained which on oxidation gave a ketone which showed carbonyl stretching absorption at 5.64 μ.[3] The fact that the hydrocarbon produced by Wolff–Kishner reduction of the ketone proved to be twist-brendane[4] (**9**) allows assignment of structure **5** to the oxetane under consideration. Although the structures of the ketone and alcohol are not uniquely defined by these

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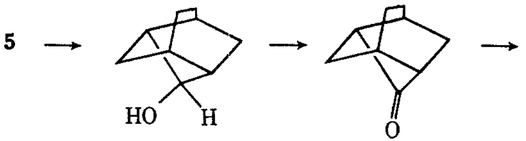
[1] R. Srinivasan, *J. Amer. Chem. Soc.*, **82**, 775 (1960); N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Lett.*, 1525 (1965).

[2] R. R. Sauers, W. Schinski, and M. M. Mason, *ibid.*, 79 (1969).

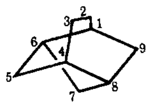
[3] This datum does not unambiguously differentiate this ketone from the other possible isomers which might be obtained from **5** and **6**. For example, cleavage of **6** to a cyclobutanol would lead to a cyclobutanone on oxidation. In a similar molecule the carbonyl group also absorbed at 5.64 μ; *cf.* G. Büchi, E. Koller, and C. W. Perry, *J. Amer. Chem. Soc.*, **86**, 5646 (1964).

[4] B. R. Vogt, *Tetrahedron Lett.*, 1579 (1968). We are indebted to Dr. Vogt for spectral data on this compound.

results, information presented below require formulae **8** and **7**, respectively, for these compounds.[5]

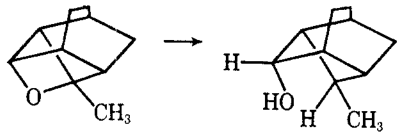


**7** **8**



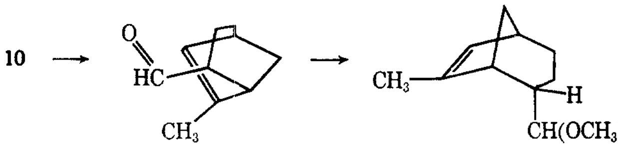
**9**

Similarly, the methyl ketone **3b** underwent smooth photocyclization to form oxetane **10**, the structure of which is assigned by analogy with the above results. This compound proved to be a versatile intermediate as evidenced by the production of the alcohol **11** on reduction with lithium aluminum hydride.[6]



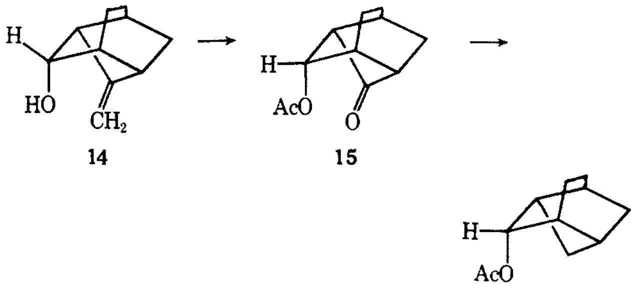
**10** **11**

Cleavage of **10** with perchloric acid in methanol similarly provided useful synthetic results. Two products were isolated and characterized from this reaction. The minor product (*ca.* 33%) was shown by analysis of nmr data to be an unsaturated dimethyl acetal. It would appear that the oxetane undergoes ring opening to form the unsaturated aldehyde **12**[7] which subsequently is converted into the acetal **13**.[5,8]



**12** **13**

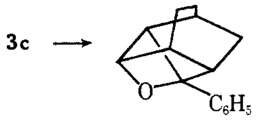
The major cleavage product proved to be an unsaturated alcohol as evidenced by the appearance of two singlets at δ 4.64 and 4.77 in the nmr spectrum ($H_2C{=}C$ protons) and the formation of an acetate on treatment with acetic anhydride. These data and mechanistic considerations are suggestive of structure **14** for this compound. In support of this structure, keto acetate **15** ($\lambda_{C=O}$ 5.63 and 5.72 $\mu$) could be produced on reductive ozonolysis of the acetate ester of **14**. Selective removal of the functional groups at $C_9$ would allow correlation of this series of compounds with those (**7** and **8**) produced from **5**. For this purpose the thioketal of **15** was prepared and subjected to Raney nickel desulfurization. The fact that the resulting ester (**16**) proved to be different from the acetate of alcohol **7** established that the mode of cleavage of **5** was in the direction indicated (*vide supra*).



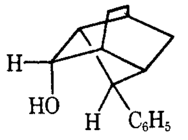
**14** **15**

**16**

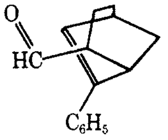
Finally, upon irradiation of the phenyl ketone **3c** an unstable oil was produced which could not be rigorously purified. From spectral data, it was clear that this material was mainly oxetane to which, by analogy, structure **17** is assigned. The crude product could be utilized synthetically as shown by its conversion with Raney nickel into a tricyclic alcohol. The most reasonable structure for this product is believed to be that of **18** on the basis of several analogies involving retention of configuration during similar hydrogenolyses.[9] Also consistent with this structure is the abnormally low field absorption in the nmr spectrum (δ 3.9) attributed to the ArCH proton. A similar deshielding was noted in the homologous series[2] and was attributed to steric deshielding by the hydroxyl group.[10,11]



**17**



**18**



**19**

The crude oxetane always displayed carbonyl absorption and it is believed that this is a product of ring opening. On treatment of the oxetane with 2,4-DNPH reagent a hydrazone was obtained which is assumed to be the derivative of **19**.[7]

In summary, these results exemplify the utility of the intramolecular oxetane reaction for the construction of complex polycyclic molecules. It should be stressed that these reactions are conveniently carried out on a relatively large scale without the need for rigorous degassing or use of highly purified starting materials. For example, the presence of *ca.* 10% *exo* isomers

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(5) The formation of only alcohol **7** from **5** has precedence from the recent work of J. Meinwald and R. A. Chapman, *J. Amer. Chem. Soc.*, **90**, 3218 (1968).

(6) The configuration about the methyl carbon is assigned by analogy with the earlier studies[1] and on the basis of the abnormal chemical shift of the tertiary proton (δ 2.72, quartet, $J = 7$ cps). This type of reduction, which has the characteristics of an electrophilic ring cleavage rather than a nucleophilic one, has also been observed in epoxide reductions; *cf.* J. P. Monthéard and Y. Chrétien-Bessière, *Bull. Soc. Chim. Fr.*, 336 (1968).

(7) *Cf.* G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4327 (1954).

(8) Treatment of **10** with acidic 2,4-dinitrophenylhydrazine produced the hydrazone of **12**.

(9) For a recent discussion and references, see A. M. Khan, F. J. McQuillin, and I. Jardine, *J. Chem. Soc., C*, 136 (1967).

(10) The analogous protons in various phenylcycloalkanes appear[9] in the δ 3.4–2.7 range. This same affect was noted in the homologous tricyclooctyl systems.[1]

(11) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5247 (1965).

can be tolerated in these syntheses owing to the fact that no volatile products are formed from them. The absence of isomeric oxetanes is also noteworthy. From a consideration of molecular models, it would appear that the relative ease of formation of the C–O bond at either $C_5$ or $C_6$ might be nearly equally efficient.[12] If this step proves to be reversible,[13,14] the product distribution would be determined by the relative ease of formation of the carbon–carbon bond. Further discussion of the details of the mechanism of the reaction will be deferred until quantitative data can be obtained.

## Experimental Section

Elemental analyses were by Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were determined in carbon tetrachloride or as noted on a Perkin-Elmer Model 21 spectrophotometer. Nuclear magnetic resonance data were obtained from a Varian Model A-60 spectrometer in carbon tetrachloride or as noted with tetramethylsilane as an internal standard. Integration data was usually accurate to within ±10% of the values reported. Unless otherwise noted, gas chromatograms (gc) were determined on an Aerograph A-90 P instrument on 0.25-in. (o.d.) columns (10–15 ft) of Carbowax 20M on Chromosorb G. Melting points were determined on a Mel-Temp apparatus and are uncorrected.

**Bicyclo[2.2.2]oct-2-ene-5-carboxaldehyde (3a).**—The aldehyde was prepared essentially by the method in ref 15 except that the heating period was changed to 48 hr at 150°. Under these conditions a yield of 80% was obtained, bp 50–51° (1 mm) [lit.[15] bp 84–85° (12 mm)]. The ratio of isomers was shown by gc analysis (160°) to be 90% *endo* to 10% *exo*.

**3-Oxatetracyclo[4.3.1.$0^{2,5}$.$0^{4,9}$]decane (5).**—A solution of 35.5 g (0.26 mol) of **3a** in 5 l. of reagent grade benzene was purged with dry, oxygen-free nitrogen for 30 min. The solution was irradiated for 14 days with a 450-W Hanovia Type L immersion lamp equipped with a Corex filter. The photolysis was interrupted after 7 days to clean the lamp. The crude oxetane was obtained by evaporation of the benzene at reduced pressure. Sublimation at 150° (60 mm) yielded 23.1 g (65%) of oxetane **5**: mp 160–163°; nmr $\delta$ 4.42 (m, 2, HCO), 3.10 (m, 1), and 2.5–0.8 (m).

*Anal.* Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.12; H, 8.68.

**7-Hydroxytricyclo[4.3.0.$0^{4,8}$]nonane (7).**—To a solution of 4.88 g (0.036 mol) of 5 in 300 ml of N-methylmorpholine was added 10 g (0.26 mol) of lithium aluminum hydride. The slurry was stirred at reflux for 60 hr at which time it was cooled and treated cautiously with methanol, water, and dilute HCl. The crude product was extracted into chloroform which was dried ($MgSO_4$) and evaporated. The resulting product was crystallized from ether–petroleum ether (bp 60–90°) to yield 1.67 g (35%) of **7**: mp 170–172°; gc (155°) indicated small amounts of three minor impurities (*ca.* 5% total); nmr $\delta$ 4.01 (s, 1, HCO), 3.53 (s, 1, HO), 2.3–1.0 (m, 10); ir (Nujol) 9.23 (s), 9.68 (m), 9.89 (m), 11.42 (m) $\mu$.

*Anal.* Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.48; H, 10.31.

**Acetylation of 7.**—The acetate of **7** was prepared in pyridine at 25° (4 hr) with acetic anhydride. A pure sample was obtained by preparative gc (150°): nmr $\delta$ 4.69 (s, 1, HCO), 1.96 (s, $CH_3$), 1.2–2.4 (m, 15); ir (film) 5.73 (s), 8.03 (s), 9.32 (m), 9.45 (m), 9.66 (m) $\mu$.

*Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.27; H, 8.75.

**Tricyclo[4.3.0.$0^{4,8}$]nonan-7-one (8).**—A solution of 1.67 g (0.012 mol) of **7** in 25 ml of acetone was treated with 2.3 ml of 8.0 *N* Jones[16] reagent over 1.5 hr with ice cooling. Isopropanol was used to destroy excess reagent and the mixture was diluted with 100 ml of water. Chloroform extracts were combined and dried ($MgSO_4$) and evaporated to give 1.065 g (63%) of **8**: mp 141–143° after sublimation at 100° (20 mm); nmr $\delta$ 1.2–2.2 (m); ir ($CCl_4$) 5.63 (s), 5.77 (m), 9.18 (m), 11.30 (m), 11.92 (m) $\mu$.

**Tricyclo[4.3.0.$0^{4,8}$]nonane (9).**—A solution of 0.457 g (0.0033 mol) of **8**, 0.25 g of potassium hydroxide, and 0.4 ml of hydrazine hydrate (85%) in 4 ml of triethylene glycol was heated at reflux for 1.5 hr. Water was allowed to boil out of the solution as the temperature approached 195–200°. The resulting solution was heated at reflux for 4 hr during which time a white solid collected in the condenser. The solid was rinsed out with pentane and the extracts were washed with water and dried. Evaporation of the pentane yielded 0.24 g (59%) of tricyclo[4.3.0.$0^{4,8}$]nonane, mp 140° (sealed cap) (lit.[4] mp 165–166°). The nmr and ir spectra were identical with those of an authentic sample.[4]

**5-Acetylbicyclo[2.2.2]oct-2-ene (3b).**—The ketone **3b** was prepared in 87% yield by heating 40 g of 1,3-cyclohexadiene and 40 g of methyl vinyl ketone at 180° for 3 days, bp 106° (20 mm) [lit.[17] bp 106–106.5° (20 mm)]. Gc analysis (165°) revealed a 90:10 ratio of the *endo* and *exo* isomers.

**2-Methyl-3-oxatetracyclo[4.3.1.$0^{2,5}$.$0^{4,9}$]decane (10).**—A solution of 64.7 g (0.43 mol) of the above mixture in 5 l. of benzene was degassed and irradiated as in the above procedure. After 164 hr, the solution was filtered to remove polymer and evaporated under reduced pressure. The residue was distilled to yield 56.5 g (88%) of oxetane **10**: bp 45° (0.5 mm); nmr $\delta$ 4.20 (m, 1, HCO), 2.7–0.9 (m, 13), 1.42 (s, $CH_3$); ir (film) 9.07 (m), 10.50 (m), 10.62 (m), 11.10 (m), 11.62 (mm) and 11.98 (m) $\mu$.

*Anal.* Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.58; H, 9.56.

***syn*-5-Hydroxy-*anti*-7-methyltricyclo[4.3.0.$0^{4,8}$]nonane (11).**—The oxetane (0.405 g) was reduced as before with 1 g of lithium aluminum hydride in N-methylmorpholine (40 ml, 48 hr at reflux) to give 0.35 g (87%) of a solid: mp 55–56°; nmr $\delta$ 3.77 (d, $J$ = 2 cps, HCO), 0.97 (d, $J$ = 7 cps, $CH_3$), 2.70 (q, $J$ = 7 cps), 2.3–1.1 (m, 11); ir (film) 3.04 (m), 9.07 (m), 9.40 (m), and 10.06 (m) $\mu$.

*Anal.* Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.73; H, 10.59.

**Cleavage of 10 with 2,4-DNPH.**—To a solution of 0.413 g of **10** in 25 ml of ethanol was added several drops of 2,4-dinitrophenylhydrazine reagent.[18] The precipitate was collected and recrystallized from methanol, mp 152–153°.

*Anal.* Calcd for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.39; H, 5.68; N, 16.85.

**Cleavage of 10 with Perchloric Acid.**—A solution containing 1.67 g (0.0011 mol) of **10** and 50 $\mu$l of 70% perchloric acid in 100 ml of methanol was kept at 25° for 24 hr. Dilution with water was followed by ether extraction. The extracts were washed with water, dried ($MgSO_4$), and evaporated to give 1.66 of an oil which showed three major peaks by gc analysis (152°): **10** (2.4%), **13** (33%), and **14** (65%). The two major components were separated by chromatography on a column of 80–200 mesh alumina. The acetal **13** was eluted with pentane and the alcohol **14** was eluted with benzene.

**2-Formyl-7-methylbicyclo[3.2.1]oct-6-ene dimethyl acetal (13)** had bp 61° (0.5 mm); nmr $\delta$ 5.39 (broad, 1, HC=), 3.91 (d, $J$ = 8 cps, HCO), 3.17 (s, 6, $CH_3O$), 1.70 (s, 3, $CH_3$), 2.5–1.2 (m); ir (film) 8.50 (m), 8.82 (s), 9.1 (s), 9.43 (vs), 10.35 (s), 11.20 (s), 12.05 (m), and 12.54 (s) $\mu$.

*Anal.* Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.70; H, 10.50.

***syn*-5-Hydroxy-7-methylenetricyclo[4.3.0.$0^{4,8}$]nonane (14)** had bp 66° (1 mm); nmr $\delta$ 4.64, 4.77 (s, 2, $H_2C$=), 3.67 (d, $J$ =

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[12] By way of a crude analogy, it has been reported that both a five- and a six-membered-ring iodolactone have been isolated from the reaction of bicyclo[2.2.2]octene carboxylic acid with iodine; see W. R. Boehme, E. Schipper, W. G. Scharpf, and J. Nichols, *J. Amer. Chem. Soc.*, **80**, 5488 (1958). The kinetically controlled product would appear to have been the five-membered-ring lactone, however.

[13] For the purpose of this discussion it is assumed that the two-step mechanism generally accepted for the intermolecular analog is applicable. For references and a discussion, see W. L. Dilling, *Chem. Rev.* **66**, 373 (1966); see also S. M. Japar, M. Pomerantz, and E. W. Abrahamson, *Chem. Phys. Lett.*, **2**, 137 (1968).

[14] Reversible complex formation between exited carbonyl groups and olefins has been postulated by several investigators: N. C. Yang, J. I. Cohen and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3264 (1968); N. J. Turro, P. A. Wriede, and J. C. Dalton, *ibid.*, **90**, 3274 (1968); L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, **91**, 897 (1969).

[15] O. Diels and K. Alder, *Ann. Chem.* **478**, 137 (1930).

[16] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[17] A. A. Petrov, *J. Gen. Chem. USSR*, **11**, 309 (1941).

[18] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley & Sons, Inc., New York, N. Y., 1957, p 219.

8 cps, 1, HCO), 2.5–1.1 (m, 11); ir (film) 2.98 (s), 3.32 (w), 9.17 (s), 9.32 (s), 9.48 (s), 9.62 (s), 10.22 (s), 11.37 (s), 11.52 (s), 12.37 (s), and 12.60 (m) μ.

*Anal.* Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.16; H, 9.63.

The acetate of **14** was prepared from 4.06 g of **14** by treatment with 3.0 ml of acetic anhydride in 10 ml of pyridine for 18 hr at 25°. After quenching with water the product was extracted into chloroform. The extracts were washed with dilute solutions of sodium hydroxide, hydrochloric acid, and water. Evaporation yielded 3.64 g (72%) of crude acetate: bp 96–99° (2.5 mm); nmr δ 1.87 (s, $CH_3$) 4.45 and 4.60 (s, 2, HC=), 4.57 (s, 1, HCO), 2.75–1.30 (m, 13); ir (film) 8.02 (m), 8.13 (m), 9.52 (m), 9.62 (m), and 11.45 (m) μ.

*Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.02, H, 8.39.

***syn*-5-Acetoxytricyclo[4.3.0.0$^{4,8}$]nonan-7-one (15).**—A solution of 1.42 g of the above acetate in 50 ml of chloroform was cooled to −78° and treated with ozone until an intense blue color persisted. The solution was allowed to warm to 25° and the excess ozone was purged by passing nitrogen through the solution. The reaction mixture was then added to a mixture of zinc dust (1.8 g) in a mixture of 300 ml of water, 75 ml of chloroform, and 3 ml of glacial acetic acid. The chloroform extract was washed with sodium carbonate solution, water, and then dried over $MgSO_4$. Upon evaporation there was obtained 0.94 g (66%) of crude **15**. Samples for spectral data were obtained from preparative gc (190°): nmr δ 4.72 (d, $J = 1$ cps, HCO), 1.93 (s, $CH_3$), 1.4–2.3 (m, 13); ir (film) 5.64 (s) and 5.77 (s) (C=O), 8.18 (s), 9.54 (w), 10.30 (m), and 11.27 (m) μ.

*Anal.* Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.32; H, 7.30.

***syn*-5-Acetoxytricyclo[4.3.0.0$^{4,8}$]nonane (16).**—A solution of 0.93 g of **16** in 5 ml glacial acetic acid was treated with 1.5 ml of ethanedithiol and 1.0 ml of boron trifluoride etherate at 25°. After 3 hr the reaction was quenched with water and sodium carbonate. The thioketal was extracted into chloroform. The dried extracts were evaporated and the crude product was dissolved in 25 ml of ethanol to which *ca.* 5 g of Raney nickel[19] had been added. After 4 hr at reflux, the mixture was filtered through Filter-Cel and the filtrate was evaporated. The residue was preparatively gas chromatographed (160°) to give 0.164 g of **16** and *ca.* 0.050 g of a second product.[20] The nmr spectrum of **16** showed a triplet ($J = 1$ cps) for the HCO proton at δ 4.63, a sharp singlet at 1.90 for the methyl group, and complex absorption extending from 2.5 to 1.2; ir (film) 5.79 (s) (C=O), 8.07 (s), 9.57 (m), 9.71 (m), and 9.92 (m) μ.

*Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.01; H, 9.00.

**5-Benzoylbicyclo[2.2.2]oct-2-ene (3c).**—A solution of 6.75 g (0.05 mol) of **3a** in 15 ml of dry ether was added dropwise to the Grignard reagent prepared from 1.4 g (0.058 g-atom) of magnesium and 9.5 g (0.06 mol) of bromobenzene in 10 ml of dry ether. The resulting mixture was heated at reflux for 1.5 hr and then kept at 25° for 18 hr. The reaction was quenched by addition to a mixture of 25 g of ice and 50 ml of 10% sulfuric acid. Separation of the layers and further ether extraction gave extracts which were washed with water and dried. Upon evaporation, 9 g of crude alcohols (**4**) were obtained. A solution of the alcohols in 500 ml of acetone was treated with 13 ml of Jones reagent[16] for *ca.* 30 min at 0.5°. Addition of 1 l. of water followed by chloroform extraction gave extracts which were washed with water and dried ($MgSO_4$). The residue on evaporation was distilled at *ca.* 100° (1 mm) to yield 7.0 g (79%) of **3c**: nmr δ 7.2–8.0 (m, 5, ArH), 6.1 (m, 2, HC=), 3.42 (t, $J = 7$ cps, 1), 3.0–1.0 (m, 9); ir (film) 3.30 (m), 5.93 (s) (C=O), 8.18 (s), 10.43 (s), 13.30 (s), and 14.45 (s) μ.

*Anal.* Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.04; H, 7.85.

**Irradiation of 3c.**—A solution of 1.0 g of **3c** in 200 ml of dry benzene was degassed with a nitrogen stream and irradiated (Pyrex filter) as before for 49 hr. The solution was filtered and evaporated to give 0.90 g of an oil. A small sample of oxetane **17** was obtained by preparative tlc (silica gel G, 20% chloroform–benzene). The material rapidly decomposed to an aldehyde on standing: nmr δ 7.27 (s, 5, ArH), 4.30 (m, 1), 3.18 (m, 1), 2.40 (s, 1), 1.0–2.0 (m, 8); ir (film) 9.56 (m), 9.81 (m), 10.23 (m), 10.43 (m), 10.63 (m), 10.94 (s), 11.92 (s), 13.26 (vs), and 14.34 vs) μ.

Treatment of the crude oxetane with 2,4-DNPH solution gave the 2,4-dinitrophenylhydrazone, mp 193–195°.

*Anal.* Calcd for $C_{21}H_{20}N_4O_4$: C, 64.27; H, 5.14; N, 14.28. Found: C, 64.09; H, 4.88; N, 13.97.

**Hydrogenolysis of 17.**—A solution of 90 mg of **17** in 15 ml of absolute ethanol was heated at reflux for 4 hr with *ca.* 0.5 g of Raney nickel.[19] The resulting solution was filtered and evaporated to yield the alcohol **18** (45 mg): mp 84–85° after crystallization from ethanol; nmr δ 7.01 (s, 5, ArH), 3.9 (broad, 2, HCO, HCAr), 0.8–2.2 (m, 11); ir ($CHCl_3$) 2.83 (w) and 2.98 (w) (OH), 9.13 (m) 9.33 (m), 9.48(m), 10.08 (m), and 14.35 (s) μ.

*Anal.* Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.84; H, 8.53.

**Registry No.**—**3c**, 21736-08-3; 2,4-DPNH of **3c**, 21736-09-4; **5**, 21746-49-6; **7**, 21746-50-9; acetate of **7**, 27146-51-0; **8**, 21746-52-1; **10**, 21746-53-2; **11**, 21736-10-7; 2,4-DNPH of **12**, 21746-54-3; **13**, 21736-11-8; **14**, 21736-12-9; acetate of **14**, 21779-11-3; **15**, 21736-13-0; **16**, 21736-14-1; **18**, 21736-15-2.

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[19] A commercial sample obtained from W. R. Grace Co. was used.

[20] This product proved to be the acetate of **11** since it could be reduced to **11** with lithium aluminum hydride. Apparently, some unreacted **14** was carried through and reduced at this stage.