Our stability studies were conducted on 3β-cholestanyl TMPDA, and less than 5% reaction was observed when this material was treated with CH_3Li-Et_2O (2.5 hr at 25°), $LiAlH_4$-Et_2O (2.5 hr at 25°), 1 N KOH-EtOH (15 hr at reflux), and 0.2 N aqueous HCl-acetone (2 hr at 25°). Prolonged treatment (12 hr at 25°) with 0.2 N aqueous HCl-acetone resulted in recovery of only 59% of the original TMPDA, but *no* 3β-cholestanol was found. Regeneration of progesteron-11α-yl TMPDA from the corresponding diketal was accomplished in 91% yield by treatment of the diketal TMPDA with 0.2 N aqueous HCl-acetone for 2 hr at 25°. The regeneration of 3β-cholestanol from its TMPDA was accomplished in *quantitative yield* after treatment with 5 equiv of *n*-butyllithium in TMEDA for 30 min at 25°.

The mechanism and stereochemical outcome of the reduction of saturated DEP and TMPDA derivatives are presently under investigation.

(8) R. E. Ireland and U. Hengartner, *J. Amer. Chem. Soc.*, 94, 3652 (1972).
(9) R. E. Ireland and S. C. Welch, *ibid.*, 92, 7232 (1970).
(10) National Defense Education Act Trainee, 1967–1971.
(11) Fellow of Stiftung für Stipendien auf dem Gebiete der Chemie, Switzerland.

Robert E. Ireland,* **David C. Muchmore,[10]** **Urs Hengartner[11]**
Contribution No. 4462, Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California 91109

Two Novel Routes to Spiro[3.4]octan-1-ones

Sir:

In this communication we outline briefly two independent syntheses of spiro[3.4]octan-1-ones **1** and **2**, representatives of a class of compounds with few previously known members.

The first approach to these spiro ketones is a photochemical one and consists simply in photolysis of the related 1-acylcyclopentenes. The resulting reaction is quite clean, and although yields are modest, the only significant volatile products are those noted below. Starting materials are readily prepared through Friedel-Crafts reaction of cyclopentene with the appropriate acyl chloride.[1] Thus, irradiation[2] of 1-cyclopentenyl isobutyl ketone (**3**)[3] for 125 min caused complete destruction of starting material and formation of **1** in 35%[5] yield. Similarly, **4**[3] gave 36%[5] of **2**.[3] This photoisomerization is most easily explained as involving abstraction of a hydrogen atom by the β carbon atom of the enone system from the β' carbon atom through a six-membered intermediate. As shown in eq 1, this process leads to a 1,4 biradical **5**, which may then collapse to the observed spiro ketone. A related intramolecular hydrogen abstraction by the β carbon atom of an α,β unsaturated ketone is responsible for the

(1) N. Jones and H. T. Taylor, *J. Chem. Soc.*, 4017 (1959), and references cited therein.
(2) Irradiations were carried out at concentrations of about 1 mg/ml in benzene solution using a Hanovia Model L mercury lamp (No. 679A-36) in a quartz immersion well and a Corning No. 3320 uranium glass filter.
(3) This new compound gave satisfactory elemental analysis for carbon and hydrogen after purification by preparative vapor phase chromatography (vpc) over Carbowax under conditions similar to those described in ref 4.
(4) W. L. Schreiber and W. C. Agosta, *J. Amer. Chem. Soc.*, 93, 3814 (1971); S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *ibid.*, in press.
(5) Yields were obtained by calibrated vpc measurements.
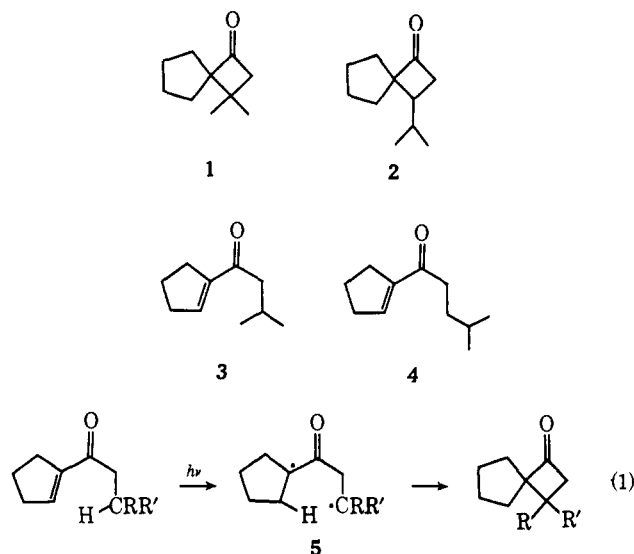
photochemical rearrangements of 4-isopentyl-4-methylcyclopentenone (**6**).[4] The suggestion that biradical **5** is an intermediate in the formation of **1** and **2** is supported by detection of ketene **7** as a concomitant product in photolysis of **3**. Infrared monitoring during this reaction revealed development of a sharp band at 2100 cm^{-1}; addition of methanol to the benzene solution after irradiation resulted in replacement of this band by new absorption at 1735 cm^{-1}, and subsequent isolation gave methyl cyclopentanecarboxylate (**8**, 25%[5]), which was identical with an authentic sample.[6,7] Formation of **7**, and presumably isobutylene, could occur most readily through simple fragmentation of biradical **5**. In connection with the mechanism (eq 1) it is noteworthy that the change of the β' carbon


6   **7**   **8**

9   **10**

a, X = O
b, X = $(OC_2H_5)_2$
c, X = NNHTs
d, X = :
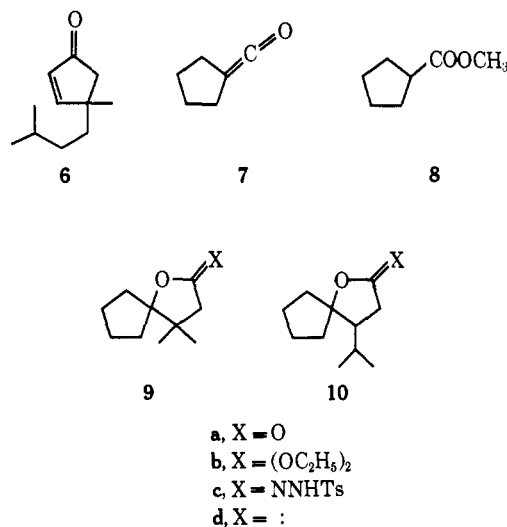
atom from tertiary to secondary in passing from **3** to **4** does not reduce the yield of spiro ketone but does suppress formation of ketene **7**.[8]

(6) D. W. Goheen and W. R. Vaughan, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 594.
(7) For preparative purposes ketene **7** can be removed by washing the benzene solution with aqueous sodium bicarbonate after irradiation, leaving **1** as the only volatile product.
(8) Apparently even abstraction of methyl hydrogen is feasible in this series, since photolysis of 1-cyclopentenyl ethyl ketone gives a low but useful yield (8%) of the parent spiro[3.4]octan-1-one as the sole volatile product. This compound was identified by comparison of its ir and nmr spectra with those of authentic material [H. H. Wasserman and D. C. Clagett, *J. Amer. Chem. Soc.*, 88, 5368 (1966)]. We are grateful to Professor Harry H. Wasserman for supplying these data.

The structures of 1 and 2 were deduced from their spectroscopic properties[9] and then confirmed through oxidation with peroxytrifluoroacetic acid[10] to the related butyrolactones 9a and 10a, which were identical with samples prepared in the following fashion. For 9a the long-known[11] carboxylic acid 11 was first converted through an Arndt–Eistert synthesis[12] to the homologous ester 12.[3] Saponification of this ester and then treatment with hot dilute hydrochloric acid led to 9a[3,9] without difficulty. For 10a, hydroxy ester 13[3] was prepared by a Reformatsky reaction[13] between cyclopentyl isopropyl ketone[14] and α-bromoacetic ester. Hydrolysis of 13 gave the related carboxylic acid, which underwent dehydration and cyclization in mineral acid to yield 10a[3,9] as well as the isomeric lactone 14.[3] These lactones were readily separated by preparative vpc.
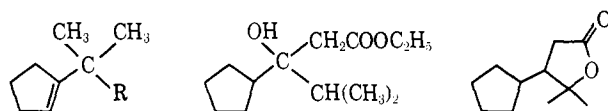
11, R = COOH
12, R = CH$_2$COOCH$_3$
13
14

Our second route to 1 and 2 starts with lactones 9a and 10a and proceeds in the reverse direction. Each lactone was converted to the related ortho lactone, 9b and 10b, respectively, on reaction[15] with triethyloxonium fluoroborate and then ethanol containing sodium ethoxide. These ortho lactones were treated[16] directly with tosylhydrazide to furnish lactone tosylhydrazones 9c[9,17] and 10c.[9,17] The dry sodium salt derived from each tosylhydrazone was then pyrolyzed at 310° to give the desired cyclobutanones 1 and 2 in yields of 42[5] and 20%,[5] respectively. This transformation, which we have discussed in some detail elsewhere,[18] presumably involves rearrangement of intermediate oxycarbenes 9d and 10d, formed on thermal elimination of molecular nitrogen and p-toluenesulfinate anion from the salts. Our previous experience included decomposition of lactone tosylhydrazone salts

having five-, six-, and seven-membered rings and indicated that the yield of cyclopentanone and cyclohexanone from appropriate precursors was significantly higher than yields of cyclobutanones. In this earlier work,[18] lactone tosylhydrazones were prepared indirectly through imino lactone salts, themselves available by various means from acyclic compounds. The noteworthy aspect of the present examples from the point of view of synthesis is the successful conversion of readily available lactones into derived tosylhydrazones and thence into cyclic ketones. Formally this constitutes a reversal of the Baeyer–Villiger oxidation;[10,19] if general, it should be a synthetically useful process.

We shall discuss additional examples of each of these reactions in later reports.

(19) C. H. Hassall, Org. React., 9, 73 (1957).

Amos B. Smith, III, A. M. Foster, William C. Agosta*
*Laboratories of The Rockefeller University
New York, New York 10021*

(9) Characterization data are given below: 1, ir 1775 cm⁻¹ (vs); nmr (220 MHz) δ 1.14 (s, 6 H), 1.36–1.81 (m, 8 H), 2.66 (s, 2 H); 2, 1775 cm⁻¹ (vs); nmr (220 MHz) δ 0.927 (d, J = 5 Hz) and 0.955 (d, J = 5 Hz) (6 H), 1.36–2.08 (m, 10 H), 2.60 (d of d, J₁ = 17, J₂ = 8 Hz, 1 H), 2.82 (d of d, J₁ = 17, J₂ = 8 Hz, 1 H); 9a, ir 1780 cm⁻¹ (vs); nmr (220 MHz) δ 1.09 (s, 6 H), 1.55–2.04 (m, 8 H), 2.26 (s, 2 H); 10a, ir 1780 cm⁻¹ (vs); nmr (220 MHz) δ 0.945 (d, J = 7 Hz) and 0.950 (d, J = 7 Hz) (6 H), 1.55–2.03 (m, 9 H), 2.03–2.27 (m, 2 H), 2.36–2.59 (m, 1 H); 9c, ir 3200, 1680, 1160 cm⁻¹; nmr (220 MHz) δ 0.93 (s, 6 H), 1.5–1.9 (m, 8 H), 2.40 (s) and 2.41 (s) (5 H), 7.28 (d, J = 8 Hz, 2 H), 7.38 (s, 1 H), 7.82 (d, J = 8 Hz, 2 H); mp 147.5–150.5°; 10c, ir 3200, 1685, 1160 cm⁻¹; nmr (220 MHz) δ 0.80 (d, J = 7 Hz, 3 H), 0.92 (d, J = 7 Hz, 3 H), 1.5–2.1 (m, 10 H), 2.32 (d of d, J₁ = 17, J₂ = 5 Hz, 1 H), 2.42 (s, 3 H), 2.72 (d of d, J₁ = 17, J₂ = 4 Hz, 1 H), 7.28 (m, 3 H), 7.80 (d, J = 8 Hz, 2 H); mp 137.5–140.5°.
(10) W. D. Emmons and G. B. Lucas, J. Amer. Chem. Soc., 77, 2287 (1955).
(11) P. B. Talukdar and P. Bagchi, J. Org. Chem., 20, 25 (1955), and references cited therein.
(12) W. E. Bachmann and W. S. Struve, Org. React., 1, 38 (1942).
(13) R. L. Shriner, ibid., 1, 1 (1942).
(14) J. Crouzet, L. Giral, G. Cauquil, and J. Rouzaud, Bull. Soc. Chim. Fr., 3722 (1967).
(15) H. Meerwein, P. Borner, O. Fuchs, H. J. Sasse, H. Schrodt, and J. Spille, Chem. Ber., 89, 2060 (1956).
(16) R. J. Crawford and R. Raap, Can. J. Chem., 43, 126 (1965); R. M. McDonald and R. A. Krueger, J. Org. Chem., 31, 488 (1966).
(17) This new compound gave satisfactory elemental analyses for carbon, hydrogen, and nitrogen.
(18) W. C. Agosta and A. M. Foster, Chem. Commun., 433 (1971); A. M. Foster and W. C. Agosta, J. Amer. Chem. Soc., in press.

Radical Chlorination of exo- and endo-Tricyclo[3.2.1.0²,⁴]octane with tert-Butyl Hypochlorite[1]

Sir:

In recent years there has been considerable interest in the characterization of radical intermediates which are structurally related to bridged carbonium ion intermediates, such as the 2-norbornyl,[2] 5-norbornenyl,[2] 7-norbornenyl,[3] and cholesteryl.[4] The reactions of these radical intermediates have, in all cases to date, been most easily explained in terms of rearranging classical intermediates, rather than by invoking bridged delocalized intermediates.

Since in an earlier study we found that radical chlorination of bicyclo[3.1.0]hexane with tert-butyl hypochlorite results in substitution at C-2 and C-3, producing a ratio of cis-3- to trans-3-chlorobicyclo[3.1.0]hexane of 2:1,[5] in spite of the steric shielding of the cis face of the ring skeleton by the cyclopropane methylene, it appeared to be of considerable interest to carry out additional studies on 3-bicyclo[3.1.0]hexyl radical intermediates. A consideration of the anchimeric assistance found in the solvolyses of exo-5-norbornenyl (10⁴),[6] anti-7-norbornenyl (10¹¹),[7] and endo-anti-tri-

(1) Financial support from the National Science Foundation is gratefully acknowledged.
(2) D. I. Davies and S. J. Cristol, Advan. Free-Radical Chem., 1, 155 (1965).
(3) J. Warkentin and E. Sanford, J. Amer. Chem. Soc., 90, 1667 (1968); G. A. Russell and G. W. Holland, ibid., 91, 3969 (1969); S. J. Cristol and A. L. Noreen, ibid., 91, 3870 (1969); H. O. Ohorodnyk and D. P. Santry, ibid., 91, 4711 (1969); Chem. Commun., 510 (1969); P. Bakuzis, J. K. Kochi, and P. J. Krusic, J. Amer. Chem. Soc., 92, 1434 (1970).
(4) S. J. Cristol and R. V. Barbour, ibid., 90, 2832 (1968).
(5) P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, J. Org. Chem., 33, 1448 (1968).
(6) S. Winstein, H. M. Walborsky, and K. Schreiber, J. Amer. Chem. Soc., 72, 5795 (1950).
(7) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, ibid., 77, 4183 (1955).