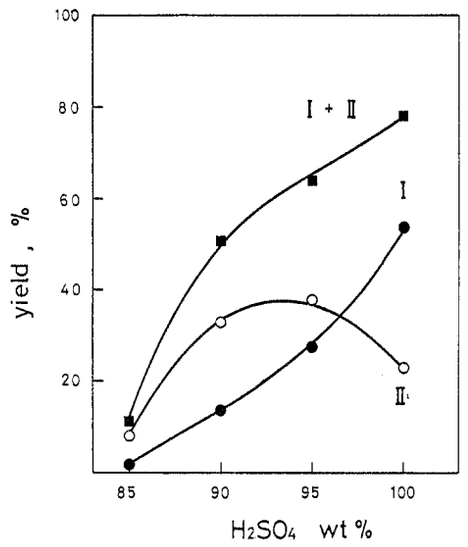


Figure 1.—The influence of H_2SO_4 concentration, with Cu_2O (0.02 mol), methylcyclohexane (0.2 mol), and hexene (0.2 mol) at 30° (2,2-dimethylpentanoic acid to 2-methyl-2-ethylbutanoic acid, 2:1).

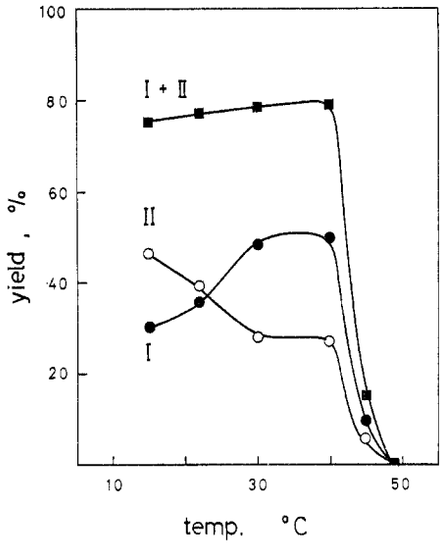
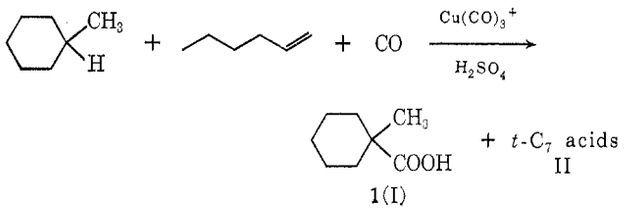


Figure 2.—The influence of reaction temperature. Cu_2O (0.02 mol), 98% H_2SO_4 (105 ml), methylcyclohexane (0.2 mol), and hexene (0.2 mol) were used.

hexene. The results are shown in Figure 1. The ratio of the product **1** *via* hydride transfer increased



with the increase of H_2SO_4 concentration. At the H_2SO_4 concentration of <80%, no reaction occurred. It is known that $Cu(CO)_3^+$ does not exist in the H_2SO_4 <80%.[6]

The influence of the reaction temperature was examined in the carbonylation of methylcyclohexane. The results are shown in Figure 2. The ratio of the product **1** *via* hydride transfer increases with an increase in temperature. However, no reaction occurred above 50°, since $Cu(CO)_3^+$, which acts as catalyst, can not exist in the reaction system above 50° at 1 atm of carbon monoxide pressure.

Experimental Section

The ir spectra were taken as neat samples using a Hitachi EPI-S2 spectrometer. ^1H nmr spectra were taken on a JEOL PS-100 at 100 MHz in CCl_4 solvent. Chemical shifts are given in δ units (parts per million) downfield from internal TMS. Glpc analyses were performed using a 3M FFAP column (10% on Chromosorb WAW). Elemental analyses were done on a Yanagimoto CHN MT-2.

Reagent.—Methylcyclohexane, methylcyclopentane, 1,4-dimethylcyclohexane, 2-methylpentane, 2-methylbutane, octane, 2,2,4-trimethylpentane, cyclohexane, 1-hexene, 1-octene, 2-propanol, *tert*-butyl alcohol, 1-hexanol, and 1-octanol were all commercial reagents and purified by distillation.

Cu_2O, CO, and H_2SO_4 were all commercial reagents, which were used without further purification.

Preparation of copper(I) carbonyl was carried out as described in previous papers.[1,6]

Carbonylation of Saturated Hydrocarbons.—The mixtures of 0.2 mol of saturated hydrocarbon and 0.2 mol of olefin (or alcohol) were added dropwise during 50 minutes to the copper(I) carbonyl suspension. Carbon monoxide was soon absorbed and reacted with carbonium ion. CO absorption was finished in 1 to 2 hr, and the reaction mixture was poured over ice–water. The products were extracted by benzene. Excess alkali was added to the benzene extract. The water phase was acidified by concentrated H_2SO_4. Carboxylic acids were again extracted by benzene and isolated by preparative glpc. The structures of products were determined by ir, nmr, and elemental analysis.

Methylcyclohexanecarboxylic acid was obtained by the carbonylation of methylcyclohexane: ir 2950, 1700 (C=O), 1460, 1250; nmr δ 1.13 (s, 3, CH_3CCOOH), 1.20~1.80 (m, 8, CH_2, HCH), 1.95~2.24 (m, 2, HCHCCOOH), 11.72 (br s, 1, COOH).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.74; H, 10.20.

Methylcyclopentanecarboxylic acid was obtained by the carbonylation of methylcyclopentane: ir 2980, 1705 (C=O), 1460, 1280, 1200; nmr δ 1.28 (s, 3, CH_3CCOOH), 1.70 (m, 6, CH_2, HCH), 2.16 (m, 2, HCHCCOOH), 11.78 (br s, 1, COOH).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 66.02, H, 9.57.

All identifications of 1,4-dimethylcyclohexanecarboxylic acid, 2-methylpropionic acid, 2,2-dimethylpentanoic acid, 2,2-dimethylbutanoic acid, 2-methyl-2-ethylbutanoic acid, and *t*-C_9 acid were made by comparison of retention time and "spiking" with authentic samples. Authentic samples were prepared by the carbonylations of olefins[1] or alcohols.[2]

Registry No.—$Cu(CO)_3^+$, 28990-05-8.

(6) Y. Souma and H. Sano, *Nihon Kagaku Zasshi*, **91**, 625 (1970).

A Photochemical Synthesis of Tetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane

PETER K. FREEMAN* AND TIMOTHY D. ZIEBARTH[1]

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

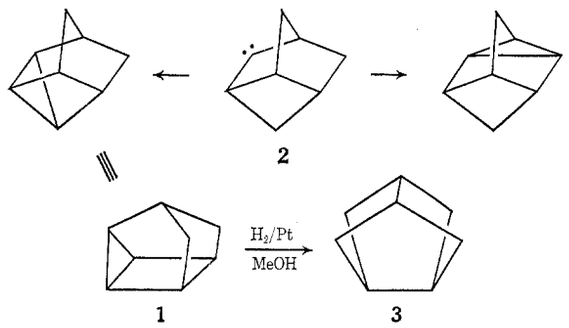
Received April 25, 1973

The synthesis of tetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (**1**) attracted our attention for several reasons. Since **1** is believed to be formed as a coproduct of the intramolecular insertion of 2-carbenatricyclo[3.2.1.0^{3,6}]octane (**2**),[2]

(1) NSF Graduate Trainee, June 1971–Sept 1972.

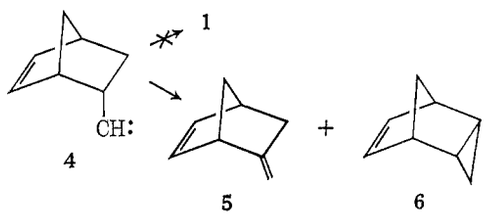
(2) P. K. Freeman, V. N. M. Rao, and G. E. Bigam, *Chem. Commun.*, 511 (1965).

an alternative synthesis is desirable to reinforce the spectroscopic and chemical evidence previously reported. In addition, the novelty of this tetracyclic hydrocarbon makes it of considerable interest in our continuing program devoted to the chemistry of small polycyclic ring systems, and the facile hydrogenolysis of **1** provides yet the best route to tricyclo[3.3.0.$0^{3,7}$]-octane (**3**),[2,3] an unusual molecule (symmetry point

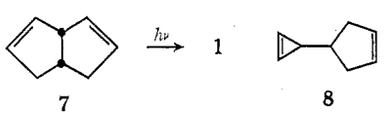


group D_2d) whose physical and chemical properties are of continuing interest.[4]

Previous synthetic efforts to prepare tetracyclooctane **1** included generation of bivalent intermediate **4**, the projected intramolecular addition to have yielded **1** directly. Unfortunately, only products arising from hydrogen migration (**5**) and endo C-3 C–H insertion (**6**) were observed.[5]

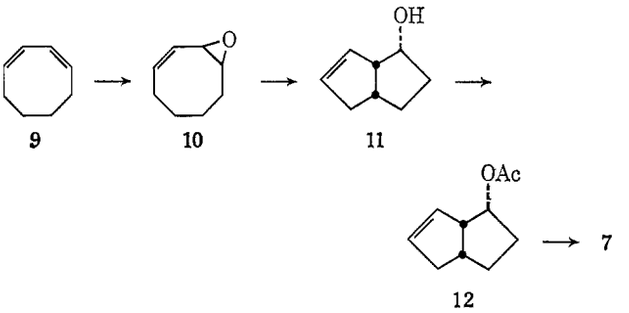


The photochemical synthesis we wish to describe relies on the intramolecular [$_\pi2_s + {}_\pi2_s$] cycloaddition[6] of diene **7**. This method was chosen for formation of **1** because of the success of similar reactions,[7,8] the proximity of the two olefinic functions in **7**,[9] and the lack of a reasonable synthesis of alternative photolytic precursor **8**.



Synthesis of key intermediate **7** was accomplished as shown in Scheme I. Monoepoxidation of *cis,cis*-1,3-

SCHEME I



cyclooctadiene (**9**) and subsequent treatment of **10** with lithium diethylamide in ether yields alcohol **11** by transannular carbene or carbenoid insertion.[10–12] Formation of acetate **12** by treatment of **11** at reflux with acetic anhydride, followed by gas-phase pyrolysis, yields required diene **7** in an overall yield of 45%.

The photolytic ring closure of diene **7** to title hydrocarbon **1** was studied in some detail. Photolysis in pentane results in tetracyclic hydrocarbon formation at a rate twice that in ether. However, periodic removal of side products is necessary for completion of the reaction. Furthermore, attempts to obtain a ratio of **1**:**7** greater than 0.5 were unsuccessful. Irradiation in ether, on the other hand, resulted in a corresponding ratio of 1.6, proceeding to this point without filtration, and resulted in a higher yield (35% *vs.* 8%) of desired photoisomer **1**. Irradiation in acetone and in the presence of benzophenone resulted in rapid loss of starting material with no concomitant production of **1**, presumably owing to bimolecular reactions such as oxetane and dimer formation. Attempts to catalyze the reaction by formation of a Cu(I) complex of **7**[13] were unsuccessful.

Overall, the yield of title hydrocarbon **1** based on 1,3-cyclooctadiene is 10%. (The yield can be increased by recycling diene **7** recovered from the photolysis if more than a single photolysis is performed.) This synthetic route has greatly facilitated the investigation of the chemistry of **1** currently in progress in our laboratory.

Experimental Section

All boiling points are uncorrected. Microanalysis was performed by Chemalytics, Inc., Tempe, Ariz. 85282. Infrared spectra were obtained using a Beckman IR-8 spectrophotometer; the nmr spectra were determined on a Varian Associates HA-100 spectrophotometer. Vpc analyses and preparative collections were performed using an Aerograph Model A-90-P gas chromatograph and the columns specified below.

Preparation of *endo*-2-*cis*-Bicyclo[3.3.0]oct-7-enyl Acetate (12).—Heating a solution of 3.0 g (2.42×10^{-2} mol) of alcohol **11**, 3.5 g (3.42×10^{-2} mol) of acetic anhydride, and 0.4 g of sodium acetate at reflux for 2 hr, followed by dilution with ether, extraction with 5% $NaHCO_3$ until no more CO_2 was evolved, and drying

(3) P. K. Freeman, R. B. Kinnel, and T. D. Ziebarth, *Tetrahedron Lett.*, 1059 (1970).

(4) R. R. Sauers and K. W. Kelly, *J. Org. Chem.*, **35**, 3286 (1970); W. T. Borden, V. V. M. Cabell, and T. Ravindranathan, *J. Amer. Chem. Soc.*, **93**, 3800 (1971); R. R. Sauers, K. W. Kelly, and B. R. Sickles, *J. Org. Chem.*, **37**, 537 (1972).

(5) P. K. Freeman and K. B. Desai, *J. Org. Chem.*, **36**, 1554 (1971).

(6) R. B. Woodward and R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(7) W. Eberbach and H. Prinzbach, *Helv. Chim. Acta*, **50**, 2490 (1967); J. Meinwald and B. E. Kaplan, *J. Amer. Chem. Soc.*, **89**, 2611 (1967); J. Meinwald and G. W. Smith, *ibid.*, **89**, 4923 (1967); R. Srinivasan and K. H. Carlough, *ibid.*, **89**, 4932 (1967); S. Moon and C. R. Ganz, *Tetrahedron Lett.*, 6275 (1968).

(8) Subsequent to the initiation of our study, G. Kaupp and K. Krieger, *Angew. Chem., Int. Ed. Engl.*, 719 (1972), have reported the observation of an analogous photoisomerization of the 3,7-diphenyl derivative of **7**.

(9) Dreiding models indicate a C_7–C_8 internuclear distance of 2.56 Å.

(10) A. C. Cope, H. H. Lee, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2849 (1958); A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6370 (1960).

(11) J. K. Crandall and L. H. Chang, *J. Org. Chem.*, **32**, 532 (1967).

(12) J. K. Crandall and L.-H. Chang, *J. Org. Chem.*, **32**, 435 (1967).

(13) No 1:1 adduct of CuCl–**7** could be obtained by the method reported for the formation of CuCl–1,5-cyclooctadiene complex.[14]

(14) J. H. van de Hende and W. C. Baird, *J. Amer. Chem. Soc.*, **85**, 1009 (1963).

over sodium sulfate–potassium carbonate, yielded 3.80 g (95%) of crude acetate upon removal of solvent at reduced pressure. This acetate was of sufficient purity (>99% by vpc analysis on a Carbowax 20M on 70/80 Anakron ABS column and nmr analysis) to be used in subsequent reactions without further purification: ir (neat) ν 3080, 2980, 2860, 2885, 1728, 1615, 1375, 1240, 1052, 714 cm^{-1}; nmr (100 MHz, CCl_4) δ 5.68 (doublet of doublets J = 6, 2 Hz, 1 H), 5.38 (doublet of doublets, J = 6, 2 Hz, 1 H), 5.01 (doublet of triplets, J = 6, 6 Hz, 1 H), 3.35 (m, 1 H), 2.66 (m, 2 H), 1.96 (s, 3 H), 2.2–1.3 (m, 5 H).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.40; H, 8.78.

Preparation of *cis*-2,7-Bicyclo[3.3.0]octadiene (7).—Acetate **12** (2.2 g, 0.0132 mol) was pyrolyzed by dropwise addition onto a 40-cm Pyrex column packed with Pyrex glass beads heated to 475° in a slow nitrogen flow. The product was trapped directly into a receiver cooled to −78°, diluted with pentane, washed once with water, once with 5% $NaHCO_3$, and once with saturated NaCl, and dried over anhydrous Na_2SO_4. Subsequent removal of solvent by distillation through a 10-cm Vigreux column, followed by distillation of the residue, yielded 1.12 g (0.0106 mol, 80% based on acetate lost) of diene **7** and 0.30 g of recovered acetate **12**. The product was pale yellow; a colorless sample having an identical ir spectrum was obtained by chromatography on alumina with pentane elution. The ir spectrum of **7** was identical with that previously reported;[15] nmr (100 MHz, CCl_4) δ 5.54 (m, 4 H), 3.66 (doublet of multiplets, J = 7.5 Hz, 1 H), 3.1–2.5 (complex multiplet, 2 H), 2.55 (doublet of multiplets, J = 7.5 Hz, 1 H), 2.04 (doublet of multiplets, J = 15 Hz, 2 H).

Preparation of Tetracyclo[3.3.0.0^{2,4}.0^{3,7}]octane (1). A. Photolysis in Pentane.—A stirred solution of 2.45 g (2.29 × 10^{-2} mol) of diene **7** in 250 ml of olefin-free pentane was purged with nitrogen for 30 min, then irradiated under nitrogen with an unfiltered 450-W Hanovia high-pressure mercury lamp using a water-cooled quartz probe. Monitoring the reaction by vpc on a β,β'-oxydipropionitrile on 30/60 Chromosorb P (AW) column indicated a buildup of a new volatile component at the rate of about 1% per hour. At the end of 16 hr, however, conversion stopped. The solution, somewhat yellow and containing a solid material, was passed through a short alumina column, and the resulting clear solution was repurged and irradiated again as above. The new volatile component again grew at the rate of 1% per hour until it was 35% of the starting diene after 40 hr total irradiation. Further manipulation of the solution as above produced no further increase in the ratio of product to starting diene **7**. The yield of **1** as indicated by an internal vpc reference was 8%.

The product was isolated by removal of *ca.* 99% of the pentane by distillation through a 40-cm spinning band column, followed by extraction of the residue with an equal volume of saturated $AgNO_3$. Vpc analysis of this procedure indicated no loss of product relative to an internal norbornane standard, whereas diene **7** was completely removed. The resulting pentane solution was subjected to preparative gas chromatography on a β,β'-oxydipropionitrile on 30/60 Chromosorb P (AW) column, the single product being identified as desired hydrocarbon **1**. Unreacted diene **7** was recovered by dilution of the $AgNO_3$ solution with a tenfold volume of water and extraction by pentane.

B. Photolysis in Ether.—A solution of 2.50 g (2.43 × 10^{-2} mol) of diene **7** was taken up in 250 ml of commercial anhydrous ether, purged with nitrogen, and irradiated as described above. Monitoring the reaction indicated conversion of **7** to **1** at a rate of 0.5% per hour until the ratio of **7**:**1** was **38**:**62** as measured by vpc integration. The resulting yellow solution was concentrated by distillation of the ether through a 40-cm Vigreux column, the residue yielding pure **1**. The yield as determined by an internal norbornane vpc reference was 35%.

Acknowledgment.—The authors gratefully acknowledge the support of this work by a grant from the National Science Foundation.

Registry No.—**1**, 4582-22-3; **7**, 41164-14-1; **11**, 41164-15-2; **12**, 40132-71-6.

(15) W. v. E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

The Synthesis of Cyclic 2-Enones from Cyclic 1,3 Diketones[1a]

GENE A. HIEGEL* AND PATRICK BURK[1b]

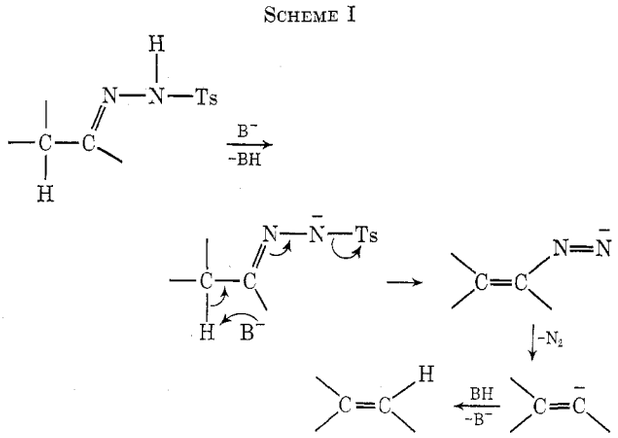
Department of Chemistry, California State University, Fullerton, California 92634

Received April 18, 1973

It has previously been shown that tosylhydrazones are converted into alkenes upon treatment with a strong base such as lithium aluminum hydride,[2] lithium hydride,[3] sodium amide,[4] or alkyllithium.[5] We have found that cyclic 1,3 diketones can be converted into cyclic 2-enones through treatment of their monotosylhydrazones with weak base. This new synthetic method is a simple, safe procedure for preparation of substituted cyclic 2-enones.

The mechanism for strong base conversion of tosylhydrazones into alkenes suggested by Shapiro[6] is outlined in Scheme I. Since the acidic sulfonamide proton (pK_a = 8.5)[7] is presumably removed first, removal of the α proton with concomitant loss of *p*-toluenesulfinate anion requires a strong base.

SCHEME I



If the α proton were more acidic than the sulfonamide proton, however, the reaction should proceed in the presence of a weak base. Since cyclic 1,3 diketones have sufficiently acidic α protons, they would be expected to undergo such a reaction.

5,5-Dimethylcyclohexane-1,3-dione (**1**, pK_a = 5.2)[8] was converted into 5,5-dimethyl-2-cyclohexen-1-one (**3**) in 52% yield on heating the crude monotosylhydrazone (**2**) in aqueous potassium carbonate solution. Enone **3** was also obtained in 53% yield from purified

(1) (a) This work was supported in part by grants from the California State University, Fullerton Foundation; (b) NSF Undergraduate Research Participant.

(2) L. Caglioti and M. Magi, *Tetrahedron Lett.*, 1261 (1962); L. Caglioti and M. Magi, *Tetrahedron*, **19**, 1127 (1963).

(3) L. Caglioti, P. Grasselli, and G. Maina, *Chim. Ind. (Milan)*, **45**, 559 (1963); L. Caglioti, P. Grasselli, and A. Selva, *Gazz. Chim. Ital.*, **94**, 537 (1964).

(4) W. Kirmse, B.-G. von Bülow, and H. Schepp, *Justus Liebigs Ann. Chem.*, **691**, 41 (1966).

(5) R. H. Shapiro and M. J. Heath, *J. Amer. Chem. Soc.*, **89**, 5734 (1967); G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

(6) R. H. Shapiro, *Tetrahedron Lett.*, 345 (1968).

(7) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

(8) G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 453.