color of the reagent persisted. The reaction mixture was extracted with ether. The ether extract was washed with water and dried over sodium sulfate, and the ether was removed on a steam bath. The residue was recrystallized from methanol to give 0.3 g (60%) of 1,5-diphenylpent-1-yn-3-en-5-one as yellow needles, mp 97°. The ir spectrum was identical with that of a sample prepared by an unambiguous route.

**Preparation of 1,5-Diphenylpent-1-yn-3-en-5-one (IX).**—A mixture of 1.3 g of phenylpropargylaldehyde and 1.2 g of acetophenone was added dropwise to a stirred solution of 2.5 g of sodium hydroxide in 20 ml of water and 16 ml of methanol. The temperature of the reaction was maintained below 20° by an ice bath. The mixture was stirred for 0.5 hr after addition was completed and filtered, yielding 0.6 g of light yellow solid. Recrystallization from methanol gave 0.5 g of lemon yellow needles, mp 97° (lit.[14] mp 101.5°).

*Anal.* Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 88.04; H, 5.23.

**Registry No.**—I, 17791-55-8; II, 17791-56-9; III, 17791-57-0; VI, 17791-58-1; VIII, 17791-59-2; 1,5-diphenylpent-1-yn-3-en-5-ol, 17791-60-5.

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# The Reductive Cyclization of 4-Tosyloxybicyclo[5.2.1]decan-10-one[1]

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The photolysis of bicyclo[5.2.1]decan-10-one (**7**) yields octamethyleneketene[3] rather than the tricyclic alcohol **8**, a product which might have been anticipated on the basis of the reported photoisomerization of monocyclic ketones to bicyclic alcohols.[4] This compound has now been synthesized by the sequence of reactions depicted in Scheme I. Employing a bishomologation ring-expansion procedure,[5] 4-hydroxycyclohexanone (**1**) was converted in 54% yield into a mixture comprised of approximately equal parts of the epimers **2** and **3**, one of which was stable in the keto alcohol form (*i.e.*, **2**) and one of which was stable in the hemiketal form (*i.e.*, **10**). Unfortunately, the hemiketal proved to be so resistant to ring opening that carbonyl derivatives could not be prepared; its utility as a synthesis intermediate being thereby limited, attention was directed to the keto alcohol **2**. This compound, isolated *via* its tosylate **4**, was shown to be epimerically related to **3** (and **10**) by acetolysis to a mixture of the olefin **5** and the actate **6** followed by methanolysis of **6** to the hemiketal **10**. Reductive cyclization of **4** with lithium in ammonia–dimethoxyethane yielded a complex mixture of products, the volatile portion of which was shown by vpc to contain two major components. One of these possesses an analysis compatible with a $C_{10}H_{16}O$ formula and has an nmr and mass spectrum interpretable in terms of the tricyclic alcohol **8**. The other material possesses an analysis compatible with a $C_{10}H_{16}O_2$ formula, has an nmr spectrum which indicates that the two oxygens are present as tertiary hydroxyl groups, and gives a periodate test which indicates the hydroxyl groups to be vicinal. The most reasonable structure commensurate with these data is the diol **9**.

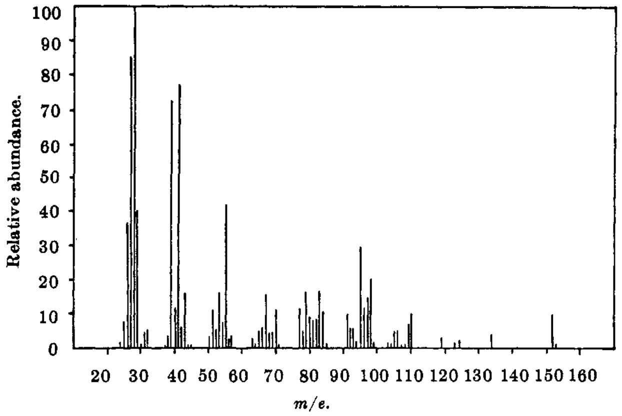

Figure 1.—Mass spectrum of tricyclo[5.2.1.0$^{4,10}$]decan-10-ol (**8**).

No attempt to unravel the details of the mechanism of the reductive cyclization was undertaken. The formation of the alcohol **8** is reasonably explained as an addition of one (or two) electrons to the carbonyl group to yield a radical anion (or a dianion) which then effects a transannular displacement of the tosyl group, a reaction having some resemblance to the reductive cyclization of keto esters which has been investigated in this laboratory.[6]

### Experimental Section[7]

**10-Oxatricyclo[5.2.1.1$^{4,11}$]undecan-11-ol (10).**—A 34.2-g (0.300 mol) sample of 4-hydroxycyclohexanone[8] in 120 ml of methanol, cooled in an ice–salt bath, was mixed with 1.0 g of powdered, anhydrous potassium carbonate. To the stirred suspension 87.0 g (0.300 mol) of N,N′-dinitroso-N,N′-dicarbethoxybutanediamine[5] in 120 ml of methylene chloride was added dropwise over a period of 70 min at a rate such that the temperature was maintained at 5–10°. After an additional 30 min 99% of the theoretical amount of nitrogen had been evolved, and the reaction mixture was processed. The combined crude product from two reactions was distilled through a 20-cm Vigreux column to give (A) 8.1 g, bp 25–96° (0.3 mm); (B) 27.5 g, bp 96–111° (0.1 mm), mainly at 109–111° (0.1 mm); (C) 34.2 g, bp 111–130° (0.15 mm); and (D) 6.1 g bp 130–145° (0.15 mm). Vpc analysis on column 1[7] of fractions A and B indicated that they contained mainly a single component, and by preparative-scale vpc separation on column 3[7] a pure sample of 10-oxatricyclo[5.2.1.1$^{4,11}$]undecan-11-ol (**10**) was obtained as a colorless solid: mp 109–111° (after three melting–solidifying cycles the melting point rose to 111–113°); $\nu^{KBr}$, in cm$^{-1}$, 3006 (hydroxyl), no absorption in carbonyl region; nmr ($CCl_4$), in ppm, 14-proton multiplet at 1.17–2.50, one-proton multiplet at 4.06–4.50 (O–CH at C-4), one-proton singlet at 4.35 (OH).

*Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.03; H, 9.53.

Attempts to make hydroxyl derivatives (benzoate and *p*-toluenesulfonate) and carbonyl derivatives (semicarbazone and

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[1] This work was supported, in part, by Grant No. DA ARO(D)-31-124-G533 from the U. S. Army Research Office.

[2] National Institutes of Health Predoctoral Fellow, 1963–1966.

[3] C. D. Gutsche and J. W. Baum, *J. Amer. Chem. Soc.*, **90**, 5862 (1968).

[4] M. Barnard and N. C. Yang, *Proc. Chem. Soc.*, 302 (1958).

[5] C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960).

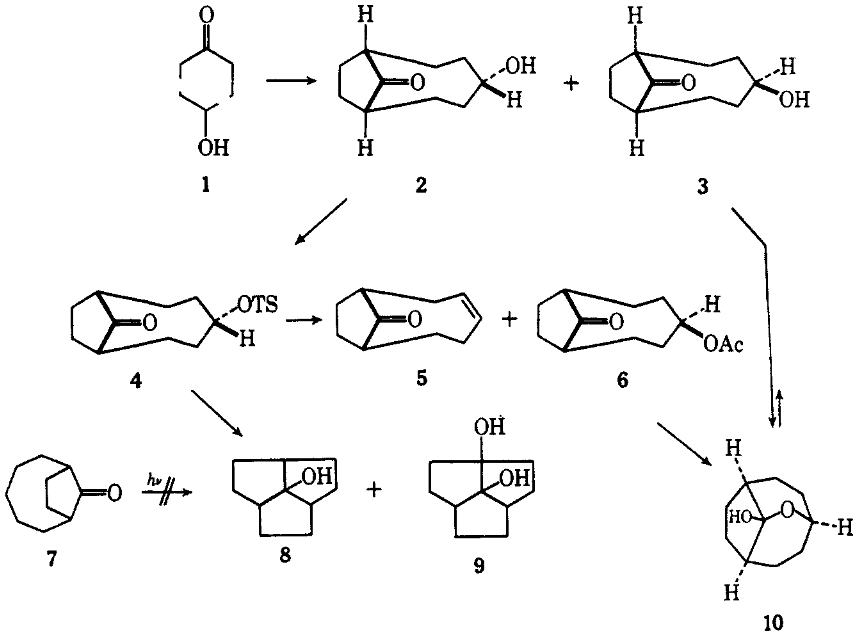
[6] C. D. Gutsche, I. Y. C. Tao, and J. Kozma, *J. Org. Chem.*, **32**, 1782 (1967).

[7] All melting points and boiling points are uncorrected. The infrared (ir) spectra were measured on a Perkin-Elmer Infracord instrument. The nmr spectra were measured on Varian HA-60 and A-60A spectrometers; the resonances are expressed in parts per million downfield shift from tetramethylsilane, present as an internal reference. Microanalyses were performed by Dr. Josef Zak, Mikroanalytisches Laboratorium, Vienna, Austria. Vpc analyses were performed on units containing thermistor detectors and using the following columns: (1) a 1/4 in. × 16 ft column packed with 15% w/w neopentylglycol sebacate polymer on 40-50 mesh type ABS Anakrom (a product of Analytical Engineering Laboratory, Inc., Hamden, Conn.); (2) a 1/4 in. × 6 ft column packed with 5% w/w Dow No. 710 silicone oil on 40-50 mesh type ABS Anakrom; (3) a 1/2 in. × 9 ft column packed with 15% w/w Dow No. 710 silicone oil on 40-50 mesh type ABS Anakrom.

[8] E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).

SCHEME I

CONVERSION OF 4-HYDROXYCYCLOHEXANONE INTO TRICYCLO[5.2.1.$0^{4,10}$]DECAN-10-OL



2,4-dinitrophenylhydrazone) of **10** were without success. Vpc analysis on column 1[7] of fraction C indicated that it contained *ca.* 65% *exo*-4-hydroxybicyclo[5.2.1]decan-10-one (**2**) and that fraction D contained *ca.* 33% **2** along with two higher boiling components presumed to be the epimers of 2-(γ-methoxypropyl)-5-hydroxycycloheptanone. On the basis of the weights of the distillation fractions and the composition as indicated by vpc analysis, the yield of the hemiketal **10** is *ca.* 30% and the yield of the hydroxy ketone **2** is *ca.* 24%.

**4-*exo-p*-Toluenesulfonyloxybicyclo[5.2.1]decan-10-one (4).**—A 22.6-g sample of fraction C described above was dissolved in 150 ml of pyridine, cooled to −5°, and treated with 26.6 g of *p*-toluenesulfonyl chloride in 100 ml of pyridine. The mixture was stirred at −5° for 4 hr and then allowed to stand at −20° for 18 hr. The crude product obtained after removal of the solvent was washed with three 50-ml portions of petroleum ether (bp 63–69°) (which removed 12.5 g of oily material) to leave 29.0 g of a semisolid. Recrystallization from acetone yielded 13.6 g (48.5%) of **4**, mp 126–128°, in the first crop and 2.7 g (10%), mp 125–127°, in the second crop. Further recrystallization from acetone yielded colorless plates: mp 127–127.5°; $\nu^{\text{KBr}}$, in cm$^{-1}$, 1734 (cyclopentanone carbonyl); nmr ($CDCl_3$), in ppm, 14-proton multiplet at 1.50–2.58 (CH and $CH_2$ of bicyclic ring), three-proton singlet at 2.45 ($CH_3Ar$), one-proton broad singlet at 4.00–4.23 (O–CH at C-4), two-proton doublet at 7.34 ($J$ = 8.5 Hz) (Ar–H), two-proton doublet at 7.74 ($J$ = 8.2 Hz) (Ar–H).

*Anal.* Calcd for $C_{17}H_{22}O_4S$: C, 63.33; H, 6.88; S, 9.94. Found: C, 63.10; H, 6.86; S, 9.76.

**Acetolysis of 4-*exo-p*-Toluenesulfonyloxybicyclo[5.2.1]decan-10-one (4).**—Following a published procedure,[9] a 0.645-g sample of **4** was refluxed for 7 hr with a mixture containing 0.500 g of sodium acetate, 2.5 ml of glacial acetic acid, and 0.5 ml of acetic anhydride. The reaction mixture was worked up to give 0.298 g of a colorless liquid, the vpc of which on column 1[7] indicated it to be a mixture of two materials. This product was dissolved in a solution containing 1.0 g of sodium methoxide in 15 ml of methanol, and the reaction mixture was refluxed overnight. The resulting product was separated by vpc on column 1[7] to yield a compound (36%), mp 113°, shown to be identical, by means of ir spectral comparison, with the hemiketal **10**, and 64% bicyclo[5.2.1]dec-3-en-10-one (**5**): $\nu^{\text{KBr}}$, in cm$^{-1}$, 1732 (cyclopentanone carbonyl); nmr ($CCl_4$), in ppm, 12-proton multiplet at 1.00–2.55 (CH and $CH_2$ of ring), two-proton multiplet at 5.33–5.91 (=CH). A 2,4-dinitrophenylhydrazone of **5** was obtained, after chromatography on alumina and recrystallization from ethanol, as red-orange plates, mp 185–187° (softening at 172° followed by resolidification).

*Anal.* Calcd for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.19; H, 5.64; N, 16.73.

**Reduction of 4-*p*-toluenesulfonyloxybicyclo[5.2.1]decan-10-one (4).**—To 650 ml of liquid ammonia (distilled from lithium) *ca.* 0.024 g of lithium and 1.6 g of the tosylate **4** were added. After addition of another 1.6 g of **4** dissolved in 10 ml of dry 1,2-dimethoxyethane, the blue color of the solution was rapidly discharged. Thereafter, small pieces of lithium and a solution of **4** in 1,2-dimethoxyethane were alternately added over a 1.5-hr period so that the blue color was just maintained. A total of 16.12 g (0.050 mol) of **4**, 2.67 g (0.385 g-atom) of lithium, and 100 ml of 1,2-dimethoxyethane was used. The mixture was cooled to −70° and treated with 20.6 g of solid ammonium chloride, whereupon the blue color was discharged and a white precipitate appeared. The ammonia was evaporated, and the residue was worked up to give a crude product which was twice distilled through a short-path apparatus, the distillate boiling up to 150° (30 mm) being collected. By means of vpc on column 2[7] the two major components of this product were isolated. One of these, mp 122–124°, was assigned the structure of **tricyclo[5.2.1.$0^{4,10}$]decan-10-ol (8)**: $\nu^{\text{KBr}}$, in cm$^{-1}$, 3350 (s), 3000 (s), 1470 (m), 1400 (w), 1320 (s), 1240 (w), 1195 (m), 1100 (w), 1040 (s), 1010 (w), 980 (vw), 955 (vw), 895 (m), 870 (w), 805 (vw), 765 (vw); nmr ($CCl_4$), in ppm, 15-proton multiplet at 1.00–2.50 (CH and $CH_2$ of ring), one-proton singlet at 3.75 (hydroxyl; band disappears after treatment of sample with $D_2O$). The mass spectrum of **2**, as illustrated in Figure 1, shows a parent peak at $m/e$ 152 which is unusually strong for a tertiary alcohol.[10]

*Anal.* Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.43; H, 10.24.

The other component, mp 133–136° after recrystallization from acetone, was assigned the structure of **tricyclo[5.2.1.$0^{4,10}$]decane-4,10-diol (9)** on the basis of a positive periodate test and its spectral characteristics: $\nu^{\text{KBr}}$, in cm$^{-1}$, 3400 (vs), 3000 (s), 1460 (m), 1420 (m), 1360 (w), 1315 (m), 1230 (m), 1180 (m), 1160 (m), 1105 (m), 1070 (s), 1040 (m), 1020 (w), 1000 (w), 982 (s), 952 (w), 920 (w), 895 (m), 790 (w); nmr ($CCl_4$), in ppm, 14-proton multiplet at 1.0–2.5 (CH and $CH_2$ of ring), two-proton singlet at 4.04 (hydroxyl; disappears after treatment of sample with $D_2O$) (note the absence of any $D_2O$-insensitive band in 3.50–4.50 region characteristic of a O–CH moiety).

*Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.45; H, 9.50.

**Registry No.**—**4**, 17790-98-6; **5**, 17790-99-7; **5** 2,4-dinitrophenylhydrazone, 17791-00-3; **8**, 17791-01-4; **9**, 17791-02-5; **10**, 17818-05-2.

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[9] F. Fleck and H. Schinz, *Helv. Chim. Acta*, **33**, 140 (1950).

[10] We are indebted to Dr. O. P. Tanner and Mr. M. T. Jackson of the Monsanto Co. for their assistance in obtaining the mass spectrum using a CEC 21-104 instrument.