TABLE IV

Starting material	Solvolysis product (registry no.)	Nmr ($CDCl_3$), δ	Mass spectrum: Calcd	Mass spectrum: Found
3 (Z = CN)	Δ^2, CN(C-7) (37741-58-5)	5.80 (m, 2, **HC=CH**)	$C_{10}H_{13}N$ M^+ 147	147, 120
3 (Z = CO_2CH_3)	Δ^2, CO_2CH_3(C-7)	5.76 (m, 2, **HC=CH**) 3.63 (s, 1, CO_2CH_3)	$C_{11}H_{16}O_2$ M^+ 180	180, 165, 148, 121, 120
3 (Z = CH_2OCH_3)	Δ^2, CH_2OCH_3(C-7) (37741-60-9)	5.71 (m, 2, **HC=CH**) 3.28 (s, 3, CH_3OCH_2) 3.17 (d, 2, J = 6 Hz, CH_2OCH_3)	$C_{11}H_{18}O$ M^+ 166	166, 124
	Δ^6, CH_2OCH_3(C-7) (37741-61-0)	5.48[a] (m, 1, HC=C-)		
3 (Z = CH_3)	Δ^2, CH_3(C-7) (2721-44-0)	5.73 (m, 2, **HC=CH**) 0.82 (d, 3, J = 6 Hz, CH_3)	$C_{10}H_{16}$ M^+ 136	136, 121
	Δ^6, CH_3(C-7) (2721-36-0)	5.40 (m, 1, HC=C-) 1.67 (s, 3, CH_3)		

[a] The nmr signal of this hydrogen is too weak to be assigned an unambiguous shift value; the shift (δ 5.48), here indicated, is compatible with the homolog multiplet on the solvolysis product of **3** (Z = CH_3).

materials, the solvolyses for preparative purposes were run with solutions 0.1 *M* in 80% aqueous acetone, in the presence of sodium carbonate, to avoid a thermodynamic equilibrium between the products of the reaction. Evaporation of the reaction mixture was easier than with aqueous ethanol, so that quantitative extraction of the reaction products was facilitated. Aqueous acetone is slightly less nucleophilic and less ionizing than 80% aqueous ethanol.[13]

We checked by vpc that the same products were obtained as those from solvolyses 0.01 *M* run in aqueous ethanol in the presence of sodium carbonate. The ratio of product without H shift/product with H shift was determined by a direct vpc evaluation of the crude product of such solvolyses. Table IV gives the nmr and mass spectral data of the products of those solvolyses studied.

Registry No.—**3** (Z = CN), 37741-64-3; **3** (Z = CO_2CH_3), 37731-04-7; **3** (Z = CH_2OCH_3), 37731-05-8; **3** (Z = CH_3), 19912-54-0; **8**, 700-58-3; **9**, 21932-98-9; **9** *exo*-methyl ester, 37741-59-6; **10**, 37731-09-2; **11**, 37731-10-5; **12**, 37731-11-6; **13**, 37731-12-7; **14**, 37731-13-8; **15**, 37731-14-9; **16**, 37731-15-0; **17**, 37731-14-9; **18**, 37731-17-2; **18** *p*-nitrobenzoate, 37731-18-3; **19**, 37731-19-4; **21**, 37741-57-4; 7-carbomethoxybicyclo[3.3.1]nonan-2-ol, 37731-21-8.

Acknowledgment.—We thank Dr. M. A. McKervey (Belfast) for a generous gift of the unsaturated acid **9**.

(13) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

Solvolysis of 9,9-Dimethylbicyclo[3.3.1]non-3-yl Tosylate. Enhancement of σ (C–H) Participation by Steric Blocking

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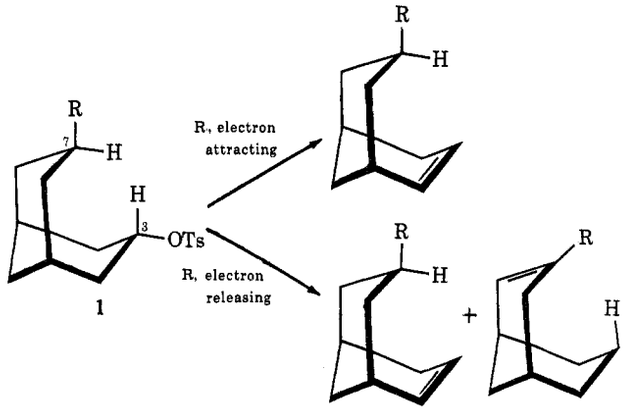
Received September 6, 1972

7,9,9-Trimethylbicyclo[3.3.1]non-3-yl tosylate (**2**, R = CH_3) undergoes solvolysis with quantitative 7–3 hydride transfer. The rate of solvolysis of **2** (R = CH_3) is four times higher than that of the lower homolog **1** (R = CH_3). This is interpreted by an anchoring of the conformation of both rings of **2** in a chair form, ensuring favorable geometry for H transfer.

We have recently shown that transannular H migrations accompanying solvolysis can produce a rate enhancement in the longifolene series[1] and in the bicyclo[3.3.1]nonane series.[2] In this last series, for instance, solvolysis of 7-substituted bicyclononyl tosylates **1** has been shown, by a Taft–Hammett treatment,[3] to be accelerated when it is accompanied by hydride migration from C-7 to C-3; there is a σ(C–H) participation in the step determining the rate of solvolysis.



However, in the bicyclononane series, this kinetic effect is less marked than in the longifolene series, and

(1) L. Stéhelin, J. Lhomme, and G. Ourisson, *J. Amer. Chem. Soc.*, **93**, 1650 (1971).

(2) L. Stéhelin, L. Kanellias, and G. Ourisson, *J. Org. Chem.*, **38**, 847 (1973).

(3) (a) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 556; (b) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **78**, 4935 (1956); "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 122, 146; (c) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4294 (1969); (d) P. G. Gassman, J. L. Marshall, J. G. Macmillan, and J. M. Hornback, *ibid.*, **91**, 4282 (1969).

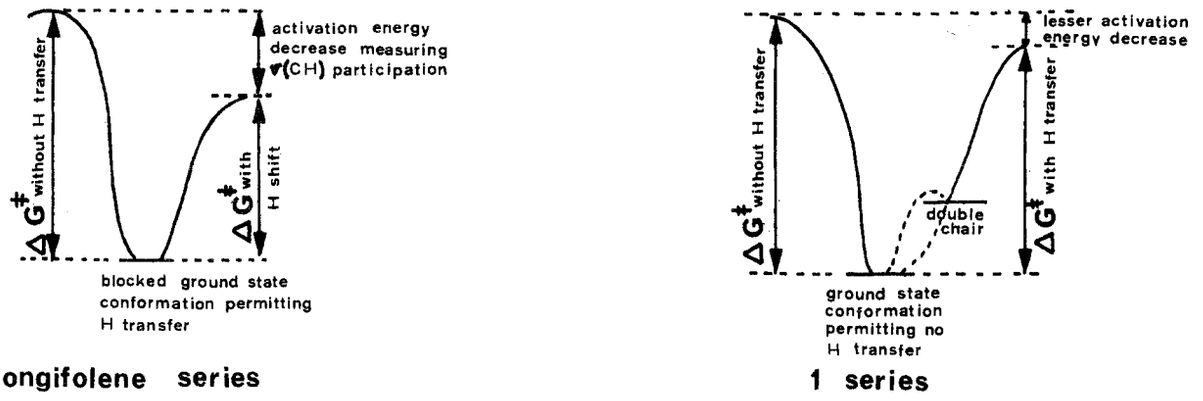
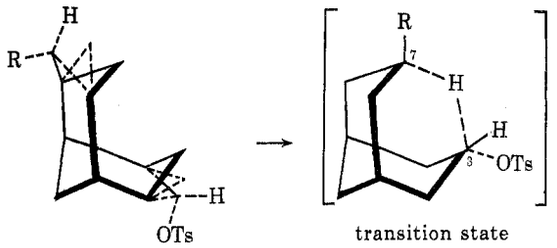


Figure 1.

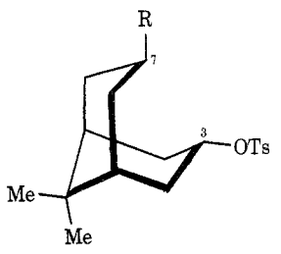
we have discussed several factors which can play a role in this quantitative difference;[2] we had concluded that it was probably due to a conformational difference. The longifolene skeleton is for all practical purposes anchored in a fixed conformation,[4] the one permitting hydride transfer from C-7 to C-3. On the contrary, both rings of bicyclononane derivatives can display conformational mobility, ranging from flattening of the rings to outright chair–boat interconversion.[5] It is only in the double-chair conformation of the solvolysis transition state that hydride transfer can take place.



1

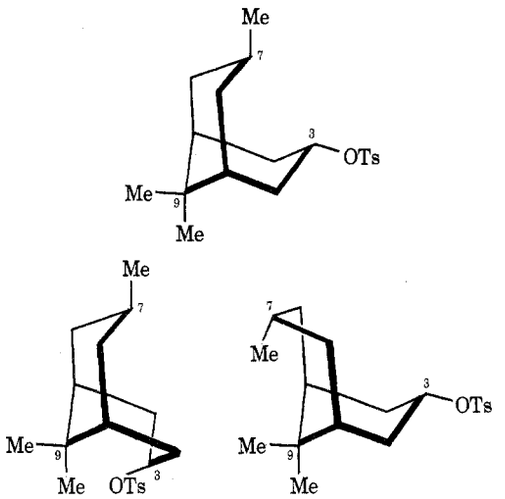
This double-chair conformation is certainly not the most stable one, owing to the H-3/H-7 interaction, and, whatever the exact geometry of the ground state, the necessary passage through the double-chair conformation must lead to an increase of the activation energy for that part of the reaction proceeding with hydride transfer during the rate-determining step. Figure 1 represents schematically the kinetic difference between the longifolene and the bicyclo[3.3.1]nonane series.

To check the validity of this interpretation, we have synthesized the 9,9-dimethyl tosylate **2** (R = CH_3).



2

In this substance, the *gem*-dimethyl group on the bridge blocks both rings into a chair conformation, effectively preventing a boat conformation from providing a way to eliminate the H-3/H-7 interaction.



The rate of solvolysis of the tosylate **2** (R = CH_3) is indeed four times higher (100% H transfer[6a]) than that of its lower homolog **1** (R = CH_3) (55% H transfer) (Table I), itself four times higher than that of the nitrile **1** (R = CN) (0% H transfer).

TABLE I

Derivative	k at 25° (80% aqueous EtOH)	H transfer, %	No H transfer, %
1 (R = CH_3)	2.28×10^{-4}	55	45
2 (R = CH_3)	9.28×10^{-4}	100	

We attribute this rate enhancement, at least in a large measure, to a σ(C–H) participation as efficient in series **2** as in the longifolene series, where a rate factor of 16 had also been found between the derivatives with a cyano and a methyl group[1] (Table I and Figure 2).

In fact, this is based on the assumption that the reaction rate in series **2** is not affected by the presence of the methyl groups as long as there is no hydride transfer, *i.e.*, for the plain solvolyses observed, in series **1**, when R is an electron-withdrawing group like CN or CO_2CH_3. This leads one to the prediction, in particu-

(4) (a) J. C. Thierry and R. Weiss, *Tetrahedron Lett.*, 2663 (1969); (b) D. Helmlinger and G. Ourisson, *Justus Liebigs Ann. Chem.*, **686**, 19 (1965).

(5) (a) W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc. C*, 1844 (1965); N. C. Webb, and M. R. Becker, *J. Chem. Soc. B*, 1317 (1967); M. R. Vegar, and R. J. Wells, *Tetrahedron Lett.*, 2847 (1971); (b) I. Fleming, S. W. Hanson, and J. K. M. Sanders, *ibid.*, 3733 (1971); J. A. Peters, J. D. Remijnse, A. van der Wiele, and H. van Bekkum, *ibid.*, 3065 (1971); P. D. Cradwick and G. A. Sim, *J. Chem. Soc. B*, 2218 (1971).

(6) (a) The product, 3,9,9-trimethylbicyclo[3.3.1]non-2-ene, was isolated, found homogeneous by gas chromatography, and characterized by nmr; (b) S. Winstein and J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955).

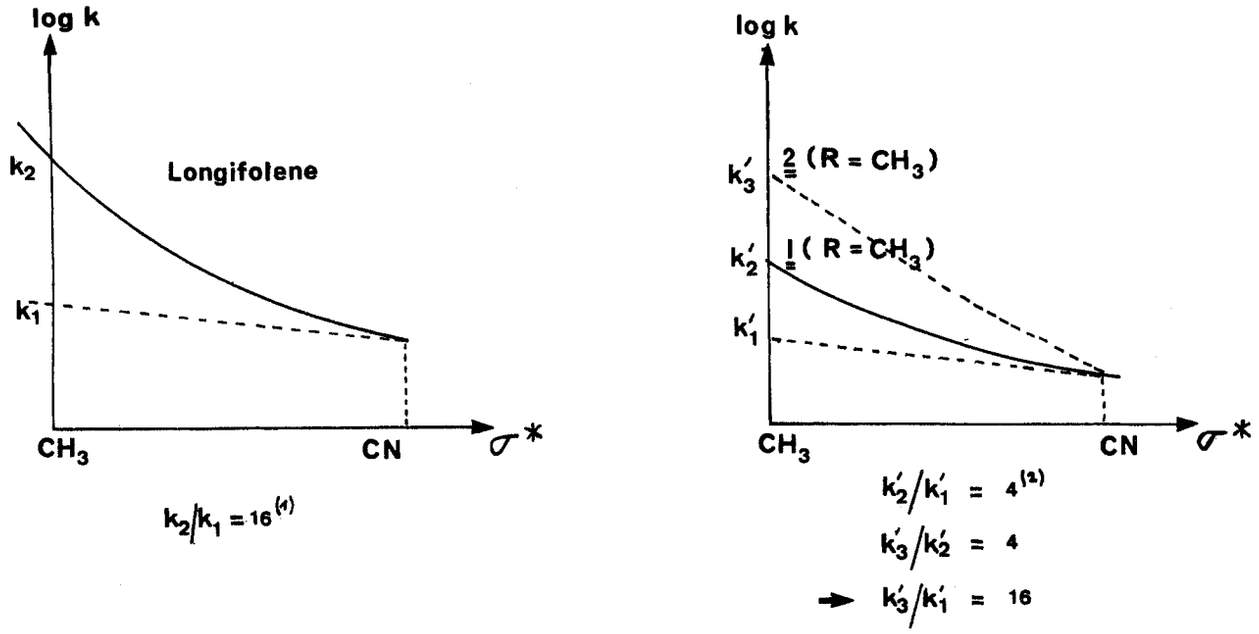
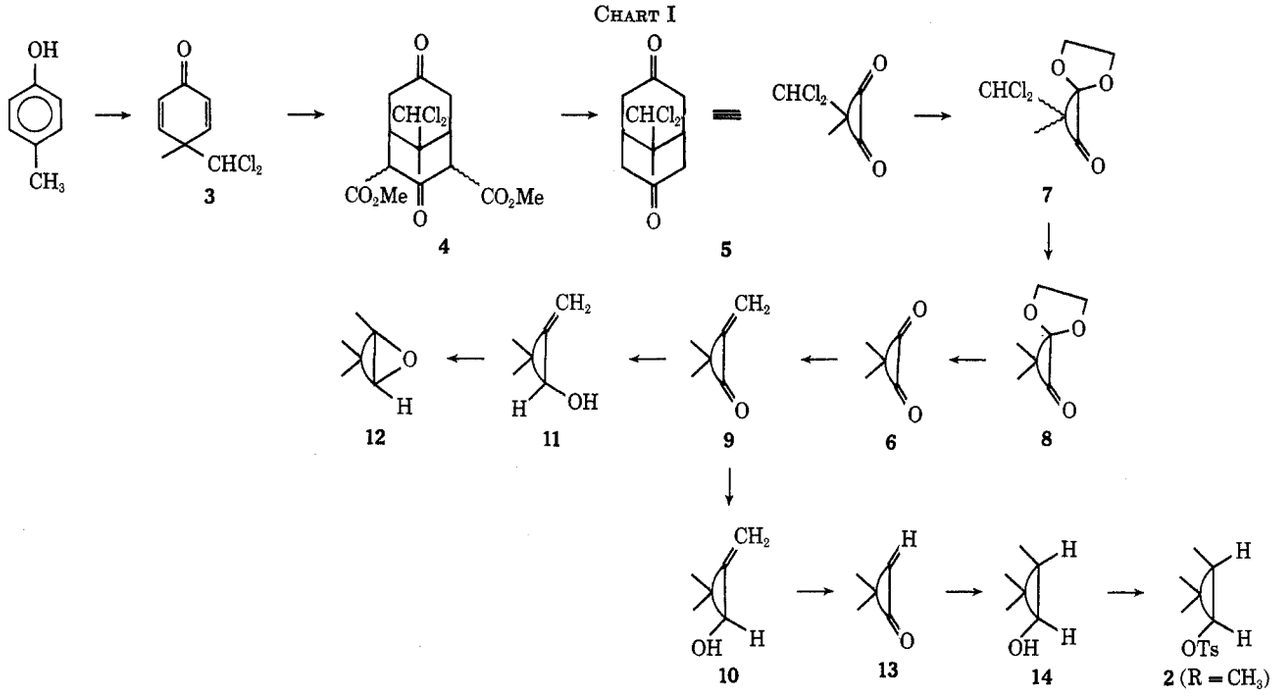


Figure 2.

CHART I



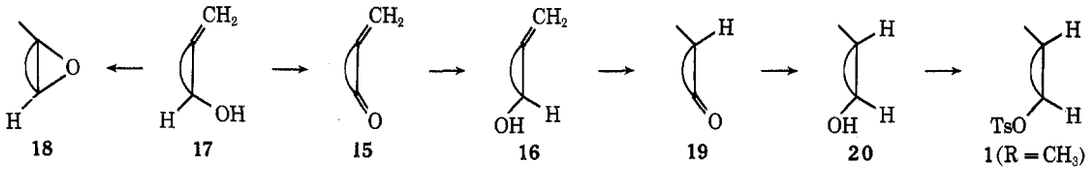
lar, that the reaction rate for solvolysis of **1** (R = CN) and **2** (R = CN) is the same. We have shunned the lengthy synthesis of **2** (R = CN) and accepted the correctness of the prediction just mentioned, on the basis of the following arguments.

The *inductive* effect of the methyl groups is certainly negligible, as even *tert*-butyl groups, in *trans*-4-*tert*-butyl and *cis*-3-*tert*-butylcyclohexyl tosylates, have practically no kinetic effect.[6b] The *field* effect of the cyano group may be more efficient in **2** (R = CN) than in **1** (R = CN), owing to the blocked conformations ensuring close proximity between C-3 and C-7; this should lead to a slight decrease of the solvolysis rate of **2** compared with **1** (R = CN), which would further increase the rate factor considered.

The other effects resulting from the presence of the axial methyl group in the ring undergoing solvolysis are taken as negligible. It appears therefore that the extent of σ(C–H) participation to the rate-determining step of solvolysis is comparable in the two series, that of longifolene and that of 9,9-dimethylbicyclo[3.3.1]-nonane, where (a) the two carbon atoms involved are situated at approximately identical distances[2] and (b) the conformations of the flexible parts of the molecules are anchored by additional substituents.

Synthesis of 2 (R = CH_3).—The synthetic route followed is summarized on Charts I and II, and described in the Experimental Section. The structures indicated are all in agreement with their physical characteristics, in particular with their nmr spectra.

CHART II



Experimental Section

We have included in some detail the preparation and/or properties of known substances, when this was found to be needed [1 (R = CH_3), 3, 4, 5, 16, 19, 20]. Microanalytical data are in agreement within ±0.3% with the calculated values for C, H, and Cl, for the indicated molecular formulas, unless explicitly indicated.

4-Dichloromethyl-4-methylcyclohexa-2,5-dienone (3).[7]—*p*-Cresol (54 g) and 15% aqueous sodium hydroxide (600 ml) were heated at 65° in a three-necked flask, with dropping funnel, stirrer, and condenser. Over 2 hr, chloroform (80 ml) was added dropwise with vigorous stirring. Stirring was maintained at the same temperature for 30 min. After cooling, the solution was extracted with chloroform, which was washed with saturated brine, dried over sodium sulfate, and evaporated. The dark, viscous residue was distilled *in vacuo*. The distillate was freed of phenols by stirring with a 1 *N* sodium hydroxide solution. The solid product was separated from the red alkaline solution by filtration and was abundantly washed with water. It was then dried *in vacuo* at room temperature. 4-Dichloromethyl-4-methylcyclohexa-2,5-dienone (3) (19.5 g, yield 20%) can be recrystallized in hexane: mp 55° (lit.[7] mp 55°); bp 70° (0.05 mm); ir ($CHCl_3$) 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.05 (m, 1), 6.85 (m, 1), 6.45 (m, 1), 6.30 (m, 1, HC=CH), 5.75 (s, 1, $CHCl_2$), 1.47 (s, 3, CH_3); mass spectrum *m/e* 190, 192, 194, 175, 177, 155, 157, 107. *Anal.* Calcd for $C_8H_8Cl_2O$: 191.06.

Methyl 9-Dichloromethyl-9-methyl-3,7-dioxobicyclo[3.3.1]nonane-2,4-dicarboxylate (4).[8]—Sodium (1.7 g) was dissolved in anhydrous methanol (40 ml) under nitrogen in a three-necked flask, with dropping funnel, stirrer, and condenser. Over 10 min, the cyclohexadienone 3 (26 g), dissolved in methanol (120 ml), was added with stirring at room temperature. Methyl acetonedicarboxylate (23.6 g) was added. The mixture was heated at reflux during 48 hr with stirring, cooled, and acidified with 1 *N* sulfuric acid (80 ml). On standing at 0°, a white precipitate was formed; it was filtered and washed at 0° with methanol and water. The diester 4 (36 g, yield 72%) was recrystallized from methanol: mp 195–197° (lit.[8] mp 189°); ir ($CHCl_3$) 1715 (ketone C=O), 1745 cm^{-1} (ester C=O); nmr ($CDCl_3$) δ 6.45 (s, 1, $CHCl_2$), 3.81 3.79 (s, 6, $COOCH_3$), 1.36 (s, 3, CH_3); mass spectrum *m/e* 364, 366, 368, 332, 334, 336, 297, 299, 261. *Anal.* Calcd for $C_{15}H_{18}O_6Cl_2$: 365.21.

9-Dichloromethyl-9-methylbicyclo[3.3.1]nonane-3,7-dione (5).[8]—The diester 4 (24.5 g) was heated at reflux temperature for 3 hr in a mixture of acetic acid (250 ml) and sulfuric acid (25 ml). After cooling at 50°, most of the acetic acid was evaporated *in vacuo*. Water (250 ml) was added at about 0°. After 12 hr at 0°, the precipitate was filtered, washed wth cold water, and dried. The decarboxylated product 5 (12.6 g, yield 75%) was dissolved in methanol at 50° and treated with carbon black. The filtered solution was evaporated to give the pure diketone 5, which was recrystallized in ethyl acetate: mp 205° (lit.[8] mp 201°); ir (KBr) 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.55 (s, 1, $CHCl_2$), 1.65 (s, 3, CH_3); mass spectrum *m/e* 248, 250, 252, 213, 215, 177. *Anal.* Calcd for $C_{11}H_{14}O_2Cl_2$: 249.14.

9,9-Dimethylbicyclo[3.3.1]nonane-3,7-dione (6). A.[9]—The diketone 5 (0.25 g) was dissolved in a 10% solution of sodium hydroxide in methanol (20 ml). In the presence of 5% palladium on barium sulfate (0.5 g), the solution was stirred in an atmosphere of hydrogen during 6 days. Water (4 ml) was added before filtration over Celite, which was washed with methanol. The filtrate was evaporated, water (10 ml) was added, and the product was extracted with chloroform. The product of hydrogenolysis 6 is obtained (0.155 g, yield 86%), but can be purified only with great difficulty, the crystals obtained from ethyl acetate, for instance, retaining impurities. The product is characterized by an exceptionally high polarity (R_f 0.1), tlc on silica gel, cyclohexane–ethyl acetate (1:1).

B.—The monodioxolane 8 (*vide infra*), treated with a mixture of methanol and a 5% solution of hydrochloric acid, gave quantitatively the same diketone 6: mp 180–190° dec; ir ($CHCl_3$) 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.42 (s, 6, CH_3); mass spectrum *m/e* 180, 165.

9-Dichloromethyl-9-methyl-7,7-ethylenedioxybicyclo[3.3.1]nonan-3-ones (7) [9-(*R*)- and 9-(*S*)-].—The diketone 5 (0.1 g) was treated in benzene (7 ml) with ethylene glycol (0.2 ml) and *p*-toluenesulfonic acid (6 mg). The solution was heated under reflux during 3 hr, with periodic withdrawal of the distillate to remove the water. After evaporation, the residue was treated with a 5% sodium carbonate–water solution and extracted with chloroform. The mixture of epimers of 7 (0.11 g, yield 93%) was obtained crystalline. Successive fractional crystallizations in a 1:9 mixture of ethyl acetate and cyclohexane give the individual 9 epimers, **7a**, and **7b**.

7a had mp 166–168°; ir ($CHCl_3$) 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.45 (s, 1, $CHCl_2$), 3.90 (m, 4, OCH_2CH_2O), 1.35 (s, 1, CH_3); mass spectrum *m/e* 292, 294, 296, 257, 259. *Anal.* Calcd for $C_{13}H_{18}Cl_2O_3$: 293.19.

7b had mp 162–164°; ir ($CHCl_3$) 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.15 (s, 1, $CHCl_2$), 3.86 (m, 4, OCH_2CH_2O), 1.40 (s, 1, CH_3); mass spectrum *m/e* 292, 294, 296, 257, 259. *Anal.* Calcd for $C_{13}H_{18}Cl_2O_3$: 293.19.

9,9-Dimethyl-7,7-ethylenedioxybicyclo[3.3.1]nonan-3-one (8).—The mixture of 9 epimers 7 (6 g), dissolved in a 10% solution of sodium hydroxide in methanol (250 ml), was stirred under hydrogen in the presence of 5% palladium on barium sulfate (2.6 g). After 8 hr, the solution was filtered over Celite, which was washed with methanol. After evaporation, water (25 ml) was added, and the product 8 (4.5 g, yield 98%) was extracted with chloroform. It was sublimed (80°, 0.5 Torr) and recrystallized in petroleum ether (bp 30–60°): mp 88–90°; ir ($CHCl_3$) 1700 cm^{-1} (C=O); nmr ($CDCl_3$) δ 3.88 (m, 4, OCH_2CH_2O), 1.2 (s, 3, CH_3), 1.15 (s, 1, CH_3); mass spectrum *m/e* 224, 209. *Anal.* Calcd for $C_{13}H_{20}O_3$: 224.29.

9,9-Dimethyl-7-methylenebicyclo[3.3.1]nonan-3-one (9).[10]—Sodium hydride suspended in paraffin oil (0.755 g) was introduced into a perfectly dry three-necked 100-ml flask, with condenser, stirrer, and serum cap. Under nitrogen, it was washed with pentane and dried. Freshly distilled dimethyl sulfoxide (7.5 ml) was injected with a syringe, and the mixture was heated at 80°, until evolution of hydrogen stops (45 min). After cooling at 0°, a solution of triphenylmethylphosphonium bromide (5.35 g) in dimethyl sulfoxide (15 ml) was injected with a syringe. After 10 min at room temperature, the diketone 6 (2.7 g), dissolved in the smallest possible volume of dimethyl sulfoxide, was slowly injected with stirring and temperature control. After one night, cold water was added, then petroleum ether, and the product was extracted. It was isolated by very careful evaporation, as it is very easily sublimable (1.853 g, yield 65%). The monoketone 9 was purified by chromatography on silica gel, and recrystallized in methanol at −20°: mp 102–105°; ir ($CHCl_3$) 1700 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.8 (m, 2, $=CH_2$), 1.25 (s, 3, CH_3), 1.20 (s, 3, CH_3); mass spectrum *m/e* 178, 163.

9,9-Dimethyl-7-methylenebicyclo[3.3.1]nonan-3-*exo*-ol (10).—The monoketone 9 (0.293 g) was reduced with lithium aluminum hydride in the usual way. The crude product (0.280 g, yield 93%) was shown by its nmr spectrum to consist of a 35:65 mixture of 3-exo and 3-endo alcohols 10 and 11. The exo alcohol 10 was obtained by chromatography on neutral alumina (Merck, activity II–III). It was recrystallized from petroleum ether at 0°: mp 106–107°; ir ($CHCl_3$) 3600, 3400 (OH), 1640, 890 cm^{-1} (=CH_2); nmr ($CDCl_3$) δ 4.70 (m, 2, $=CH_2$), 4.55 (m, 1,

(7) K. von Auwers, *Ber.*, **35**, 4211 (1902).
(8) H. Stetter and J. Mayer, *Chem. Ber.*, **92**, 2664 (1959).
(9) R. B. Woodward, *J. Amer. Chem. Soc.*, **62**, 1208 (1940).
(10) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

CHOH), 1.13 (s, 3, CH_3), 1.08 (s, 3, CH_3); mass spectrum *m/e* 180, 165. *Anal.* Calcd for $C_{12}H_{20}O$: 180.28. Chromatography on silica gel transforms **11** [nmr ($CDCl_3$) δ 4.93 (m, 2, $=CH_2$), 3.66 (m, 1, CHOH), 1.08 (s, 3, CH_3), 0.97 (s, 3, CH_3)] into the cyclic ether **12**, evaporated at 25° (0.01 Torr): nmr ($CDCl_3$) δ 3.95 (m, 1, CHO), 1.22 (s, 9, CH_3); mass spectrum *m/e* 180, 165. *Anal.* Calcd for $C_{12}H_{20}O$ (180.28): C, 79.94; H, 11.18. Found: C, 79.44; H, 11.32.

9,9,7-*exo*-Trimethylbicyclo[3.3.1]nonan-3-one (13).[11,12]—To the exo alcohol **10** (0.28 g) in methanol (4 ml) was added a 50% solution of sulfuric acid in water. After a few minutes, water was added, and the product was extracted by continuous ether extraction. It was ketone **13**: mp 54–55°; ir ($CHCl_3$) 1690 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.15 (s, 6, CH_3), 0.88 (degenerate d, 3, CH_3); mass spectrum *m/e* 180, 165.

9,9,7-*exo*-Trimethylbicyclo[3.3.1]nonan-3-*exo*-ol (14).—By reduction of ketone **13** (0.1 g) with lithium in liquid ammonia, followed by chromatography on silica gel, alcohol **14** was obtained (0.07 g, yield 70%): mp 101–102°; ir (KBr) 3300 cm^{-1} (OH); nmr ($CDCl_3$) δ 4.35 (m, 1, CHOH), 1.07 (s, 3, CH_3), 0.97 (s, 3, CH_3), 0.88 (degenerate d, 3, CH_3); mass spectrum *m/e* 164 $(M - H_2O)^+$.

9,9,7-*exo*-Trimethylbicyclo[3.3.1]nonyl 3-*exo*-Tosylate (2) (R = CH_3).—A solution of alcohol **14** (0.035 g) in pyridine (1.5 ml) was treated with *p*-toluenesulfonyl chloride (0.054 g). The product **2** (R = CH_3) was isolated in the usual way, pyridine being removed only with water (no acid wash!). It is very unstable, but can be recrystallized in petroleum ether at −20°: mp 58° dec; nmr (CCl_4) δ 5.13 (m, 1, CHOTs), 1.17 (s, 3, CH_3), 1.07 (s, 3, CH_3), 1.03 (degenerate, d, 3, CH_3); mass spectrum *m/e* 172 ($TsOH^+$), 155 (Ts^+).

7-Methylenebicyclo[3.3.1]nonan-3-*exo*-ol (16).—7-Methylenebicyclo[3.3.1]nonan-3-one (**15**), obtained by fragmentation of 1,3-dibromoadamantane[13] was reduced with lithium aluminum hydride in ether.[14] The crude product was shown by nmr spectroscopy to be a 15:85 mixture of the 3-exo alcohol **16** and the 3-endo alcohol **17**. By chromatography on neutral alumina (Merck, activity II–III), the exo alcohol **16** was obtained pure. It was recrystallized from petroleum ether at 0°: mp 93–94°; ir ($CHCl_3$) 3600, 3400 (OH), 1640, 880 cm^{-1} ($=CH_2$); nmr ($CDCl_3$) δ 4.63 (m, 2, $=CH_2$), 4.56 (m, 1 CHOH); mass spectrum *m/e* 152, 137.

By chromatography on silica gel, the endo alcohol **17** [nmr (CCl_4) δ 4.95 (m, 2, $=CH_2$), 3.78 (m, 1, CHOH)] was transformed into the cyclic ether **18**, evaporated at 26° (0.1 Torr): nmr ($CDCl_3$) δ 4.05 (m, 1, CHO), 1.07 (s, 3, CH_3); mass spectrum *m/e* 152, 137, 134. *Anal.* Calcd for $C_{10}H_{16}O$: 152.23.

7-*exo*-Methylbicyclo[3.3.1]nonan-3-one (19).—The exo alcohol **16**, treated with acid in the manner described above for the obtention of **13** from **10**, gives the ketone **19**:[11] mp 57–58°; ir ($CHCl_3$) 1690 cm^{-1} (C=O); nmr ($CDCl_3$) δ 0.82 (d, 3, J = 5 Hz, CH_3); mass spectrum *m/e* 152, 137. *Anal.* Calcd for $C_{10}H_{16}O$ (152.23): C, 78.89; H, 10.59. Found: C, 78.54; H, 10.50.

7-*exo*-Methylbicyclo[3.3.1]nonan-3-*exo*-ol (20).—Ketone **19**, reduced with lithium in liquid ammonia, gives the exo alcohol **20**: mp 72–75°; ir ($CHCl_3$) 3600 and 3420 cm^{-1} (OH); nmr ($CDCl_3$) δ 4.34 (m, 1, CHOH), 0.83 (d, 3, J = 5 Hz, CH_3); mass spectrum *m/e* 154, 136, 121. *Anal.* Calcd for $C_{10}H_{18}O$ (154.24): C, 77.86; H, 11.76. Found: C, 77.35; H, 11.57.

7-Methylbicyclo[3.3.1]nonyl 3-*exo*-Tosylate (1) (R = CH_3).—The exo alcohol **20**, treated with *p*-toluenesulfonyl chloride in pyridine, gives after extraction (avoiding any acidic washing), the corresponding, very unstable tosylate **1** (R = CH_3), which is recrystallized in hexane: mp 64° dec; nmr ($CDCl_3$) δ 5.24 (m, 1, CHOTs), 0.82 (d, 3, J = 5 Hz, CH_3); mass spectrum *m/e* 172 ($TsOH^+$), 155 (Ts^+).

Kinetics.—Solvolysis was carried out in a 80:20 (v/v) mixture of ethanol and water on solutions 0.002 *M*. After orientation runs, at least duplicate measurements were carried out for the determination of rate constants, up to more than 95% of completion. The progress of reaction was followed by the decrease of extinction at 262 nm,[15] on a Cary 14 spectrophotometer.

Registry No.—**1** (R = CH_3), 19912-54-0; **2** (R = CH_3), 37741-04-1; **3**, 6611-78-5; **4**, 37741-06-3; **5**, 22899-25-8; **6**, 37741-08-5; **7a**, 37741-09-6; **7b**, 37805-66-6; **8**, 37741-10-9; **9**, 37741-11-0; **10**, 37741-12-1; **11**, 37741-13-2; **12**, 37741-14-3; **13**, 37741-15-4; **14**, 37741-16-5; **15**, 19933-29-8; **16**, 1712-41-0; **17**, 1905-15-3; **18**, 6508-22-1; **19**, 37741-56-3; **20**, 37741-57-4; *p*-cresol, 106-44-5.

Acknowledgments.—We thank the Université Louis Pasteur for a Visiting Assistantship (L. K.), the CNRS for a Research Attachéship (L. S.), Messr. F. Hoffmann-La Roche et Cie, Bâle, for a generous gift of substance **3** and for partial support of this work, and Professors D. Goldsmith and W. Parker for useful discussions.

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