hours, cooled, and worked up as before. (b) A solution of 0.431 g of **3** in 30 ml of acetic acid-O-*d* buffered with 0.1 *M* sodium acetate was heated at 110.00° for 75.5 min (39% reaction), cooled, and worked up as before. In each case the crude product was chromatographed through silica gel with benzene–ether to give an acetate fraction and a tosylate fraction. The acetate fraction was purified by preparative vpc (15% didecyl phthalate on Chromosorb P) in the case of a and by distillation (bp 75°, 0.25 mm) in the case of b. The infrared spectra of the acetates from a and b were identical, but were different from that of **15**. The tosylate fractions were purified by recrystallization from hexane (mp 97.0–98.0°). The infrared spectra of the tosylates from a and b were different from one another and from that for **3**; that from b was intermediate between that from a and that of **3**. The nmr pattern of the tosylate from b was identical with that of **3**, except that the intensity of a signal masked by the aryl methyl group was diminished. Mass spectral analyses indicated a monodeuterio percentage of 54% for the tosylate from a and 34% deuterium incorporation for the tosylate from b.

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The Acetolysis of the Epimeric 3,3-Dimethyl-7-tosyloxybicyclo-[2.2.1]heptan-2-ones. The Interaction between Incipient Carbonium Ions and Neighboring Nonenolizable Ketones[1]

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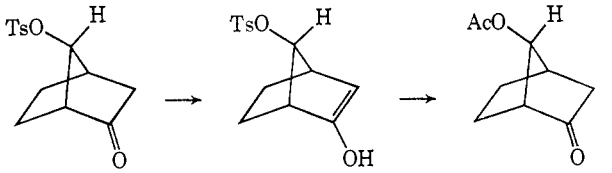
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received April 16, 1969*

Abstract: 3,3-Dimethyl-*syn*-7-tosyloxybicyclo[2.2.1]heptan-2-one and 3,3-dimethyl-*anti*-7-tosyloxybicyclo[2.2.1]-heptan-2-one have been prepared by nine and seven step synthetic sequences, respectively, starting with *dl*-camphor. The *anti* isomer underwent acetolysis *ca.* 20 times faster than the *syn* isomer and *ca.* six times faster than 7-tosyloxynorbornane. Whereas the *syn*-tosylate gave predominately a mixture of *syn*- and *anti*-7-acetoxy-3,3-dimethylbicyclo-[2.2.1]heptan-2-ones, the *anti*-tosylate gave the ring opened product, (Δ-2-cyclopentenyl)-2,2-dimethylacetic acid, as the only isolable compound. This behavior is contrasted with the corresponding acetolysis of *syn*- and *anti*-7-tosyloxybicyclo[2.2.1]heptan-2-one, where the enolizable character of the carbonyl function accounts for a drastically different rate comparison and product composition.

In the preceding paper[4] we discussed in detail the role of enolization in neighboring group participation of carbonyl functions. Although the small amount of enol present is generally not involved in ketone neighboring group participation,[5] we have found that in rigid bicyclic systems, where participation of the π and nonbonding electrons of the carbonyl group is stereochemically prohibited from interacting with the incipient carbonium ion center, this enol content can be the overriding factor in determining the rates and products of solvolysis. This point is dramatically illustrated by the case of the epimeric 7-tosyloxybicyclo[2.2.1]heptan-2-ones. Acetolysis of *anti*-7-tosyloxybicyclo[2.2.1]heptan-2-one (**1**) occurred 10^4 times faster than acetolysis of *syn*-7-tosyloxybicyclo[2.2.1]heptan-2-one (**2**). In addition **1** gave only *anti*-7-acetoxybicyclo[2.2.1]heptan-2-one (**3**), while **2** gave a mixture of **3** and *syn*-7-acetoxybicyclo[2.2.1]heptan-2-one (**4**). Solvolysis in acetic acid-O-*d* provided definitive evidence that **1** and **2** were solvolyzing by different mechanisms with enolization to **5** being the rate-determining step in the acetolysis of **1**. This example of rate and product dependence on the stereochemical relationship of the leaving tosylate function and the enolizable carbonyl group was instructive



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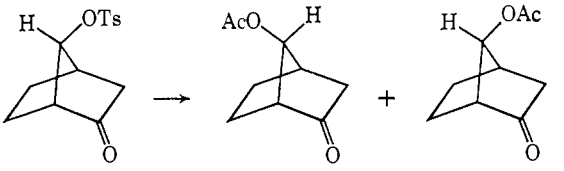
insofar as it unequivocally established the importance of considering the enol form in any study of carbonyl

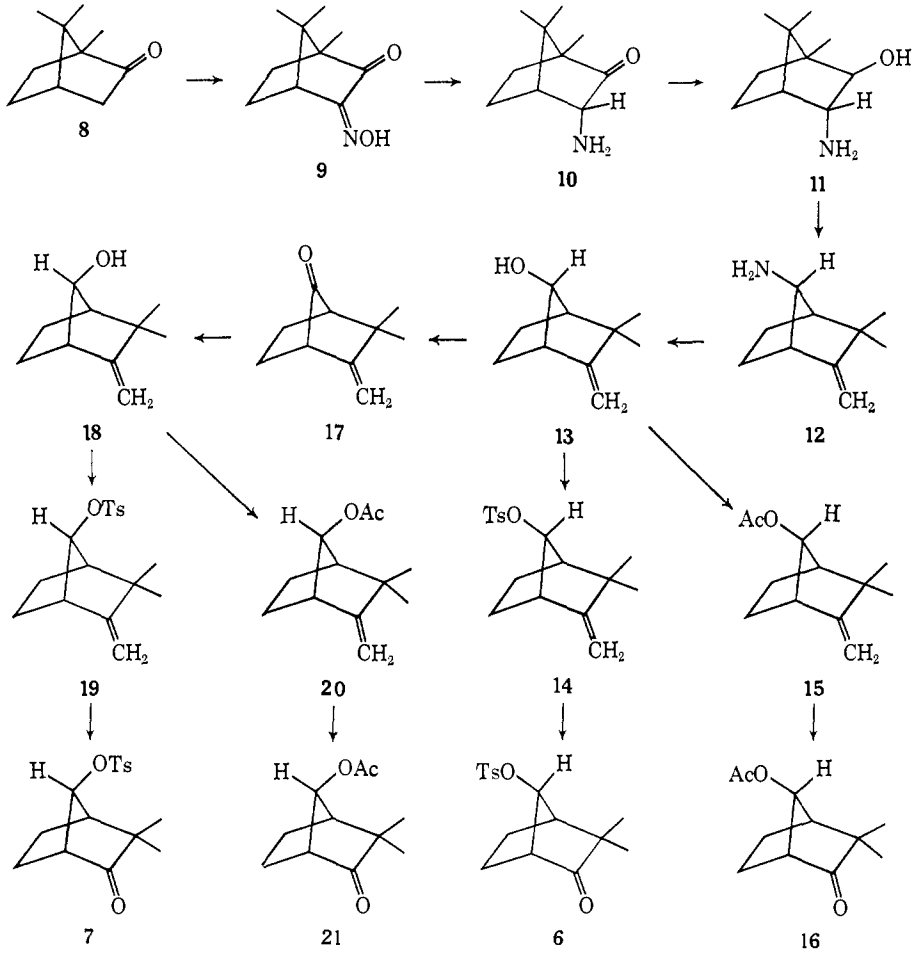


2 3 4

neighboring group participation. This unusual example raised the question of the chemical consequences of the stereochemical relationship between a leaving tosylate function and a nonenolizable ketone. The present paper describes the synthesis and solvolysis of model compounds which allow a critical evaluation of the interaction of nonenolizable ketones with incipient carbonium ion centers in rigid molecules.

(1) For a preliminary communication of part of this work, see P. G. Gassman and J. M. Hornback, *Tetrahedron Letters*, 1325 (1969).
(2) Alfred P. Sloan Research Fellow, 1967–1969.
(3) National Science Foundation Trainee, 1965–1968.
(4) P. G. Gassman, J. L. Marshall, and J. M. Hornback, *J. Am. Chem. Soc.*, 91, 5811 (1969).
(5) D. J. Pasto and M. P. Serve, *ibid.*, 87, 1515 (1965); D. J. Pasto, K. Garves, and M. P. Serve, *J. Org. Chem.*, 32, 774 (1967); H. R. Ward and P. D. Sherman, Jr., *J. Am. Chem. Soc.*, 90, 3812 (1968).

Scheme I



Synthesis and Solvolysis

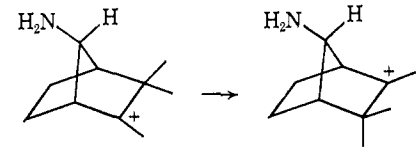
In view of the clear-cut distinction between the modes of solvolysis of **1** and **2** and the role of **5** in the acetolysis of **1**, it appeared that an evaluation of the interaction of nonenolizable ketones could be obtained if the α positions in **1** and **2** could be blocked in a manner which would prevent enolization. 3,3-Dimethyl-*anti*-7-tosyloxybicyclo[2.2.1]heptan-2-one (**6**) and 3,3-dimethyl-*syn*-7-tosyloxybicyclo[2.2.1]heptan-2-one (**7**), in which the *gem*-dimethyl groups would render enolization impossible, seemed to be ideal models for our study.

The synthesis of **6** and **7** is outlined in Scheme I. Treatment of *dl*-camphor (**8**) with sodium amide in liquid ammonia–ether solution to give the anion, followed by reaction of the anion with isoamyl nitrite, gave isonitrosocamphor (**9**).[6] Reduction of **9** with zinc and sodium hydroxide gave α-aminocamphor (**10**).[7] Catalytic hydrogenation of **10** over Adam's catalyst by a modification of the procedure of van Tamelen and Judd[8] gave α-aminoborneol (**11**) which was converted to *anti*-7-aminocamphene (**12**) by treatment with phosphorus pentachloride followed by the addition of base.[9,10] Nitrous acid deamination of **12** gave *anti*-7-hydroxycamphene (**13**).[9] The conversions of **13** into the corresponding tosylate,[8] **14**, and acetate, **15**, were accomplished by reaction of **13** with *p*-toluenesulfonyl chloride in pyridine and acetic anhydride in pyridine, respectively. Ozonolysis of **14** in absolute methanol at -70 to $-80°$ gave **6**. Similar ozonolysis of **15** gave **16**.

7-Ketocamphene (**17**)[8] was prepared by Sarett oxidation[11] of **13**. Sodium borohydride reduction of **17** gave *syn*-7-hydroxycamphene (**18**)[8] which upon reaction with *p*-toluenesulfonyl chloride in pyridine[12] and acetic anhydride in pyridine gave **19** and **20**, respectively. Ozonolysis of **19** and **20** gave **7** and **21**, respectively.

The solvolysis of 3,3-dimethyl-*anti*-7-tosyloxybicyclo[2.2.1]heptan-2-one (**6**) and 3,3-dimethyl-*syn*-7-tosyloxybicyclo[2.2.1]heptane-2-one (**7**) was studied in acetic acid buffered with sodium acetate. Table I lists the

(6) F. S. Legagneur, *Ann. Chim.* (Paris), 7, 385 (1927).
(7) P. Duden and W. Pritzkow, *Ber.*, 32, 1538 (1899).
(8) E. E. van Tamelen and C. I. Judd, *J. Am. Chem. Soc.*, 80, 6305 (1958).
(9) P. Duden and A. E. MacIntyre, *Ann.*, 313, 59 (1900).
(10) When *d*-camphor was used instead of *dl*-camphor complications arose in the rearrangement step. Apparently the dehydration–rearrangement of **11** occurred *via* the intermediacy of a which through a Nametkin-type of methyl migration gave the mirror image ion, b. This resulted in partial racemization. Owing to this partial racemization subsequent



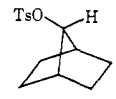
a b

compounds in the series, which were a mixture of *d* and *dl* forms, were not readily crystallized or purified. This difficulty was avoided through the use of *dl*-camphor as starting material.
(11) G. I. Poos, G. E. Arth, R. E. Beylor, and L. H. Sarett, *J. Am. Chem. Soc.*, 75, 422 (1953).
(12) R. S. Tipson, *J. Org. Chem.*, 9, 235 (1944).

Table I. Acetolysis Rates of 7-Norbornyl Tosylates

Compd	Ref	Temp, °C	Rate, sec^{-1}	k_{rel} at 200°	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
6		210.0 ± 0.1	$(7.12 \pm 0.09) \times 10^{-4}$			
		200.0 ± 0.1	$(3.03 \pm 0.03) \times 10^{-4}$	56	34.6	−2.4
		190.0 ± 0.1	$(1.43 \pm 0.01) \times 10^{-4}$			
7		220.0 ± 0.1	$(7.02 \pm 0.08) \times 10^{-5}$			
		210.0 ± 0.1	$(3.24 \pm 0.03) \times 10^{-5}$		34.4	−8.8
		200.0 ± 0.1	$(1.52 \pm 0.02) \times 10^{-5}$	3		
2	4	200.0 ± 0.1	$(5.45 \pm 0.19) \times 10^{-6}$	1	34.9	−9.8
22	13	200.0	5.49×10^{-5}	10	35.7	−3.5

rates of acetolysis, and the associated thermodynamic parameters, of **6** and **7**, together with the rates of *syn*-7-tosyloxybicyclo[2.2.1]heptan-2-one (**2**) and 7-tosyloxybicyclo[2.2.1]heptane[13] (**22**) for comparison purposes. In general, the rates of solvolysis of **6**, **7**, **2**, and **22** were not very different, the fastest being only 56 times more rapid than the slowest. Both **2** and **7** were slower than **22**, which would be expected on the basis of the rate-retarding inductive effect of the carbonyl group in the 2 position of both **2** and **7**. The surprising feature of the rate comparison was that **6** was *ca.* six times faster than **22** even though the presence of the carbonyl group



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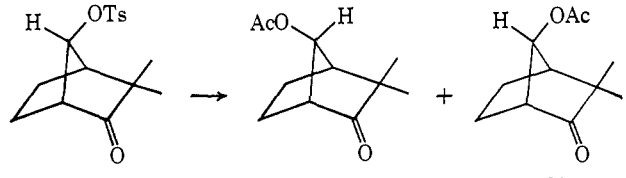
in the 2 position of **6** should have exerted a rate-slowing influence similar to that observed for **2** and **7**. The enhanced rate of acetolysis of **6** implied either an unusual effect of the carbonyl dipole or a change in the mechanism of the reaction.

Analysis of the products obtained from the acetolyses of **6** and **7** indicated that these tosylates were solvolyzing by different mechanisms. The acetolysis of **7** was extremely complex since extensive decomposition occurred at the temperature required for acetolysis and a mixture of twelve components was formed even on very short reaction times. When the products were analyzed after less than 5% reaction of **7** the 12-product

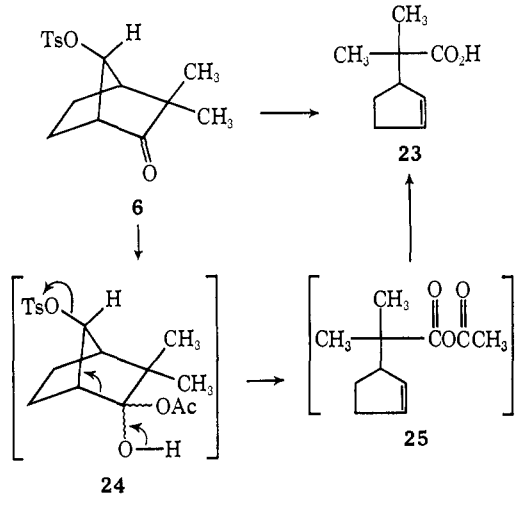


7 **16** **21**

mixture was found to contain 50% **16** and 20% **21**, with the ten unidentified components constituting the remaining 30%. The extensive decomposition and formation of numerous side products, observed in the acetolysis of **7**, were similar to the results obtained in the solvolysis of **2**. It is interesting to note that although **2** and **7** appear to solvolyze by the same mechanism to give a mixture of *syn*-7- and *anti*-7-acetoxybicyclo[2.2.1]heptan-2-one derivatives, **7** gave less inversion than **2**. Unfortunately, the available experimental data do not permit an evaluation of the factors which control retention or inversion of stereochemistry at the 7 position of **2** and **7**.

(13) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, 77, 4183 (1955).

Solvolysis of **6** in sodium acetate buffered glacial acetic acid gave only one isolable product in 67% yield. This product was shown to be an acid by ir spectroscopy. The formation of an acid implied a dramatic change in solvolytic mechanism and required that the bicyclic starting material undergo bond cleavage.

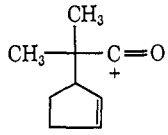


Mechanistic considerations led to **23** as the most likely acid product. That the acid obtained from acetolysis of **6** was (Δ-2-cyclopentenyl)-2,2-dimethylacetic acid (**23**) was verified by nmr spectroscopy. The spectrum of **23** showed the two methyl groups as three proton singlets at τ 8.83 and 8.88. The two separate methyl resonances were expected for a *gem*-dimethyl grouping next to an asymmetric center by analogy with the findings of Mislow and coworkers.[14] The tertiary allylic proton appeared as a multiplet centered at τ 6.90. The remaining four protons on saturated carbons appeared as a broad two-proton multiplet at τ 8.19 due to the non-allylic methylene protons, and a multiplet centered at τ 7.60 (2 H) due to the allylic methylene protons. The vinyl protons appeared as multiplets at τ 4.12 and 4.32 (1 H each). Irradiation of either the τ 6.90 or 7.60 multiplet resulted in simplification of the multiplets due to the vinyl protons. When the τ 6.90 and 7.60 multiplets were simultaneously irradiated, the vinyl proton multiplets collapsed to an AB quartet with a coupling constant of 6 cps. In general the over-all vinyl hydrogen pattern was the same as that which has been established as being characteristic of 3-substituted cyclopentenes.[15]

The formation of **23** in the acetolysis of **6** could have occurred by either of two mechanisms. Addition of

(14) R. A. Lewis, O. Korpium, and K. Mislow, *ibid.*, **89**, 4786 (1967).
(15) P. G. Gassman and K. T. Mansfield, *ibid.*, **90**, 1517 (1968).

acetic acid to the carbonyl group of **6** would give **24** which could undergo concerted cleavage to yield **25**. Under the work-up conditions **25** would be expected to hydrolyze to **23**. An alternate mechanism would involve concerted ionization–bond cleavage of **6** to give the acylium ion **26**, which would react with the solvent to give **25** and, after hydrolysis, **23**.



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Discussion of Results

Both the rates and the products of the acetolysis of **6** and **7** indicated that these molecules, which only differ in the stereochemistry of the tosylate function, solvolyze by different mechanisms. Although the steric environment of the leaving group was somewhat more crowded in **7** than in **6**, it is felt that this steric factor was relatively unimportant in determining the over-all mechanistic features of the acetolyses. Undoubtedly, the controlling factor was the stereochemical relationship between the carbonyl group in the 2 position and the leaving tosylate function. In **6**, where the leaving tosylate group was *trans* to the C_1–C_2 bond, concerted cleavage was favored. In **7**, where the leaving group was oriented in a *cis* position relative to the C_1–C_2 bond, the major products had the bicyclic skeleton intact. This change in reaction mechanism with change in stereochemical relationship between leaving group and carbonyl group clearly illustrated the role which can be played by a nonenolizable ketone function. A nonenolizable ketone group can be a critical neighboring group participant even when this "participation" is not involvement of the π or nonbonding electrons of the carbonyl. This principle, so clearly demonstrated by the comparison of the acetolysis of **6** and **7**, is one that bears serious consideration in all cases where the stereochemical arrangement of an incipient carbonium ion and a carbonyl group is such that "neighboring group participation," in the classical sense of the term, is considered unlikely.

Experimental Section[16]

α-Aminocamphor (10). *dl*-Camphor (**8**) was converted into isonitrosocamphor (**9**)[6] and **9** was subsequently reduced to α-aminocamphor (**10**) according to the procedure of Duden and Pritzkow.[7] The unstable α-amino ketone was used in the next step without purification. The over-all yield of **10** from **8** was generally *ca.* 80%.

α-Aminoborneol (11). The preparation of **11** was accomplished by a modification of the procedure of van Tamelen and Judd.[6] A solution of 32.0 g of crude **10** in 100 ml of anhydrous ethanol was swirled over grade VI Raney nickel and the Raney nickel was removed by filtration. The filtrate was mixed with 2.5 g of platinum oxide and the resulting mixture was hydrogenated on a Parr hydrogenator. After 48 hr the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration and the solvent was distilled off under reduced pressure. Recrystallization of the crystalline residue from mixed hexanes (Skelly B) gave 22.6 g (70%) of **11**, mp 186–189°.

If the crude crystalline residue was dissolved in anhydrous ether and hydrogen chloride gas was bubbled through the solution, **11** was precipitated as its hydrochloride. Filtration and drying of this precipitate generally gave a higher over-all yield of **11** (as the hydrochloride salt).

anti-7-Hydroxycamphene (13). The hydrochloride salt of **11** was converted into *anti*-7-aminocamphene (**12**) and **12** was subsequently converted into **13** according to the procedure of Duden and MacIntyre.[9]

anti-7-Tosyloxycamphene (14). The method of Tipson[12] was used to convert **13** into **14**.[8]

anti-7-Acetoxycamphene (15). To a cold solution of 0.50 g of **13** in 10 ml of pyridine was added 1.0 g of acetic anhydride and the solution was allowed to stand overnight at 5°. The solution was poured into 250 ml of water and extracted with three 75-ml portions of ether. The combined extracts were washed with dilute hydrochloric acid solution, water, and saturated sodium chloride solution, followed by drying over anhydrous magnesium sulfate. Removal of the drying agent by filtration, followed by removal of the solvent, gave a residue which on fractional distillation yielded 0.54 g (84%) of **15**, bp 84–87° (3.6 mm). An analytical sample was obtained by preparative vpc on a 5 ft × 3/8 in. 20% butanediol succinate on firebrick column, n^{25}D 1.4700.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.23; H, 9.28. Found: C, 74.00; H, 9.39.

3,3-Dimethyl-*anti*-7-tosyloxybicyclo[2.2.1]heptan-2-one (6). A solution of 6.0 g (0.020 mole) of **14** in 50 ml of anhydrous methanol at −70 to −80° was ozonized until a total of 0.019 mole of ozone had been added. The ozonolysis mixture was poured into an ice cold solution of 16 g of sodium iodide and 8 ml of acetic acid in 50 ml of methanol. The reaction mixture was stirred for 4 hr, poured into 1 l. of water, and sodium bisulfite was added until the iodine color disappeared. Sodium carbonate was added until the solution was slightly basic and the reaction mixture was extracted with three 250-ml portions of chloroform. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, and the drying agent removed by filtration. The solvent was removed under reduced pressure and the solid product was recrystallized several times from *n*-hexane to give 3.4 g (57%) of **6**, mp 108–110°.

Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.34; H, 6.49; S, 10.39. Found: C, 62.34; H, 6.65; S, 10.24.

anti-7-Acetoxy-3,3-dimethylbicyclo[2.2.1]heptan-2-one (16). A solution of 0.40 g of **15** in 20 ml of anhydrous methanol at −70 to −80° was exhaustively ozonized. The ozonolysis solution was poured into a rapidly stirred solution of 4 g of sodium iodide and 2 ml of acetic acid in 15 ml of methanol. After stirring for 4 hr the reaction mixture was poured into 500 ml of water, sodium bisulfite was added until the iodine color disappeared, and sodium carbonate was added until the solution was basic. The basic solution was extracted with three 150-ml portions of ether and the combined ethereal extracts were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent was distilled off under reduced pressure. Distillation of the residue gave 0.35 g (87%) of **16**, bp 99–104° (0.6 mm). An analytical sample was prepared by preparative vpc on a 5 ft × 3/8 in. 20% butanediol succinate on firebrick column, n^{25}D 1.4687.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.35; H, 8.16. Found: C, 67.38; H, 8.22.

syn-7-Hydroxycamphene (18). Sarett oxidation converted **13** into 7-ketocamphene (**17**). Sodium borohydride reduction of **17** according to the literature procedure[8] gave **18** in 81% over-all yield from **13**.

syn-7-Tosyloxycamphene (19). The alcohol, **18**, was converted into **19** according to the method of van Tamelen and Judd.[8]

syn-7-Acetoxycamphene (20). The acetate, **20**, was prepared from **18**, as described above for the preparation of **15**, in 81% yield, bp 80–84° (3 mm), n^{25}D 1.4733.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.23; H, 9.28. Found: C, 74.42; H, 9.52.

3,3-Dimethyl-*syn*-7-tosyloxybicyclo[2.2.1]heptan-2-one (7). A methanolic solution of **19** was ozonized as described above for the preparation of **6**. Work-up in the manner described above gave a 25% yield of **7**, mp 79–81° after several recrystallizations from mixed pentanes.

Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.34; H, 6.49; S, 10.39. Found: C, 62.28; H, 6.68; S, 10.27.

syn-7-Acetoxy-3,3-dimethylbicyclo[2.2.1]heptan-2-one (21). Ozonolysis of **20**, as described above with **15**, gave **21** in 79% yield, bp 101–113° (0.9 mm). An analytical sample was prepared as described above for **16**.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.35; H, 8.16. Found: C, 67.30; H, 8.28.

(16) Melting points and boiling points are uncorrected.

Kinetics. The kinetic procedures used were the same as those described in the preceding paper.[4]

Acetolysis Product Analysis of 3,3-Dimethyl-*anti*-7-tosyloxybicyclo[2.2.1]heptan-2-one (6). A solution of 0.50 g of **6** in 20 ml of 0.1 *M* sodium acetate in acetic acid was sealed in an ampoule and heated in a bath at 200° for 3 hr (*ca.* 5 half-lives). After cooling to room temperature the ampoule was opened and the contents were poured into 250 ml of water. The acidic solution was neutralized with sodium bicarbonate and extracted with three 150-ml portions of ether. The ethereal extracts were combined and dried over anhydrous magnesium sulfate. Removal of the drying agent by filtration and distillation of the solvent gave a residue which on short-path distillation gave 0.16 g (67%) of a colorless liquid which was clearly identified as a carboxylic acid by its infrared spectrum.[17] Vpc analysis on a 3% FFAP on Chromosorb G column showed this acid to be greater than 95% pure. Nmr spectroscopy showed this acid to be (Δ-2-cyclopentenyl)dimethylacetic acid (**23**). An analytical sample was obtained by preparative vpc on a 5 ft × $^3/_8$ in. 5% SE-30 on Firebrick column.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 70.16; H, 9.17.

Vpc analysis of the reaction mixture after 10 min at 200° (*ca.* 5% reaction) showed the same product composition as obtained at the completion of the reaction. That **23** was not arising from the decomposition of either **16** or **21** under the reaction conditions was shown by separate control experiments in which **16** and **21** were subjected to the reaction conditions for 30 min at 200°. Relatively little decomposition of **16** or **21** occurred during the 30-min period. However, on prolonged heating at 200°, **16** and **21** did decrease in quantity.

Product Analysis of the Acetolysis Mixture from 3,3-Dimethyl-*anti*-7-tosyloxybicyclo[2.2.1]heptan-2-one. Because of the instability of **16** and **21** to the reaction conditions employed in the acetolysis of **7**, the product determination could not be made at the conclusion of the reaction. A solution of 0.051 g of **7** in 2 ml of 0.1 *M* sodium acetate buffered glacial acetic acid was sealed in a solvolysis tube and heated to 200° for 30 min ($t_{1/2}$ 760 min at 200°). After cooling to room temperature the solution was poured into 40 ml of water and neutralized with 5 g of sodium bicarbonate. The neutralized solution was extracted with two 20-ml portions of ether and the combined extracts were dried over anhydrous magnesium sulfate. Removal of the drying agent and solvent gave a liquid residue. Vpc analysis showed the solvolysis mixture to consist of 50% **16**, 20% **21**, and ten other components which constituted the remaining 30%. The identity of the two major components was established by comparison of vpc retention times on three columns with different liquid phases (PDEAS, XF-1150, and FFAP).

Acknowledgment. We are indebted to the Petroleum Research Fund administered by the American Chemical Society for a grant which supported this work.

(17) It is interesting to note that this carboxylic acid could be readily extracted from sodium bicarbonate solution which had completely neutralized the acetic acid solvent. The crude product, prior to distillation, corresponded to a quantitative yield of **23**. Sodium hydroxide solution neutralized **23**. In addition **23** was readily converted to its methyl ester with diazomethane. We wish to acknowledge the assistance of Dr. Richard Steppel in the identification of **23**.

The Peroxide Route to Pentaoxyphosphoranes[1]

Donald B. Denney and Donald H. Jones[2]

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Abstract: A variety of pentaoxyphosphoranes have been prepared by allowing trisubstituted phosphites to react with diethyl peroxide. In one case the same pentaoxyphosphorane was prepared by condensation of β-naphthoquinone and triethyl phoshite and by reaction of the phosphite, **3**, with diethyl peroxide. The relative rates of formation of the pentaoxyphosphoranes have been obtained as a function of structure. Decomposition of five-membered ring containing pentaoxyphosphoranes gives epoxides in a stereospecific process.

The syntheses of the first pentaoxyphosphoranes were reported nearly simultaneously in 1958 by Birum and Dever[3] and Kukhtin.[4] These compounds were prepared by condensation of α-dicarbonyl compounds with trisubstituted phosphites. Since that time Ramirez and coworkers have conducted extensive studies of this method of producing these and related substances.[5] Their preparation has been reviewed.[6] Other reviews on the structures and properties of pentacoordinated compounds have appeared in the recent literature.[7]

In 1964, Denney and Relles[8a] found that diethyl peroxide and triethylphosphite reacted to give a substance which was characterized as pentaethoxyphosphorane (**2**). Subsequently pentamethoxyphosphorane and an

$$(C_2H_5O)_2 + (C_2H_5O)_3P \longrightarrow (C_2H_5O)_5P$$
$$\mathbf{1} \qquad\qquad \mathbf{2}$$

oxyphosphorane containing a six-membered ring were prepared by the phosphite–peroxide reaction.[8b]

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