The two mechanism shown above have been distinguished by use of deuterium oxide to quench the reaction mixture. The ratio of phenylcyclopropane to other products (measured by glpc) was 9:91, regardless of whether the deuterium oxide was added immediately after mixing the reactants or after the reaction mixture had been held for 2 hr under reflux. The phenylcyclopropane contained no detectable deuterium, in spite of the known stabilities of cyclopropyllithiums in ether.[4] The cyclopropene mechanism is thus virtually ruled out, and the Wawzonek mechanism or some variant of it remains the simplest interpretation of the facts. One modification of this mechanism which might improve it would be to eliminate the intermediate carbanion (*i.e.*, to make the reaction one concerted process). It is not obvious that there should be simple addition to the double bond in the sense observed, since phenyllithium does not add to simple olfins.[5] The higher yields of cyclopropanes when γ-alkyl substituents are present[1] are also in the wrong direction with respect to the expected relative stabilities[6] of the intermediate carbanions proposed by Wawzonek.

Another mechanism which cannot be ruled out is heterolytic dissociation of the allylic chloride followed by reaction of the allylic cation at the 2 position with phenyllithium. The reaction path lacks good precedent, but could be regarded as the mechanistic reverse of the formation of allylic cations from cyclopropyl halides.

Experimental Section[7]

Reaction of Allyl Chloride with Phenyllithium.—To a stirred solution of 100 ml of 1.2 *M* (0.12 mole) phenyllithium in 70:30 benzene–ether was added dropwise, over a 10-min period, 7.65 g (0.10 mole) of allyl chloride. The reaction temperature was maintained at 20–25° by use of an ice bath. Immediately after the addition, 10 ml of deuterium oxide (99.5%) was added cautiously. The mixture was poured into water, and then extracted with ether. The organic phase was dried over sodium sulfate, filtered, and concentrated. Phenylcyclopropane was collected by preparative glpc on a 10-ft column of 20% Apiezon L on Anakrom ABS at 155°, flow rate 100 ml/min. Analytical glpc on a 10-ft 10% Apiezon L column at 150° and 80 ml/min showed major peaks at 2.7, 4.15, and 7.8 min, the last being phenylcyclopropane. The relative peak areas were 1.84:8.54: 1.00, respectively. In a similar run, the reaction mixture was heated under reflux for 2 hr before addition of deuterium oxide, and in this case, the peak areas observed were 1.83:8.49:1.00. The phenylcyclopropane peak was established by the identity of the infrared spectrum with that of an authentic sample[8] and by the identity of the nmr (carbon tetrachloride) spectrum with the published spectrum.[9] There was no absorption in the infrared from 1950 to 2800 cm^{-1} to show any deuterium incorporation, and a falling-drop deuterium analysis also showed no deuterium in the sample from immediate deuterium oxide work-up.

Acknowledgment.—The authors are indebted to the National Science Foundation for support of this work, and to Professor Wawzonek for details of his experimental procedure.

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(4) (a) D. E. Applequist and A. H. Peterson, *J. Am. Chem. Soc.*, **83**, 862 (1961); (b) H. M. Walborsky, *Rec. Chem. Progr.* (Kresge-Hooker Sci. Lib.), **23**, 75 (1962).

(5) (a) S. J. Cristol, J. W. Ragsdale, and J. S. Meek, *J. Am. Chem. Soc.*, **73**, 810 (1951); (b) N. P. Neureiter and F. G. Bordwell, *ibid.*, **81**, 578 (1961).

(6) D. E. Applequist and D. F. O'Brien, *ibid.*, **85**, 743 (1963).

(7) Deuterium analyses by the falling-drop method were performed by Mr. Josef Nemeth.

(8) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(9) N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., Spectrum 528.

The Acylation of Cycloheptene[1]

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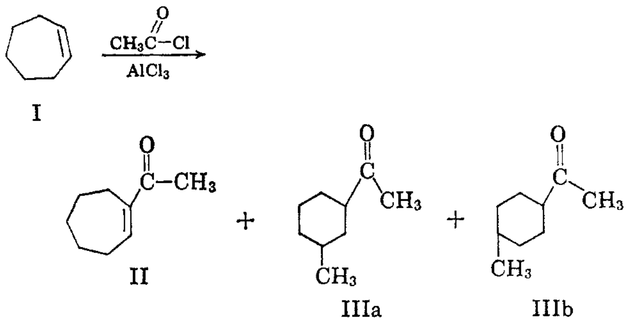
The aluminum chloride catalyzed acylation of cycloheptene (I) has been shown[2–6] to produce a variety of products depending upon the reaction conditions. At 10°, acetylation with acetyl chloride in methylene chloride gave[4] 1-acetylcycloheptene (II), while at reflux temperatures in cyclohexane or isopentane, Friess and Pinson[5] and Nenitzescu and his co-workers[6] obtained 3- and 4-methylacetylcyclohexane (IIIa,b). It was suggested[6] that the saturation of the rearranged products was the consequence of an intermolecular hydrogen transfer from the solvent.



In the course of attempting to synthesize II using polyphosphoric acid (PPA),[7] it was surprising to find, instead, the products shown in Table I. Although the ketones, 2-methyl-1-acetylcyclohexene (IV) and 2-methyl-3-acetylcyclohexene (V) represent rearrangement of the cycloheptyl ring skeleton, they do not correspond to the rearranged products obtained by the aluminum chloride catalyzed reaction. The ester VI and hydrocarbon VII were produced without a skeletal rearrangement.

The formation of these products can be visualized as arising from several carbonium ion processes. Electrophilic attack on the olefin by the acylium ion, from the reaction of acetic acid with PPA, would give rise to the intermediate ion, IIa. Rearrangement to the tertiary ion involving a 1,2-hydride ion shift[8] and elimination of proton H_a or H_b would yield the ketonic products IV and V.

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(1) (a) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966. (b) Taken in part from a dissertation submitted by R. J. Dolinski to the University of Detroit Graduate School in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) N. Jones, E. J. Rudd, and H. T. Taylor, *J. Chem. Soc.*, 2354 (1963).

(3) W. Taub and J. Szmuszkowicz, *J. Am. Chem. Soc.*, **74**, 2117 (1952).

(4) N. Jones, H. T. Taylor, and E. J. Rudd, *J. Chem. Soc.*, 1342 (1961).

(5) S. L. Friess and R. Pinson, Jr., *J. Am. Chem. Soc.*, **73**, 3512 (1951).

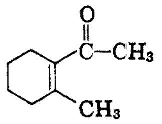
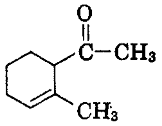
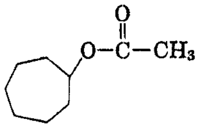
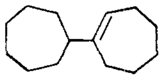
(6) C. D. Nenitzescu, I. Pogany, and G. Mihai, *Acad. Rep. Populare Romine Studii Cercetari Chim.*, **6**, 375 (1958).

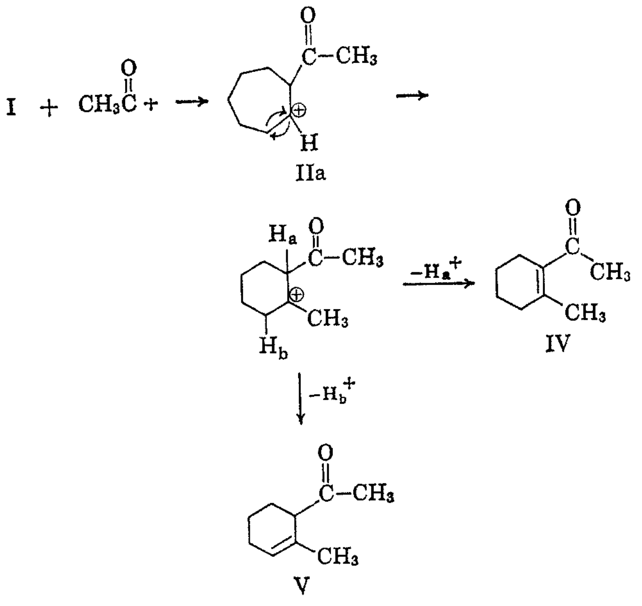
(7) F. D. Popp and W. E. McEwen, *Chem. Rev.*, **58**, 321 (1958).

(8) C. D. Nenitzescu and A. J. Balaban, "Friedel-Crafts and Related Reactions", Vol. III, Part 2, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 1066 ff.

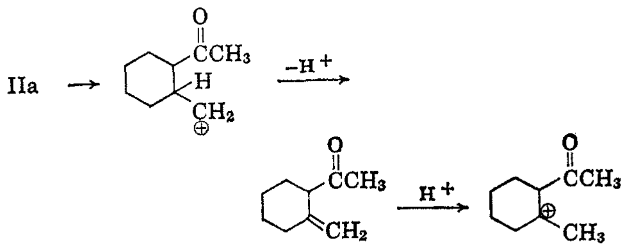
TABLE I

RESULTS OF THE CYCLOHEPTENE–ACETIC ACID REACTION IN PPA AT 50°

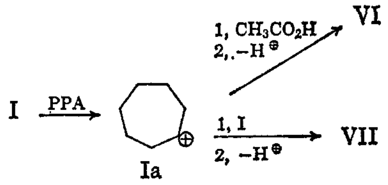
Product	% yield (based on olefin)
 IV	23.0
 V	0.6
 VI	4.8
 VII	0.6



However, an alternative mechanism involving proton elimination and readdition of the proton to give the intermediate tertiary carbonium ion cannot be excluded.



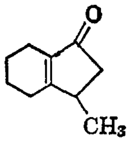
In addition to effecting acylium ion formation, the PPA appears capable of protonating the double bond of I to form the cycloheptyl ion, Ia. This ion may then



react with acetic acid to yield VI or react with cycloheptene to give the hydrocarbon, VII.

The absence of rearrangement of the cycloheptyl cation has been demonstrated[9] in the acid-catalyzed dehydration of cycloheptanol at 195° and in the products of the first-order acetolysis of cycloheptyl tosylate.[10,11]

The reaction of olefins with α,β-unsaturated carboxylic acids in PPA has been shown to yield bicyclic ketones. For example, the reaction[12] of cyclohexene with crotonic acid in PPA yields 3-methylbicyclo-[4.3.0]-8(9)-nonen-1-one (VIII). The reaction of I

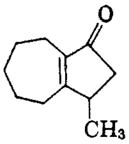
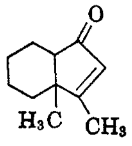
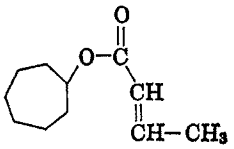
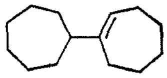


VIII

with crotonic acid in PPA was investigated and the products are shown in Table II.

TABLE II

PRODUCTS FROM THE CYCLOHEPTENE–CROTONIC ACID REACTION IN PPA AT 50°

Products	% yield (based on olefin)
 IX	5.7
 X	18.2
 XI	4.7
 VII	1.1

The unrearranged ketone (IX), 3-methylbicyclo-[5.3.0]-9(10)-decen-1-one, probably results from acyla-

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[9] A. C. Cope, T. A. Liss, and G. W. Wood, *J. Am. Chem. Soc.*, **79**, 6287 (1957).

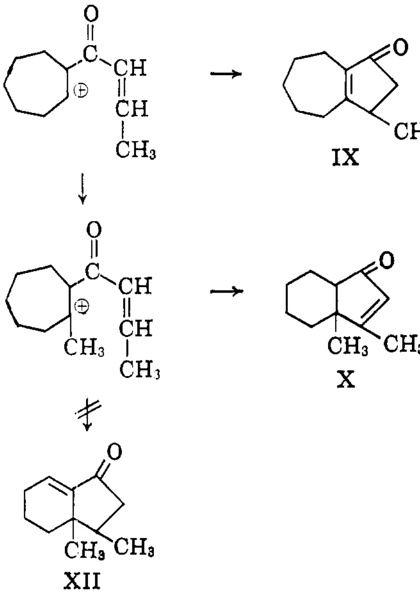
[10] R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955).

[11] H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956).

[12] S. Dev., *J. Indian Chem. Soc.*, **34**, 169 (1957).

tion and subsequent cyclization. The yield of this product, however, compared with that of the rearranged ketone, X, was low. The structure of the latter, 3,9-dimethylbicyclo[4.3.0]-2-nonen-1-one was based on its ultraviolet, infrared, and nmr spectra. The presence of a vinyl methyl group precluded XII.

The formation of the ketones is visualized as resulting from the following sequence.



Cycloheptyl crotonate (XI) and VII also were isolated in the reaction and are thought to arise from processes similar to those described for I and acetic acid.

Experimental Section

Infrared spectra were measured on a Beckman IR-5 spectrophotometer. Ultraviolet spectra were measured on a Beckman Model DU spectrophotometer in ethyl alcohol solutions. The nmr were measured on a Varian A-60 spectrometer.[13] Thin layer chromatography (tlc) was performed using Camag silica gel without binder. The polyphosphoric acid was obtained from Victor Chemical Co.

Cycloheptene (I) and Acetic Acid Reaction.—Into a 3-necked flask equipped with a condenser, drying tube, and high-torque stirrer was added 9.6 g (0.1 mole) of cycloheptene, 6.0 g (0.1 mole) of acetic acid, and 100 g of polyphosphoric acid. The mixture was stirred for 1 hr in a water bath maintained at 50° and then poured onto approximately 100 g of crushed ice and 100 g of water in order to decompose the complex. After adding 50 g of ammonium sulfate, the aqueous solution was extracted with three 50-ml portions of ether and the ether washed successively with 50 ml of water, two 50-ml portions of 5% ammonium hydroxide solution, and 50 ml of brine. The ether was dried over anhydrous sodium sulfate, evaporated in *vacuo*, and distilled. After a forerun of 2.9 g (31%) of unreacted I, a fraction consisting of 0.75 g (4.8%) of cycloheptyl acetate was obtained, bp 86–88° (18 mm), n^{26}D 1.4498 [lit.[14] bp 76–78° (11 mm), n^{20}D 1.4510]. The infrared spectrum of this material was identical with an authentic sample.[14] Hydrolysis with aqueous 10% sodium hydroxide gave cycloheptanol bp 184–185°, n^{25}D 1.4684 [lit.[15] bp 85–87° (15 mm), n^{20}D 1.4705]. The second fraction consisted of a mixture of 3.2 g (23.0%) of 2-methyl-1-acetylcyclohexene (IV) and 0.08 g (0.6%) of 2-methyl-3-acetylcyclohexene (V), determined by vapor phase chromatography. The mixture had bp 90–92° (18 mm), n^{25}D 1.4870 [lit.[16] IV, bp 89.5–90° (17 mm), n^{25}D 1.4872; V, bp 83–83.5° (17 mm), n^{25}D 1.4740]. The semicarbazones were prepared and fractionally crystallized from ethanol: IV semicarbazone, mp 226–227° (lit.[16] mp 227–227.5°); V semicarbazone, mp 159–161° (lit.[16] mp 160–162°). Similarly, the 2,4-dinitrophenylhydrazones were obtained from ethanol: IV 2,4-DNP, mp 124–125° (lit.[16] mp 124°); V 2,4-DNP, mp 112–113° (lit.[16] mp 113°). The last fraction consisted of 0.06 g (0.6%) of cycloheptyl cycloheptene (VII), bp 150–152° (17 mm), n^{25}D 1.5001 [lit.[17] bp 140–141° (12 mm), n^{20}D 1.5021].

Cycloheptene (I) and Crotonic Acid Reaction.—Following the above procedure, 19.2 g (0.2 mole) of cycloheptene and 17.2 g (0.2 mole) of crotonic acid in 200 g of PPA were allowed to react for 1 hr at 50°. Evaporation of the ether and distillation of the residue gave four fractions. The first fraction consisted of 1.7 g (4.7%) of cycloheptyl crotonate, bp 112–114° (18 mm). Hydrolysis with 10% aqueous sodium hydroxide gave equivalent amounts of cycloheptanol, bp 88–89° (18 mm), n^{25}D 1.4688 [lit.[15] bp 85–87° (16 mm), n^{20}D 1.4705] and crotonic acid, mp 71–72° (lit.[18] mp 72°). The second fraction consisted of 5.97 g (18.2%) of a material identified as 3,9-dimethylbicyclo[4.3.0]-2-nonen-1-one (X), bp 128–131° (18 mm), n^{25}D 1.5033. Vpc showed it to be contaminated with 5% of five other materials. The crude ketone had a $\lambda_{\max}^{\mathrm{EtOH}}$ 226.5 mμ and $\lambda_{\max}^{\mathrm{NaCl}}$ 5.96 μ indicative of the presence of an α,β-unsaturated ketone.[19,20] After unsuccessful attempts to purify the material, the 2,4-dinitrophenylhydrazone was prepared and separated by tlc (3:2 benzene–hexane), mp 157–158°, $\lambda_{\max}^{\mathrm{EtOH}}$ 390 mμ (log ε 4.41). The nmr spectrum was measured in carbon tetrachloride using tetramethyl silane (TMS) as the internal standard. Bands were obtained at δ 1.12 (bridgehead methyl), δ 1.96 (vinyl methyl), and at δ 5.80 (vinyl hydrogen).[21]

Anal. Calcd for $C_{17}H_{20}N_4O_4$: C, 59.29; H, 5.85. Found: C, 59.22; H, 5.92.

The third fraction contained 1.8 g (5.7%) of 3-methylbicyclo-[5.3.0]-9(10)-decen-1-one (IX), bp 144–145° (18 mm), n^{25}D 1.5117 [lit.[22] bp 140° (15 mm), n^{20}D 1.5138]. The 2,4-dinitrophenylhydrazone was obtained and recrystallized from ethanol, mp 235–237° (lit.[22] mp 236°). The final fraction contained 0.2 g (1.1%) of VII, bp 150–153° (18 mm), n^{25}D 1.5000.

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[13] The authors are grateful to Dr. John Oliver for the determination of the nmr spectra.

[14] M. Koblet, P. Barman, V. Prelog, and L. Ruzicka, *Helv. Chim. Acta*, **32**, 256 (1949).

[15] H. Pines, A. Edeleanu, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **67**, 2193 (1945).

[16] R. B. Turner and D. M. Voitle, *ibid.*, **73**, 1403 (1951.)

[17] S. I. Khromov, I. M. Kuznetsova, and E. S. Balenkova, *Zh. Obshch. Khim.*, **26**, 3302 (1956).

[18] M. Julia and J. Bullot, *Compt. Rend.*, **246**, 3648 (1958).

[19] A. R. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold Publishers, Ltd., London, 1955, p 92.

[20] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 42.

[21]. L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," The Macmillan Co., New York, N. Y., 1959, Chapter 4.

[22] E. A. Braude and W. F. Forbes, *Nature*, **168**, 874 (1951).

Conformational Analysis. VIII.[1,2] Relative Stabilities of 5-Cyanobicyclo[2.2.2]octenes and 5-Acetylbicyclo[2.2.2]octenes

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As part of a continuing effort to determine the relative stabilities of substituted bicyclic compounds,[3] we have sought to relate the factors governing these stabilities to the conformational preferences of substituents in the cyclohexane system. Substituted cyclohexanes have been investigated extensively and the conformational preferences of many substituents are

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[1] Part VII: R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, **31**, 587 (1966).

[2] The authors acknowledge Grant No. 2410-A4 from the Petroleum Research Fund of the American Chemical Society in support of this research.

[3] R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, **30**, 423 (1965).