isolate these components. The mixture (2.82 g, 0.0172 mole) was hydrolyzed in aqueous hydrochloric acid as before, and gave 1.08 g (59%) of benzaldehyde. Neutralization and treatment in ether with dry hydrogen chloride afforded N-methylbenzylamine hydrochloride (0.88 g, 43%).

Electrolysis of N-Benzyldiethanolamine in Methanol.—N-Benzyldiethanolamine (100 g, 0.5 mole) in 400 ml of methanol containing 10 g of potassium hydroxide was electrolyzed at 5.5 amp and 20° for 5.5 hr. After removal of solvent and inorganic salts there remained 125 g of viscous oil. Vpc analysis indicated at least four components existing as three distinct peaks in the ratio of 9:1:10. (One constituent of the mixture was a shoulder on the largest peak.)

The oil (52 g) was distilled and gave the following fractions: fraction 1, bp 90–95° (1.5 mm), 4.5 g, fraction 2, bp 110–115° (1.5 mm), 8.6 g; fraction 3, bp 125° (1 mm), 16 g; pot residue, 20 g (tarry). Fraction 1, the second largest of the components by vpc, was identified as 3-benzyloxazolidine by comparison of the nmr and infrared spectra of this oil with that of authentic material. Fractions 2 and 3 were redistilled (spinning-band column). A fraction, bp 110–120° (0.25 mm), 6.5 g, $n^{20}D$ 1.5471, was obtained which was pure according to vpc analysis. The infrared spectrum had strong, broad absorption for hydroxyl at 3300–3400 cm^{-1}, while the nmr spectrum exhibited a characteristic ArCHO band at τ 5.21. The integrated ratio of areas for aromatic H to ArCHO to all others was 5:1:8 in agreement with the structural assignment for this material as 3-(β-hydroxyethyl)-2-phenyloxazolidine.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.63; H, 7.94; N, 7.21.

A solution of 3.2 g (0.017 mole) of this fraction in dilute, aqueous hydrochloric acid afforded 1.7 g (94%) of benzaldehyde while neutralization gave 0.75 g (42%) of diethanolamine (compared with authentic material by infrared).

A mixture of 11 g of the crude electrolysate in 50 ml of 10% hydrochloric acid was kept at 25° for 0.5 hr. Ether extraction provided 1.5 g (30%) of benzaldehyde and on neutralization 5.7 g of a mixture of amino alcohols.

Acknowledgments.—The authors wish to thank Professor B. Belleau and Professor R. R. Fraser of the University of Ottawa for helpful advise and nmr spectra, respectively.

Competitive Carbonium Ion Processes. Catalysis of Acylation and Acetoxylation Reactions by Polyphosphoric Acid

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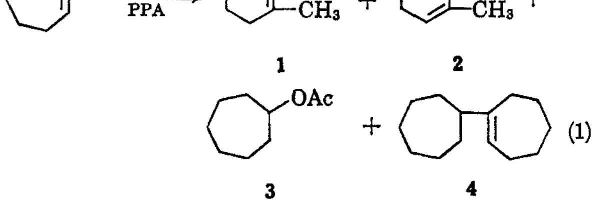
The reaction of simple cycloalkenes with acetic acid in polyphosphoric acid (PPA) is shown to give rise to the acetylation product, 1-acetylcycloalkene, and to the cycloalkyl acetate as well as minor products. Evidence is presented to indicate that an increase in the ratio of the yields of ester to ketone is a function of an increase in the stability of the carbonium ion resulting from protonation of the olefin. Cyclopentene, cyclohexene, and cyclooctene each leads to ketonic and ester mixtures, whereas norbornene, α-pinene, and β-pinene each gives predominantly esters. In a series of styrenes, higher relative yields of ketones are obtained the more sterically hindered the vinyl group. In certain instances, higher reaction temperatures increase the yield of ketone, as does a higher equivalent of P_4O_{10} in the PPA.

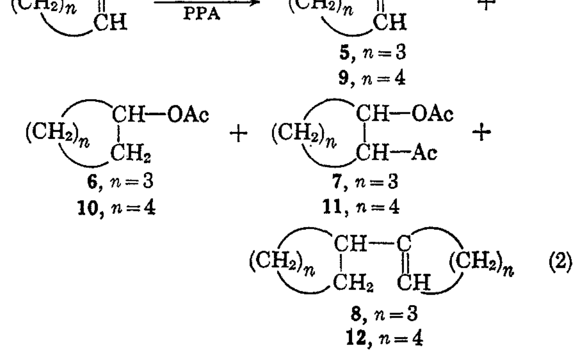
The acetylation of olefins with carboxylic acids, using polyphosphoric acid (PPA) as the catalyst, is not an uncommon procedure.[2] In appropriately structured molecules, the PPA also serves to induce cyclization, aromatization, dehydration, and carbonium ion rearrangements. It was surprising, however, to find[3] that the attempted acylation of cycloheptene with acetic acid in PPA gave the products shown in eq 1, but no 1-acetylcycloheptene. One of the major products, 1-acetyl-2-methylcyclohexene (1), reflects rearrangement, as does the unconjugated ketone (2) which was produced in smaller yield. In contrast, the other main and minor products, cycloheptyl acetate (3) and the hydrocarbon, 1-cycloheptylcycloheptene (4), respectively, did not suffer rearrangement.



In view of the unexpected products obtained with cycloheptene, it was considered worthwhile to ascertain whether other cyclic olefins also gave rise to similar complex mixtures, and to determine more fully the catalytic behavior of PPA.

Discussion of Results

Reaction of cyclopentene with acetic acid in PPA gave two major products, 1-acetylcyclopentene (5) and cyclopentyl acetate (6). In addition, 2-acetylcyclopentyl acetate (7) and 1-cyclopentylcyclopentene (8) were obtained as minor products. Similarly, reaction



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[1] Taken from the Ph.D. Dissertation of R. J. Dolinski, University of Detroit, Detroit, Mich., 1966.

[2] (a) F. D. Popp and W. E. McEwen, *Chem. Rev.*, **58**, 321 (1958); (b) F. Uhlig and H. R. Snyder, *Advan. Org. Chem.*, **1**, 35 (1960).

[3] L. Rand and R. J. Dolinski, *J. Org. Chem.*, **31**, 3063 (1966).

[4] Similar products were proposed from the reaction of cyclohexene with acetyl chloride and silver perchlorate or with acetic anhydride and perchloric acid: H. Burton and P. F. G. Praill, *Chem. Ind.* (London), 75 (1954).

of cyclohexene and acetic acid resulted[4] in formation of 1-acetylcyclohexene (**9**) and cyclohexyl acetate (**10**) together with smaller amounts of 2-acetylcyclohexyl acetate (**11**) and 1-cyclohexylcyclohexene (**12**). The structure of **7** and **11** was confirmed by degradation to cyclopentanone and cyclohexanone, respectively, through hypoiodite oxidation, saponification, chromic acid oxidation, and decarboxylation, as well as by infrared comparison with authentic samples.

For this initial set of reactions, a temperature of 50° was selected on a rather arbitrary basis. To determine the effect of temperature on the product yields, cyclopentene and cyclohexene each were allowed to react with acetic acid in PPA at various temperatures for 1 hr. The yield of the ester and ketone, based on three runs having a maximum deviation from the mean of ±7%, are shown in Table I. These data show a temperature effect, with the ester predominating at the lower temperature and the ketone at the higher, thus suggesting that ester formation is kinetically controlled while ketone formation is probably thermodynamically preferred.

TABLE I
RESULTS OF THE CYCLOALKENE–ACETIC ACID REACTION IN PPA AS A FUNCTION OF TEMPERATURE[a]

		Rel product %[b]	
Compd	Temp, °C	1-Acetylcyclopentene	Cyclopentylacetate
Cyclopentene	0	8.2 (2.5)	91.8 (27.0)
	40	60.1 (27.4)	39.9 (17.2)
	50	65.4 (31.6)	34.6 (15.6)
	60	72.7 (37.2)	27.3 (12.9)
	100	93.7 (63.1)	6.3 (4.1)
		Rel product %[b]	
Compd	Temp, °C	1-Acetylcyclohexene	Cyclohexylacetate
Cyclohexene	0	1.1 (7.2)	98.9 (20.8)
	40	70.8 (35.5)	29.2 (12.5)
	50	71.6 (41.1)	18.3 (9.1)
	60	83.8 (50.2)	16.2 (8.4)
	100	98.8 (81.4)	1.2 (0.7)

[a] Yield of hydrocarbon averaged 1%; keto ester up to 0.3% above 50°. [b] Number in parentheses is per cent yield based on olefin.

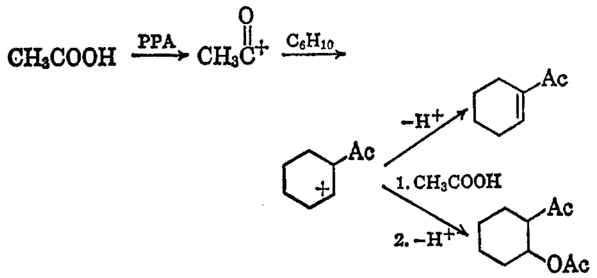
If the formation of ester follows a path similar to that of the acid-catalyzed hydration of olefins,[5] which proceeds smoothly at low temperatures, the first step requires protonation of the double bond. The resulting cycloalkyl cation can then react with the carboxylic acid to give the ester after loss of a proton.

On the basis of the temperature studies, all subsequent reactions were performed at 50°. Using cyclohexene and acetic acid, the product distribution was determined as a function of time. These data, shown in Table II, indicate a decreasing ester yield after 3 hr with a concurrent rise in ketone concentration. When a mixture of either cyclopentyl or cyclohexyl acetate and the respective olefin was stirred with PPA for 3 hr, the corresponding ketone was formed in a yield close to 25% of that obtained by direct acylation in 1 hr. The conversion of ester to ketone may be explained by the reverse of the sequence equation suggested for ester formation (eq 4) followed by eq 3.

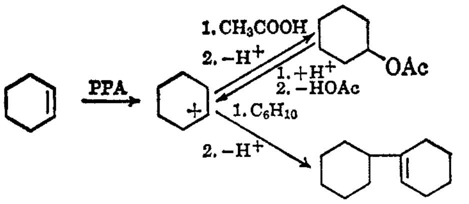
TABLE II
RESULTS OF THE CYCLOHEXENE–ACETIC ACID REACTION IN PPA AS A FUNCTION OF TIME

	Yield (based on olefin), %	
Time, hr	1-Acetylcyclohexene	Cyclohexylacetate
1	41.1	9.1
2	50.4	9.7
3	56.4	11.9
4	56.9	10.6
5	58.2	9.8

The reactions between an olefin and a carboxylic acid in PPA can be visualized as stemming mainly from two carbonium ion processes. One is an electrophilic attack by an acylium ion, formed by the reaction of the carboxylic acid with PPA, on the olefin (eq 3). The second is the protonation of the olefin by PPA to give the cycloalkyl carbonium ion which can then react with the carboxylic acid to yield ester or alternatively with unreacted olefin to yield the hydrocarbon (eq 4).



(3)



(4)

Acid-catalyzed additions of carboxylic acids to olefins is documented,[6] although ester formation has not been reported previously as occurring in PPA-catalyzed acylation reactions.

Acylation–cyclization reactions resulting from acrylic, crotonic, or benzoic acids and cyclopentene or cyclohexene with PPA have been studied by Dev.[7] In addition to the ketones, Table III shows that uncyclized esters are also produced in significant amounts, generally 20–25% of the yield of ketone. The total yields with the α,β-unsaturated acids are generally lower than are obtained with acetic acid because of vinyl polymerization.[8]

The products from treating cyclooctene with acetic acid in PPA consist of rearranged ketones and unrearranged ester and hydrocarbon. The compound, 3,3-dimethyl-4-acetylcyclohexene (**13**), which also was isolated by Nenitzescu[9] from acetylation of cyclooctene with acetyl chloride and $AlCl_3$, is apparently the result

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[5] R. W. Taft, *J. Am. Chem. Soc.*, **74**, 5372 (1952).

[6] (a) J. Bertram and L. Walbaum, *J. Prakt. Chem.*, **49**, 1 (1894); (b) J. M. Mavity, U. S. Patent 2,584,102 (1952); *Chem. Abstr.*, **46**, 4702 (1952); (c) M. M. Bortnick, U. S. Patent 3,037, 052 (1962); *Chem. Abstr.*, **57**, 6125 (1964); (d) H. Dreyfus, U. S. Patent, 2,217,735 (1941); *Chem. Abstr.*, **35**, 1066 (1941).

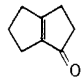
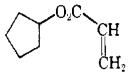
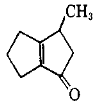
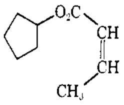
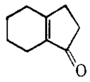
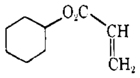
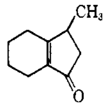
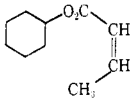
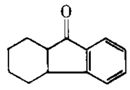
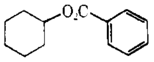
[7] S. Dev, *J. Indian Chem. Soc.*, **33**, 703 (1956); **34**, 169 (1957).

[8] S. M. McElvain and J. W. Langston, *J. Am. Chem. Soc.*, **66**, 1759 (1944).

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

TABLE III

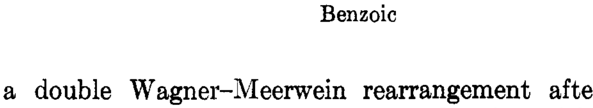
RESULTS OF THE CYCLOALKENE–α,β-UNSATURATED ACID REACTION IN PPA

Olefin	Acid	Ketone (%)	Ester (%)
Cyclopentene	Acrylic	 (21.0)	 (5.7)
	Crotonic	 (25.1)	 (5.9)
Cyclohexene	Acrylic	 (13.2)	 (2.7)
	Crotonic	 (48.3)	 (8.0)
	Benzoic	 (52.0)	 (10.3)

of a double Wagner–Meerwein rearrangement after initial formation of the 2-acetylcyclooctyl cation. The bicyclic ketone, 2-acetylbicyclo[3.3.0]octane (**14**), results from a transannular proton elimination.[10]

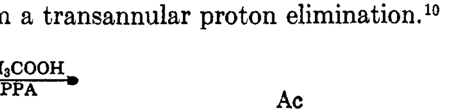
$C_8H_{14} \xrightarrow[PPA]{CH_3COOH}$ **13** + **14** + $C_8H_{15}OAc$ (5)

From the cyclic olefins, the relative amounts of products derived from each of the two carbonium ion processes appear to be fairly uniform. However, the yield of 1-methyl-1-cyclohexyl acetate (**15**) relative to ketone **16** from the reaction of 1-methylcyclohexene with acetic acid in PPA (eq 6) was more than twice the yield of cyclohexyl acetate and 1-acetylcyclohexene from cyclohexene. This result suggests that the rate of ester formation is increased the more stable the carbonium ion which is produced by proton transfer from the PPA to the olefin. Norbornene, which likewise affords a stable carbonium ion upon protonation,[11] gives only *exo*-norbornyl acetate (**17**) upon reaction with acetic acid. Similarly, the PPA-catalyzed reaction of acetic acid and α- or β-pinene, which affords stable carbonium ions,[12] yields no acetylation products.



(6)

15 **16**



(7)

17

As shown in Table IV, the pinene isomers give approximately identical product mixtures as would be anticipated, since an identical ionic intermediate is a consequence of protonation. The steps involved in the conversion of the pinene to limonene (**18**), bornyl acetate (**19**), fenchyl acetate (**20**), camphene (**21**), and isobornyl acetate (**22**) are in accord with the isomerizations expected from mineral acids.[13]

TABLE IV

RESULTS OF THE α- AND β-PINENE–ACETIC ACID REACTION IN PPA

	Product, %			
Compd	Bornyl acetate	Fenchyl acetate	Isobornyl acetate	Limonene
α-Pinene	50.0	8.2	1.0	13.2
β-Pinene	51.0	8.2	1.9	11.8

Further evidence for the relationship between carbonium ion stability and ester formation was obtained by determining the ester–ketone yields from the reaction between 2-, 2,6-, or β-substituted styrenes with acetic acid in PPA. In this series, increasing the size of the substitutent effectively serves to decrease interaction between the ring and the vinyl p orbitals, thereby decreasing the stability of the benzylic cation derived from the protonation of the vinyl group.[14] The product distribution, showing decreased yield of ester and corresponding increase in yield of ketone as a function of substituents, is shown in Table V. That the observed effect is a result mainly of a sterically induced destabilization of the benzylic ion is indicated by obtaining only the ester from 4-methylstyrene. Ester formation is eliminated completely by the presence of 2-ethyl or 2,6-dimethyl groups. While the *trans*-β-methylstyrene gave rise only to ester, the *cis* isomer gave some ketone in addition to ester. The latter result can be explained[15] by both the steric interaction of the β-methyl group with the ring and by

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[10] C. D. Nenitzescu and A. T. Balaban in "Friedel-Crafts and Related Reactions," Vol. III, Part 2, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 1046.

[11] (a) A. Streitwieser, *Chem. Rev.*, **56**, 571 (1956); (b) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **71**, 2953 (1949).

[12] (a) J. A. Berson in "Molecular Rearrangements," P. Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3; (b) H. Meerwein, *Ann.*, **405**, 129 (1914); (c) M. de Bollemont, *Compt. Rend.*, **136**, 239 (1903).

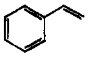
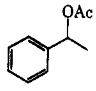
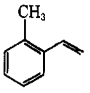
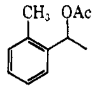
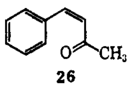
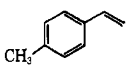
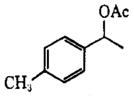
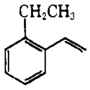
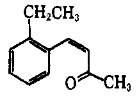
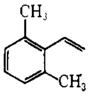
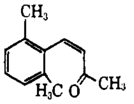
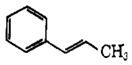
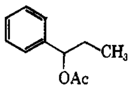
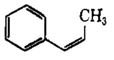
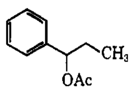
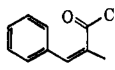
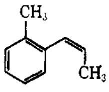
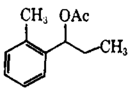
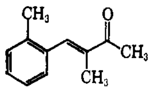
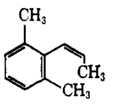
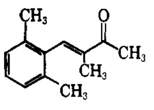
[13] (a) G. Bouchardat and J. La Font, *Ann. Chim.* (Rome), **9**, 507 (1886); (b) M. Delepine, *Compt. Rend.*, **178**, 2088 (1924); (c) M. Delepine, *ibid.*, **179**, 175 (1924).

[14] (a) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754, 3773 (1955); (b) E. A. Braude and C. J. Timmons, *ibid.*, 3766 (1955).

[15] M. E. Kronenberg and E. Havinga, *Rec. Trav. Chim.*, **84**, 17 (1965).

Table V

Results of the Substituted Styrene–Acetic Acid Reaction in PPA

Compd	Ester	Yield %[a]	Ketone	Yield %[a]
	 23	100 (15.8)	...	
 24	 25	18.6 (1.8)	 26	81.4 (7.7)
 27	 28	100 (13.7)	...	
 29	...		 30	100 (8.1)
 31	...		 32	100 (9.2)
 33	 34	100 (1.4)	...	
 35	 36	70 (0.3)	 37	30 (0.1)
 38	 39	31.9 (1.1)	 40	68.1 (4.6)
 41	...		 42	100 (0.7)

[a] Numbers in parentheses are yields based on styrene.

the preferred *trans* conformation of the acetyl group to the ring.

Polyphosphoric Acid.—Establishing the role of PPA in facilitating ester and ketone formation is hindered by the indefinite composition of the PPA. Thilo[16] has demonstrated that mixtures which contain up to 85% of P_4O_{10} are composed only of linear polyphosphoric acids while at higher anhydride content there is extensive cross linking and cyclization of the chains. Since commercially available PPA contains 82–84% P_4O_{10}, it probably consists of a mixture of the linear chains.

Synthetic mixtures made from 85% syrupy H_3PO_4 and P_4O_{10}, in which the percentage of the P_4O_{10} was varied, were used in the cyclohexene–acetic acid reaction. The changes in the ester–ketone product yields, as a function of the P_4O_{10} content of the PPA, are shown in Table VI. The amount of 1-acetylcyclohexene increases with a corresponding decrease in the amount of cyclohexyl acetate when the P_4O_{10} equivalent is increased. Since the number of protons available is lessened[17] as the P_4O_{10} content is increased, the extent of protonation of olefin, required for ester formation, is lessened. Furthermore, since the yield of ketone rises, the role of the PPA in acylium ion formation must not be protonolysis of the acetic acid. Indeed, when strong mineral acids, such as 96% H_2SO_4, 85% H_3PO_4, and *p*-toluenesulfonic acid, were used in lieu of PPA, no ketone was obtained (Table VII).

Table VI

Results of the Cyclohexene–Acetic Acid Reaction in PPA with Different P_4O_{10} Equivalents

P_4O_{10} equivalent, %	Ketone, %	Ester, %
72.5	0	29.2
77.5	5.6	22.5
80.8	21.0	11.9
82–84	41.1	9.1
91.0	62.9	2.8

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[16] E. Thilo and R. Sauer, *J. Prakt. Chem.*, **4**, 324 (1957).

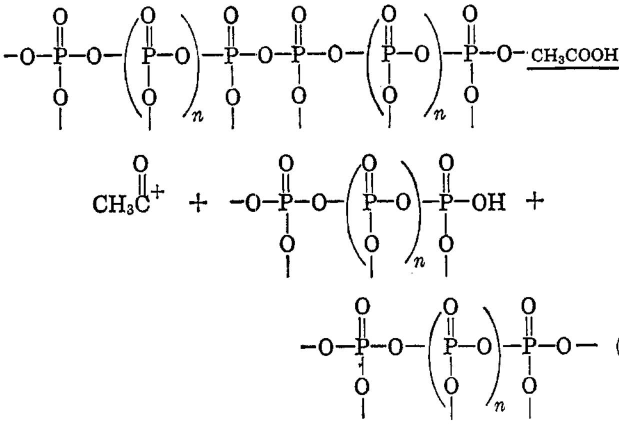
[17] H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Princeton, N. J., 1960, p 336.

TABLE VII

RESULTS OF THE CYCLOHEXENE–ACETIC ACID REACTION CATALYZED BY STRONG ACIDS

Acid	Reacn time, hr	Temp, °C	Cyclohexyl acetate, %
H_2SO_4	1	50	42.3
H_2SO_4	3	25	14.8
H_2SO_4	3	75	40.1
H_2SO_4	4	50	66.9
p-TsOH	3	50	15.5
H_3PO_4	1	50	29.2

The addition of P_4O_{10} to H_3PO_4 (or to PPA) apparently results in decreasing the number of protons, and thereby increasing the number of sites which can function as Lewis acids.[18] Acylium ion formation in this modified PPA may occur through a process similar to that represented in eq 8.



(8)

A 10:1 weight ratio of PPA–olefin has been considered optimum,[2] and this is confirmed by the results in Table VIII. While a larger excess may give too high a dilution of the reactants, a lower ratio may reduce the number of sites necessary for generation of the reaction intermediates.

TABLE VIII

RESULTS OF THE CYCLOHEXENE–ACETIC ACID REACTION WITH VARIOUS CONCENTRATIONS OF PPA

Weight ratio of PPA/olefin	Ketone, %	Ester, %
2.5	0.2	12.3
5.0	1.3	16.8
10.0	22.7	17.5
20.0	16.1	15.2

Experimental Section

Polyphosphoric acid was obtained from Victor Chemical Co. Infrared spectra were measured on a Beckman Model IR-5, ultraviolet spectra were taken on a Beckman Model DU spectrophotometer, nmr spectra were recorded on a Varian A-60 spectrometer, and mass spectra were obtained on a Bendix time-of-flight mass spectrometer.

Reaction of Olefins with Carboxylic Acids in PPA.—The general procedure was a modification of the method of Dev.[7] Into a 500-ml flask fitted with a condenser, drying tube, and high-torque stirrer was added PPA in an amount ten times the weight of the olefin. The flask was placed in a bath maintained at 50° unless otherwise stated. To the flask were added equimolar amounts of the olefin and the carboxylic acid and the mixture was stirred for 1 hr and poured onto ice water, and the solution was saturated with ammonium sulfate. The aqueous solution was extracted with ether and the ether layer was washed successively with water, twice with 5% ammonium hydroxide, and then with brine, and finally dried over anhydrous sodium sulfate. The ether was evaporated *in vacuo* and the products were isolated from the residue either by distillation or by vapor phase chromatography. In the latter cases, identification was by comparison of retention times with authentic samples; yields were determined by measurement of peak areas after preparing concentration/area curves.

Cyclopentene and Acetic Acid.—The ether residue was subjected to vpc analysis which showed four components. Distillation separated two of the components, cyclopentyl acetate (**6**), bp 160–162°, n^{25}_{D} 1.4285 [lit.[19] bp 50° (12 mm), n^{25}_{D} 1.4288], and 1-acetylcyclopentene (**5**), bp 167–168° (lit.[20] bp 168°). The ester was further identified by basic hydrolysis to cyclopentanol, bp 139–141° (lit.[21] bp 139–140°), and by comparison of infrared spectra and vpc retention times with those of an authentic sample. A 2,4-dinitrophenylhydrazone of **5** was prepared, mp 201–202° (lit.[20] mp 203°).

After obtaining a sufficient amount of the minor products from several trials, they were identified as 2-acetylcyclopentyl acetate (**7**) and 1-cyclopentylcyclopentene (**8**). The keto ester was degraded following the procedures of Werber[22] and Alder[23] to cyclopentanone, 2,4-dinitrophenylhydrazone mp 142–143° (lit.[24] mp 142°). The hydrocarbon (**8**), bp 80–83° (17 mm), n^{25}_{D} 1.4856 [lit.[24] bp 75–79° (14 mm), n^{25}_{D} 1.4858], was synthesized by the method of Cordon, Knight, and Cram[25] and its infrared spectrum and vpc retention time were identical with those of **8**.

Cyclopentene was treated with acetic acid at various temperatures and the yields of **5** and **6** are shown in Table I.

Cyclopentene with Acrylic and Crotonic Acids.—The ether residue obtained with each of these acids was distilled and the ester and ketone fractions were collected. With acrylic acid, cyclopentyl acrylate, bp 114–115°, n^{25}_{D} 1.4499 [lit.[26] bp 75–76° (31 mm), n^{25}_{D} 1.4500], and bicyclo [3.3.0.]-7(8)-octen-1-one, bp 97–98° (20 mm), n^{25}_{D} 1.5222, 2,4-dinitrophenylhydrazone mp 220–221° (lit.[7] bp 87° (12 mm), n^{25}_{D} 1.5221, mp 221°], were obtained in yields shown in Table III. Similarly, crotonic acid gave cyclopentyl crotonate, bp 80–82° (13 mm), n^{25}_{D} 1.4563 [lit.[26] bp 84–85° (13 mm), n^{25}_{D} 1.4562], and 3-methylbicyclo-[3.3.0.]-7(8)-octen-1-one, bp 102–105° (13 mm), n^{25}_{D} 1.5062, 2,4-dinitrophenylhydrazone mp 214–215° [lit.[7] bp 85–92° (3 mm), n^{29}_{D} 1.5045, mp 214–215°]. Both esters upon basic hydrolysis gave cyclopentanol.

Cyclohexene and Acetic Acid.—Distillation of the ether residue gave cyclohexyl acetate (**10**), bp 174–175°, n^{25}_{D} 1.4373 [lit.[27] bp 42° (5 mm), n^{20}_{D} 1.4406], and 1-acetylcyclohexene (**9**), bp 202°, n^{25}_{D} 1.4883 [lit.[28] bp 64–67° (5 mm), n^{22}_{D} 1.4893].

Cyclohexene was allowed to react with acetic acid at various temperatures for 1 hr and the yields of **9** and **10** are given in Table I.

Table II shows the results from the reaction of cyclohexene and acetic acid at 50° for various time intervals.

Cyclohexene and acetic acid were allowed to react in polyphosphoric acids of various compositions. These acids, prepared by heating the appropriate amount of phosphoric anhydride and phosphoric acid at 100° for 6 hr using the procedure of Gilmore and Horton,[29] were used as described for commercial PPA. The product distributions using these acids are given in Table VI.

Table VII summarizes the results of the reaction of cyclohexene with acetic acid in the presence of various strong acids.

Cyclohexene with Acrylic, Crotonic, and Benzoic Acids.—The method of Dev[7] was used with each of these acids to yield the ketones and esters shown in Table III. The ketones were identical with those previously prepared by this method. The esters were saponified to cyclohexanol.

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(18) R. Truffault, *Compt. Rend.*, **200**, 406 (1935).

(19) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

(20) N. Jones and H. T. Taylor, *J. Chem. Soc.*, 4017 (1959).

(21) C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **48**, 1080 (1926).

(22) F. X. Werber, J. E. Jansen, and T. C. Gresham, *ibid.*, **74**, 532 (1952).

(23) K. Alder and M. Schumacher, *Ann.*, **565**, 148 (1949).

(24) C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **48**, 1084, (1926).

(25) M. Corden, J. D. Knight, and D. J. Cram, *ibid.*, **76**, 1643 (1954).

(26) J. Lal and R. Green, *J. Org. Chem.*, **20**, 397 (1955).

(27) (a) M. Kolbelt, P. Barman, V. Prelog, and L. Ruzicka, *Helv. Chim. Acta*, **32**, 256 (1949); (b) V. N. Ipatieff, *Ber.*, **45**, 3217 (1912).

(28). E. E. Royals and C. M. Hendry, *J. Org. Chem.*, **15**, 1147 (1950).

(29) R. C. Gilmore and W. J. Horton, *J. Am. Chem. Soc.*, **73**, 1411 (1951).

Cyclooctene and Acetic Acid.—Distillation of the ether residue gave 11.4% of cyclooctyl acetate, bp 93–95° (10 mm), $n^{25}\mathrm{D}$ 1.4556 [lit.[27] bp 95–96° (11 mm), $n^{20}\mathrm{D}$ 1.4593]. The residue after distillation of the cyclooctyl acetate was subjected to gas chromatography on a 28 ft × 1/8 in. column at 160° packed with 3% E-4000 (Dow Chemical Co.) on firebrick. Eight compounds were obtained, each exhibiting a parent peak at m/e 152 in their mass spectra. The major component, representing 10.1% based on its vpc peak area, was identified by spectral methods as 3,3-dimethyl-4-acetylcyclohexene (**13**). In its mass spectrum, it had a base peak at m/e 43 ($CH_3C{=}O$) and prominent peaks at masses 79, 94, 107, 109, 122, and 137 (loss of CH_3 and/or $CH_3C{=}O$). In the infrared, λ_{max} 5.84 (C=O), 6.03 (C=C), and 7.28 μ (doublet, *gem*-dimethyl) were observed. The nmr spectrum (d_6-acetone *vs.* TMS) gave the following signals: δ 0.9 (CH_3C), 2.3 ($CH_2C{=}O$), 2.5 (CHC=OR), and 5.4 (C=CH), along with ring protons. No vinyl methyl protons at δ 1.6 were observed. The compound was essentially transparent in the ultraviolet region, exhibiting only weak absorption at 280 mμ (ϵ 17, unconjugated ketone).

The other compounds having parent peaks at m/e 152 appeared to be isomers of **13**. A base peak at m/e 43 was evident for each, and the cracking patterns for six of the seven isomers were consistent with dimethyl-substituted acetylcyclohexenes. The remaining compound, which showed no mass spectral evidence for methyl groups (except $CH_3C{=}O$), was 1-acetylbicyclo-[3.3.0.]octane (**14**). This compound was isolated in 2.1% yield by distillation in a separate trial, bp 98–99° (10 mm), $n^{25}\mathrm{D}$ 1.4655, semicarbazone mp 181–183° [lit.[30] bp 94–95° (10 mm), $n^{25}\mathrm{D}$ 1.4655, mp 181–182.4°]. A final fraction consisted of 3.8% of 1-cyclooctylcyclooctene, bp 128–130° (1 mm) [lit.[31] bp 135–140° (2 mm)], which exhibited a parent peak at m/e 220. A trace amount (0.1%) showed a parent peak at m/e 330 which may be a trimer of cyclooctene.

Norbornene and Acetic Acid.—Distillation of the ether residue gave only *exo*-norbornyl acetate (**17**) with no ketone detectable by vpc, bp 73–75° (8 mm), $n^{25}\mathrm{D}$ 1.4566 [lit.[32] bp 80° (11 mm), $n^{25}\mathrm{D}$ 1.4563]. The yields of **17** with varying temperature based on the olefin were 40°, 44.8%; 50°, 65.6%; 60°, 72.1%. Basic hydrolysis and sublimation of the product at 50° (10 mm) gave predominantly *exo*-norbornyl alcohol, mp 121–122°, phenylurethane, mp 146–147° (lit.[32] mp 120–123°, 146–147°).

1-Methylcyclohexene and Acetic Acid.—The ether residue gave 14.2% of 1-methyl-1-cyclohexyl acetate (**15**), bp 175–176°, $n^{25}\mathrm{D}$ 1.4357 (lit.[27] bp 176°, $n^{18}\mathrm{D}$ 1.4386), and 31.1% of 2-methyl-1-acetylcyclohexene (**16**), bp 90–92° (18 mm), $n^{25}\mathrm{D}$ 1.4870 [lit.[33] bp 89.5–90° (17 mm), $n^{25}\mathrm{D}$ 1.4872).

α- and β-Pinene with Acetic Acid.—The isomers were separated to approximately 95% purity by fractionation through a column packed with glass helices. The yields of the products as determined by vpc are shown in Table IV. The materials obtained were limonene (**18**), bp 65–66° (15 mm), $n^{21}\mathrm{D}$ 1.4727 (lit.[13a] mp 178–180°, $n^{20}\mathrm{D}$ 1.4731), bornyl and isobornyl acetates (**19** and **22**), bp 105–106° (15 mm), $n^{21}\mathrm{D}$ 1.4638 [lit. for **19**[34] bp 86° (6 mm), $n^{25}\mathrm{D}$ 1.4620; for **22**[13b] bp 106° (15 mm)], and fenchyl acetate (**20**), bp 150–152° (15 mm) [lit.[13c] bp 125–127° (5 mm)].

Reaction of Acetic Acid and Substituted Styrenes.—Acetic acid and a series of *ortho*-substituted and β-methylstyrenes, prepared by previously reported methods, were reacted in PPA following the procedure used for the simple olefins. The esters obtained were saponified to the corresponding alcohols, and the ketones were identified either by their conversion to iodoform and the substituted cinnamic acid or by the preparation of ketone derivatives. The yields of the products obtained are given in Table V. The reactions of acetic acid with the indicated styrene are as follows.

A. **Styrene.**—This olefin gave only acetate ester **23**, bp 200–202° (10 mm) [lit.[34] bp 80° (4 mm)]. Basic hydrolysis gave the alcohol, bp 104–105° (15 mm) [lit.[35] bp 94° (12 mm)].

B. **2-Methylstyrene** (**24**).—This substituted styrene gave the corresponding acetate ester (**25**), bp 120–123° (23 mm) [lit.[36] bp 126° (23 mm)], which gave the alcohol upon saponification, bp 110–112° (23 mm) [lit.[36] bp 107.8–108° (20 mm)], and ketone **26**, bp 178–180° (23 mm), $n^{25}\mathrm{D}$ 1.5867, 2,4-dinitrophenylhydrazone mp 229–230° [lit.[14] bp 84 (0.1 mm), $n^{25}\mathrm{D}$ 1.5906, 231°].

C. **4-Methylstyrene** (**27**).—The reaction of acetic acid with this compound gave only acetate ester **28** which gave the alcohol, bp 120–121° (19 mm), $n^{25}\mathrm{D}$ 1.5202 [lit.[37] bp 105–106° (13 mm), $n^{25}\mathrm{D}$ 1.5203].

D. **2-Ethylstyrene** (**29**).—With acetic acid, this styrene gave only ketone **30**, bp 200–203° (25 mm), $n^{25}\mathrm{D}$ 1.5755 [lit.[38] bp 94–96° (0.1 mm), $n^{20}\mathrm{D}$ 1.5774]. Oxidation with potassium hypoiodite gave 2-ethylcinnamic acid, mp 147–150° (lit.[38] mp 151–152°).

E. **2,6-Dimethylstyrene** (**31**).—Reaction of this olefin with acetic acid gave ketone **32**, bp 200–202° (21 mm), $n^{25}\mathrm{D}$ 1.5759, 2,4-dinitrophenylhydrazone mp 212–214° [lit.[14a] bp 94° (0.1 mm), $n^{23}\mathrm{D}$ 1.5764, mp 212–214°].

F. ***trans*-β-Methylstyrene** (**33**).—This compound was treated with acetic acid to yield ester **34**, bp 122–123° (27 mm), $n^{25}\mathrm{D}$ 1.4890 [lit.[39] bp 82° (4 mm), $n^{25}\mathrm{D}$ 1.4893]. Saponification yielded the corresponding alcohol, bp 120–124° (24 mm), $n^{25}\mathrm{D}$ 1.5204 [lit.[39] bp 105–106° (12 mm), $n^{25}\mathrm{D}$ 1.5203].

G. ***cis*-β-Methylstyrene** (**35**).—With acetic acid, this material gave ester **36**, bp 120–123° (25 mm), $n^{25}\mathrm{D}$ 1.4891, and ketone **37**, bp 150–151° (25 mm), $n^{25}\mathrm{D}$ 1.5690 [lit.[40] bp 143–145° (18 mm), $n^{17}\mathrm{D}$ 1.5720]. Oxidation of the ketone gave α-methylcinnamic acid, mp 78–79° (lit.[41] mp 77–78°). The semicarbazone was prepared, mp 218–219° (lit.[41] mp 218–219°). The infrared spectrum of the ketone was consistent with that previously reported.

H. **2-Methyl-β-methylstyrene** (**38**).—This substituted styrene was reacted with acetic acid to give the alcohol after saponification of the ester (**39**), bp 120–121° (24 mm), $n^{25}\mathrm{D}$ 1.5311 [lit.[42] bp 116–117° (19 mm), $n^{20}\mathrm{D}$ 1.5328], and the ketone (**40**) which was oxidized, without prior isolation, to *o*-α-dimethylcinnamic acid, mp 123–124° (lit.[43] mp 123°).

I. **2,6-Dimethyl-β-methylstyrene** (**41**).—Reaction of this compound with acetic acid gave a material thought to be the ketone (**42**). One compound was observed on the vpc, λ_{max} 5.97 μ (conjugated C=O). Also, this material formed iodoform when treated with potassium hypoiodite.

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[30] R. Granger, P. F. G. Nau, and J. Nau, *Bull. Soc. Chim. France*, 1811 (1959).

[31] W. Reppe, O. Schlicting, P. Westphal, and A. Amann, U. S. Patent 2,759,926 (1956); *Chem. Abstr.*, **51**, 5371 (1957).

[32] R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

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

[34] J. M. Wilkinson, U. S. Patent, 2,485,125 (1949); *Chem. Abstr.*, **44**, 2027 (1950).

[35] R. Klages, *Ber.*, **36**, 1632 (1903).

[36] F. Eisenlohr and L. Schultz, *ibid.*, **57**, 1808 (1924).

[37] D. J. Mowry, M. Renoll, and W. F. Huber, *J. Am. Chem. Soc.*, **68**, 1105 (1946).

[38] A. C. Cope, T. A. Liss, and D. S. Smith, *ibid.*, **79**, 240 (1946).

[39] C. G. Overberger and D. Tanner, *ibid.*, **77**, 369 (1955).

[40] M. Metayer, *Ann.*, **4**, 196 (1949).

[41] H. Midorikawa, *Bull. Chem. Soc., Japan*, **27**, 131 (1954); *Chem. Abstr.*, **50**, 244 (1956).

[42] R. Ya Levina and I. Kh Grinberg, *J. Gen. Chem. USSR*, **7**, **2308** (1937); *Chem. Abstr.*, **32**, 509 (1938).

[43] R. Fusco and S. Rossi, *Gazz. Chim. Ital.*, **78**, 524 (1948); *Chem. Abstr.*, **43**, 1744 (1949).