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ORGANIC REACTIONS WITH POLYPHOSPHORIC ACID—IX

ADDITION OF ACETIC ACID TO OLEFINS[*][†]

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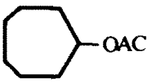
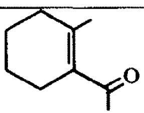
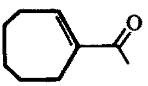
Abstract—It is shown that, in presence of PPA, acetic acid adds on to olefins to furnish the corresponding acetates in excellent yields.

IT HAS been described[1] that the action of AcOH on cycloheptene in polyphosphoric acid (PPA) proceeds with ring-contraction to yield 2-methyl-Δ^1-acetylcyclohexene as the main product. In an effort to by-pass ring-contraction, the molar ratio of AcOH/cycloheptene was increased,[2] when at 5:1 ratio, some Δ^1-acetylcycloheptene was indeed formed. When still higher proportions of AcOH were employed, it was found that the acylation reaction was suppressed and a new product, identified as cycloheptyl acetate,[3] resulted. The present communication deals with the results of these experiments and further exploration of this reaction.

The reaction of cycloheptene with varying proportions of AcOH in PPA was carried out under the usual conditions (55–60°; 1 hr) and the product of the reaction analysed by GLC. It was found that when the molar ratio of AcOH (to cycloheptene) was raised to 10, the reaction product contained 86% cycloheptyl acetate, besides

TABLE 1 REACTION OF CYCLOHEPTENE AND ACETIC ACID IN PPA[*]

Molar ratio of reactants[*]		Total yield (%)	Product composition (GLC)§ (%)		
	AcOH				
0·1	0·1	30[†]	—	98	—
0·1	0·5	45[†]	7	84	9
0·1	1·0	75[‡]	86	7	5
0·1	2·0	92[‡]	93	3	2

[*] PPA from P_2O_5 (70 g) and 85% H_3PO_4 (30 ml); reaction temp.: 55–60°; reaction time: 1 hr.

[†] Computed as methyl ketone.

[‡] Computed as the acetate.

[§] Column temp 160°; gas press 15 psi.

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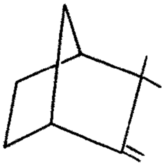
[†] Abstracted from the Ph.D thesis (Bombay University. 1966) of S B. Kulkarni.

some Δ^1-acetyl-2-methylcyclohexene and Δ^1-acetylcycloheptene. When the proportion of AcOH was increased still further, the yield of cycloheptyl acetate improved further. These results have been summarized in Table 1.

The reaction was next extended to cyclopentene, cyclohexene and (±)-camphene (I) and in each case excellent yields of the expected acetate—cyclopentyl acetate,[4] cyclohexyl acetate[5] and (±)-isobornyl acetate (II)[6]—were obtained. The identification of the products was carried out by comparison (GLC, IR) with authentic samples. The results have been summarized in Table 2.



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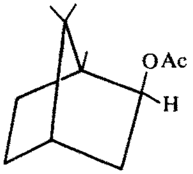

II

The action of this reagent (PPA + excess AcOH) on methylcyclohexene was investigated to see, if tertiary acetates can also result under these reaction conditions. When methylcyclohexene was treated with 20 or 40 mole equivalent of AcOH in PPA at ~60°, the product consisted essentially (~80%) of the corresponding methyl ketone (2-methyl-Δ^1-acetylcyclohexene). However, when the reaction was carried out at room temp (~28°), much more of the tert-acetate[7] resulted. These results are also included in Table 2.

TABLE 2 ACTION OF ACETIC ACID–POLYPHOSPHORIC ACID ON SOME OLEFINS

Olefin	Molar ratio of reactants*		Reaction conditions		Total yield † (%)	Product composition (GLC) (%) ‡	
	Olefin	AcOH	Temp.	Time (hr)		Acetate	Methyl ketone
Cyclopentene	0·1	2·0	55–60°	1	60	95	5
Cyclohexene	0·1	2·0	55–60°	1	81	92	8
	0·1	2·0	55–60°	0·5	75	92	8
	0·1	4·0	55–60°	1	65	98	2
Camphene	0·1	2·0	55–60°	1	74	80	—
	0·1	4·0	55–60°	2	85	80	—
	0·2	8·0	55–60°	2	90	85	—
Methyl-cyclohexene	0·1	2·0	55–60°	1	52	10	80
	0·1	4·0	40–45°	1	65	10	80
	0·1	4·0	28–30°	1	50	70	22

* PPA from 70 g P_2O_5 and 30 ml 85% H_3PO_4.

† Computed as the acetate.

‡ The balance represents other products (not investigated). In the case of camphene-AcOH-PPA reaction, the balance material is a hydrocarbon. GLC was carried out at a column temp. of 150° and gas press of 15 psi.

It is clear from the above that with increasing ratio of AcOH to PPA, the concentration of acylium cation is effectively cut down, and with this change, proton addition, rather than acetylium ion addition, occurs to the olefin, the resulting carbonium ion reacting with AcOH to furnish the acetate.[8]

EXPERIMENTAL

For general remarks see Part VII of this series.

Addition of acetic acid to olefins

General procedure. To PPA (70 g P_2O_5 and 30 ml 85% H_3PO_4) maintained at 55–60°, gl. AcOH (120 g, 2 moles) was added rapidly with stirring, and the contents brought to the desired reaction temp. To this, the olefin (0·1 mole) was added (5 min) with stirring and the reaction mixture stirred for 1 hr at that temp. The product was cooled, poured onto ice-water slush (800 g) and extracted with pet. ether (30 ml × 5). The extract was washed with water, $NaHCO_3$aq and brine and dried. The solvent was removed and the residue distilled. The products obtained this way, from various olefins, had the following characteristics [for purity see Tables 1 and 2; reference is to experiments with AcOH–olefin ratio of 20, reaction temp 55–60°, reaction time 1 hr except for camphene (AcOH–olefin ratio 40; 2 hr) and 1-methylcyclohexene (AcOH–olefin ratio 40; 28–30°; 1 hr)].

Olefin	b.p./mm	n_D^{30}	IR absorption, cm^{-1} (acetate)
Cyclopentene	75–76°/40	1·4278	1748, 1250
Cyclohexene	85–88°/35	1·4414	1738, 1245
Cycloheptene	120–124°/50	1·4522	1740, 1250
1-Methylcyclohexene	80–90°/30	1·4589	1750, 1245
(±)-Camphene	115–20°/30	1·4615	1742, 1245

Authentic acetates. The authentic samples of acetates were prepared from the corresponding alcohols by the acetic anhydride and pyridine method according to the reference procedures cited.

REFERENCES

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[2] The amount of PPA was kept constant.

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[7] T. D. Nevitt and G. S. Hammond, *J. Am. Chem. Soc.* **76**, 4124 (1954).

[8] For addition of AcOH to olefins of these types see: G. F. Bloomfield, *J. Chem. Soc.* 3329 (1953); P. E. Peterson and G. Allen, *J. Org. Chem.* **27**, 1505 (1962); P. E. Peterson and E. V. P. Tao, *Ibid.* **29**, 2322 (1964).