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ORGANIC REACTIONS WITH POLYPHOSPHORIC ACID—VIII

INTRAMOLECULAR ACYLATION WITH LACTONES (FURTHER EXTENSION), HYDROXY ACIDS AND ESTERS*†

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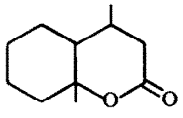
Abstract—Intramolecular acylation with lactones in polyphosphoric acid has been extended to γ- and δ-lactones with angular methyls. It is further shown that hydroxy acids can conveniently replace the corresponding lactones in such reactions. The reaction has also been applied to simple esters.

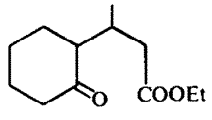
THE preparative utility of intramolecular acylations of lactones in polyphosphoric acid, a reaction first announced in 1955,[1] is now well demonstrated.[2–6] The present work was undertaken to explore its possible extension to the synthesis of cyclopentenones with an angular Me group, to the preparation of cyclohexenones and cycloheptenones and, to examine the action of PPA on hydroxy acids (instead of corresponding lactones) and simple esters.

Lactones with an angular methyl group

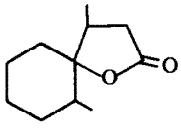
In order to prepare the δ-lactone I, action of MeMgI on ethyl β-(2-oxocyclohexyl) butyrate (II)[3] was investigated. The product was shown by GLC to consist of at least six components, besides some unchanged II. By a combination of fractionation and column chromatography (SiO_2 gel) four of these could be obtained pure, while another was obtained in a form of acceptable purity (~90%). Their relevant spectral characteristics are given in Table 1. On the basis of these data and the elemental



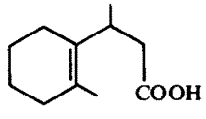
I



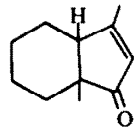
II



III



IV



V

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† Abstracted from the Ph.D Thesis (Bombay University, 1966) of S. B. Kulkarni.

analysis it is clear that component **2** is the spirolactone (III), **3** is the unsaturated acid IV, while **4**, **5** and **6** represent three of the four racemates possible for I.*

When the above total reaction product was treated with PPA (65°, 3 hr), essentially a single ketone resulted. The ketone ($\nu^{C=O}$ 1709 cm^{-1}; λ_{max} 232 mμ, ε 10,350; 2,4-dinitrophenylhydrazone, m.p. 140–142°) shows in its PMR spectrum one quaternary Me (3H singlet at 63 c/s), one vinylic Me (3H doublet centred at 124 c/s, J = 1·5 c/s) and an olefinic proton (1H multiplet centred at 342 c/s). These characteristics are in accord with the expected structure V. It has been mentioned elsewhere[7]

TABLE 1. PRODUCTS FROM THE ACTION OF MeMgI ON II

		GLC peak number				
	2†	3	4	5	6‡	7
RRT*	1·22	1·44	1·77	2·07	2·30	2·96
% of total product	7	3	9	35	25	5
$\nu^{C=O}$ (cm^{-1})	1780	1718 (also: ν^{OH} at 2618 cm^{-1})	1751	1745	1748	—
PMR spectrum§						
$C\underline{H}_3$—CH	56 (d) 62 (d)	64 (d) —	57 (d) —	60 (d) —	57 (d) —	
$C\underline{H}_3$—C(—)—	—	—	80 (s)	88 (s)	77 (s)	
$C\underline{H}_3$—C≡C	—	103 (s)	—	—	—	
—$C\underline{H}_2$—C(=O)—O—	142 (m)	136 (s)	140 (m)	140 (m)	140 (m)	
Others	—	702 (1H, s) (COOH)	—	—	—	

* Retention time relative to II (temp 200°; H_2 flow: 50 ml/min).

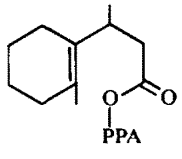
† Peak 1 is unreacted II. (Besides II, three very minor peaks also appear earlier.)

‡ GLC purity ~90%.

§ Spectra taken in CCl_4 and values are reported in c/s from TMS; s = singlet, d = doublet, m = multiplet. In case of doublets and multiplets, the centre is indicated. J = 6 c/s for all doublets.

that this compound is identical with one of the products of condensation of cycloheptene and crotonic acid. In view of the arguments presented there, the ketone should have *cis*-ring fusion.

The fact that the unsaturated acid IV, the γ-lactone III and the various isomeric



VI

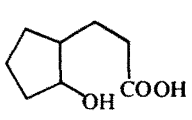
* Equilibration of the total lactone mixture with *p*-toluenesulphonic acid in boiling toluene led to the formation of the γ-lactone (III) at the expense of the component **5** (δ-lactone).

δ-lactones I, all on treatment with PPA give rise to the same ketone would suggest that in its formation all these compounds pass through the same intermediate. The mechanism of conversion of lactones into cyclopentenones has been discussed[2] and the present results support the earlier suggestion that the reaction proceeds through an intermediate of type VI.

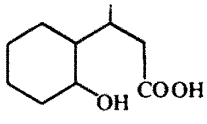
Hydroxy acids

The extension of lactones → cyclopentenones sequence to the closure of 6- and 7-membered rings, would obviously involve the preparation of lactones with rings larger than 6-membered. Since the preparation of ε-lactones and higher lactones, in condensed phase, may be expected to lead to considerable intermolecular reactions, it was thought desirable to investigate, if hydroxy acids could be directly employed in PPA condensations.

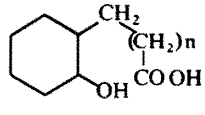
The use of the hydroxy acids, instead of the corresponding lactones was first investigated for the closure of cyclopentenone ring, as the latter readily result from the corresponding lactones by reaction with PPA. The crude hydroxy acid VII,[2] obtained by $NaBH_4$ reduction of cyclopentanone-2-β-propionic acid, reacted with PPA at 60 ± 2° to give the expected bicyclo[0.3.3]Δ^7-octen-1-one(X) in 76% overall yield. Likewise, the crude hydroxy acid VIII,[3] on interaction with PPA, first at 60° and then at 100°, yielded the corresponding bicyclic ketone XI, along with some



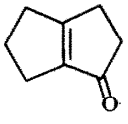
VII



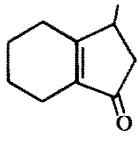
VIII



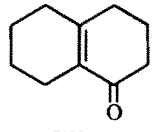
IXa (n = 2)
IXb (n = 3)



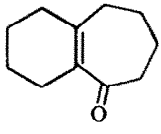
X



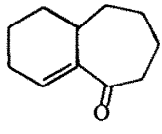
XI



XII



XIII



XIV

δ-lactone;* these results parallel closely the results obtained by Jacob and Dev[3] in the lactone-PPA reaction. The bicyclic ketone XI, thus prepared, has properties (b.p., n, λ_{max}, m.p. of its 2,4-DNP) indistinguishable from those recorded by the earlier workers[3] and is homogeneous (GLC). However, it displays a split CO frequency

* When the reaction is carried out only at 60°, the lactone portion consists of three components (GLC) (γ- and δ-lactones, $\nu^{C=O}$ 1750, 1780 cm^{-1}), which on further treatment with PPA at 100° gives more of XI and the lactone part now contains only one component (with highest retention time; $\nu^{C=O}$ 1750 cm^{-1}). Thus, different lactones undergo intramolecular acrylation at different rates. This point has an important bearing on the mechanism of intramolecular acylation and deserves further study.

($\nu^{C=O}$ 1700, 1720 cm^{-1}; $\nu^{C=C}$ 1655 cm^{-1}). Its PMR spectrum shows no vinylic Me or olefinic proton, thus confirming its homogeneity. Hence, the splitting of the CO frequency must be attributed to Fermi resonance.[8]

The method was next extended to the construction of a cyclohexenone ring. γ-(2-Oxocyclohexyl) butyric acid[9] was reduced with $NaBH_4$, and the crude γ-(2-hydroxycyclohexyl) butyric acid (IXa) treated with PPA (65°, 3 hr) to yield, in 78% yield, an unsaturated ketone (λ_{max} 244 mμ, ε 12,400; $\nu^{C=O}$ 1678 cm^{-1}; $\nu^{C=C}$ 1650 cm^{-1}; no vinyl protons in the PMR spectrum) of the expected structure XII. This ketone has been synthesized by several authors[10–12] earlier and the simplicity of the present procedure may be contrasted with the earlier methods.

The attention was next directed to see if the higher homologous acid IXb[13] can, with PPA, cyclize to a cycloheptenone. Reaction of IXb with PPA (80°, 3 hr) gave in only 15% yield a product shown by GLC to be ~1:1 mixture of two unsaturated ketones (broad UV absorption with λ_{max} 236 mμ, ε 7000 and a slight shoulder at 251 mμ, ε 5700; $\nu^{C=O}$ 1709, 1680 cm^{-1}; $\nu^{C=C}$ 1650, 1615 cm^{-1}) which were not examined further in detail because of the low yields obtained.*

From the above work, it can be reasonably concluded that hydroxy acids may be conveniently employed, instead of the corresponding lactones for intramolecular acylation to cyclopentenones and cyclohexenones.

Esters

Since lactones are only intramolecular esters, it was thought worthwhile to examine the action of PPA on simple esters. When cyclohexyl acetate was treated with PPA (55–60°, 1 hr), Δ^1-acetylcyclohexene could be isolated in ~50% yield. The reaction was next extended to cyclopentyl acetate, cycloheptyl acetate, 1-methyl-cyclohexyl-1-acetate and n-butyl acetate, as typical substrates, derived from secondary, tertiary and primary alcohols. In all cases, the corresponding α,β-unsaturated methylketones were formed, though in unsatisfactory yields in some cases. These results are summarized in Table 2. The methyl ketones were identified by comparison (IR; GLC)

TABLE 2. ACTION OF PPA ON SOME ACETATES

No.	Acetate	Reaction conditions*		Total yield (wt. basis) %	% Composition (GLC)		
		Temp	Time (min)		Methyl ketone	Unreacted acetate	Unidentified
1	Cyclopentyl	40–45°	45	40	72	14	14
2	Cyclohexyl	55–60°	60	50	92	8	—
3	Cycloheptyl	55–60°	60	25	95	—	5
4	1-Methyl cyclohexyl	40–45°	30	60	90	2	8
5	n-Butyl	100–10°	120	25	65	35	—

* 35 g P_2O_5 and 15 ml phosphoric acid for 0·05 mole of the acetate.

* A mixture of ketones XIII and XIV has been obtained by the PPA cyclization of (Δ^1-cyclohexenyl) valeric acid.[13] For the pure ketones XIII and XIV, these authors report λ_{max} 250 and 241 mμ respectively; their 2,4-DNP have m.p. 170–171° and 177–178° respectively. However, the 2,4-DNP prepared from our mixture has m.p. 184–185°, which is higher than that of either one of these. For a possible explanation see Refs. 13, 14.

with authentic samples, with the exception of ketone from n-butyl acetate, which was identified by comparison of m.ps of its derivatives with those described in the literature. It may be noted that the product from cycloheptyl acetate was 2-methyl-Δ^1-acetylcyclohexene, as might have been expected in view of our earlier findings.[7]

As discussed earlier, for intramolecular acylation with lactones, the intermediary of an olefinic acid derivative has been postulated[2] for the PPA-induced reactions. Since, it is only reasonable to expect that the conversion of acetates into the corresponding unsaturated methyl ketones, also proceed by the same mechanism, the reaction boils down to the acylation of an olefin, wherein the olefin and the acylating species are generated, first, from the acetate. Thus, one would expect competition with another added olefin. That this indeed is so was demonstrated by carrying out the reaction of cyclopentyl acetate with PPA with added cyclohexene, when the product of reaction was found to consist of 1:1 mixture of Δ^1-acetylcyclohexene and Δ^1-acetylcyclopentene.

EXPERIMENTAL

For general remarks, see Part VII of this series.

GLC was carried out on "Aerograph" model A-350-B, using H_2 as the carrier gas and a 2 meter × 6 mm column, packed with 20% diethylene glycol polysuccinate on Chromosorb W.

SiO_2 gel used for column chromatography was of mesh size −100, +200, and was repeatedly washed with hot, distilled water, dried and activated at 120–130° for 6 hr.

Ethyl β-(2-oxocyclohexyl) butyrate (II)

β-(2-Oxocyclohexyl)butyric acid[3] was esterified with EtOH and H_2SO_4, using benzene as the entrainer, in the usual manner: b.p. 135–137°/2·5 mm, n_D^{25} 1·4625.

Action of methyl magnesium iodide on II

To the above keto ester (8·0 g, 0·04 mole) in thiophene-free benzene (25 ml), a soln of MeMgI (from 1·2 g Mg, 8 g MeI and 20 ml ether) was introduced, at 0–5°, during 20 min with stirring. After stirring for another hr at 0–5°, the reaction mixture was allowed to attain room temp (~25°) and then refluxed for 5 hr. After the usual work up with 1:1 HCl aq the product was taken up in ether, washed with $Na_2S_2O_3$ aq and finally with brine and dried. Removal of solvent gave a product, b.p. 116–122°/1 mm, yield 5·2 g; GLC (200°; 50 ml/min) showed it to consist of at least 7 components (cf. Table 1).

The above product (30 g) was carefully fractionated on a spinning-band column,[15] under total reflux, at 2 mm, while following the course of fractionation by GLC. In this way the appropriate fractions were combined to give the following cuts:

Cut No.	Fractions pooled	b.p./1 mm	Wt. (g)	Remarks
A	1–9	−120°	1·1	1* and 2 with lower b.p. impurities.
B	10–12	120–121°	2·0	1 and 2, 1:1 mix.
C	13–16	121–122°	2·0	Mix. of 1, 2, 4
D	17–21	122–123°	8·2	Mix. of 4, 5, 6
E	22–37	123–124°	10·3	Essentially 5 and 6 with some 3.
F	38–39	124–125°	1·0	3, 5, 6, with 3 accounting for 30%.

* These numbers refer to GLC peak No. (cf. Table 1).

Spirolactone (III, *GLC component* 2). The above cut B (1 g) was chromatographed on silica gel (55 cm × 1·5 cm):

Fraction 1:	Pet. ether–50% C_6H_6	4 × 25 ml	5 mg, rejected.
Fraction 2:	Pet. ether–75% C_6H_6	7 × 25 ml	120 mg of III, 90% pure.
Fraction 3:	C_6H_6	8 × 25 ml	420 mg of pure III
Fraction 4:	C_6H_6–1% MeOH	6 × 25 ml	430 mg of II

Fraction 3 was distilled to give pure III: b.p. 130–140° (bath)/3 mm, n_D^{30} 1·4323, yield 375 mg. (Found: C, 72·32; H, 9·85. $C_{11}H_{18}O_2$ requires: C, 72·49; H, 9·96%.)
Fraction 4 was identified (IR, GLC) as the unreacted keto ester II.

2-Methyl- Δ^1*-Cyclohexenyl-β-butyric acid* (IV, *GLC component* 3). Cut F (950 mg) was chromatographed on silica gel (50 cm × 1·5 cm):

Fraction 1:	Pet. ether	2 × 25 ml	—
Fraction 2:	Pet. ether–50% C_6H_6	4 × 25 ml	—
Fraction 3:	C_6H_6	6 × 25 ml	35 mg of 80% pure IV
Fraction 4:	C_6H_6–0·5% MeOH	8 × 25 ml	225 mg of pure IV
Fraction 5:	C_6H_6–1% MeOH	10 × 25 ml	700 mg of 1:1 **5** and **6**

Fraction 4 solidified (m.p. 50–53°) and was recrystallized from acetone, m.p. 52–53°. (Found: C, 72·73; H, 9·95. $C_{11}H_{18}O_2$ requires: C, 72·49; H, 9·96%.)

GLC component 4 (I). When 1·2 g of cut D was chromatographed over SiO_2-gel (50 cm × 1·5 cm) as above, benzene (8 × 25 ml) eluted 70 mg of **4**, contaminated only with the GLC component 1 (II). This was refluxed with 1% alc. KOH (5 ml) for 3 hr, the alcohol removed, the residue diluted with water, and acidified with HCl aq. The acidic soln was warmed on a steam-bath (15 min), cooled and the product extracted with ether. The ether extract was washed with $NaHCO_3$ aq. to remove the keto acid, and the ether phase worked up to give pure **4**, b.p. 130–140° (bath)/2 mm. (Found: C, 72·64; H, 10·22. $C_{11}H_{18}O_2$ requires: C, 72·49; H, 9·96%.)

Benzene–0·5% MeOH (5 × 25 ml) eluted 400 mg of a mix containing all the 4 components. Benzene–1% MeOH (8 × 25 ml) eluted 670 mg of a mix of **5** and **6**; this was mixed with the Fraction 5 of the above chromatography (isolation of IV) and the total employed for the separation of **5** and **6**, as described below.

GLC components **5** *and* **6** (I). Chromatography of the above mixture (1·3 g) of **5** and **6** on silica gel (75 cm × 1·5 cm) led to their partial separation. Pet. ether–75% C_6H_6 (10 × 50 ml) eluted fractions rich in **5**, the central one (~30 mg) of these being GLC pure. (Found: C, 72·43; H, 9·93. $C_{11}H_{18}O_2$ requires C, 72·49; H, 9·96%.) Elution was continued with C_6H_6 (10 × 50 ml) and later with C_6H_6–1% MeOH (10 × 50 ml). The last few fractions gave **6** in ~90% purity. (Found: C, 72·30; H, 9·90. $C_{11}H_{18}O_2$ requires: C, 72·49; H, 9·96%.)

Isomerization of lactone mixture

A mixture of δ-lactones (cut D, 0·2 g) and *p*-toluenesulphonic acid (20 mg) was heated for 2 hr at 100°, cooled, diluted with water, extracted with ether and the extract, after washing with Na_2CO_3 aq was dried. Solvent was flashed off and the residue distilled: b.p. 130–140° (bath)/2 mm, yield 100 mg. GLC (200°; 50 ml/min) of this material showed **2**, **4**, **5** and **6** in the ratio 2:1:3:4.

Action of PPA on the crude lactone mixture

To PPA (from 7 g P_2O_5 and 3 ml of 85% H_3PO_4), maintained at 65 ± 2°, the crude lactone mixture (product obtained by the action of MeMgI on II, b.p. 116–121°/1 mm; 1·0 g) was added and the reaction mixture heated and stirred at that temp for 3 hr. The mixture, while still warm, was poured onto ice–water slush (100 ml) and the product extracted with ether (10 ml × 4). The extract was washed with water, $NaHCO_3$ aq, brine and dried. The solvent was removed and the residue distilled: b.p. 130–140° (bath)/1 mm, n_D^{30} 1·4985, yield 0·79 g; GLC showed essentially a single component. (Found: C, 80·00; H, 9·71. $C_{11}H_{16}O$ requires: C, 80·44; H, 9·83%.)

2,4-*Dinitrophenylhydrazone* (HCl method). Crude product, m.p. 135–137°; after 3 crystallizations from EtOH it was obtained as a red powder, m.p. 140–142°. (Found: N, 16·02. $C_{17}H_{20}O_4N_4$ requires: N, 16·27%.)

Action of PPA on 2-hydroxycyclopentyl -β-propionic acid (VII)

2-Oxocyclopentyl-β-propionic acid[2] (27·5 g) was dissolved in water (150 ml) containing 17·6 g $NaHCO_3$, and to the resulting soln (~20°) $NaBH_4$ (3·4 g) was added in small lots (45 min), with swirling; during the addition the temp rose to ~50°. The mixture was left aside as such, at room temp overnight (12 hr) and then acidified with HCl aq to pH 2, when a heavy oil separated. This was taken up in ether (20 ml × 6; the aq portion was saturated with ammonium sulphate), the extracts washed with brine, dried and freed of solvent to give the crude hydroxy acid (27 g).

To PPA (450 g P_2O_5 and 180 ml 85% H_3PO_4) maintained at 60 ± 2°, the above hydroxy acid (47·4 g)

was introduced in one lot and stirred for a few min to effect thorough mixing. The stirrer was stopped and the resulting brown reaction mixture heated at the same temp for 4·5 hr; during this heating period, the reaction mixture was stirred 4 times for 2 min every time. The reaction mixture was worked up as described earlier[2] to give X[2] as a colourless liquid, b.p. 75–77°/1·5 mm, n_D^{22} 1·5202, yield 28 g (76·5%); the product crystallized on cooling, m.p. 19–20°, IR spectrum: C=O 1697; C=C 1641 cm^{-1}.

Action of PPA on 2-hydroxycyclohexyl-β-butyric acid (VIII)

2-Oxocyclohexyl-β-butyric acid[3] (2·0 g) was reduced with $NaBH_4$ (200 mg) as detailed above to give 1·8 g of crude VIII. This was treated with PPA (14 g P_2O_5 and 6 ml 85% H_3PO_4), as already described, first at 60° (3 hr) and later at 100° (2 hr) and then worked up to give a product (1·5 g), b.p. 140–160° (bath)/1 mm; this was separated into the lactone and the ketone parts, as reported.[3] The pure ketone had: b.p. 115–116°/6 mm, n_D^{25} 1·5105, yield 0·7 g; λ_{max} 236 mμ, ε 13,300; PMR spectrum: CH_3–CH, a doublet centred at 69 c/s with J = 6·5 c/s.

2,4-Dinitrophenylhydrazone (HCl method). The crude product, m.p. 237–239°; after two recrystallizations from EtOH gave bright red leaflets m.p. 242–243°; mixed m.p. with an authentic sample[3] remained undepressed.

Action of PPA on 2-hydroxycyclohexyl-γ-butyric acid (IXa)

γ-(2-Oxocyclohexyl) butyric acid was prepared essentially by the procedure of Cook and Lawrence[9] with some modifications: Ethyl cyclohexanone-2-carboxylate (16·9 g, 0·1 mole) in toluene (20 ml) was added to Na dust (2·5 g) covered with toluene (50 ml), with ice-cooling. The reaction was finally completed by heating in an oil-bath (130–140°) for 2 hr. The Na enolate was cooled and ethyl γ-bromocrotonate[16] (17·1 g, 0·1 mole) introduced with stirring. The reaction mixture was finally heated in a bath at 130–140° for 4 hr and then worked up in the usual manner to give the required product (16·4 g) as an oil, b.p. 160–165°/1·5 mm. This diester (10 g) was hydrogenated over PtO_2 (200 mg) in EtOH (50 ml) at room temp and press to give the dihydro ester (10 g), which was hydrolyzed and decarboxylated by refluxing with HCl aq (50 ml)–AcOH (15 ml) for 20 hr. The usual work-up gave γ-(2-oxocyclohexyl) butyric acid as a viscous liquid (4·1 g), b.p. 150–153°/1·5 mm. (Found: C, 64·92; H, 9·05. $C_{10}H_{16}O_3$ requires: C, 65·19; H, 8·75%.)

The above keto acid (3·6 g) was reduced with $NaBH_4$ (0·4 g), as detailed for VII and the crude IXa directly used in the next step.

To PPA (7 g P_2O_5 and 3 ml 85% H_3PO_4) maintained at 65 ± 2°, the above hydroxy acid (1·0 g) was added, well-mixed and heated at that temp for 3 hr. Usual work up gave a product (0·68 g), b.p. 110–120° (bath temp)/0·8 mm, n_D^{25} 1·5100; 2,4-dinitrophenylhydrazone (HCl) method): dark red leaflets (alc), m.p. 268–269° (Lit.[12], m.p. 264·5–265°). (Found: N, 16·60. $C_{16}H_{18}O_4N_4$ requires: N, 16·96%.)

Action of PPA on 2-hydroxycyclohexyl-δ-valeric acid (IXb)

The acid IXb, was prepared according to Conley and Czaja,[13] except that the reduction of 2-oxocyclohexyl-δ-valeric acid was carried out with $NaBH_4$, as described for VII.

Crude IXb (2·25 g) was added to PPA (15 g P_2O_5 and 6 ml 85% H_3PO_4), maintained at 80 ± 2° and the mixture heated and stirred at that temp for 3 hr. After working up, a viscous material was obtained, which on distillation gave a mobile liquid (0·25 g), b.p. 140–160° (bath temp)/0·8 mm and much residue. The product readily gave a *2,4-dinitrophenylhydrazone* (HCl method): m.p. of crude product 165–169°; two crystallizations from EtOH furnished dark red needles, m.p. 184–185°, with very poor recovery. (Found: N, 15·90. $C_{17}H_{20}O_4N_4$ requires: N, 16·27%.)

Action of PPA on simple esters

The details are given below for the reaction of cyclohexyl acetate[17] with PPA, as a typical example.

To PPA (35 g P_2O_5 and 15 ml 85% H_3PO_4), maintained at 55–60°, cyclohexyl acetate (7·1 g, 0·05 mole) was added in one lot and the mixture stirred at the same temp for 1 hr. The resulting dark red coloured product was poured onto ice–water mixture (200 g), saturated with ammonium sulphate and extracted with ether (30 ml × 3). The combined extracts were washed with $NaHCO_3$ aq, brine and then dried. The solvent was removed and the residue distilled: b.p. 115–120°/40 mm, yield 3·5 g. IR Spectrum: >C=O 1667; C=C 1648 cm^{-1}.

In a similar fashion cyclopentyl acetate,[18] cycloheptyl acetate,[19] 1-methylcyclohexyl acetate[20] and n-butyl acetate were reacted with PPA and the products analysed (Table 2). The product (1·03 g) from

the reaction of n-butyl acetate (5·8 g) was characterized by the preparation of its *semicarbazone*, m.p. 196–197° (Lit.[21] m.p. 198°) and *2,4-dinitrophenylhydrazone*, orange-red needles (alc. acetone), m.p. 191–192°. (Found: N, 20·27. $C_{12}H_{14}O_4N_4$ requires: N, 20·14%.)

Action of PPA on cyclopentyl acetate in presence of cyclohexene

A mixture of cyclopentyl acetate (3·2 g, 0·025 mole) and cyclohexene (2·05 g, 0·025 mole) was added to PPA (17 g P_2O_5 and 8 ml 85% H_3PO_4), maintained at 40–42°. After stirring at the same temp for 0·5 hr, it was worked up, as described to give a product (1 g), b.p. 80–91°/35 mm. GLC (column temp 130°; gas press: 15 psi) showed it to consist of ~1:1 mixture.

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