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FACILE ESTERIFICATION OF CARBOXYLIC ACIDS WITH ORGANOPHOSPHORUS REAGENTS.
NOVEL APPLICATION OF ALKYLPHOSPHORIC ESTERS (APE) **

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Abstract - A mixture of alkyl phosphate esters (APE) obtained from P_4O_{10} and alkanols taken in 1:6 mole ratio is an excellent esterification reagent for several classes of carboxylic acids. This new reagent offers several advantages compared to conventional reagents.

Recent publications in this Journal[1] and elsewhere[2,3] concerning synthetic applications of phosphorus reagents to effect esterification of carboxylic acids, prompt us to report our own results on a novel application of organophosphoric esters, obtained from the hitherto poorly studied[4] reaction of alkanols with P_4O_{10}.

The extensive applications of organophosphorus reagents in synthetic methodology are well documented[5]. Among them, those of polyphosphoric acid (PPA)[6] and polyphosphoric esters (PPE)[6c] have generated a rich literature. Since the first report concerning the reaction of P_4O_{10} with diethyl ether was made several decades ago[7], there have been many studies addressed to formation[8], structure[8a,9] and synthetic applications of this versatile reagent. It has been used successfully for several conversions of biochemical interest[9a, 10a], dehydration of amides[10b], Fischer indole synthesis[10c], Bischler-Napierlaski reaction[8c,8d,8e,11], Beckmann rearrangement[12], and condensation reactions involving 1,2-bifunctional nucleophiles[13,14]. In contrast to such diverse applications of PPE derived from P_4O_{10} and diethyl ether, the reagent obtained from P_4O_{10} and alkanols singularly lacks detailed investigations either of its structure or its synthetic utility. Just a handful of investigations refer to its formation[4a,15], structure[15c,16], and synthetic uses. The reagent obtained from P_4O_{10} and alkanol (1:1.25-3.00) has been used for efficient dehydration of oximes to nitriles and secondary alkanols to olefins[15a]. With a 1:4 ratio of P_4O_{10} and alkanol, the reagent brings about nitrogen and carbon alkylation[15c,17]. In these early investigations, neither any

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** Part IX of the series Reactions of Cyclic Anhydrides.

specific structure is assigned for the reagents formed nor are the mechanistic details indicated. Without adducing any evidence, a suggestion is made[15c] that this reagent might be intermediate in structure between PPA and PPE. Nevertheless the superior reactivity of this reagent to effect alkylation over trialkylphosphates and tetraalkylpyrophosphates appears established[15c].

In connection with our work related to generation of heterocycles[18] from suitably ortho substituted anilic esters, we were in need of a dependable method for formation of anilic esters. After the conventional direct esterification methods for conversion of carboxylic acids to esters failed in our trials to provide acceptable yields of the esters, we turned to PPE for this purpose. The reagents obtained from P_4O_{10}-diethyl ether[8c] or P_4O_{10}-chloroform-alkanol[15c] caused either decomposition or imide formation of the anilic acids. In the fewer cases where it worked, the yield and purity of the product were far from satisfactory. After some trials, we realised[18] that nitro anilic acids obtained from nitro-aniline and maleic anhydride undergo smooth conversion to the esters in excellent yield when treated with a mixture of 1 mole of P_4O_{10} taken in 6 moles of alkanols. Encouraged by these results, we made a systematic study of the utility of this new reagent for esterifying other sensitive anilic acids, and more generally mono and dicarboxylic acids. The present report describes our results.

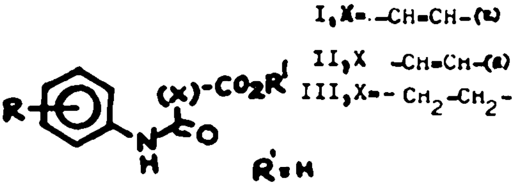
We prepared the reagent by careful portionwise addition of 1 mole of P_4O_{10} to 6 moles of anhydrous methanol at 0-5°C. The reagent thus obtained is stable for several days. Aliquots of the reagent can be conveniently used for esterification of carboxylic acids by refluxing them with the reagent for 3 hours. For liquid acids, the best results were obtained by using P_4O_{10} and alkanol in the ratio 1:6. With solid acids, a higher ratio of alkanol was employed to ensure homogeneous solution, when necessitated by the poor solubility of anilic acids. Even in the latter cases, that the operative composition of the reagent was nevertheless one portion of P_4O_{10} to 6 of alkanol, was clarified by running the reaction with this reagent, solution being effected by an inert solvent such as dioxane. We therefore believe that the nature of the species obtained from interaction of P_4O_{10} with alkanol is critically dependent on the stoichiometry of the components. In the amounts taken in this work, the reagent formed presumably consists of an equimolar mixture of monoalkyl and dialkyl phosphates[16,20]. The

$$P_4O_{10}+6ROH \longrightarrow$$
$$2(RO)\,P(O)\,(OH)_2+2(RO)_2\,P(O)\,(OH)$$

detailed studies on the hydrolytic behaviour of mono and dialkyl phosphates under acidic conditions clearly point out their efficiency as alkyl transfer reagents[21]. As of now, we choose not to venture into a more detailed discussion of the precise nature of the active reagent;

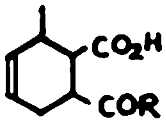
instead we report on the synthetic potential of this reagent.

Table I contains details of several successful conversions of acids into esters. The classes examined include saturated and unsaturated aliphatic mono and dicarboxylic acids, halocarboxylic acids and an amino acid. Table II lists similar conversions for a large number of maleanilic (I), fumaranilic (II) and succinanilic (III) acids. An examination of data of these tables reveals the versatility of this reagent. A few noteworthy features of this reagent deserve mention: i) The amount of reagent obtained from 1 mole of P_4O_{10} esterifies 6 moles of mono carboxylic acids. As such, the transfer efficiency of this reagent is very high compared to trimethyl phosphate[22], trimethyl phosphite[23], dimethyl sulphate[24] and the 'rediscovered' dimethyl sulphite[25]. ii) Direct esterification of carboxylic acids using ROH/H_2SO_4 often fails to provide esters of higher alkanols. We found this to be particularly true of anilic acids. This difficulty was overcome by using the alkylphosphate reagents of the present work. iii) The reagent has a good solvent action for solid acids such as nitro-anilic acids which otherwise are less soluble in alkanols. iv) With dicarboxylic acids, invariably the reaction resulted in formation of diesters even when the stoichiometry was deliberately adjusted to cause only mono-esterification. In such cases, it turned out that only half the initial acid underwent diesterification, the otherhalf being quantitatively recovered. In the case of maleic acid (entry No.10, Table I) esterification was accompanied by isomerisation as well, the Z:E ratio being 84:16; however, the related citraconic acid (entry No.11, Table I) furnished only the "Z" isomer (resisting isomerisation). v) This reagent cuts down the reaction time from 12-24 hours required to esterify certain acids (entry 1,6,7,8,12; Table I) to a uniformly short period of three hours, the yield in general being comparable or better; the need to remove water formed during the reaction by azeotropic distillation can also be avoided.

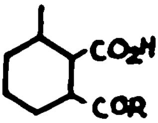


The present method of esterification is not without some limitations. Thus the reagent failed to furnish acceptable yields of some aromatic esters for e.g., nitro and amino benzoic acids; besides, some of the maleanilic acids not containing nitro function often displayed a tendency to form imides rather than the expected esters. A similar problem was faced with phthalanilic (IV) curanilic-400 (Va) and curanilic-600 (Vb) acids.

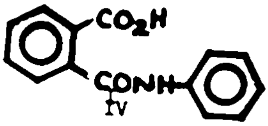
R= -NHAr



Va



Vb



IV

The ready formation of imides in the latter cases can be a consequence of the relatively higher nucleophilicity of nitrogen and/or the favourable proximity of the interacting groups. In fact, the latter systems IV-V have so far defied our attempts at direct esterification by variety of methods.

In summary, the reagent obtained from 1 mole of P_4O_{10} and 6 moles of alkanol satisfactorily brings about the direct esterification of a wide variety of carboxylic acids in good to excellent yields. This new reagent provides a technique complementary to the available ones. Even though the precise composition of the reagent is yet to be ascertained, its synthetic utility appears promising. At this stage mechanistic speculations are premature and must await the results of studies currently on hand in our laboratories.

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EXPERIMENTAL

Melting points recorded are uncorrected. The IR spectra are recorded in nujol on a Perkin-Elmer R37 spectrophotometer(ν_{max} in cm^{-1}), PMR spectra in $CDCl_3$ on Perkin-Elmer R_{32} spectrophotometer using TMS as internal standard (chemical shifts in δ ppm).

Preparation of Alkyl phosphate reagent:

Anhydrous methanol (240 ml,6mol) was cooled to 0-5° and phosphorus pentoxide (284 gm,1mol,calculated as P_4O_{10}) gradually added with constant stirring (internal temperature less than 10°; higher temperature caused decomposition of the reagent resulting in a brown solution). The addition was carried out preferably in an inert atmosphere(N_2). After the addition was over, the reaction mixture was stirred for another 20 minutes. The clear viscous solution thus obtained can be stored under seal to keepout moisture and used in aliquots. The hygroscopic reagent is stable for periods upto three weeks at room temperature.

Esterification of liquid carboxylic Acids :

A typical reaction is described : Glacial acetic acid (0.6 mole, 36.0 gm) was added to 0.1 mole equivalent of the reagent prepared as above, and the reaction mixture refluxed for 3 hours on a water bath, ice-cold water being circulated through the condenser. The reaction mixture was allowed to come to room temperature, extracted with ether (2 x 100 ml), the organic layer washed (aq.$NaHCO_3$ 2 x 100 ml) and dried (Na_2SO_4). After removal of solvent, the residual liquid was distilled through a fractionating column to yield 90% (39 gm) of methyl acetate b.p. 54-56°.

Esterification of solid acid :

Phenylacetic acid (82.2 gm, 0.6 mol) was added to the reagent prepared as above. In this case, any required alkanol was added to ensure homogeneous solution. The reaction mixture was refluxed for 3 hours. It was then diluted with water (100 ml) extracted with ether (2 x 100 ml), the organic layer washed (aq.$NaHCO_3$, 2 x 100 ml) and dried (Na_2SO_4). After removal of solvent, the residual liquid was distilled off to yield 86% (85 gm) of ethyl phenyl acetate, b.p. 224-226°. Data concerning other methyl and ethyl esters thus prepared are collected in Table I.

Identical procedure was adopted for maleanilic (I) and fumaranilic(II) acids. For succinanilic acids (III), the reaction was brought about by stirring the acid and the reagent at room temperature for four hours. The products obtained from anilic acids thus esterified are reported in in Table II. In case of alkanols immiscible with water, after concentrating the solution by distilling off most of the solvent, light petroleum (60-80) was added and the mixture allowed to stand, when the product crystallised out. The spectral and analytical data of the esters prepared are furnished in Table III and IV.

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Table I Esterification of Carboxylic Acids with alkylphosphate esters (APE). Data concerning methyl/ethyl esters.[a]

No.	Carboxylic acid	Methyl Ester B.P./M.P.	Methyl Ester Yield %	Ethyl Ester B.P./M.P.	Ethyl Ester Yield %
1.	Acetic	54-56	90	74-76	56
2.	Propionic	74-76	86	96-98	66
3.	Butyric	99-101	80	117-19	66
4.	isoValeric	114-16	70	131-33	72
5.	Phenylacetic	250-52	89	224-26	86
6.	Oxalic	54[b]	95	181-83	68
7.	Succinic	193-95	60	214-16	63
8.	Crotonic	117-19	70	122-24	68
9.	Cinnamic	32[b]	78	138-41/12mm	73
10.	Maleic[d]	201-3	73	101-3/14mm	70
11.	Methylmaleic[d]	98-102/14mm	68	118-20/20mm	65
12.	Fumaric	101-2[b]	72	134-36/19mm	60
13.	Chloroacetic	128-30	78	141-43	90
14.	Aminoacetic	172-74[c]	65	143-44[c]	90
15.	Benzoic	191-93	70	209-11	24
16.	3,5-Dinitrobenzoic	111-12[b]	36	89-90[b]	30
17.	3-Methyl-hexahydro-phthalic	149-50/33mm	71	165-70/15mm	85
18.	3-Methyl-Δ^4-tetrahydro phthalic	155-60/20mm	73	115-20/10mm	79

a. Yields are not optimised. The m.p./b.p. of the esters were checked against literature values. All new compounds were characterised by elemental analysis and/or ir/pmr spectra.

b. Solid esters; melting points are reported.

c. For the hydrochloride.

d. For entry 10, mixture of esters (16 % E, 84 % Z); for entry 11, only Z-isomer.

Table II. Esterification of maleanilic, fumaranilic and succinanilic acids with alkyl phosphate esters (APE)[a]

No	R_1	(X)=-CH=CH-$_{(Z)}$[b]		(X)=-CH=CH-$_{(E)}$[b]		(X)=-CH_2-CH_2-	
		M.P.	Yield %	M.P.	Yield %	M.P.	Yield %
1	2-CH_3	72-74	c	143-45	68	78-80	50
2	4-CH_3	149-50	c	143-44	67	114-16	68
3	2-OCH_3	137-39	c	118-120	64	56-57	62
4	4-OCH_3	142-45	c	174-75	65	108-09	80
5	4-Cl	-	-	178-80	70	142-45	68
6	2-NO_2[d]	74-76	85	123-24	85	124-5	50
		(55-56)	78	(98-100)	80		
7	3-NO_2	125-26	87	174-76	84	139-40	72
		(118-19)	77	(138-39)	78		
8	4-NO_2	130-31	89	250-51	87	140-41	66
		(93-94)	78	(218-19)	80		
9	2-NO_2-4OCH_3	98-100	88	134-36	89	88-90	70
		(83-84)	78	(139-40)	80		
10	2-NO_2-4-CH_3	103-4	87	111-13	85	84-86	
				(121-23)	78		80

a. Yields are not optimised. The m.p. of the esters were checked against literature values. All new compounds were characterised by elemental analysis and/or ir/pmr spectra.

b. The first row relates to data on methyl esters, the second row to ethyl esters.

c. In these cases, esters were not formed; the data given are for imides (see text)

d. For entry 6, the following higher esters in E-series have also been prepared.

i) iso-propyl ester - m.p. 81-83°
ii) n-propyl ester - m.p. 83-84°
iii) n-Butyl ester - m.p. 79-80°
iv) cyclohexyl ester - m.p. 134-36.

Table III Analytical and spectral data for representative esters.

No.	Compound	%	Calc.	Found.	PMR ppm
1	I;R=2-NO_2;R^1=Me ($C_{11}H_{10}N_2O_5$)	C H N	52.80 04.00 11.20	52.85 04.02 11.32	3.82(3H,s,$-OCH_3$);6.30(1H,d,J=13Hz, vinylic H);6.56(1H,d,J=13Hz,vinylic H) 7.2-8.8(4H,m,Ar-H);10.7(1H,bs,exch, D_2O-NH-CO-).
2	II;R=2-NO_2;R^1=Me ($C_{11}H_{10}N_2O_5$)	C H N	52.80 04.00 11.20	53.10 04.03 11.01	3.82(3H,s,$-OCH_3$);6.95(1H,d,J=18Hz, vinylic H);7.07(1H,d,J=18Hz vinylic H); 7.1-8.8(4H,m,Ar-H);10.7(1H,bs,exch, D_2O-NH-CO-).
3	II;R=2-NO_2;R^1=Et ($C_{12}H_{12}N_2O_5$)	C H N	54.55 04.54 10.60	54.35 04.56 09.95	1.3(3H,t,$-CH_3$);4.3(2H,q,$-CH_2$;6.95(1H, d,J=18Hz vinylic H);7.00(1H,d,J=18Hz, vinylic H);7.1-8.3(4H,m,Ar-H); 10.7 (1H,bs,exch,D_2O,-NH-CO-).
4	II;R=4-NO_2;R^1=Et ($C_{12}H_{12}N_2O_5$)	C H N	54.55 04.54 10.60	54.25 04.50 10.71	1.3(3H,t,$-CH_3$);4.3(2H,q,$-CH_2$);6.22(1H d,J=18Hz vinylic H);6.44(1H,d,J=18Hz, vinylic H);7.7-8.3(4H,m,Ar-H);11.5 (1H,bs,exch,D_2O,-NH-CO-).
5	II;R=4-NO_2;R^1=Me ($C_{11}H_{10}N_2O_5$)	C H N	52.80 04.00 11.20	52.95 04.05 11.15	3.88(3H,s-OCH_3);6.27(1H,d,J=18Hz, vinylic H);6.47(1H,d,J=18Hz vinylic H), 11.5(1H,bs,exch,D_2O,-NH-CO-).
6	II;R=2-CH_3;R^1=Me ($C_{12}H_{13}NO_3$)	C H N	65.75 05.93 06.39	65.99 06.11 06.52	2.18(3H,s,Ar-CH_3);3.17(3H,s,$-OCH_3$); 6.78(1H,s,vinylic H);6.94(1H,s, vinylic H);7.04-7.08(4H,m,Ar-H);7.68 (1H,bs,exch,D_2O,-NH-CO-).
7	Entry 11-Table I Methyl ester				2.07(d,J=1.8 Hz long range coupling with olefinic proton, 3H);3.7(s,3H); 3.8(s,3H);3.9(q,J=1.8 Hz).
8	Entry 17-Table I Methyl ester				1.05(d,J=9 Hz,3H);1.3-2.1(m,6H); 2.23(sext,1H);2.48(t,1H);2.88(m,1H); 3.6(s,6H).
9	Entry 18-Table I Methyl ester				1.20(d,J=9 Hz,3H);2.2-3.2(complex m,5H);3.5-3.7(two close singlet,6H); 5.3-5.8(m,2H).

IR spectra of 1-6 displayed NH bands at ~3300 cm^{-1}, ester carbonyl at ~1710 cm^{-1} and amide I and II bands at ~1670 and ~1630 cm^{-1} respectively.

Table IV Analytical and spectral data for anilic esters.

No.	Compound	%	Calc.	Found.	IR cm^{-1}
1	II;R=2-NO_2-4-OMe R^1=Me	C H N	51.42 04.26 10.00	51.62 04.38 09.62	3300, 1710, 1670.
2	I;R=2-NO_2-4OMe R^1=Me	C H N	51.42 04.26 10.00	51.48 04.29 09.83	3300, 1715, 1675.
3	II;R=2-NO_2; R^1=n-Pr	C H N	56.10 05.03 10.07	56.00 04.91 09.60	3300, 1710, 1670.
4	III;R=4-OCH_3; R^1=Me	C H N	60.75 06.32 05.91	60.69 06.41 05.82	3370, 1680, 1740.
5	III;R=4-Cl;R^1=Me	C H N	54.77 06.32 05.91	54.70 06.41 05.82	3350, 1710, 1680.
6	III;R=3NO_2;R^1=Me	C H N	52.38 04.76 11.11	52.28 04.81 10.94	3350, 1670, 1710.
7	III;R=4-NO_2; R^1=Me	C H N	52.38 04.76 11.11	52.40 04.70 10.59	3350, 1605,
8	I;R=2-Me(imide)	C H N	70.58 04.81 07.48	70.69 04.71 07.19	1700.
9	I;R=4-Me;(imide)	C H N	70.58 04.81 07.48	 07.36	1700.
10	I;R=4-OCH_3(imide)	C H N	65.02 04.43 06.89	 06.67	1700.
11	I;R=2-NO_2-4-CH_3; R^1=Me	C H N	54.55 04.54 10.60	54.50 04.50 10.52	3460, 1710, 1630.
12	II;R=2NO_2-4-Me; R^1=Me	C H N	54.50 04.54 10.60	54.35 04.50 10.40	3340, 1740, 1680.

Table IV(Contd)

No	Compound	%	Calc.	Found.	IR cm^{-1}
13	II;R=2-NO_2-4CH_3 R^1=Et	C	56.11	56.09	3320, 1725, 1675, 1640.
		H	05.03	05.60	
		N	10.07	09.91	
14	II;R=2-NO_2;R^1=Bu	C	57.53	57.39	3320, 1720, 1680.
		H	05.47	05.46	
		N	09.62	09.33	
15	II;R=2-NO_2 R^1=Cyclohexyl	C	60.37	60.31	3275, 1660, 1675, 1730.
		H	05.66	05.84	
		N	08.75	08.34	
16	II;R=2-NO_2; R^1=isoPropyl	C	56.10	56.32	3340, 1715, 1680.
		H	05.03	05.09	
		N	10.11	10.58	
17	I;R=3-NO_2;R^1=Et	C	54.54	54.50	3340, 1620, 1680.
		H	04.54	04.65	
		N	10.60	10.41	
18	I;R=3-NO_2;R^1=Me	C	52.80	52.71	3345, 1680, 1700.
		H	04.00	04.01	
		N	11.20	11.52	
19	I;R=4-NO_2;R^1=Me	C	52.80	52.68	3300, 1650, 1710.
		H	04.00	04.10	
		N	11.20	11.35	
20	II;R=2-NO_2-4OCH_3 R^1=Me	C	53.07	52.91	3325, 1650, 1710.
		H	04.76	04.96	
		N	09.52	09.41	
21	III;R=2-Me;R^1=Me	C	65.15	65.05	3280, 1680, 1745.
		H	06.78	06.91	
		N	06.31	06.16	
22	III;R=4-Me;R^1=Me	C	65.15	65.19	3320, 1655, 1730.
		H	06.78	06.93	
		N	06.31	06.20	