[CONTRIBUTION FROM THE MALONEY LABORATORY, THE CATHOLIC UNIVERSITY OF AMERICA]

USE OF PARANITROPHENYLACETYL CHLORIDE FOR THE IDENTIFICATION OF ALCOHOLS, ETHERS, PHENOLS, AND AMINES[1]

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The purpose of this investigation was to determine whether *p*-nitrophenylacetic acid is a suitable reagent for the identification of alcohols, ethers, phenols, and amines. It was found that the acid, in the form of the acid chloride, reacts readily with the first three classes of organic compounds to give esters of *p*-nitrophenylacetic acid, and with amines to yield amides. Since most of the esters and amides are new compounds, they were prepared in quantity by the usual methods for analysis and characterization.

The experimental part describes procedures for making the derivatives of alcohols, phenols, and amines with *p*-nitrophenylacetyl chloride in small amounts adapted to the purposes of organic qualitative analysis.

EXPERIMENTAL

p-Nitrophenylacetyl chloride. Equimolar amounts of phosphorus pentachloride and *p*-nitrophenylacetic acid were mixed and heated gently until the evolution of hydrogen chloride had ceased. The liquid mixture of the acyl chloride and phosphorus oxychloride was poured onto a large watch glass and allowed to solidify. The crude *p*-nitrophenylacetyl chloride was then transferred to a clay plate and rubbed with a spatula in order to remove the last traces of phosphorus oxychloride, after which it was recrystallized from benzene. Yellowish-white crystals, m.p. 45–46°, were obtained.

Alcohol derivatives of p-nitrophenylacetic acid. One gram of *p*-nitrophenylacetyl chloride was treated with 6 to 8 drops of the alcohol, and heated in boiling water for 15 minutes. The mixture was diluted with 10 ml. of distilled water and cooled in an ice-bath to precipitate the ester. The solid esters were washed and recrystallized from alcohol-water mixtures. Liquid esters were extracted and purified by distillation. Larger quantities of liquid esters were prepared by refluxing 0.05 mole of *p*-nitrophenylacetic acid (9 g.) with 0.1 to 0.6 mole of the alcohol in the presence of 0.5 ml. of concentrated sulfuric acid.

Table I summarizes the data on the alkyl esters of *p*-nitrophenylacetic acid. The equivalent weights were determined by potentiometric titration after alkaline hydrolysis, and the percentages of nitrogen by the micro-Kjeldahl method.

Ether derivatives of p-nitrophenylacetic acid. The *p*-nitrophenylacetyl derivatives of diethyl ether and of dipropyl ether were prepared after the method of Underwood, Baril, and Toone (1), using 4 g. of *p*-nitrophenylacetyl chloride, 10 ml. of the ether, and 0.2 g. of anhydrous zinc chloride. The derivatives were the ethyl and propyl esters of *p*-nitrophenylacetic acid.

The method gives the same esters with ethers as with the corresponding alcohols, but is not suitable for mixed ethers.

Phenol derivatives of p-nitrophenylacetic acid. In a test tube 1.5 g. of the *p*-nitrophenylacetyl chloride and 0.25 g. of the phenol were heated together on a water-bath for twenty

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minutes at 100°. The mixture was poured into 200 ml. of cold water and stirred. The precipitate was washed and recrystallized from alcohol.

TABLE I

ALKYL ESTERS OF *p*-NITROPHENYLACETIC ACID

ESTER	B.P./5 mm., °C	M. ., °C	$d_{4°}^{28°}$	$n_D^{20°}$	EQUIVALENT WT.		PER CENT N	
					Theor.	Found	Theor.	Found
Methyl		52.4–53.3			195	197	7.18	7.12
Ethyl		62.8–63.3			209	215	6.70	6.67
n-Propyl		36.5–37.5			223	227	6.28	6.34
Isopropyl		33.9–34.7			223	220	6.28	6.28
n-Butyl	158–160	15.8–16.4	1.135	1.5154	237	246		
Isobutyl	168–169	10.0–13.2		1.5138	237	232		
Sec.-Butyl	162–164	−12 to −11		1.5178	237	242		
n-Amyl	176–178	3.8–4.6	1.107	1.5107	251	254		
n-Hexyl	186–189	5.8–6.4	1.083	1.5077	265	275		
n-Heptyl	208–211	19.2–20.4	1.066	1.5038	279	278		
n-Octyl		27.0–28.2	1.060	1.5028	293	290		
Benzyl		90.7–91.8					5.17	5.14

TABLE II

PHENOL DERIVATIVES OF *p*-NITROPHENYLACETIC ACID

DERIVATIVES	M.P., °C	PER CENT NITROGEN	
		Calculated	Found
Phenol	90.5– 91.2	5.45	5.59
o-Cresol	71.5– 72.3	5.17	5.21
m-Cresol	60.2– 61.2	5.17	5.13
p-Cresol	80.5– 81.6	5.17	5.21
Thymol	54.7– 55.2	4.47	4.53
α-Naphthol	144.6–145.2	4.56	4.53
β-Naphthol	125.4–126.4	4.56	4.62
4-Hydroxy-1,3-dimethylbenzene	99.9–101.1	4.91	4.85
2-Hydroxy-1,4-dimethylbenzene	101.0–101.4	4.91	4.98
4-Hydroxy-1,2-dimethylbenzene	98.2– 98.9	4.91	5.05
2-Hydroxy-1,3-dimethylbenzene	105.9–106.6	4.91	4.87
o-Dihydroxybenzene	141.4–142.9	6.43	6.40
m-Dihydroxybenzene	149.0–151.0	6.43	6.45
p-Dihydroxybenzene	245.0–249.0	6.43	6.50
Guaiacol	107.1–107.8	4.88	4.87

In the case of dihydric phenols, the di-ester was obtained if an excess of *p*-nitrophenylacetyl chloride was used, but it was contaminated by a small amount of the mono-ester and was purified only after repeated recrystallization.

Amine derivatives of p-nitrophenylacetic acid. A mixture of 0.01 mole of *p*-nitrophenylacetyl chloride and 0.02 mole of amine was melted together and kept liquid in a bath for about 20 minutes. The mixture was poured into 50 ml. of distilled water and stirred. The solid, after washing, was recrystallized from alcohol. Color was removed with charcoal.

TABLE III

AMINE DERIVATIVES OF *p*-NITROPHENYLACETIC ACID

DERIVATIVE	M.P., °C	PER CENT NITROGEN	
		Calculated	Found
Aniline	211.7–213.2	10.93	10.72
o-Toluidine	207.8–208.8	10.37	10.14
m-Toluidine	167.8–168.2	10.37	10.36
p-Toluidine	208.3–210.0	10.37	10.26
o-Chloroaniline	216.8–218.8	9.65	9.68
m-Chloroaniline	162.2–163.2	9.65	9.59
p-Chloroaniline	231.2–232.7	9.65	9.58
m-Nitroaniline	186.6–187.6	13.98	13.48
p-Nitroaniline	248.0–250.0	13.98	13.49
α-Naphthylamine	225.4–226.9	9.15	8.93
β-Naphthylamine	236.6–239.1	9.15	9.04
Ethylenediamine	110.1–111.7	14.52	14.42
o-Phenylenediamine	255.7–257.1	12.90	12.60
Isoamylamine	108.1–110.6	11.16	11.00
4-Amino-1,3-dimethylbenzene	203.4–204.4	9.83	9.84
Benzylamine	185.0–186.2	10.37	10.33
p-Benzylaniline	86.0– 86.8	8.09	8.09
p-Bromoaniline	228.7–231.2	8.37	8.32

SUMMARY

The preparation and properties of 27 esters and 18 amides of *p*-nitrophenylacetic acid has been described.

Most of the alkyl esters are liquids at room temperature but it has been shown that the aryl esters and amides are easily prepared solids with sharp melting points, not too high, and not too close together for easy identification.

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REFERENCE

(1) UNDERWOOD, BARIL, AND TOONE, *J. Am. Chem. Soc.*, **52**, 4087 (1930).