proximately 2 moles of isopropylmagnesium chloride was allowed to react with 0.5 mole of α-phenylbutyric acid. To the mixture there was added 1.6 moles of cyclohexanone. The yield was 62%; m.p. 125–128° after recrystallization from benzene-petroleum ether (60–70°).

Anal. Calcd. for $C_{16}H_{22}O_3$: C, 73.26; H, 8.45; neut. equiv., 262.2. Found: C, 73.12; H, 8.68; neut. equiv., 261.8.

The following esters were obtained by the use of diazomethane.

Methyl α-phenyl-α-(1-hydroxycyclohexyl)acetate. The yield was 81%; m.p. 84° after recrystallization from petroleum ether (60–70°).

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.29; H, 8.08.

Methyl α-phenyl-α-(1-hydroxy-4-methylcyclohexyl)acetate. The yield was 77%; m.p. 113–114° after recrystallization from petroleum ether (90–100°).

Anal. Calcd. for $C_{16}H_{22}O_3$: C, 73.26; H, 8.45. Found: C, 73.60; H, 8.89.

Methyl α-phenyl-α-(1-hydroxycyclooctyl)acetate. The ester was obtained in 74% yield; m.p. 93–95° after recrystallization from petroleum ether (60–70°).

Anal. Calcd. for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.85; H, 8.53.

The following hydrazides were prepared by heating the required methyl esters with a fourfold excess of hydrazine monohydrate on a steam bath until a homogeneous solution was obtained.

α-Phenyl-β-hydroxypropionhydrazide. The yield was 81%; m.p. 169–171° after recrystallization from water.

Anal. Calcd. for $C_9H_{12}O_2N_2$: C, 59.98; H, 6.71. Found: C, 60.14; H, 6.75.

α-Cyclohexyl-β-hydroxypropionhydrazide. This compound melted at 213–214° (dec.) after recrystallization from water; yield 60%.

Anal. Calcd. for $C_9H_{18}O_2N_2$: C, 58.04; H, 9.74. Found: C, 58.33; H, 9.76.

Base-catalyzed cleavage. The required acid (0.02 mole) was dissolved in 50 cc. of aqueous sodium hydroxide solution which contained 1.6 g. (0.04 mole) of sodium hydroxide, the solution was refluxed for 16 hours and then extracted with ether (nonacidic fraction). The alkaline solution was then acidified and the precipitate (acidic fraction) was filtered; ether extraction of the filtrate yielded an additional amount of acidic fraction.

The acidic fraction was composed of the acid formed by cleavage, the original acid, or a mixture of the two acids. Each acid was characterized by a mixed melting point and by a neutralization equivalent.

In those instances in which cleavage occurred, the carbonyl compound, found in the nonacidic fraction, was identified by its boiling point and/or the melting point of a known derivative.

COLLEGE OF PHARMACY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICH.

Aromatic Nucleophilic Substitution Reaction in Qualitative Organic Chemistry: The Reaction of 2,4-Dinitrofluorobenzene with Phenols

JOHN D. REINHEIMER, JAMES P. DOUGLASS,[1]
HOWARD LEISTER,[1] AND MARTHA B. VOELKEL[1]

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The preparation of derivatives of phenols, for identification purposes, by reactions of the corresponding sodium phenoxides with 2,4-dinitrochlorobenzene is described or mentioned in several texts and laboratory manuals[2–6] for organic qualitative analysis. The procedure, based upon work of Bost and Nicholson,[7] appears to be simple but the products obtained are frequently oils rather than crystalline solids. The 2,4-dinitrophenyl ether has therefore not found favor as a derivative in the identification of phenols.

The reason for the formation of the oils lies in the choice of solvent for this reaction. In the alcohol water solvent used, there are generally three nucleophilic ions present, hydroxide, phenoxide, and ethoxide.[8] Since the nucleophilic attacking power of these ions is in the order ethoxide > phenoxide > hydroxide,[8] one generally obtains two ethers, 2,4-dinitrophenetole as well as the expected substituted diphenyl ether. Any phenol formed by the reaction with an excess of hydroxide ion is readily removed from the desired derivative by washing with dilute base. However, the two ethers cannot be separated by this simple washing, so that an oil results. If Bost and Nicholson's procedure is carefully followed so that equimolar amounts of NaOH, phenol, and 2,4-dinitrochlorobenzene are used, little ethoxide ion is present and only one ether, a crystalline derivative, is obtained. A more promising method of obtaining crystalline derivatives is to use a solvent which does not give nucleophilic ions by reacting with hydroxide ion, or to use an aqueous solvent and remove the 2,4-dinitrophenol which is the by-product.

The change in solvent to water was not practical with the solid 2,4-dinitrochlorobenzene for the heterogeneous reaction at room temperature is slow. However, the liquid, 2,4-dinitrofluorobenzene, contains the more highly activated fluorine atom,[9] so that a Schotten-Bauman reaction at room temperature was possible. Fifteen ml. of 5% NaOH (an excess), 0.005 mole of phenol, and 0.005 mole of 2,4-

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(1) From the independent study theses submitted to the College of Wooster in partial fulfillment of the degree of Bachelor of Arts, of James P. Douglas, 1954, Howard Leister, 1955, and Martha B. Voelkel, 1956.

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TABLE I

New 2,4-Dinitrophenyl Ethers of Phenols

Phenol Used	Derivative[a] M.P., ° C.	Yield, %	Formula	Analytical Data[b] % N		% C		% H	
				Obsvd.	Calcd.	Obsvd.	Calcd.	Obsvd.	Calcd.
2,4-Dimethylphenol	101.5–102.5	92	$C_{14}H_{12}O_3N_2$	9.50	9.72	58.2	58.3	4.38	4.20
Resorcinol monomethyl ether	87–88.5	95	$C_{13}H_{10}O_6N_2$	9.78	9.65	54.0	53.8	3.41	3.47
Resorcinol monoethyl ether	113.5–115.0	92	$C_{14}H_{12}O_6N_2$	9.20	9.21	55.5	55.3	3.84	3.98
o-Hydroxy diphenyl	113.0–114.0	90	$C_{18}H_{12}O_5N_2$	8.45	8.33	64.5	64.3	3.60	3.60
3,4-Dimethylphenol	105.0–105.5	96	$C_{14}H_{12}O_5N_2$	9.90	9.72	58.4	58.3	4.03	4.20
o-Cyclohexylphenol	76.0–77.0	94	$C_{18}H_{18}O_5N_2$	8.25	8.18	63.5	63.2	5.57	5.30
3,5-Dimethylphenol	100.0–100.5	95	$C_{14}H_{12}O_5N_2$	9.86	9.71	58.4	58.3	4.24	4.20
8-Hydroxy quinoline	165–165.5 d.p.	90	$C_{15}H_9O_5N_3$	13.40	13.50	58.3	57.9	3.21	2.91
p-Benzylphenol	74.5–76.0	96	$C_{19}H_{14}O_5N_2$	7.83	8.00	65.1	65.0	4.10	4.03
p-*t*-Butylphenol	108.5–110.0	90	$C_{16}H_{16}O_5N_2$	9.04	8.86	61.1	60.8	4.98	5.10
Catechol	136.0–138.0	72	$C_{18}H_{10}O_{10}N_4$	12.6	12.7	48.8	48.9	2.36	2.28
Orcinol	152.7–153.9	92	$C_{19}H_{12}O_{10}N_4$	11.1	12.3	49.9	50.0	3.07	2.63
Hydroquinone monobenzyl ether	129.0–130.0	95	$C_{19}H_{14}O_6N_2$	7.42	7.65	62.6	62.3	3.71	3.85
p-Cyclohexylphenol	100.0–101.0	94	$C_{18}H_{18}O_5N_2$	8.14	8.18	63.5	63.2	5.20	5.30

[a] All melting points taken with a calibrated thermometer. [b] Analyses by C. Weiler and F. B. Strauss.

dinitrofluorobenzene were shaken for 5 min. in a glass-stoppered bottle. Crystalline precipitates which gave literature melting points after one or two recrystallizations were obtained. The drawback with this simple, rapid procedure was that the more acidic phenols gave low yields. This procedure was not applied to dihydric phenols.

The second change in solvent used was to replace alcohol with acetone, and to use triethyl amine as the reaction catalyst. This procedure, using 2,4-dinitrofluorobenzene, gave high yields (80–95%) with most monohydric phenols and good yields (60–80%) with the dihydric phenols used. The crude products crystallized immediately when the acetone was removed. Those phenols whose derivatives crystallized more slowly were: *p*-cyclohexyl phenol, 15 min.; resorcinolmonomethyl ether and *o*-cyclohexylphenol, 1 hr.; thymol, overnight; while carvacrol and pyrogallol did not crystallize. It should be noted that the last phenols used were of technical or practical grades. The reaction procedure was used on 41 phenols with satisfactory results in 38 cases. The data for the reaction is summarized in Tables I and II.

The substituted 2,4-dinitrophenyl ethers are recommended as good derivatives of phenols since: (1) the reagent is available, (2) the yield of derivative is high and the procedure is simple, (3) the melting points of the ethers formed are high, (4) phenols which melt at nearly the same temperatures give derivatives which have different melting points, (5) the ethers are pure so that constant melting points are obtained after one or two recrystallizations.

TABLE II

2,4-Dinitrophenyl Ethers of Phenols

Phenol Used	Derivative, M.P., °C. Obsvd.	Lit., ref.	No Recryst.	Yield, %
m-Cresol	73–74	74[4]	2	. . .
o-Chlorophenol	99–100	100[4]	2	79
o-Bromophenol	87–88	89[4]	1	82
o-Cresol	88–89	90[4]	2	94
m-Chlorophenol	73.5–75.5	75[3]	2	93
p-Cresol	93–93.5	93[4]	2	71
Guaicol	92.5–94.0	97[3]	3	100
2,4-Dibromophenol	135–135.5	135[4]	1	76
p-Chlorophenol	125–125.5	126[4]	2	68
Phenol	70.0–71.5	69[4]	2	62
2,4-Dichlorophenol	118–118.5	119[3]	2	81
o-Iodophenol	93.5–94.0	95[4]	1	88
o-Nitrophenol	139–140.5	142[4]	2	82
Eugenol	114–115.5	115[4]	2	94
Thymol	64.5–66.5	67[3]	2	84
Hydroquinone monomethyl ether	111–112.0	110[10]	2	94
p-Bromophenol	140–141.5	141[4]	2	89
2,4,6-Trichlorophenol	134.5–135	135[4]	2	75
α-Naphthol	127–128.0	128[4]	2	80
m-Nitrophenol	135–135.5	138[4]	2	95
2,4,6-Tribromophenol	137.5–138	138[3]	2	75
p-Nitrophenol	118–119.0	120[3]	2	90
Resorcinol	191–192.0	194[4]	1	60
β-Naphthol	94–94.5	95[4]	2	94
Hydroquinone	243–246 (d.p.)	240[11]	. . .	84
Isoeugenol	127.5–128	130[4]	2	97

EXPERIMENTAL

Whalley[12] used a similar procedure for the reaction of alcohols and 2,4-dinitrofluorobenzene. He used no solvent

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(10) E. T. Burrows, J. C. Clayton, B. E. Hems, A. G. Long, *J. Chem. Soc.*, Suppl. Issue, 1, 198 (1949).

(11) Beilstein, "*Handbuch der Organischen Chemie*," 4th ed., Julius Springer, Berlin, 1923, Vol. 6, 845.

(12) W. B. Whalley, *J. Chem. Soc.*, 2241 (1950).

for liquid alcohols, but ether or benzene was used to dissolve solid alcohols.

Procedure. The phenol, 0.005 mole (±10 mg.) was dissolved in 5 ml. of acetone, and 0.50 ml. of triethyl amine was pipetted into the reaction flask. The 2,4-dinitrofluorobenzene (0.005 mole, ± 10 mg.) was dissolved in 5 ml. of acetone. The two solutions were mixed at room temperature, then refluxed for 0.5 hr. in a water bath. The acetone was removed by evaporation, followed by the addition of 10 ml. of 5% HCl. The derivative crystallized and was filtered and washed several times with water. The precipitate was then ground under 15 ml. of 5% NaOH in a mortar, filtered, and washed several times with water. The crude product was dried for 24 hr. in a vacuum desiccator over "drierite". The best solvent for recrystallization of derivatives melting below 120° was ethanol or ethanol-water, while acetic acid or acetic acid–water was preferred for those melting above 120°.

The reaction procedures failed with 2,4-dinitrophenol because of low yield, while pyrogallol and carvacrol gave oils which did not crystallize.

The samples of phenols were either technical, practical, or purified grades. The technical and practical grades were not further purified before use.

SEVERANCE CHEMISTRY LABORATORY
THE COLLEGE OF WOOSTER
WOOSTER, OHIO

Reactions of *O*-Benzoyl-9-*aci*-nitrofluorene[1]

EMIL H. WHITE[2] AND WILLIAM J. CONSIDINE

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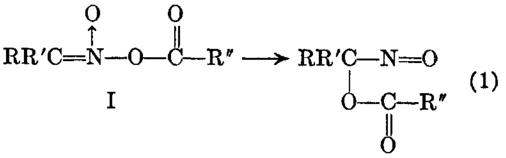
Salts of secondary alkyl nitroparaffins react with acid chlorides to yield the products shown in equation one.[3] In the alkyl series, the nitronic anhydrides I are relatively unstable and at temperatures well below 0°[3] they rearrange to the nitroso derivatives II. The nitronic anhydrides of more highly conjugated nitroparaffins are relatively stable, on the other hand, presumably because a rearrangement to II would result in a decrease in resonance energy. Two compounds of this type are known.[4]

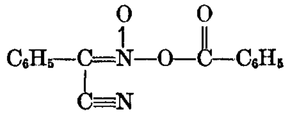
$$RR'CNO_2^- + R''COCl \longrightarrow$$



$$RR'C=\overset{\substack{O\\ \uparrow}}{N}-O-\overset{\substack{O\\ \|}}{C}-R'' \longrightarrow RR'\underset{\substack{|\\ O-\underset{\substack{\|\\ O}}{C}-R''}}{C}-N=O \qquad (1)$$

I II

The first, *O*-benzoyl-*aci*-nitrophenylacetonitrile (III), was synthesized by Thurston and Shriner[5]



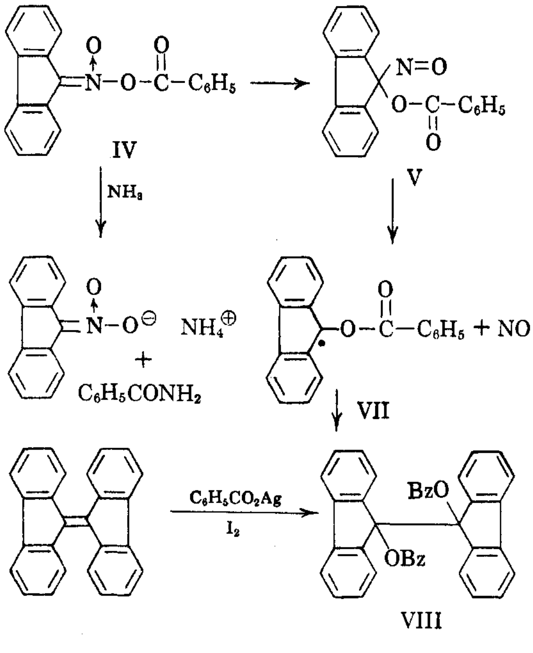
$$C_6H_5-\underset{\substack{|\\ C\equiv N}}{C}=\overset{\substack{O\\ \uparrow}}{N}-O-\overset{\substack{O\\ \|}}{C}-C_6H_5$$

III

and its structure was proved by the same authors. The second, *O*-benzoyl-9-*aci*-nitrofluorene (IV), was first synthesized by Nenitzescu and Isacescu.[6] In this paper we present evidence for its structure and list several of its reactions.

O-Benzoyl-9-*aci*-nitrofluorene was prepared by the reaction of benzoyl chloride with sodium 9-fluorenenitronate. The infrared spectrum of IV had intense absorption bands at 5.67 and 6.16 μ; this set of bands in the double bond stretching region of the spectrum is characteristic of nitronic anhydrides.[3] The isolation of benzamide and ammonium 9-fluorenenitronate from the ammonolysis of IV further confirms the structure assigned.

When a solution of IV in carbon tetrachloride was refluxed, nitric oxide was evolved and 9,9'-dibenzoyloxy-9,9'-bifluorenyl (VIII) was formed. The first step in this reaction is probably the formation of the nitroso compound V, since this is the sequence that has been established for the corresponding alkyl nitronic anhydrides.[3] Homolysis of the carbon-nitrogen bond of V would yield nitric oxide and the relatively stable radical VII, the dimerization of which would yield VIII. The last



VIII

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(1) Taken in part from a thesis submitted by William J. Considine to the faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree. Presented before the Division of Organic Chemistry at the 130th Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, New Jersey, September 21, 1956.

(2) Author to whom inquiries are to be sent (The Johns Hopkins University, Baltimore 18, Md.).

(3) E. H. White and W. J. Considine, *J. Am. Chem. Soc.*, in press.

(4) A compound isolated from the reaction of benzoyl chloride with the potassium salt of 3-nitroindene may be a third example [W. Wislicenus and K. Pfeilsticker, *Ann.*, **463**, 40 (1924)]. The authors proposed that the product was 1-benzoyl-3-nitroindene, but in view of the oxygen acylation observed with the related nitrofluorene, the product is probably *O*-benzoyl-3-*aci*-nitroindene.

(5) J. Thurston and R. Shriner, *J. Org. Chem.*, **2**, 183 (1937).

(6) C. D. Nenitzescu and D. A. Isacescu, *Bull. Soc. Chim. Romania*, 14, 53 (1932); *Chem. Abstr.*, **27**, 964 (1934).