Conclusions

1. A number of 2,3-diaryl-1,4-dioxanes have been synthesized for the first time.
2. The reaction of alkylmagnesium halides with 2,3-dichloro-1,4-dioxane produces *p*-dioxene, a new compound, of which the structure has been proved.
3. The reactions of *p*-dioxene have been studied.
4. Monochloro-*p*-dioxane has been obtained for the first time, and a mechanism for the chlorination of dioxane proposed.
5. Monophenyl-*p*-dioxane has been prepared.
6. The work is being continued.

Evanston, Illinois Received July 29, 1935

[Contribution from the Chemical Laboratory of the University of North Carolina]

The Identification of Phenols with 2,4-Dinitrochlorobenzene

By R. W. Bost and Frank Nicholson

Although numerous reagents have been proposed for the identification of phenols,[1-5] nevertheless serious objections may be raised against most of them. The method of Koelsch[5] is perhaps the best but many of his derivatives melt so close together that identification is difficult, whereas the *o*- and *p*-nitrophenols were not obtained.

The value of 2,4-dinitrochlorobenzene as a reagent for the identification of mercaptans has been shown in previous communications.[6,7] Since the reactions of mercaptans and phenols are similar in many respects, it seemed desirable to study the usefulness of 2,4-dinitrochlorobenzene as a reagent for phenols. In a few cases 2,4-dinitrophenyl ethers occur in the literature and in such cases the melting points and literature references are given in the table. In cases where discrepancies occur between the melting points of those reported in the literature and of those obtained in our study, analyses were made and herein recorded.

Procedure

0.01 Mole of the phenol is added to 0.01 mole of sodium hydroxide dissolved in 5 cc. of water. The resulting solution of sodium phenolate is added to 0.01 mole of 2,4-dinitrochlorobenzene dissolved in 30 cc. of ethyl alcohol (95%). In some cases with difficultly soluble compounds more alcohol must be added to keep the substance in solution. The solution at this point is always highly colored. In most cases it turns dark red in color; however in some cases it is almost black. The solution is then heated under reflux on a steam-bath until the red color is discharged and a copious precipitate of salt appears. (Usually one-half hour is sufficient.) The reaction mixture is diluted with an equal part of water whereupon the 2,4-dinitrophenyl ether is precipitated, then filtered, washed with water and finally recrystallized from alcohol. As a rule one recrystallization is sufficient.

Discussion of Results

There are times when a precipitate occurs at the point when the aqueous solution of the phenolate is added to the alcoholic solution of the reagent. This precipitate is not to be confused with the precipitate of salt which appears after heating for some time. It has been shown[8] that 2,4-dinitrochlorobenzene forms addition products with certain phenols, and apparently the precipitate first formed in our work is of such a nature, since it contains both nitrogen and chlorine. Upon heating, it loses chlorine as well as its color, and sodium chloride is precipitated.

The 2,4-dinitrophenyl ethers which were obtained are easily purified, highly crystalline, and possess sharp melting points widely enough separated to ensure identification. An exception is noted only in the case of derivatives of 2,4-dibromophenol and 2,4,6-tribromophenol, which have the same melting point. However, in this case, the original phenols melt 56° apart. With the exception of the derivatives of thymol, carvacrol and hexylresorcinol, all are precipitated from the reaction mixture as solids. The reagent is superior to the isocyanates in that the presence of water in the phenol does not interfere with the formation of the derivative. The melting points are high enough so that very few are obtained as oils, again indicating the superiority of the reagent. 2,4-Dinitrochlorobenzene is more stable than both

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[1] Herzog, *Ber.*, **40**, 1831 (1907).

[2] Reid, This Journal, **39**, 304 (1917); Lyman and Reid, *ibid.*, **42**, 615 (1920).

[3] Brown and Kramers, *J. Am. Pharm. Assoc.*, **11**, 607 (1922).

[4] French and Wertel, This Journal, **48**, 1736 (1926).

[5] Koelsch, *ibid.*, **53**. 304 (1931).

[6] Bost, Turner and Norton, *ibid.*, **54**, 1985 (1932).

[7] Bost, Turner and Conn, *ibid.*, **55**, 4456 (1933).

[8] Buehler, Hisey and Wood, *ibid.*, **52**, 1939 (1930).

2,4-DINITROPHENYL ETHERS

Phenol	Color	Crystal form	M. p., °C. Obsd.	M. p., °C. Lit.	Analyses, % N Calcd.	Analyses, % N Found
Phenol[a]	Faint yellow	Fine needles	69	70	10.76	10.62
o-Cresol	Faint yellow	Prisms	90		10.22	10.03
m-Cresol	Pale greenish-yellow	Prismatic needles	74		10.22	10.45
p-Cresol[b]	Faint yellow	Flat needles	93.5	93	10.22	10.08
Thymol	Faint yellow	Prismatic needles	67		8.85	8.57
Guaiacol	Faint yellow	Prismatic needles	97		9.65	9.40
α-Naphthol	Pale yellow	Very fine needles	128		9.03	9.12
β-Naphthol[c]	Colorless	Hair-like needles	95	95	9.03	8.93
p-Hydroxydiphenyl	Faint greenish-yellow	Needles	118		8.33	7.92
Resorcinol[d]	Buff	Granular	194	184	12.67	13.00
Eugenol[e]	Yellow	Very fine needles		114–115		
Isoeugenol[e]	Sulfur yellow	Needles	130	129–130		
Vanillin[e]	Colorless	Needles		131		
o-Nitrophenol[f]	Buff	Granular	142	119	13.81	14.00
m-Nitrophenol[g]	Light yellow	Prismatic needles	138	136	13.81	13.81
p-Nitrophenol	Light yellow	Fine needles	120	114	13.81	14.08
2-Chloro-5-hydroxytoluene	Faint greenish-yellow	Needles	112		9.07	8.80
o-Iodophenol	Faint yellow	Small plates	95		7.22	7.01
					Analyses, % halogen	
o-Chlorophenol	Faint greenish-yellow	Needles	99		12.04	11.85
m-Chlorophenol	Faint yellow	Needles	75		12.04	11.90
p-Chlorophenol	Light yellow	Small needles	126		12.04	12.11
2,4-Dichlorophenol	Faint yellow	Very short needles	119		21.87	21.72
2,4,6-Trichlorophenol	Pale yellow	Rhombic crystals	136		29.26	29.40
o-Bromophenol	Faint greenish-yellow	Small prisms	89		23.58	23.20
p-Bromophenol	Faint yellow	Fine needles	141		23.58	23.70
2,4-Dibromophenol	Pale yellow	Fine needles	135		38.28	38.48
2,4,6-Tribromophenol	Faint greenish-yellow	Long needles	135		48.26	48.10
p-Iodophenol[h]	Light yellow	Needles		156		

[a] Willgerodt, *Ber.*, **12**, 764 (1879); Cook, THIS JOURNAL, **32**, 1291 (1910). [b] Cook, *ibid.*, **32**, 1289 (1910). [c] Ernst, *Ber.*, **23**, 3429 (1890). [d] Nietzki and Schundelen, *ibid.*, **24**, 3586 (1891). [e] Einhorn and Frye, *ibid.*, **27**, 2457 (1894). [f] Willgerodt and Huetlin, *ibid.*, **17**, 1765 (1884). [g] German Patent 28,053 (1914); *Chem. Zentr.*, **86**, **I**, 74 (1915). [h] Willgerodt and Weigand, *Ber.*, **42**, 3764 (1909).

the isocyanates and the nitroacyl halides and possesses an advantage in this respect. The procedure is simple and requires no special degree of skill. Good results may be obtained in the hands of a beginner.

Summary

1. 2,4-Dinitrochlorobenzene reacts with phenols forming highly crystalline stable solids, easily purified, and possessing sharp melting points.

2. The procedure is simple and requires no unusual of technique.

3. Derivatives of twenty-eight phenols are given.

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RECEIVED AUGUST 12, 1935