CHARACTERIZATION OF DINITROALKYL PHENOLS[1]

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ABSTRACT

Amine salts of dinitroalkyl phenols have been suggested as herbicides and insecticides. A selection of such amine salts was examined as to their suitability for characterizing dinitroalkyl phenols. The following new salts are described: the piperidine, morpholine, and cyclohexylamine salts of each of 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol, 2,6-dinitro-4-methylphenol, 4,6-dinitro-2-isopropylphenol, 2,6-dinitro-4-isopropylphenol, 4,6-dinitro-2-(*sec*-butyl)-phenol, 2,6-dinitro-4-(*tert*-butyl)-phenol, and 2,6-dinitro-4-(*tert*-amyl)-phenol. In addition, the preparation of 4,6-dinitro-2-isopropylphenol and 2,6-dinitro-4-isopropylphenol does not appear to have been previously described. The use of these salts, and similar ones with other amines, is recommended for the preparation of crystalline derivatives of dinitrophenols.

INTRODUCTION

Dinitroalkyl phenols have been shown to be effective as insecticides (2, 3) and selective weed killers (6). In connection with a study of such compounds as herbicides a selection of dinitroalkyl phenols has been prepared. The amine salts of these dinitroalkyl phenols were prepared and were found to be excellent derivatives for the characterization of these compounds.

The reported method of preparing such amine salts (4) (sodium salt of phenol + amine hydrochloride) has given in our hands crystalline mixtures of the phenol and the desired salt. The discrepancies between the reported melting points of some of these salts (4) and those described here are attributed to this cause. Bell's melting point (1) of 171° C. for piperidinium 2,4-dinitrophenoxide agrees well with our figure of 172° C.

EXPERIMENTAL

The phenols selected for nitration were 2-and 4-methylphenol, 2- and 4-isopropylphenol, 4-(*tert*-butyl)-phenol, and 4-(*tert*-amyl)-phenol. The latter two were prepared by the method of Putnam (5) and the remainder, together with 2,4-dinitrophenol and 2,4-dinitro-2-(*sec*-butyl)-phenol, were obtained as commercial products.

4,6-Dinitro-2-isopropylphenol

2-Isopropylphenol (25 gm.) was dissolved in glacial acetic acid (60 cc.) and this solution was added dropwise, with constant stirring, to a solution of nitric acid (40 cc., $d = 1.5$) and glacial acetic acid (75 cc.) which had been cooled to $-15°$ C. in a stainless steel beaker. The addition took about three quarters of an hour, after which time the mixture was allowed to come slowly to room temperature over a period of one and a half hours. The solution was kept at room temperature for one half hour and then poured onto cracked ice.

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The yellow precipitate which resulted was filtered off, dissolved in chloroform, and carefully washed to remove all trace of acid. The chloroform solution was then dried over magnesium sulphate and after removal of the solvent, the residual oil was distilled under high vacuum to give the 4,6-dinitro-2-isopropylphenol as a clear yellow oil boiling at 132° C. (0.15 mm.). The oil solidified on cooling and on recrystallization from ethanol gave a yellow solid, m.p. 54° C., yield, 65%.

In a similar manner all the other dinitrophenols were prepared and the results shown in Table I.

TABLE I

DINITROALKYL PHENOLS

Phenol	M.p., °C.	Yield, %
2,4-Dinitro	114	*
4,6-Dinitro-2-methyl	86	67
2,6-Dinitro-4-methyl	82	60
4,6-Dinitro-2-isopropyl	54	66
2,6-Dinitro-4-isopropyl	68	65
4,6-Dinitro-2-(*sec*-butyl)	42	*
2,6-Dinitro-4-(*tert*-butyl)	95	80
2,6-Dinitro-4-(*tert*-amyl)	66	50

**Commercial sample.*

Piperidine Salt of 4,6-Dinitro-2-methylphenol

4,6-Dinitro-2-methylphenol (0.5 gm.) was placed in an Erlenmeyer flask and a small excess of piperidine (0.75 gm.) was added. Benzene (10 cc.) was then added and the mixture gently warmed for five minutes. Petroleum ether (25 cc., 30–60° C.) was then added when the salt crystallized as colored flakes. The precipitate was filtered off, washed with petroleum ether, and recrystallized from a mixture of benzene (five parts), ethanol (one part), and petroleum ether (two parts).

In a similar way the piperidine, morpholine, and cyclohexylamine salts of all the dinitrophenols were prepared and these are listed in Tables II, III, and IV.

TABLE II

PIPERIDINE SALTS OF DINITROALKYL PHENOLS

Phenol	Formula	M.p., °C.	Nitrogen, %		Description
			Calc.	Found	
2,4-Dinitro	$C_{11}H_{15}N_3O_5$	172*	15.61	15.54	Orange needles
4,6-Dinitro-2-methyl	$C_{12}H_{17}N_3O_5$	157	14.83	14.93	Yellow needles
2,6-Dinitro-4-methyl	$C_{12}H_{17}N_3O_5$	195	14.83	14.86	Orange needles
4,6-Dinitro-2-isopropyl	$C_{14}H_{21}N_3O_5$	204	13.50	13.52	Yellow needles
2,6-Dinitro-4-isopropyl	$C_{14}H_{21}N_3O_5$	218	13.50	13.44	Orange plates
4,6-Dinitro-2-(*sec*-butyl)	$C_{15}H_{23}N_3O_5$	154	12.92	12.93	Yellow needles
2,6-Dinitro-4-(*tert*-butyl)	$C_{15}H_{23}N_3O_5$	232	12.92	12.92	Orange needles
2,6-Dinitro-4-(*tert*-amyl)	$C_{16}H_{25}N_3O_5$	198	12.39	12.54	Orange plates

* *Ref.(1).*

TABLE III

MORPHOLINE SALTS OF DINITROALKYL PHENOLS

Phenol	Formula	M.p., °C.	Nitrogen, %		Description
			Calc.	Found	
2,4-Dinitro	$C_{10}H_{13}N_3O_6$	169	15.49	15.36	Yellow needles
4,6-Dinitro-2-methyl	$C_{11}H_{15}N_3O_6$	189	14.74	14.76	Red plates
2,6-Dinitro-4-methyl	$C_{11}H_{15}N_3O_6$	217	14.74	14.73	Orange plates
4,6-Dinitro-2-isopropyl	$C_{13}H_{19}N_3O_6$	204	13.42	13.54	Orange needles
2,6-Dinitro-4-isopropyl	$C_{13}H_{19}N_3O_6$	216	13.42	13.55	Yellow flakes
4,6-Dinitro-2-(*sec*-butyl)	$C_{14}H_{21}N_3O_6$	147	12.84	12.89	Red needles
2,6-Dinitro-4-(*tert*-butyl)	$C_{14}H_{21}N_3O_6$	232	12.84	12.92	Orange needles
2,6-Dinitro-4-(*tert*-amyl)	$C_{15}H_{23}N_3O_6$	174	12.32	12.22	Yellow plates

TABLE IV

CYCLOHEXYLAMINE SALTS OF DINITROALKYL PHENOLS

Phenol	Formula	M.p., °C.	Nitrogen, %		Description
			Calc.	Found	
2,4-Dinitro	$C_{12}H_{17}N_3O_5$	158	14.83	14.85	Yellow needles
4,6-Dinitro-2-methyl	$C_{13}H_{19}N_3O_5$	171	14.13	14.23	Yellow needles
2,6-Dinitro-4-methyl	$C_{13}H_{19}N_3O_5$	193	14.13	14.16	Orange needles
4,6-Dinitro-2-isopropyl	$C_{15}H_{23}N_3O_5$	207	12.92	12.95	Yellow needles
2,6-Dinitro-4-isopropyl	$C_{15}H_{23}N_3O_5$	213	12.92	12.99	Orange needles
4,6-Dinitro-2-(*sec*-butyl)	$C_{16}H_{25}N_3O_5$	210	12.38	12.44	Yellow needles
2,6-Dinitro-4-(*tert*-butyl)	$C_{16}H_{25}N_3O_5$	230	12.38	12.39	Orange needles
2,6-Dinitro-4-(*tert*-amyl)	$C_{17}H_{27}N_3O_5$	219	11.90	11.93	Yellow needles

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