TABLE I

Acyl chloride	1,2-Dihydroquinaldonitriles									Hydrolysis with H_2SO_4, *N*	Aldehyde		
	Yield, %	% Alc. solvent	M. p., °C.	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found		Yield, %	*p*-Nitrophenylhydrazone M. p., °C.	*p*-Nitrophenylhydrazone Yield, %
Acetyl-	74	50	96 - 97	72.7	72.8	5.04	5.02	14.1	14.0	5, dist.	Not isol.	127.5–128	99
Propionyl-[a]	10	50	49 - 50	73.6	73.7	5.66	5.82	13.2	13.3	5, dist.	Not isol.	128–129	92
Butyryl-	64	70	97.5–98	74.3	74.2	6.20	6.20	12.4	12.6	5, dist.	Not isol.	90– 91	97
Isobutyryl-[a]	28	80	129 –129.5	74.3	74.3	6.20	6.21	12.4	12.5	5, dist.	Not isol.	131.5–132	98
n-Valeryl-[b]											Not isol.	96–98[c]	42[c]
Isovaleryl-	64	60	90 - 90.5	75.0	75.2	6.66	6.60	11.6	11.7	5, st. dist.	Not isol.	122–123[c]	98
2-Methoxybenzoyl-	66	60	164 –164.5	74.5	74.4	4.83	4.90	9.66	9.80	10, st. dist.	97	208	92
4-Methoxybenzoyl-	88	50	120.5–121.5	74.5	74.7	4.83	4.65	9.66	9.64	10, st. dist.	98	162	95
o-Chlorobenzoyl-	80	70	165 –166	69.4	69.2	3.74	3.66	9.53	9.53	10, st. dist.	94	247–248	98
m-Chlorobenzoyl-[a]	28	60 and 90	116 –119	69.4	69.3	3.74	3.67	9.53	9.53	10, st. dist.	96	220	91
p-Chlorobenzoyl-	77	70	140 –143	69.4	69.2	3.74	3.82	9.53	9.53	10, st. dist.	92	219	95
Cinnamoyl-[d]	91	96	154 –155	79.7	80.0	4.89	4.93	9.79	9.80	10, st. dist.	82	169.5–170.5	92
Benzoyl-[d]	96	96	154 –155							10, st. dist.	Not isol.	193–194	98

[a] Direct preparation without isolation of the 1-acyl-1,2-dihydroquinaldonitrile improved the yields as follows: propional 36%, isobutanal 56%, *m*-chlorobenzaldehyde 65%. [b] Intermediary *n*-valeryl-1,2-dihydroquinaldonitrile not isolated. [c] M. p. and yield refer to 2,4-dinitrophenylhydrazone. [d] Previously prepared according to Reissert,[1,3] and checked by mixed m. p.

quinaldonitrile is not easily soluble in ether, it may partially crystallize out during this operation. After evaporation of the ether and crystallization of the residue from a mixture of ethanol and water, the 1-acyl-1,2-dihydroquinaldonitrile was obtained. The percentage of alcohol in the solvent for the recrystallization, melting point, yield and analytical data of the 1-acyl-1,2-dihydroquinaldonitriles are given in the accompanying table, with the corresponding acyl groups.

Hydrolysis.—The hydrolysis of the 1-acyl-1,2-dihydroquinaldonitriles was carried out with 5 to 10 *N* sulfuric acid. Where aldehydes with boiling points below 100° were to be obtained, 0.01 mole of the substance was boiled with 30 cc. of 5 *N* sulfuric acid down to half volume, and the escaping aldehyde precipitated in a solution of *p*-nitrophenylhydrazine (or 2,4-dinitrophenylhydrazine) in 2 *N* hydrochloric acid for quantitative measurement. Aldehydes with boiling points over 100° were obtained in a similar way by steam distillation of 0.01 mole of substance in 10 *N* sulfuric acid and the aldehyde was isolated in the usual way.

Summary

A number of 1-acyl-1,2-dihydroquinaldonitriles were prepared by the interaction of acid chlorides, hydrocyanic acid and 2 moles of quinoline in nonaqueous media. On acid hydrolysis the corresponding aldehydes and quinaldinic acid were obtained in excellent yields. For the purpose of preparing aldehydes, the intermediary 1-acyl-1,2-dihydroquinaldonitriles need not be isolated. The reaction mixture may be steam distilled with sulfuric acid, thus yielding the aldehyde in one operation from the corresponding acid or acid chloride.

TORONTO, CANADA RECEIVED MAY 14, 1941

NOTES

Removal of Acyl Groups

BY RICHARD BALTZLY AND JOHANNES S. BUCK

It has been shown recently, especially by Reichstein,[1] that esters often can be cleaved under much milder alkaline conditions than had generally been supposed. As the authors were interested in compounds stable only in the absence of alkalinity, the generality of a similar exchange reaction with an acid catalyst was examined. The literature gave some indications that such a method was feasible. Thus Fischer[2] reported the formation of α-methyl glucoside when pentaacetylglucose stood for three days in methanolic hydrogen chloride, and Mannich[3] found that acetyl groups were removed from a catechol derivative under similar conditions.

Some esters of acetic and propionic acids were therefore examined, the esters being chosen so that both they and the corresponding alcohols had melting points satisfactory for identification.

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[1] Reichstein and Euw, *Helv. Chim. Acta*, **21**, 1181 (1938).

[2] Fischer, *Ber.*, **26**, 2400 (1893).

[3] Mannich and Hahn, *ibid.*, **44**, 1542 (1911).

Procedure.—One-hundredth mole of ester was dissolved in 35–50 cc. of methanol and the catalyst added. After standing for twenty-four hours at room temperature (sixty hours in the case of α-naphthyl acetate) the solution was evaporated at 25–40° under the vacuum of a good water-pump. The residual alcohol or phenol had the correct melting point and was frequently of exceptional purity. As catalyst, 5 cc. of concentrated hydrochloric acid may be used. However, ethanolic hydrogen chloride is preferable, 0.5 g. of 38% solution (wt./wt.) being effective.

Catechol diacetate, β-naphthyl acetate, pentaerythritol tetraacetate and hydroquinone dipropionate were found to be completely cleaved under very mild conditions. α-Naphthyl acetate was also cleaved but required a longer time. Benzoyl and carbethoxy groups appear to react more slowly.

When low fatty acid esters of relatively nonvolatile alcohols are concerned, the method offers the advantage that all other components of the solution can be removed under reduced pressure, at or near room temperature, permitting the isolation of the product without further manipulation.

From the foregoing it is evident that considerable caution is necessary in working with alcoholic solutions of esters, particularly acetyl compounds, when small amounts of strong acid are present.

BURROUGHS WELLCOME & CO. U. S. A.
EXPERIMENTAL RESEARCH LABORATORIES
TUCKAHOE, N. Y.
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Methylanilines by Demethylation of Dimethylanilines

BY WILLIAM S. EMERSON

Since dimethyl-2,4,6-trisubstituted anilines are readily obtained,[1] they offer a convenient starting point for the preparation of the corresponding monomethyl derivatives. We have found that when three of these compounds are treated with nitrous acid the N-nitroso derivative of the secondary amine is produced in each case in quantitative yield in contrast to dialkylanilines where not all of the active positions are blocked.[2] The nitroso group is easily removed by one of the standard methods employed when secondary amines are purified through this derivative.[3] Since it has been shown that a methyl group is removed less readily with nitrous acid than an ethyl group,[2] this method should be capable of extension to other dialkyl-2,4,6-trisubstituted anilines.

Experimental

N-Nitroso-N-methyl-2,4,6-tribromoaniline.—2,4,6-Tribromoaniline was reductively alkylated with formaldehyde and formic acid by the method of Clark, Gillespie and Weisshaus.[1a] In this way 10 g. (92%) of N,N-dimethyl-2,4,6-tribromoaniline, b. p. 134–138° (15 mm.), was obtained from 10 g. of the primary amine. Its physical properties, which have never been reported, are n^{20}_{D} 1.6244, d^{20}_{20} 1.998, M^{20}_{D} calcd. 64.3, M^{20}_{D} found 63.5. Its perbromide melted at 123–124° (124°).[4]

After 5.5 g. of N,N-dimethyl-2,4,6-tribromoaniline had been dissolved in 30 cc. of concentrated hydrochloric acid and 20 cc. of water, a solution of 7 g. of sodium nitrite in 10 cc. of water was added over a one-half hour period. During the addition the mixture was cooled in ice and shaken occasionally. It was then allowed to stand sixteen hours at room temperature before the N-nitroso-N-methyl-2,4,6-tribromoaniline was collected on a filter, washed with water and dried; yield 5.7 g. (100%) of practically pure material. After two crystallizations from aqueous alcohol an analytical sample melted at 91.5–92.0°.

Anal.[5] Calcd. for $C_7H_5ON_2Br_3$: N, 7.50. Found: N, 7.62.

N-Methyl-2,4,6-tribromoaniline.—When 5.7 g. of the N-nitroso-N-methyl-2,4,6-tribromoaniline was treated with stannous chloride and hydrochloric acid essentially according to the procedure for N-ethyl-*m*-toluidine,[3] 4.5 g. (85%) of N-methyl-2,4,6-tribromoaniline was obtained. It boiled at 178–179° (30 mm.) and melted at 36–37° (39°).[4] Its acetyl derivative melted at 97.5–98.5° (101°)[4] after one crystallization from aqueous alcohol.

N-Nitroso-N-methyl-2,4,6-trichloroaniline.—N,N-Dimethyl-2,4,6-trichloroaniline was prepared from 2,4,6-trichloroaniline by reductive alkylation with formaldehyde and formic acid.[1a] The 10 g. of tertiary amine obtained from 10 g. of the primary represented a yield of 83%. It boiled at 128–138° (20 mm.); n^{20}_{D} 1.5649 (1.5660).[6] The perbromide prepared by Fries' method[4] melted at 112–113°.

Anal. Calcd. for $C_8H_9NCl_3Br_3$: C, 20.6; H, 1.93. Found: C, 20.9; H, 1.93.

Treatment of 7.5 g. of the N,N-dimethyl-2,4,6-trichloroaniline with nitrous acid as described above yielded 8.0 g. (100%) of practically pure N-nitroso-N-methyl-2,4,6-trichloroaniline. An analytical sample melted at 66.5-67.0° after two crystallizations from aqueous alcohol and one from aqueous methyl alcohol.

Anal. Calcd. for $C_7H_5ON_2Cl_3$: N, 11.7. Found: N, 11.5.

N-Methyl-2,4,6-trichloroaniline was prepared by the reduction of 7.5 g. of the nitroso derivative with stannous chloride and hydrochloric acid. The yield of 6 g. (90%)

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[1] (a) Clark, Gillespie and Weisshaus, THIS JOURNAL, **55**, 4571 (1933); (b) Emerson, Neumann and Moundres, *ibid.*, **63**, 972 (1941).

[2] Crowley, Milton, Reade and Todd, *J. Chem. Soc.*, 1286 (1940).

[3] Buck and Ferry, "Organic Syntheses," Vol. 18, 1938, p. 40.

[4] Fries, *Ann.*, **346**, 128 (1906).

[5] The analyses in this paper are microanalyses and were carried out by Mr. L. G. Fauble and Miss Mary S. Kreger.

[6] Emerson, Dorf and Deutschman, THIS JOURNAL, **62**, 2159 (1940).