+93.5° (22°; *c*, 5; abs. $CHCl_3$),[5] spec. rot. +96° (25°; *c*, 1; EtOH; no mutarotation).

The compound crystallized as elongated prisms and was very soluble in chloroform and acetone and was moderately soluble in ether, alcohol and boiling water. It reduced Fehling solution on warming and reduced a neutral solution of copper acetate. In aqueous solution at room temperature it quickly restored the color to Schiff reagent.

Anal. Calcd. for $C_{12}H_{14}O_{11}\ (CH_3CO)_8$: C, 49.56; H, 5.64; CH_3CO, 11.8 cc. 0.1 *N* NaOH per 100 mg. Found: C, 49.49; H, 5.63; CH_3CO, 11.8 cc.

aldehydo-**Maltose Octaacetate Monoethyl Alcoholate.**—This substance was obtained on recrystallization of *aldehydo*-maltose octaacetate from absolute ethanol or on working up the demercaptalation reaction with absolute ethanol in place of ether and petroleum ether. Pure material was obtained on several recrystallizations from absolute ethanol; m. p. 66–67°, spec. rot. +85° (21°; *c*, 5; abs. $CHCl_3$; no mutarotation), spec. rot. +90° (25°; *c*, 1; abs. EtOH; no mutarotation).

The substance was not very stable and slowly decomposed on long standing, with the liberation of alcohol and acetic acid. The product crystallized as long, lustrous needles and was very soluble in chloroform and acetone, moderately so in alcohol and warm ether, and was practically insoluble in water and ligroin. It reduced Fehling solution.

Anal. Calcd. for $C_{12}H_{14}O_{11}(CH_3CO)_8(C_2H_5OH)$: C, 49.7; H, 6.12; OC_2H_5, 6.22; CH_3CO, 11.0 cc. 0.1 *N* NaOH per 100 mg. Found: C, 49.5; H, 6.14; OC_2H_5, 6.16; CH_3CO, 11.0 cc.

aldehydo-**Maltose Oxime Octaacetate.**—*aldehydo*-Maltose octaacetate (4 g.) was dissolved in 400 cc. of boiling water, filtered and a solid mixture of 0.9 g. of hydroxylamine hydrochloride and 1.8 g. of potassium acetate was added to the filtrate. A crystalline product separated on cooling; yield 1.5 g., m. p. 89–92°, spec. rot. +100° ($CHCl_3$). Pure material was obtained on two recrystallizations from water; yield 0.7 g., m. p. 93–94°, spec. rot. +107° (24°; *c*, 3; U. S. P. $CHCl_3$), spec. rot. +100° (24°; *c*, 3; EtOH). Recrystallization of the product from ether or aqueous alcohol did not alter the constants.

The product crystallized as fine rectangular rods and was soluble in chloroform, acetone, alcohol, ether and boiling water. It was insoluble in the hydrocarbon solvents.

Anal. Calcd. for $C_{12}H_{15}O_{11}N(CH_3CO)_8$: N, 2.02; CH_3CO, 11.5 cc. 0.1 *N* NaOH per 100 mg. Found: N, 2.00; CH_3CO,[6] 11.5 cc.

We are indebted to Mr. John Walker (W. P. A. Project 18062) for assistance rendered in the analytical determinations. We also acknowledge assistance rendered by Mr. F. B. Moody.

Summary

1. The synthesis of the first crystalline *aldehydo*-acetate in the disaccharide series, *aldehydo*-maltose octaacetate, is reported.

2. *aldehydo*-Maltose octaacetate forms a crystalline oxime and a crystalline compound containing one mole of ethanol.

3. *aldehydo*-Maltose octaacetate shows no detectable mutarotation in ethanol solution and its ethanol compound shows no detectable mutarotation in chloroform or ethanol solution.

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[5] All rotations are recorded to the D-line of sodium light, 22° is the temperature, *c* is the concentration in g. per 100 cc. soln.

[6] M. L. Wolfrom, M. Konigsberg and S. Soltzberg, THIS JOURNAL, **58**, 490 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Disproportionation in Aryloxymalonic Acid Syntheses

BY JOSEPH B. NIEDERL AND ROSLYN T. ROTH[1]

In the course of the studies of substituted phenylmalonic acids[2,3] studies of various phenoxymalonic acids were undertaken as well. Mono- and di-phenoxymalonic acids, with and without substituents in the phenyl or the malonyl radical, were prepared.

In the preparation of the mono-phenoxymalonic acids from the diethyl mono-bromomalonate by the Williamson synthesis, a "disproportionation" phenomenon was encountered. Thus it was found that the di-phenoxy compounds result in about equal quantities with the monophenoxy products despite the use of equimolar quantities of sodium phenolate and diethyl mono-bromomalonate. On the other hand, no such disproportionation took place when the diethyl mono-chloromalonate was used instead of the bromo compound.

Although the mono- and diphenoxy-malonic acid esters had been prepared previously by Conrad and Brueckner[4] and the mono- and di-*p*-

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[1] The material presented in this paper is taken from Part III of the thesis presented by Roslyn T. Roth to the Faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] J. B. Niederl, R. T. Roth and A. Plentl, THIS JOURNAL, **59**, 1901 (1937).

[3] J. B. Niederl and R. T. Roth, *ibid.*, **60**, 2140 (1938).

[4] M. Conrad and C. A. Brueckner, *Ber.*, **24**, 2993 (1891).

nitrophenoxy malonic acid esters and acids by C. A. Bischoff[5] from the respective mono- and di-bromomalonic acid esters, neither one had reported the simultaneous formation of mono- and di-phenoxy derivatives from the mono-bromo ester. Formation of di-substituted malonic acid esters from equimolecular reactants of the monosodium salt of methyl malonate, or ethyl acetoacetate and mono-bromomalonic acid ester, while mono-substituted malonic acid derivatives were formed using the corresponding mono-chloromalonic acid ester, have previously been reported.[6,7]

While it is simple enough to state the formation of the mono phenoxymalonic acid esters from the respective sodium phenolates and the diethyl mono-bromomalonate (reaction A), interpretation of the disproportionation process (reaction B) is certainly more complicated and might be expressed in its simplest form as follows.

Reaction A

$$\mathrm{ROOC_2CH}\boxed{\mathrm{Br + Na}}\mathrm{OC_6H_4R} \longrightarrow \mathrm{NaBr + (ROOC)_2CH{\cdot}O{\cdot}C_6H_4R}$$

Reaction B

$$\mathrm{2(ROOC)_2CHBr + 2NaOC_6H_4R} \longrightarrow \mathrm{2NaBr + (ROOC)_2C(OC_6H_4R)_2 + (ROOC)_2CH_2}$$

In the course of this investigation there were prepared the ethyl esters of the mono- (Ia) and the di-phenoxymalonic acids, the mono- (IIa) and di-*m*-cresoxymalonic acids (IIIa), the mono- and di-*p*-nitrophenoxy-malonic acids and the *p*-nitrophenoxy-methylmalonic acid (IVa), then several of the free acids (I, II, III, IV) and some of the amides (Ib, IIb). The various mono- as well as di-phenoxymalonic acid esters were subjected to rearrangement processes according to J. B. Niederl[8] and E. Wallis.[9] These attempts proved to be negative inasmuch as no carbon-arylated malonic acid could be obtained, the respective phenoxyacetic acids resulting from the mono derivatives. Of particular interest in this respect is the *p*-nitrophenoxy-methyl-malonic acid (IV) and ester (IVa), on account of its being a tertiary alkyl phenyl ether and yet being unable to undergo any rearrangement.

Experimental

Diethyl Aryloxymalonates.—These esters were prepared by refluxing until neutral 0.125 mole of diethyl monochloromalonate and the respective sodium phenolate, or cresylate, in absolute alcohol. The mixture was then poured into water and extracted with ether. The ether extract was fractionally distilled under reduced pressure. In this manner were prepared: diethyl phenoxymalonate (Ia) (yield 60%, the crystals were crystallized from methyl alcohol), and diethyl *m*-cresoxymalonate (IIa) (yield 60%). The diethyl di-*m*-cresoxymalonate (IIIa) was prepared by the method of M. Conrad and C. A. Brueckner[4] (yield 50%): the diethyl *p*-nitrophenoxy-methylmalonate was prepared according to the method of C. A. Bischoff[5] using xylene as the solvent (yield, 50–60%; the crystals were recrystallized from methyl alcohol).

Mono-aryloxymalonic Acids.—The individual free acids were prepared by hydrolyzing the respective esters with 5% alcoholic potassium hydroxide solution. The potassium salts which usually precipitated out were redissolved in water and the free acids were precipitated out of these solutions by subsequent acidification. Purification of the acids was effected by dissolving the acids in ether, extracting the ether solution with 5% aqueous sodium carbonate solution, precipitating the acids from the carbonate solution and re-extracting with ether. Upon concentration of the ether extracts at room temperature, the acids crystallized out on standing. The phenoxy and *m*-cresoxymalonic acids (I, II) were recrystallized from toluene, the *p*-nitrophenoxy-methylmalonic acid (IV) from a mixture of ether and petroleum ether. The free acids were hygroscopic. Upon heating and also on prolonged standing the acids lost carbon dioxide and were converted into the respective aryloxyacetic acids.

Di-aryloxymalonic Acids.—These acids also were prepared by hydrolysis of the corresponding esters. Usually only a short period of refluxing was required for the saponification of the ester. The di-*m*-cresoxymalonic acid (III) precipitated out on acidification in a partially hydrated state. The acid was recrystallized from hot water in the form of a tri-hydrate ($\mathrm{III_1}$). On further heating or on long standing it lost water, forming the anhydrous acid (III). The anhydrous acid also was obtained from the ether solution of the acid or by precipitation by petroleum ether from the solution of the acid in benzene.

The di-aryloxymalonic acids upon heating underwent decomposition yielding the respective phenol, carbon dioxide, water and a non-volatile resin.

Mono-aryloxymalonic Acid Amides.—One gram of the aryloxymalonic acid ester (Ia, IIa) was shaken with 10 cc. of concentrated aqueous ammonium hydroxide solution for five minutes. The amide crystallized out in about 80% yield and was recrystallized from 30% alcohol (Ib, IIb).

Disproportionation.—The reactions between the sodium salts of the respective phenols (phenol, *m*-cresol, *p*-nitrophenol) and diethyl mono-bromomalonate (b. p. 125–127° (15 mm.)) were carried out with and without solvents. The solvents were ethyl alcohol (85%, 95% and absolute) and xylene. The mixtures were refluxed until they reacted neutral to litmus paper. They were then poured into water and the resulting aqueous mixtures were extracted with ether. The ether extract was separated and subjected to fractional distillation *in vacuo* (phenol and *m*-cresol). The fraction boiling above 140° (4 mm.) (a)

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[5] C. A. Bischoff, *Ber.*, **40**, 3134, 3150 (1907).

[6] C. A. Bischoff, *ibid.*, **29**, 1276 (1896).

[7] A. Gault and L. Klees, *Bull. soc. chim.*, [4] **39**, 1000 (1926).

[8] J. B. Niederl and co-workers, THIS JOURNAL, **53**, 1928 (1931); **54**, 1063 (1932).

[9] E. Wallis and co-workers, *ibid.*, **56**, 1715 (1934).

TABLE I

CHEMICAL CONSTANTS AND ANALYSES OF COMPOUNDS

Compound	M. p. or b. p. °C. (uncor.)	Formula	Carbon % Calcd.	Carbon % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen % Calcd.	Nitrogen % Found	Neut. equiv. Calcd.	Neut. equiv. Found
		Phenoxymalonic acid								
I Acid	124 (dec.)	$C_9H_8O_5$	55.07	55.19	4.08	4.12			98	97
(a) Ethyl ester	52–53	$C_{13}H_{16}O_5$	61.88	61.94	6.37	6.24				
(b) Amide	214–215	$C_9H_{10}N_2O_3$	55.67	55.65	5.15	5.20	14.42	14.43		
		m-Cresoxymalonic acid								
II Acid	138 (dec.)	$C_{10}H_{10}O_5$							105	103
(a) Ethyl ester	154–156 (4 mm.)	$C_{14}H_{18}O_5$	63.16	63.11	6.77	6.94				
(b) Amide	216–217	$C_{10}H_{12}N_2O_3$	57.69	57.60	5.76	5.80	13.46	13.54		
		Di-*m*-cresoxymalonic acid								
III Acid	148 (dec.)	$C_{17}H_{16}O_6$							158	158
(1) Acid-hydrate	87	$C_{17}H_{22}O_9$							185	183
(a) Ethyl ester	202–205 (3 mm.)	$C_{21}H_{24}O_6$	67.70	67.85	6.46	6.67				
		p-Nitrophenoxymethylmalonic acid								
IV Acid	142 (dec.)	$C_{10}H_9NO_7$	47.04	46.88	3.57	3.39	5.49	5.52	128	128
(a) Ethyl ester	50–51	$C_{14}H_{17}NO_7$	54.07	53.95	5.47	5.59	4.50	4.59		

and 150° (4 mm.) (b) were reserved for examination. In the case of the *p*-nitrophenol (c) the esters crystallized out of the reaction mixture upon dilution with water when alcohol was used as the solvent; otherwise the solvent (xylene) had to be distilled off first.

(a) **Mono- and Di-phenoxymalonic Acids.**—The weighed esters as obtained above were first hydrolyzed with 20% aqueous potassium hydroxide solution and the solution acidified afterward. The di-phenoxymalonic acid (m. p. 173°) (the acetal) precipitated out and was weighed, while the monophenoxymalonic acid (I) (the ether) remained in solution. The second method for the determination of the proportion of mono- (ether) to the di-phenoxymalonic acid (acetal) involved treatment of the weighed ester mixture with concd. aqueous ammonium hydroxide solution. Only the mono acid (the ether) yielded an amide (Ib) which alone crystallized out and was then weighed.

The proportion of ether to acetal was two to three in absolute alcohol, xylene and no solvent. In 95 and 85% alcohols it changed to a one to one and a three to two ratio.

(b) **Mono- and Di-*m*-cresoxymalonic Acids.**—The proportion of mono- (ether) to the di-acid (acetal) was ascertained by determining the saponification equivalent of a weighed amount of the distillate. The second method involved determination of the refractive index of the ester mixture and comparing the value obtained with those of standard mixtures of the two components. Diethyl mono-*m*-cresoxymalonate: $n^{23°}_{\mathrm{D}}$ 1.4895; sapon. equiv., 133. Diethyl di-*m*-cresoxymalonate: $n^{22°}_{\mathrm{D}}$ 1.5221; sapon. equiv., 186. The proportion of ether to acetal was three to one using 95% alcohol as solvent.

(c) **Mono and Di-*p*-nitrophenoxymalonic Acid.**—The crude ester mixture was recrystallized from methyl alcohol. The melting point range of the mixture was then compared with those of a series of standard mixtures of the two components, which were prepared according to C. A. Bischoff[5] using diethyl mono-chloromalonate (b. p. 118–119° (16 mm.)) for the ether and diethyl di-bromomalonate (b. p. 140–143° (18 mm.)) for the acetal. The two esters were also separated by fractional crystallization from methyl alcohol in which solvent the ether compound is much more soluble than the acetal. Diethyl mono-*p*-nitrophenoxymalonate: m. p. 86°; diethyl di-*p*-nitrophenoxymalonate: m. p. 144°. The proportion of ether to acetal was two to three in absolute and 95% alcohol, three to two in 85% alcohol and one to one in xylene and without a solvent.

Summary

1. A disproportionation phenomenon involving abnormal aryloxylation has been described.
2. Various mono- and di-aryloxymalonic acids, their esters and amides have been prepared and their behavior on heating as well as under conditions which normally would lead to carbon arylation has been studied.

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