The *l*-acid was obtained in a similar manner from the crude soluble salt. The free acid was recrystallized from absolute methyl alcohol; melting point 220–221°.

Rotation. *l*-Acid, 0.1544 g. made up to 25 cc. with pyridine at 20° gave α_D −0.31; $l = 2$; $[\alpha]_D^{20}$ −25.1.

Racemization Experiments.—A solution of 0.1817 g. of *d*-acid made up to 25 cc. with pyridine at 20°, α_D +0.40, $l = 2$, $[\alpha]_D^{20}$ +27.5, was refluxed for twenty-four hours. No change in initial rotation was observed.

A solution of 0.1990 g. of *d*-acid in 50 cc. of 0.1 *N* sodium hydroxide gave an initial rotation of α_D +0.19; $l = 2$; $[\alpha]_D^{20}$ +23.9; upon boiling for eighty-four hours the rotations were as follows: nine hours, α_D +0.14, $l = 2$, $[\alpha]_D^{20}$ +17.6; forty-eight hours, α_D +0.12, $l = 2$, $[\alpha]_D^{20}$ +15.1; seventy-two hours, α_D +0.07, $l = 2$, $[\alpha]_D^{20}$ +8.8; eighty-four hours, α_D +0.06, $l = 2$, $[\alpha]_D^{20}$ +7.5.

Summary

1. N,N′,2,5,2′,5′-Tetramethyl-3,3′-dicarboxydipyrryl has been prepared by condensing N-amino-2,5-dimethyldicarboethoxypyrrole with 3-carboethoxy-2,5-dimethylhexadione.

2. The product was resolved through the brucine salt and the active forms were found to be unusually resistant to racemization.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

THE REDUCTION OF AROMATIC NITRO AND NITROSO COMPOUNDS WITH SODIUM ALCOHOLATES. II.

BY F. B. DAINS AND W. O. KENYON

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The reduction of aromatic nitro compounds with sodium or potassium hydroxide in alcohol solution or with sodium alcoholates has been studied by a number of investigators from the time of Mitscherlich to the present.[1] Under various conditions there have been obtained amines, azoxybenzene, azobenzene and in the case of *p*-nitrotoluene stilbene derivatives. In addition, Suter and Dains have found that the reduction of *o*-halogen nitrobenzenes with sodium propylate or butylate gave an unexpected product, a substituted amino acid.[2]

$$o\text{-}ClC_6H_4NO_2 + n\text{-}C_3H_7ONa \longrightarrow o\text{-}ClC_6H_4NHCH(CH_3)COONa + H_2O$$

[1] E. Mitscherlich, *Ann.*, **12**, 311 (1834); Rasenack, *Ber.*, **5**, 364 (1872); Zinin, *J. prakt. Chem.*, [I] **36**, 98 (1845); Klinger, *Ber.*, **15**, 865 (1882); Schultz and Smith, *Ann.*, **207**, 328 (1881); Holleman, *Rec. trav. chim.*, **35**, I (1915); Blom, *Helv. Chim. Acta*, **4**, 297 (1921); Fry and Cameron, THIS JOURNAL, **49**, 864 (1927); Heumann, *Ber.*, **5**, 911 (1872); Brand, *J. prakt. Chem.*, [II] **68**, 208 (1903); Richardson, *J. Chem. Soc.*, 522 (1926); McMasters and Magill, THIS JOURNAL, **50**, 3038 (1928); Perkin, *J. Chem. Soc.*, **37**, 546 (1880); Goldschmidt, *Ber.*, **11**, 1624 (1878); Buchka and Schachtebeck, *ibid.*, **22**, 834 (1889); Schmidt, *ibid.*, **32**, 2919 (1899); Green, Davies and Horsfall, *J. Chem. Soc.*, **91**, 2076 (1907); Brühl, *Ber.*, **37**, 2066 (1904); Lyons and Pleasant, *ibid.*, **62**, 1723 (1929).

[2] Suter and Dains, THIS JOURNAL, **50**, 2733 (1928).

The present paper is a continuation of their investigation and was undertaken with the following purposes: (1) to study the reducing action in benzene solution of polyhydric alcohols and of ketones which are capable of forming sodium derivatives; (2) to ascertain whether ortho groups other than halogen atoms will cause the formation of amino acids; (3) to compare the action of nitroso compounds as oxidizing agents; (4) to ascertain the amount of halogen removed from the ring.

Experimental

The method outlined by Dains and Suter was used in most cases. When the reduction was complete the separation of products was carried out as outlined in their paper. The benzene layer of the distillate contained the unchanged nitro compounds.

The amine formed was estimated by the method of Francis and Hill.[3] The brominated amine thus formed was used for identification wherever possible.

After separation of azo or azoxy derivatives, acidification with sulfuric acid precipitated the amino acids, organic acids, or phenolic products. These were removed, the filtrate diluted to a definite volume and the halogen removed was estimated by a Volhard titration of an aliquot portion. When soluble organic acids were present which would affect the titration, they were removed by making the solution alkaline, evaporating to dryness and fusing the residue until all carbon was removed. The melt was then dissolved and the halogen estimated.[4]

Table I gives a résumé of the laboratory results and in the later discussion references are made to the particular experiments involved. All melting points are uncorrected.

Discussion

The Effect of Added Amines upon Reduction.—The work of Fry and Cameron and of Fry and Bowman[5] has shown that when pyridine or other organic bases such as aniline are present in the reaction mixture, they increase the reduction of nitrobenzene by sodium methylate.

In benzene solution it was found that nitrobenzene is reduced to only a slight extent (Ia) and the presence of an equimolar amount of aniline has only slight effect on the amount of reduction (Ib).

In the case of *p*-chloronitrobenzene and sodium propylate, Suter has shown that 33% of the nitro compound goes to the *p,p'*-dichloroazoxybenzene. A series of reductions (IIIa, b, c, d) in the presence of organic bases gives yields almost twice as great as when no base is added. In

[3] Francis and Hill, THIS JOURNAL, **46**, 2488 (1924).

[4] All products with chlorine in the ring had been removed before fusion.

[5] Fry and Bowman, THIS JOURNAL, **52**, 1531 (1930).

TABLE I

EXPERIMENTAL RESULTS

300 Cc. of Benzene in Each Experiment

No.	Nitro compd., moles	Alcohol, moles	Sodium, moles	Amine formed, %	Azoxy formed, %	Nitro recovered, %	Acids and other products	Halogen removed, %
Ia	0.1 $C_6H_5NO_2$	0.6 C_2H_5OH	0.2	6.24	Tar	73.17		
b	.1 $C_6H_5NO_2$ .1 $C_6H_5NH_2$	.6 C_2H_5OH	.2	8.25		82.93		
c and d	.1 $C_6H_5NO_2$	.6 $(CH_3)_2CO$	.2	36.13	36.2 Tar			
e	.1 $C_6H_5NO_2$	.6 $C_3H_5(OH)_3$	.2 NaOH	1.06	Azobz. 22.0		0.0044 mole oxalic, 0.0487 mole formic, 0.0153 mole acetic, 0.0004 mole oxalic	
f	.5 $C_6H_5NO_2$	.3 $C_3H_5(OH)_3$	.1	39.83		49.0		
g	.1 $C_6H_5NO_2$	.6 $C_2H_4(OH)_2$	.2 NaOH	17.46	Azobz. 43.50		0.0024 mole oxalic, 0.006 mole vol. acids	
h	.1 $C_6H_5NO_2$	.6 $C_2H_4(OH)_2$	.2	9.00	Azobz. 28.10	3.20	0.0017 mole oxalic, 0.0054 mole vol. acid	
IIa	0.1 o-$ClC_6H_4NO_2$	0.6 C_2H_5OH	0.2	20.40	29.85	6.33	Tar	7.25
b	.1 o-$ClC_6H_4NO_2$	.2 $C_2H_5OC_2H_4OH$	.2	4.35		0.6	Tar	
c	.1 o-$ClC_6H_4NO_2$	.2 $CH_3COCH_2COOC_2H_4$	.2	16.34[b]			CO_2	20.48
d	.1 o-$ClC_6H_4NO_2$	.2 $CH_2(CO_2C_2H_5)_2$	.2	7.5	Tar		CO_2	5.33
IIIa[a]	0.1 p-$ClC_6H_4NO_2$	0.6 n-C_3H_7OH	.2	18.70	60.00	10.76	Tar	12.72
b	.1 p-$ClC_6H_4NO_2$ .1 $C_6H_5NH_2$	.6 n-C_3H_7OH	.2	30.00	67.10			
c	.1 p-$ClC_6H_4NO_2$ .1 p-$ClC_6H_4NH_2$	.6 n-C_3H_7OH	.2	12.00 Lost	74.63	12.66		
d	.1 p-$BrC_6H_4NH_2$ .1 p-$ClC_6H_4NH_2$	.6 n-C_3H_7OH	.2	9.67	69.50			
e	.1 p-$ClC_6H_4NO_2$	50 cc. $C_2H_4(OH)_2$	.2 NaOH		82.20			
f	.1 p-$ClC_6H_4NO_2$	0.6 $(CH_3)_2CO$	.2	44.50				
g	.05 p-$ClC_6H_4NO_2$	.1 $C_6H_5COCH_2C_6H_5$	.1	3.68	Trace	6.33	Benzoic trace, Benzilic	18.75

TABLE I (*Continued*)

No.	Nitro compd., moles	Alcohol, moles	Sodium, moles	Amine formed, %	Azoxy formed, %	Nitro recovered, %	Acids and other products	Halogen removed, %
h	0.1 *p*-$ClC_6H_4NO_2$	0.2 $CH_3COCH_2CO_2C_2H_5$	0.2	14.48[b]	16.42	61.40	CO_2 acetone, oxalic acid, 0.397 mole	12.61
i	.1 *p*-$ClC_6H_4NO_2$	.08 $C_6H_5COCH_2CO_2C_2H_5$	.08	7.71	Tar			3.78
j	.1 *p*-$ClC_6H_4NO_2$	.2 $CH_2(CO_2C_2H_5)_2$	.2	7.13	26.27	47.50		2.52
IVa	20 g. 3,4-Dichloro-1-nitrobenzene	200 cc. C_2H_5OH	40 g. KOH		90.48			Trace
b	10 g. "	100 cc. 95% C_2H_5OH	4.6 Na		43.45			7.68
c and				5.45	55.95			21.60
d	0.1 "	0.6 C_2H_5OH	0.2	25.70	61.90			Trace
e	0.1 "	0.6 *n*-C_3H_7OH	0.2	3.78	61.90		Tar	17.64
f	0.1 "	100 cc. *n*-C_3H_7OH	4.6 g.		41.66		CO_2	Trace
g[c]	20 g. "	50 cc. $C_6H_5CH_2OH$	40 g. NaOH	3.04	49.50		0.0594 mole benzoic acid	
h	0.1 "	0.6 $C_6H_5CH_2OH$	0.2	2.80	67.50		0.166 mole benzoic acid	11.59
Va	0.1 2,5-Dichloro-1-nitrobenzene	0.6 C_2H_5OH	.2	13.43	26.70	26.56	Tar, trace of phenols	
VIIa	0.1 *o*-nitrotoluene	0.6 *n*-C_3H_7OH	.2	48.00		18.26	Tar	
VIIIa	0.1 *p*-nitrotoluene	0.6 CH_3OH	.2	32.70		13.87	0.0194 mole formic acid	Stilbene, 61.60
b	.1 *p*-nitrotoluene	0.6 C_2H_5OH	.2	36.21	46.02		0.009 mole formic, 0.013 mole acetic	Stilbene, 3.00
c	.1 *p*-nitrotoluene	0.6 $C_2H_5OC_2H_4OH$	.2	7.95		1.46		Stilbene, 85.30
d	.1 *p*-nitrotoluene	0.3 $CH_3COC_6H_5$	.1	83.03	Trace	14.60	0.025 mole benzoic acid	
IXa	0.1 2-chloro-6-nitro-toluene	0.6 *n*-C_3H_7OH	.2	29.70	Tar	8.15		

TABLE I (*Concluded*)

No.	Nitro compd., moles	Alcohol, moles	Sodium, moles	Amine formed, %	Azoxy formed, %	Nitro recovered, %	Acids and other products	Halogen removed, %
Xa	0.4 4-chloro-2-nitro-toluene	0.6 C_2H_5OH	0.2	15.00	13.50	2.3	Tar	8.36
XIa	.1 2-chloro4-nitro-toluene	.6 C_2H_5OH	.2	7.70		3.5		Stilbene, 58.70
b	.1 "	.6 n-C_3H_7OH	.2	9.33		4.70		Stilbene, 61.80
XIIIa	.1 o-nitroanisol	.6 n-C_3H_7OH	.2	3.01	Tar		Tar	
XIVa	.1 o-nitrodiphenyl ether	.6 n-C_3H_7OH	.2	12.85		4.18	Tar	
XVa	.1 o-nitrodiphenyl	.6 n-C_3H_7OH	.2	21.00	34.10		Tar	
XVIa	.1 p-nitrodiphenyl	.6 n-C_3H_7OH	.2	2.17	93.72	5.00		
XVIIa	.05 m-Nitrobenzylidine aniline	.3 n-C_3H_7OH	.1	63[b]			Tar	
XIXa	.1 m-nitrobenzaldehyde	.6 n-C_3H_7OH	.2				97 m-Nitrobenzoic acid	
XXa	.1 o-Nitrobenzaldehyde	.6 n-C_3H_7OH	.2				Tar	
XXIa	.1 p-Nitroethyl benzoate	.6 n-C_3H_7OH	.2		86.5 Azoxybenzoic acid			
XXIIa	.1 o-Nitroacetanilide	.6 n-C_3H_7OH	.2	13.13[c]	Resins			
XXIIIa	.1 Nitrosobenzene	.6 n-C_3H_7OH	.2	10.00	Tar			
XXIVa[d]	.05 p-Nitroso-toluene	200 cc. C_2H_5OH	10 g. NaOH		95.2			
b	.05 "	0.3 n-C_3H_5OH	0.1	8.07	83.00			
XXVa	.5 p-Nitrosodimethylaniline	.3 n-C_4H_9OH	.1	44.00	46.5			

[a] 0.1 Mole of pyridine added to solvent benzene. [b] Aniline. [c] 25 cc. of water as solvent. [d] 40 cc. of water as solvent. [e] Diamine.

(IIIc), 0.1 mole of amine was added to the reaction mixture but only 88% of this could be recovered.

The Action of Glycol and Glycerol.—The reductions using glycerol and sodium in benzene were very slow due to the formation of two layers in the reaction medium. In the case of sodium or sodium hydroxide with glycol and glycerol in an excess of the alcohol (Ie, g, h), the formation of azobenzene is unique and rather surprising. In contrast to this, *p*-chloronitrobenzene with glycol and alkali yields mainly *p,p'*-dichloroazoxybenzene (IIIe). The formation of oxalic and volatile acids is also to be noted.

The Oxidation of Ketones and Ketone Acids.—The sodium salt of acetone is a powerful reducing agent (Ie, d, IIIf) and gives from 36 to 44% amines, but otherwise thick tars. Acetophenone behaves in an analogous manner (VIIId).

With phenyl benzyl ketone (IIIg) there was observed the interesting formation of benzilic as well as benzoic acid. This is due to oxidation of the ketone to benzil, which in part is oxidized to benzoic acid but mainly undergoes rearrangement in the alkaline solution during the steam distillation[6] to benzilic acid.

Ethyl acetoacetate (IIc, IIIh) was not only oxidized by *o*- and *p*-chloronitrobenzenes, but was able to replace the chlorine in the ring by hydrogen, since the amine recovered was practically all aniline, which was not the case with benzoylacetic ester (IIIi) or malonic ester (IId, IIIj).

Reactions with 3,4-Dichloronitrobenzene.—The series IVa-h deals with the reduction of the 3,4-dichloronitrobenzene. Three different alcohols were used, the reactions being carried out in various ways and the product, aside from small amounts of the corresponding amine, was tetrachloroazoxybenzene. A typical experiment is as follows.

Preparation of 3,4,3',4'-Tetrachloroazoxybenzene.—Sodium (4.6 g.) was dissolved in a mixture of benzene (300 cc.) and *n*-propyl alcohol (45 cc.). To this was added 3,4-dichloronitrobenzene (19.2 g.) dissolved in a little benzene. The mixture was refluxed for two hours.

After distillation, the distillate showed 3.78% of 3,4-dichloroaniline. The residue in the flask gave 10.4 g. of brown material. This was extracted with ether–alcohol and recrystallized from carbon disulfide and benzene. The melting point is 137–138°; 61.9% yield.

Anal. Calcd. for $C_{12}H_6ON_2Cl_4$: Cl, 42.2. Found: Cl, 42.02, 42.08.

The molecular weight in benzene by the freezing point method gives 372; calculated. 336. In no case under the conditions employed was any evidence obtained for the formation of ethers of 4-nitro-3-chlorophenol such as were described by McMaster and McGill[7] as resulting from the interaction of sodium alcoholates on this dichloronitrobenzene.

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[6] Klinger, *Ber.*, **19**, 1867 (1886).

[7] McMaster and McGill, THIS JOURNAL, **50**, 3041 (1928).

The Nitrobenzaldehydes, Acids and Phenols.—*o*-Nitrobenzaldehyde and sodium propylate (XXa) gave only tars, while the *m*-nitrobenzaldehyde (XIXa) was changed almost quantitatively to *m*-nitrobenzoic acid. Evidently in the alkaline solution it undergoes the Cannizzaro reaction and then the nitrobenzyl alcohol, in turn, with dilute alkali is oxidized to the acid. *o*-, *m*- and *p*-nitrobenzoic acids (XVIIIa) gave no reduction products, though the ethyl ester of *p*-nitrobenzoic acid (XXIa) was reduced (86%) to the *p,p'*-azoxybenzoic acid, identified by its properties and analysis of its silver salt. *o*-Nitrophenol was not reduced but went over into the red sodium salt of the acid form.

Formation of Amino Acids.—Suter and Dains[2] showed that such amino acids resulted from the reduction of *o*-halogen nitro compounds. Thus far this seems to be an essential condition since no amino acids have been isolated with the following ortho substituents: CH_3, OH, OCH_3, OC_6H_5, C_6H_5, CHO and $NHCOCH_3$ (in IXa, Xa, XIIIa, XIVa, XVa, XXIIa).

Since ethyl alcohol failed to give an amino acid with dichloronitrobenzene, while propyl did, it is evident that a 3-carbon alcohol at least is necessary for this synthesis. The following illustrates, however, the synthesis of such acids.

α-2,5-Dibromoanilinopropionic Acid, $CH_3CH(NHC_6H_3Br_2)COOH$.—Sodium (4.6 g.) is dissolved in a mixture of benzene (250 cc.) and *n*-propyl alcohol (45 cc.) and 2,5-dibromonitrobenzene (28.1 g.) in 50 cc. of benzene is slowly added. When the violent reaction subsides, the mixture is refluxed on the water-bath for two hours. The amine present (21.65%) is removed by steam distillation and the residue filtered. Acidification precipitated the acid as an oil which later solidified. This crude material was dissolved in alcohol, boiled with norite and the product precipitated by dilution of the hot filtered solution with water. It forms colorless crystals, m. p. 156°, which became brown on contact with air.

Anal. Calcd. for $C_9H_9O_2NBr_2$: Br, 49.49. Found: Br, 49.59, 49.37.

Its constitution was further proved by its synthesis from dibromoaniline and α-bromopropionic acid on refluxing in water solution until the mixture was homogeneous. A mixed melting point showed identity.

In connection with the method of determining the amount of 2,5-dibromoanilinc formed (method of Francis and Hill) in the preceding reduction, it was found necessary to synthesize the possible product. When bromine water is added to a dilute sulfuric acid solution of 2,5-dibromoaniline, the 2,4,5,6-tetrabromoaniline is found. The crystals from alcohol melt at 118°.

Anal. Calcd. for $C_6H_3NBr_4$: Br. 78.21. Found: Br, 78.08.

α-2-Chloro-5-methylanilinopropionic Acid.—This was formed in 49.18% yield together with 8.43% of amine from the chloronitrotoluene and sodium propylate in benzene solution. The white crystals from hot water melt at 158°.

Anal. Calcd. for $C_{10}H_{12}O_2NCl$: Cl, 16.57. Found: Cl, 16.64, 16.72.

The same acid was synthesized from α-bromopropionic acid and 3-amino-4-chlorotoluene.

In a previous paper[8] it was suggested that the formation of these amino acids may be due to an increased ability of the *o*-nitroso group to add an aldehyde complex and then rearrange. This does not seem to be true of the *p*-nitroso derivatives (XXIIIa, XXIVa, XXVa), since they exhibit strong oxidizing properties, yielding amines and azoxy compounds.

Halogen Removal.—While varying amounts of halogen were removed in many cases, no definite phenols were isolated. This is probably due to the interaction of the intermediate nitroso compounds with such phenols, yielding tarry products.

Summary

1. A study has been made of the action of sodium alcoholates (or tautomeric substances) on nitrobenzene, substituted nitrobenzenes and nitrosobenzenes in anhydrous benzene solution.

2. The products are normally amines or the corresponding azoxy derivatives, though polyhydric alcohols tend to form azo compounds.

3. Sodium derivatives of tautomeric substances are often good reducing agents, being oxidized usually at the methylene bond.

4. When *p*-nitrotoluene or its substitution products are used, stilbenes may be formed.

5. No substituting groups other than halogen form α-amino acids.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPHENYLS. PREPARATION AND PROPERTIES OF 4,4′-DICARBOXY-1,1′-DIANTHRAQUINOYL. XVII[1]

BY W. M. STANLEY AND ROGER ADAMS

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It was pointed out in a previous paper[2] that it should be possible to resolve a 2,2′-disubstituted diphenyl derivative into optical antipodes, provided the two substituting groups are sufficiently large and assuming that a hydrogen atom may serve as a blocking group. Diphenyl-2,2′-disulfonic acid[3] was investigated but it could not be resolved. In the present investigation 4,4′-dicarboxy-1,1′-dianthraquinoyl (I) and its di-*l*-menthyl ester were synthesized in order to determine whether the CO group in a quinone ring would be a sufficiently large 2-substituted group to cause inter-

[8] Ref. 2, p. 2738.

[1] For the two previous papers in this series see Shildneck and Adams, THIS JOURNAL, **53**, 2203 (1931); Chang and Adams, *ibid.*, **53**, 2353 (1931).

[2] Stanley and Adams, *ibid.*, **52**, 1200 (1930).

[3] Stanley and Adams, *ibid.*, **52**, 4471 (1930).