Notes

A department for short papers of immediate interest.

The Three Symmetrical Hydrazophenols

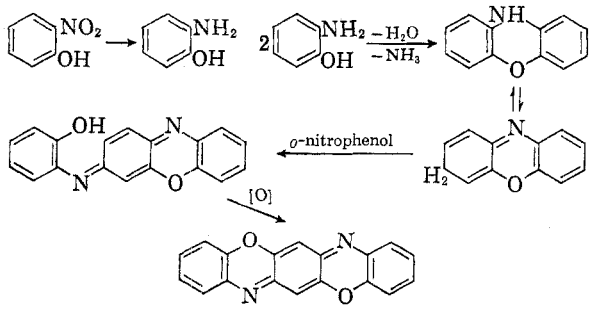
M. KHALIFA AND (IN PART) W. H. LINNELL

Received April 1, 1957

p-Hydrazophenol could not be prepared by the method reported for the ortho isomer.[1] However, acyl derivatives of the three hydrazophenols were obtained by reducing the corresponding azo or azoxy compounds according to Jacobson's method.[2] In the course of the reduction we have observed that substituents which increase the electron density of the azo- group favor reductive fission, while those which lower this density or at least do not increase it above that of azobenzene favor the reduction to the hydrazo stage only. The same applies to Jacobson's reported results.[2,3]

The intermediate azo- and azoxyphenols were prepared from the corresponding nitrophenols according to Willstatter's fusion method.[4] The formation of such compounds probably takes place through the reduction[5] of part of the nitrophenol to aminophenol and condensation of the latter with the nitro-body giving rise to the azoxy compound which may be reduced further to the azo compound. That such a mechanism is possible is supported by the fact that azoxy and azo compounds are prepared by fusing aromatic amines together with aromatic nitro compounds in the presence of powdered caustic alkalis.[6-8]

The formation of the by-product triphenodioxazine from *o*-nitrophenol probably takes place according to the following scheme:



Triphenodioxazine

The above scheme besides being in conformity with the one given for the formation of the azo and azoxy compounds gives a reasonable answer to the evolution of ammonia in the course of the fusion process. This suggested scheme finds support in the formation of phenoxazine[9] through the condensation of *o*-aminophenol and catechol and in the fact that triphenodioxazine itself had been prepared from 4,6-diaminoresorcinol and *o*-aminophenol[10]

EXPERIMENTAL[11]

2,2'-Dihydroxyazobenzene and 4,4'-dihydroxyazobenzene were prepared according to a method described in the literature.[4]

3,3'-Dihydroxyazoxybenzene was obtained instead of the corresponding azo compound when the method[4] reported for the preparation of the latter was adopted.

Acetylation and benzoylation. The above compounds were acetylated by acetyl chloride in presence of glacial acetic acid and benzoylated according to Schotten-Baumann method of benzoylation. Yields were almost theoretical.

Reduction. The acyl derivatives were reduced in 80 to 90% yields by Jacobson's procedure[2] which was modified by stirring briskly the reaction mixture and concentrating the alcoholic filtrate[12] containing the hydrazo compound before its dilution with cold water.

Acknowledgment. Thanks are due to Messrs. J. R. Geigy of Basle, Switzerland, for the microanalyses of the new compounds and to Prof. Y. M. Abou-Zeid of the Faculty of Pharmacy, Cairo University for the facilities during this work.

CHEMISTRY DEPARTMENT
FACULTY OF PHARMACY
CAIRO UNIVERSITY

(1) Sen and Sadasivam, *J. Indian Chem. Soc.*, **9**, 405 (1932).
(2) Jacobson and Steinbrenk, *Ann.*, **303**, 384 (1898).
(3) Jacobson and Hönigsberger, *Ber.*, **36**, 4093 (1903).
(4) Willstatter and Benz, *Ber.*, **39**, 3495 (1906).
(5) The hydrogen for the reduction probable comes from the breaking down of part of the starting material.
(6) Martynoff, *Compt. rend.*, **223**, 747 (1946).
(7) Martynoff, *Compt. rend.*, **225**, 1332 (1947).
(8) Sidgwick, *Organic Chemistry of Nitrogen*, Oxford University Press, 1942, p. 436.
(9) Ref. 8, p. 75.
(10) Seidel, *Ber.*, **23**, 188 (1890).
(11) All melting points recorded here are uncorrected.
(12) The filtrate containing diacetyl-*o*-hydrazophenol instantaneously acquired a green coloration probably due to contamination with the very unstable *p*-diaminohydroquinone resulting from triphenodioxazine which is a by-product in the preparation of *o*-azophenol.

TABLE I

ACYL DERIVATIVES OF AZO- AND AZOXYPHENOLS

Acryl Derivative	Solvent of Crystln.[a]	Color	M.P., °C.	Formula	Analysis: Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
2,2′-Diacetoxyazobenzene	A	Orange	154–155	$C_{16}H_{14}N_2O_4$	64.42	64.23	4.69	4.58	9.39	9.45
3,3′-Diacetoxyazoxybenzene	B	Reddish brown	102–103	$C_{16}H_{14}N_2O_5$	61.14	61.16	4.45	4.58	8.92	8.82
4,4′-Diacetoxyazobenzene[b]	C	Golden yellow	198–199	$C_{16}H_{14}N_2O_4$						
2,2′-Dibenzoyloxyazobenzene	A	Orange	172–173	$C_{26}H_{18}N_2O_4$	73.93	73.88	4.26	4.20	6.63	6.67
3,3′-Dibenzoyloxyazoxybenzene	B	Yellowish brown	174–175	$C_{26}H_{18}N_2O_5$	71.23	71.10	4.11	4.06	6.39	6.47
4,4′-Dibenzoyloxyazobenzene[b]	A	Reddish yellow	210–211 249–251	$C_{26}H_{18}N_2O_4$						

[a] A, benzene; B, alcohol; C, glacial acetic acid. [b] Willstatter and Benz, *Ber.*, **40**, 1582 (1907).

TABLE II

ACYL DERIVATIVES OF THE THREE SYMMETRICAL HYDRAZOPHENOLS

Acyl Hydrazophenol	Solvent of Crystln.[a]	M.P., °C.	Formula	Analysis: Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Diacetyl-*o*-hydrazophenol[b]	A	146–147	$C_{16}H_{16}N_2O_4$	64.00	64.09	5.33	5.11	9.33	9.36
Diacetyl-*m*-hydrazophenol	A	136	$C_{16}H_{16}N_2O_4$	64.00	64.05	5.33	5.27	9.33	9.38
Diacetyl-*p*-hydrazophenol-[c]	B	138–140	$C_{16}H_{16}N_2O_4$	64.00	63.81	5.33	5.17	9.33	9.29
Dibenzoyl-*o*-hydrazophenol	C	169–170[d]	$C_{26}H_{20}N_2O_4$	73.58	73.52	4.71	4.64	6.60	6.50
Dibenzoyl-*m*-hydrazophenol	A	146–147	$C_{26}H_{20}N_2O_4$	73.58	73.72	4.71	4.75	6.60	6.69
Dibenzoyl-*p*-hydrazophenol	C	188–190	$C_{26}H_{20}N_2O_4$	73.58	74.11	4.71	4.65	6.60	6.56

[a] A, aq. alc.; B, benzene–pet. ether (80–100°); C, alcohol. [b] Purified by refluxing its alcoholic solution with charcoal in an atmosphere of nitrogen. [c] Hydrolysis with 5% sodium hydroxide did not yield the free hydrazophenol, but instead afforded the oxidation product viz. *p*-azophenol. [d] Ref. 1, m.p. 186°.

Reduction of Organic Compounds by Lithium in Low Molecular Weight Amines. V. The Mechanism of Formation of Cyclohexanes. Utility of the Reducing Medium in Effecting Stereospecific Reductions

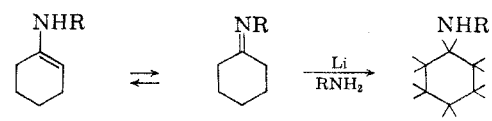
ROBERT A. BENKESER, JAMES J. HAZDRA, ROGERS F. LAMBERT, AND PATRICK W. RYAN

Received October 9, 1958

It was reported in a previous paper[1] in this series that reduction of aromatic nitro compounds with the lithium-amine reagent stops rather cleanly at the aromatic amine. On the other hand, aromatic amines (primary, secondary, or tertiary) are reduced by excess lithium in ethylamine to cyclohexane derivatives principally. This unusual behavior was shown to be due to the generation of alkyl amide ions during the reduction of the nitro group. These maintain the aromatic amino group as the anilide ion which resists further reduction. However, when one starts with an aromatic amine, the ring is reduced rapidly at first, since little or no amide ion is present, and hence reasonably good yields of reduction product can be realized in many instances.

In extending this work, we have found that all three isomeric toluidines are reduced to methylcyclohexylamines with excess lithium. In every case the most stable cyclohexane isomer was the predominant product (all substituent groups equatorial). Hence it appears that the lithium-amine reducing system should prove a valuable tool in the stereospecific synthesis of certain cyclohexanes.[2]

It was suggested previously[1] that complete saturation of the aromatic ring of certain 1° and 2° amines occurs because of the facile reduction of imine intermediates, arising from the isomerization of 1-aminocyclohexene isomers (enamines). Fur-



(1) R. A. Benkeser, R. F. Lambert, P. W. Ryan, and D. G. Stoffey, *J. Am. Chem. Soc.*, **81**, 228 (1959).

(2) We have observed also that certain of the xylidines undergo what appear to be similar stereospecific reductions. Details of these, and other stereospecific reductions will be published later.