Acknowledgment.—Microanalyses for carbon, hydrogen and nitrogen were performed by Miss H. Beck, Mrs. C. White and Miss J. Sorenson. This investigation was made possible by a grant-in-aid of research by American Viscose Corporation.

EVANSTON, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

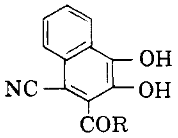
Studies on 4-Substituted-β-naphthoquinones

BY WILLIAM IBRAHIM AWAD AND MOHAMED SHAWKEY HAFEZ

RECEIVED FEBRUARY 10, 1958

The infrared curves of 1,2-dihydroxy-3-aceto-4-cyanonaphthalene and 2,3-dihydroxyacetophenone are discussed. A comparison between the ultraviolet curves of 1,2-diacetoxy-4-cyanonaphthalene and 1,2-diacetoxy-3-aceto-4-cyanonaphthalene is discussed. The photochemical reaction of some aldehydes with β-naphthoquinone, 4-cyanomethyl-1,2-naphthoquinone, 4-chloro-1,2-naphthoquinone and 4-aryloxy-1,2-naphthoquinones is investigated. The 4-aryloxy-1,2-naphthoquinones are prepared by the interaction of 4-chloro-1,2-naphthoquinone and phenols in the presence of pyridine.

Schönberg, Awad and Mousa[1] found that when 4-cyano-1,2-naphthoquinone was exposed to sunlight in the presence of an aliphatic aldehyde, *e.g.*, acetaldehyde or propionaldehyde, an orange compound of constitution I was obtained.



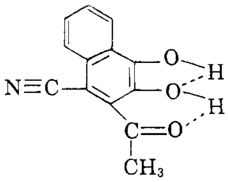
Ia, R = $-CH_3$
Ib, R = $-C_2H_5$

The chemical evidence supporting structure I has been described before.[1] Spectroscopic data of I and some related compounds are discussed here. The infrared[2] curve of Ia shows that the carbonyl group stretching frequency is at 1640 cm.$^{-1}$, which corresponds to a chelated carbonyl group. Similar values have been observed with *o*-hydroxyacetophenone (1639–1613 cm.$^{-1}$)[3a] and 3-hydroxy-2-acetonaphthalene (1657 cm.$^{-1}$).[3b] Compound Ia shows also strong absorption due to the —C≡N radical at (2190 cm.$^{-1}$)[4a]; no free –O–H stretching frequency (3650–3690 cm.$^{-1}$)[4b] could be observed. In similar cases the absence of free –OH absorption in the fundamental region has been reported (ref. 3b, p. 91).

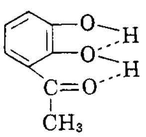
The absorption at 3460 cm.$^{-1}$ (which persists in concentrated and dilute chloroform solution) is to be attributed to hydrogen bonding by the hydroxyl group in the α-naphthyl position to the other hydroxyl group in the β-naphthyl position. The chelated hydroxyl group (*i.e.*, that in the β-naphthyl position) would be expected to give a broad band extending over the region (3400–2600 cm.$^{-1}$).[5] The wide base of the peak with maximum at 3460 cm.$^{-1}$ on its low frequency side, clearly indicates the presence of such a broad peak of relatively low intensity.

These data show that a sort of double chelation exists in the molecule and the structure of Ia is thus better represented as II.

A similar hydrogen bond was assigned to pyrogallol by Pauling[6] to account for its infrared spectrogram (overtone region).



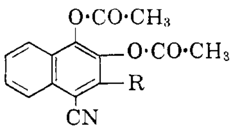
II



III

Further evidence for structure II is deduced by comparing its infrared curve (potassium bromide technique) and that of 2,3-dihydroxyacetophenone (III); III shows absorption bands at 1640 cm.$^{-1}$ (chelated carbonyl group) and at 3300 cm.$^{-1}$ (which is to be attributed to hydrogen bonding by the hydroxyl group). Again no free –OH stretching frequency could be observed.

More evidence for structure II is deduced from the comparison of the ultraviolet[7] curve of its diacetate IV and the ultraviolet[7] curve of 1,2-diacetoxy-4-cyanonaphthalene (V) prepared according to reference 1. These ultraviolet curves show that both IV and V are of analogous structure.



IV, R = $COCH_3$
V, R = H

	λ_{max}	E_{max}	λ_{max}	E_{max}	λ_{max}	E_{max}
IV	243	42200	305	6400	329	3600
V	231	50600	299	7600	328	3300

The colors of II (orange-red)[1] and III (deep-yellow)[8] have been attributed to the contribution of *o*-quinonoid structure VI, since the diacetates of II and III are colorless. If this assumption is valid *o*-

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[1] A. Schönberg, W. I. Awad and G. A. Mousa, THIS JOURNAL, **77**, 3850 (1955).

[2] Baird Double beam instrument with sodium chloride prism using the potassium bromide wafer technique on solids. The cell was 0.5 mm. and the concentration was 0.5% in potassium bromide wafer.

[3] (a) W. Gordy, *J. Chem. Phys.*, **8**, 516 (1940); (b) compare L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," first edition, reprinted 1956, Methuen and Co. Ltd., London, p. 124.

[4] (a) *Ibid.*, p. 223; (b) *ibid.*, p. 84.

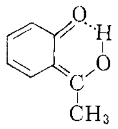
[5] *Cf.* M. St. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957), with special reference to p. 29. This idea and reference were suggested by one of the referees.

[6] Linus Pauling, "The Nature of the Chemical Bond," 2nd. ed., Geoffrey Cumberlege, Oxford University Press, London, 1950, p. 325.

[7] Unicam Spectrophotometer, cell 1 cm., using ethyl alcohol as a solvent.

[8] H. v. Krannichfeldt, *Ber.*, **46**, 4017, 4018 (1913).

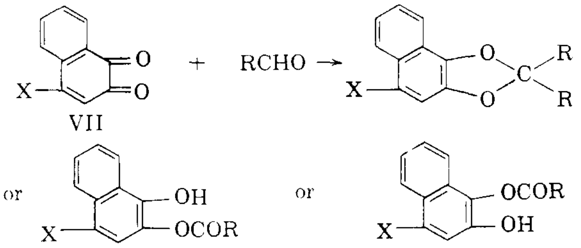
hydroxyacetophenone should be colored, whereas in fact it is colorless. A comparison of the colors of the different dihydroxyacetophenones shows that 2,3-dihydroxyacetophenone is dark yellow, 2,4-dihydroxyacetophenone is colorless[9a] and 2,5-dihydroxyacetophenone is stated to be yellowish-green.[9b] However, 2,5-dihydroxypropiophenone is almost colorless and we believe that the yellowish-green color of 2,5-dihydroxyacetophenone, which persists after rigorous purification and decolorization (charcoal), is not genuine. It seems very plausible to suggest that although the *o*-quinonoid unperturbed structure is not excluded, the presence of the second hydrogen bond may be a more important contributor to the color of these compounds (II and III).



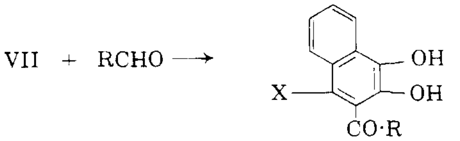
VI

The photochemical reaction leading to compound I is in fact the first example of attack by the aldehyde on the naphthalene ring, instead of at the carbonyl oxygen of the *o*-quinonoid system, as reported by Klinger[10a] and others.[10b,11] Two reaction patterns for the photochemical reaction therefore exist: *i.e.*, attack on the nucleus, and attack at the carbonyl oxygen. It is of interest therefore, to study the effects on reaction course of various substituents in position 4. The two reaction patterns are shown in Scheme A and Scheme B.

Scheme A



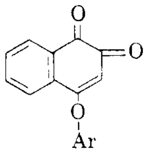
Scheme B



The photochemical products obtained according to Scheme A are (i) colorless or almost colorless, (ii) do not give any color with alcoholic ferric chloride solution.[1,10a,b,11] The photochemical products obtained according to Scheme B are (i) colored (red, or orange-red), (ii) give a green color with alcoholic ferric chloride solution which changes to red on the addition of sodium carbonate solution.[1]

When VII (X = H), β-naphthoquinone; or X = CH_2CN, namely 4-cyanomethyl-1,2-naphthoquinone; or when X = Cl, namely 4-chloro-1,2-naphthoquinone is allowed to react with acetaldehyde in sunlight no crystalline product was isolated. When VII (X = Cl) is allowed to react with *p*-nitrobenzaldehyde, it gives a photochemical addition product according to Scheme A.

The introduction of a group with +T effect in position 4 such as an aryloxy group has been achieved by allowing 4-chloro-1,2-naphthoquinone to react with phenols in the presence of pyridine to give VIII.



VIIIa, Ar = $-C_6H_5$
VIIIb, Ar = $-C_6H_4CH_3(m)$
VIIIc, Ar = $-C_6H_4CH_3(p)$
VIIId, Ar = $-C_6H_3(CH_3)_2(3,4)$
VIIIe, Ar = $-C_6H_3(CH_3)_2(3,5)$
VIIIf, Ar = $-C_6H_3(CH_3)_2(2,5)$
VIIIg, Ar = $-C_6H_4Cl(p)$
VIIIh, Ar = $-C_6H_4NO_2(o)$
VIIIi, Ar = $-C_{10}H_7(\beta)$

The constitution of VIII is assigned on the basis of (i) analytical data, (ii) quinoxaline formation, (iii) reductive acetylation to its diacetate. Compounds VIIIe and VIIIf react with acetaldehyde to give colorless crystals in sunlight indicating that the reaction goes *via* Scheme A; VIIIe also gives a colorless product with anisaldehyde; VIIIi reacts with anisaldehyde to give almost colorless addition product and consequently the above-mentioned reactions proceed *via* Scheme A.

From the above discussion we can conclude that in order for an acyl group to attack the ring (compare Scheme B), a strong electron-attracting group such as a cyano group (−I, −T) should be present in position 4.

The absence of the cyano group (VII, X = H) or its isolation from the conjugated system of the ring (VII, X = CH_2CN) or the presence of chlorine (−I > + T) (VII, X = Cl) in position 4 prevents the reaction from taking place *via* Scheme B.

The presence of an aryloxy group (+T) in position 4 as in the case of VIIIe or VIIIf facilitates the reaction *via* Scheme A whether the aldehyde used is aliphatic or aromatic.

Experimental[12]

General Considerations.—The benzene for the photochemical experiments was thiophene free and dried over sodium. The photochemical reactions were carried out in a Schlenk[13] tube (Monax or Pyrex glass) in carbon dioxide atmosphere.

The photochemical experiments were carried out in direct sunlight. Parallel experiments in the dark were made in all cases and were negative.

Photochemical Reduction of 4-Cyano-1,2-naphthoquinone.—Four-tenths gram of the quinone[14] was suspended in 20 ml. of isobutyl alcohol and was exposed to sunlight for 2 months (December–January). It was filtered off, and concentrated, when a light brown deposit was obtained. The product was filtered and recrystallized from benzene in colorless crystals, m.p. 208° (yield 0.25 g.), undepressed on admixture with an authentic specimen.[14]

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[9] (a) N. A. Lange, "Handbook of Chemistry," seventh edition, Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 636; (b) Heilbron and Bunbury, "Dictionary of Organic Compounds," Vol. III, Eyre and Spottiswoode, London, 1946.

[10] (a) H. Klinger, *Ann.*, **249**, 137 (1888); (b) A. Schönberg and R. Moubasher, *J. Chem. Soc.*, 1430 (1939).

[11] R. F. Moore and William A. Waters, *ibid.*, 238 (1953).

[12] Microanalyses were carried out by Aldred Bernhardt, Germany. The melting points are not corrected.

[13] Compare J. Houben, "Die Methoden der Organischen Chemie," second edition, Vol. 4, Georg Thieme, Leipzig, 1924, p. 960.

[14] W. Bradley and R. Robinson, *J. Chem. Soc.*, 1484 (1934).

TABLE I

4-ARYLOXY-1,2-NAPHTHOQUINONES

Compound[a]	M.p., °C.	Yield,[d] %	Color of crystals	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Color with concd. H_2SO_4
VIIIa[a]	168	75	Orange	$C_{16}H_{10}O_3$	76.79	76.92	4.03	4.32	Orange-red
VIIIb[a]	197	76	Orange-red	$C_{17}H_{12}O_3$	77.26	77.24	4.58	4.72	Orange-red
VIIIc[c]	163	65	Orange	$C_{17}H_{12}O_3$	77.26	77.53	4.58	4.49	Orange-red
VIIId[b]	209	70	Orange	$C_{18}H_{14}O_3$	77.68	77.33	5.07	5.00	Brown-red
VIIIe[a]	191	74	Orange	$C_{18}H_{14}O_3$	77.68	77.23	5.07	5.19	Dark red
VIIIf[b]	159	68	Orange	$C_{18}H_{14}O_3$	77.68	76.97	5.07	5.03	Red
VIIIg[a]	179	65	Dark orange	$C_{16}H_9O_3Cl^e$	67.48	67.24	3.16	3.45	Orange-red
VIIIh[a]	222	75	Dark orange	$C_{16}H_9O_5N^f$	65.09	65.09	3.07	3.25	Orange-red
VIIIi[a]	192	65	Brown	$C_{20}H_{12}O_3$	79.99	80.04	4.03	4.02	Brown

[a] Crystallized from: benzene, [b] methyl alcohol, [c] benzene–petroleum ether (40–60°). [d] Yield is calculated as pure material. [e] Calcd.: Cl, 12.47. Found: Cl, 12.03. [f] Calcd.: N, 4.74. Found: N, 4.69.

TABLE II

QUINOXALINE DERIVATIVES OF 4-ARYLOXY-1,2-NAPHTHOQUINONES

Compound[a]	M.p., °C.	Yield,[g] %	Formula[i]	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Color with concd. H_2SO_4
VIIIa[b]	203	50	$C_{22}H_{14}ON_2$	81.97	81.52	4.38	4.66	8.69	8.74	Olive-green
VIIIb[c]	168	55	$C_{23}H_{16}ON_2$	82.12	82.07	4.79	4.61	8.33	8.73	Olive-green
VIIIc[b]	212	55	$C_{23}H_{16}ON_2$	82.12	81.90	4.79	4.90	8.33	8.56	Olive-green
VIIId[c]	172	50	$C_{24}H_{18}ON_2$					8.00	8.66	Olive-green
VIIIe[b]	169	55	$C_{24}H_{18}ON_2$					8.00	7.86	Olive-green
VIIIf[d]	203	45	$C_{24}H_{18}ON_2$	82.26	81.87	5.18	5.08	8.00	8.22	Olive-green
VIIIg[e]	230	59	$C_{22}H_{13}ON_2Cl^h$					7.85	7.49	Brown
VIIIh[f]	223	64	$C_{22}H_{13}O_3N_3$	71.95	72.06	3.54	3.78	11.44	11.45	Brown-red
VIIIi[a]	221	54	$C_{26}H_{16}ON_2$	83.85	83.90	4.33	4.26	7.52	7.32	Brown

[a] Crystallized from: [a] benzene, [b] methyl alcohol, [c] petroleum ether (60–80°), [d] petroleum ether (40–60°), [e] glacial acetic acid, [f] benzene–methyl alcohol. [g] Yield is calculated as pure material. [h] Calcd.: Cl, 9.41. Found: Cl, 9.95. [i] All crystals (VIIIa–VIIIi) were colored yellow.

TABLE III

PHOTOCHEMICAL REACTION BETWEEN 4-SUBSTITUTED-1,2-NAPHTHOQUINONES AND ALDEHYDES

Quinone (g.)	Aldehyde	Time of exposure to sunlight, days (month)	Solvent of crystln.	M. p., °C.	Yield,[d] %	Color of crystals	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Color with concd. H_2SO_4
4-Chloro-β.naptho-quinone (1.0)	p-Nitro-benzaldehyde (1.0)	10 (Oct.)	[a]	205	38	Yellow	$C_{17}H_{10}O_5N^eCl^f$	59.4	59.9	2.9	3.2	Yellow
VIIIi (0.5)	Anisaldehyde (0.5)	1 (June)	[b]	164	56	Pale yell.	$C_{28}H_{20}O_5$	77.1	77.65	4.6	4.8	Or.-red
VIIIe (0.5)	Acetaldehyde (1.0)	1 (Aug.)	[c]	129	42	Colorless	$C_{20}H_{18}O_4$	74.5	74.6	5.6	5.7	Brown
VIIIe (0.5)	Anisaldehyde (0.5)	1 (Sept.)	[b]	136	51	Pale yell.	$C_{26}H_{22}O_5$	75.4	76.15[g]	5.4	5.5	Brown
VIIIf (0.5)	Acetaldehyde (1.0)	1 (Nov.)	[c]	133	82	Colorless	$C_{20}H_{18}O_4$	74.52	74.68	5.63	5.79	Brown

[a] Benzene. [b] Benzene-petroleum ether (40–60°). [c] Petroleum ether (40–60°). [d] Yield is calculated as pure material. Calcd.: N, 4.1. Found: N, 3.9. [f] Calcd.: Cl, 10.3. Found: Cl, 10.3. [g] No better analytical data could be obtained.

Photochemical Reaction between 1,2-Naphthoquinone or 4-Cyanomethyl-1,2-naphthoquinone[15] and Acetaldehyde.—A mixture of the quinone and acetaldehyde (1 mol to 1 mol) was suspended in benzene and exposed to sunlight for 2 months. The solution was concentrated under reduced pressure and allowed to cool. No crystalline product was obtained even after triturating with petroleum ether (40–60°) or with methyl alcohol.

General Procedure for the Preparation of 4-Aryloxy-1,2-naphthoquinones.—A mixture of the phenol (1 mol) and 4-chloro-1,2-naphthoquinone[16] (1 mol) was dissolved in sufficient quantity of pyridine; the solution became warm. It was then heated on a water-bath for 15 minutes and cooled in ice. A crystalline product separated out, little absolute ethyl alcohol was added. The product was filtered off, washed with little absolute ethyl alcohol and crystallized from a suitable solvent (compare Table I).

General Procedure for the Preparation of Quinoxalines of 4-Aryloxy-1,2-naphthoquinones.—Quinoxalines were prepared in the normal way, using acetic acid as a medium (compare Table II).

Reductive Acetylation of VIIIa.—One gram of VIIIa was dissolved in hot acetic anhydride (25 ml.), then a mixture of zinc dust (1.5 g.) and fused sodium acetate (0.5 g.) was added. The color changed from orange to dark blue, then the bluish color faded gradually to a colorless solution. The reaction mixture was refluxed for a further half-hour, poured on ice while hot and left overnight. The colorless product thus obtained was crystallized from petroleum ether (40–60°) in colorless needles, m.p. 110–111° (yield 1.0 g.). The substance gave a dark brown color with concentrated sulfuric acid.

Anal. Calcd. for $C_{20}H_{16}O_5$: C, 71.42; H, 4.80; acetyl group (for 2), 25.6. Found: C, 71.70; H, 5.07; acetyl group, 27.68.

Reductive Acetylation of VIIIe.—Similar treatment of VIIIe gave colorless crystals, m.p. 154°. The substance gave a caramel-brown color with concentrated sulfuric acid.

Anal. Calcd. for $C_{22}H_{20}O_5$: C, 72.5; H, 5.5; acetyl group (for 2), 23.6. Found: C, 72.7; H, 5.8; acetyl group, 25.9.

General Procedure for the Photochemical Reaction between 4-Substituted-1,2-naphthoquinones and Aldehydes.—A mixture of the quinone and aldehyde was suspended in benzene (20–25 ml.) and exposed to sunlight. At the end of the experiment, the solution was filtered, concentrated under reduced pressure and allowed to cool (compare Table III). All the products investigated gave no color with alcoholic ferric chloride.

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[15] M. Gates, R. B. Woodward, W. F. Newhall and Rosemarie Künzli, THIS JOURNAL, **72**, 1144 (1950).

[16] L. F. Fieser and J. T. Dunn, *ibid.*, **59**, 1019 (1937).

The authors wish to express their thanks and gratitude to Messrs P. Sadtler and Son, Inc., Research Laboratories, Philadelphia, U.S.A., for kindly carrying out the infrared spectrograms. The infrared measurements of Ia were also carried out by Mr. Nagib Doss, Chemistry Department, Ohio State University, U.S.A., to whom we are highly indebted.

ABBASSIA, CAIRO, EGYPT

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE U. S. VITAMIN CORPORATION]

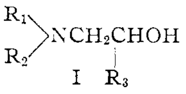
Aminophenylethanols and Related Compounds

BY SEYMOUR L. SHAPIRO, HAROLD SOLOWAY AND LOUIS FREEDMAN

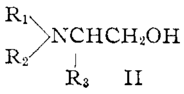
RECEIVED MAY 15, 1958

Aminophenylethanols of the types I and II, and the corresponding halides were required as synthetic intermediates. The alcohols of the type I were prepared by condensation of styrene oxide and secondary amines, while the alcohols of the type II were prepared by amination of 2-bromo-2-phenylethanol. Treatment of the alcohols I or II with thionyl chloride in ether afforded the identical chloride which in the instance of the isomeric pyrrolidino alcohols proved to be 1-(2-chloro-2-phenylethyl)-pyrrolidine hydrochloride.

In connection with the broad study of the pharmacological activity of substituted α- and β-phenylethylamines, we required a number of alcohols of the type represented by I and II.



$\begin{matrix}R_1\\R_2\end{matrix}\!>\!NCH_2\underset{R_3}{\underset{|}{C}}HOH$ I



$\begin{matrix}R_1\\R_2\end{matrix}\!>\!N\underset{R_3}{\underset{|}{C}}HCH_2OH$ II

The groups R_1 and R_2 were varied as alkyl, aralkyl, aryl and cycloalkyl, and R_3 was retained principally as phenyl but was also varied as *p*-chlorophenyl, *p*-tolyl, α-naphthyl and cyclohexyl.

Reports of derivatives of the structures I and II in a variety of pharmacological categories such as methadon analogs,[1] antihistamines, antispasmodics and anesthetics[2] will be detailed in subsequent papers. Derivatives of this type have received but scant inspection.[3,4]

The synthesis of the aminoalcohols of the type I was effected by condensation of the appropriate secondary amine with styrene oxide or the related oxide; the compounds prepared are described in Table I.

It has been clearly established that with secondary amines[5,6] styrene oxide forms only secondary alcohols of the type I. From Table I it is seen that bulky groups attached to the secondary amine tend to give lower yields. When a steric effect was anticipated, the reaction was carried out at a higher temperature and for a longer heating period.

It is of interest that controlled studies[7] of the reaction of diethylamine and styrene oxide at 60° showed virtually no reaction at 6 hours and about 70% of the reactants remained after 12 hours. These workers concluded that styrene oxide reacts only sluggishly with amines, although they noted vigorous interaction of diethanolamine with styrene oxide which was attributed to the catalytic effect of the hydroxyl groups of the reactant amine. In contrast to these observations, a 92% yield (compound 14, Table I) with diethylamine was obtained after 16 hours reaction time. These data suggest that after the 6-hour induction period a catalytic effect is obtained from the formed aminoalcohol of the reaction.

The amino alcohols represented by II and described in Table II were prepared from secondary amines and 2-bromo-2-phenylethanol using the method of King, *et al.*,[8] and Golumbic and Cottle[9] with slight modification.

The amino alcohols of the type I, as well as their hydrochlorides were readily converted to the corresponding chloride hydrochlorides (Table III) by treatment with thionyl chloride in ether.

When the amino alcohol of the type II as the hydrochloride was treated similarly with thionyl chloride, the chloride obtained in 72% yield was identical with that obtained using the secondary alcohol I as the reactant.

Using the isomeric amino alcohols (compound 25, Table I, and compound 3, Table II), the series of reactions reflecting the rearrangement and the identity of the chloride formed is shown in Scheme I.

In the rearrangement of the product from the amino alcohol II, liberation from its salt[10] was not required for conversion to Ia. With no noted formation of sulfur dioxide during the thionyl chloride treatment of II, and evolution of sulfur dioxide upon subsequent handling of this initial reaction product IIb, the 2-pyrrolidino-2-phenethyl chlorosulfite hydrochloride could form Ia directly or yield Ia through the ethylenimonium chloride IIa.[10]

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(1) S. L. Shapiro, H. Soloway and L. Freedman, Meeting-in-Miniature, Westchester Section, American Chemical Society, April 21, 1955.

(2) S. L. Shapiro, H. Soloway, E. Chodos and L. Freedman, THIS JOURNAL, in press.

(3) G. A. Alles and P. K. Knoefel, *Arch. intern. pharmacodynamie*, **47**, 96 (1934).

(4) C. S. Marvel and V. du Vigneaud, THIS JOURNAL, **46**, 2093 (1924).

(5) W. Emerson, *ibid.*, **67**, 516 (1945).

(6) A. Funke and G. Benoit, *Bull. soc. chim. France*, **20**, 1021 (1953).

(7) L. Shecter, J. Wynstra and R. P. Kurkjy, *Ind. Eng. Chem.*, **49**, 1107 (1957).

(8) L. C. King, N. W. Berst and F. N. Hayes, THIS JOURNAL, **71**, 3498 (1949).

(9) C. Golumbic and D. L. Cottle, *ibid.*, **61**, 996 (1939).

(10) (a) E. M. Schultz and J. M. Sprague, *ibid.*, **70**, 48 (1948); (b) R. C. Fuson and C. L. Zirkle, *ibid.*, **70**, 2760 (1948); (c) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 121-124; (d) in ref. 10a, 2-dimethylamino-1-chloropropane did not rearrange immediately when liberated from its hydrochloride at room temperature, but did change to the isomeric 1-dimethylamino-2-chloropropane upon distillation, b.p. 64-67° (97-100 mm.). In turn, ref. 10b reported that when 1-ethyl-2-chloromethylpyrrolidine is liberated from its hydrochloride salt, it rearranges at room temperature to 1-ethyl-3-chloropiperidine.