

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

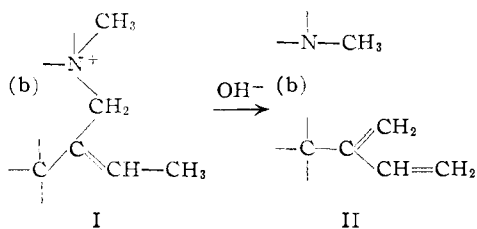
A Single Hofmann Degradation of C-Curarine-I and its Structural Implications^{1,2}

BY V. BOEKELHEIDE, O. CEDER, M. NATSUME AND A. ZÜRCHER

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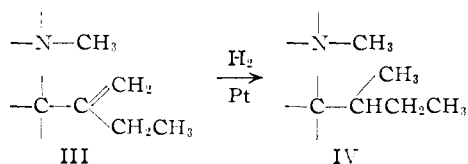
A Hofmann degradation of C-curarine-I under mild conditions gives a monoquaternary product whose composition corresponds to $C_{40}H_{46}ON_4^+$ and thus provides independent proof of the correctness of the C_{40} -formula for this alkaloid. Cleavage of des-C-curarine-I with acid gives C-curarine-III which establishes the C_{20} -formula for the latter alkaloid.

Aside from the fragments obtained through the drastic treatment of zinc dust distillation,³ there is relatively little direct evidence regarding the carbon skeleton of C-curarine-I. The presence of an ethylidene group is revealed by ozonolysis^{4,5} and the relationship of this group to that of the ammonium nitrogen (N_b) has been clearly shown to be that given in partial structure I.⁶ As would be expected, cleavage of the allylic group occurs readily with base. This reaction was first observed by Wieland, Pistor and Bähr⁶ who gave the name Ditertiary Ether Base to the product. Later, Schmid, Ebnöther and Karrer recognized that the reaction was a Hofmann degradation and assigned partial structure II to the product. Subsequently, with the development of the molecular formula $C_{40}H_{44-46}ON_4^{++}$ for C-curarine-I,⁷ it has been assumed that the environment of both quaternary nitrogens is the same and so C-curarine-I has been regarded as having two halves, which are structurally alike.



In order to extend our knowledge of the environment of N_b , we began an investigation of C-curarine-I using other methods of carbon-nitrogen bond cleavage in the hope that one of the bonds other than the allylic one might be broken. The Emde reaction was first studied and it was observed that a crystalline tertiary base (partial structure III) was produced in high yield when C-curarine-I chloride was subjected to hydrogenation over platinum in the presence of excess alkali. The composition of the product ($C_{40}H_{46-48}ON_4$) was in accord with that to be expected if a simple Emde cleavage had occurred at both quaternary nitrogens. The presence of the terminal methylene

group was evidenced from the infrared spectrum (absorption band at 11.2μ) and this was confirmed by oxidation of the corresponding quaternary salt with osmium tetroxide and periodate⁸ to give formaldehyde, isolated as its 2,4-dinitrophenylhydrazone in 46% yield. Also, a qualitative micro Kuhn-Roth determination⁹ yielded both propionic and acetic acids. On hydrogenation, the Emde base absorbed two moles of hydrogen and the resulting product was identical in all respects with the octahydro base (partial structure IV) obtained by hydrogenating Wieland's ditertiary ether base.⁶ It is clear, therefore, that the Emde reaction results in cleavage of the same carbon-nitrogen bond as does the Hofmann and the addition of hydrogen occurs with an allylic shift as shown by III. This is analogous in part to the behavior encountered on reduction of C-curarine-I with sodium and amyl alcohol^{5,6} but is in contrast with the results of Bernauer, Schmid and Karrer on the Emde reduction of isocalebassine.^{10,11}



After the initial experiments in which the crystalline Emde product was obtained in high yield, further investigation revealed that the reaction conditions had to be specified very rigorously in order to obtain reproducible results and the yield of the Emde product was highly dependent on the activity of the catalyst, the concentration of alkali and the nature of the containing vessel. In the course of sorting out these variables, it was observed that in those cases where catalyst activity was low, a second product was formed which was not soluble in ether or water but dissolved in benzene, chloroform and methanol. The yield of this unusual product increased when the hydrogen atmosphere was replaced by nitrogen and it became apparent that this substance was the des-base resulting from a single Hofmann degradation. Subsequently, a more rational procedure—the heating of a mixture of C-curarine-I chloride and C-curarine-I hydroxide in ethanol—was developed which allowed the isolation of crystalline des-C-curarine-I (partial structure V) in good and reproducible yields.

(1) This investigation was supported by a research grant (B-671) from the National Institute of Neurological Diseases and Blindness of the National Institutes of Health, Public Health Service.

(2) Paper III in this series; for the preceding communication, see A. Zürcher, O. Ceder and V. Boekelheide, *THIS JOURNAL*, **80**, 1500 (1958).

(3) H. Schmid, A. Ebnöther and P. Karrer, *Helv. Chim. Acta*, **33**, 1486 (1950).

(4) Th. Wieland and H. Fritz, *Naturwissenschaften*, **42**, 297 (1955).

(5) W. von Philipsborn, H. Schmid and P. Karrer, *Helv. Chim. Acta*, **38**, 1067 (1955).

(6) H. Wieland, H. J. Pistor and K. Bähr, *Ann.*, **547**, 140 (1941).

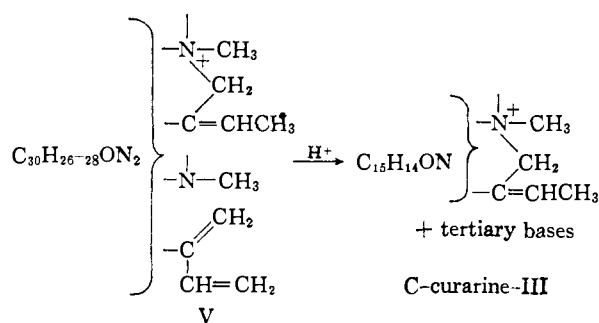
(7) W. von Philipsborn, H. Schmid and P. Karrer, *Helv. Chim. Acta*, **39**, 913 (1956).

(8) R. Pappo, D. S. Allen, R. U. Lemieux and W. S. Johnson *J. Org. Chem.*, **21**, 478 (1956).

(9) H. Bickel, H. Schmid and P. Karrer, *Helv. Chim. Acta*, **38**, 649 (1955).

(10) K. Bernauer, H. Schmid and P. Karrer, *ibid.*, **40**, 731 (1957).

(11) Isocalebassine is also known as C-toxiferine-III; cf. Th. Wieland, H. Fritz and K. Hasspacher, *Ann.*, **588**, 1 (1954).



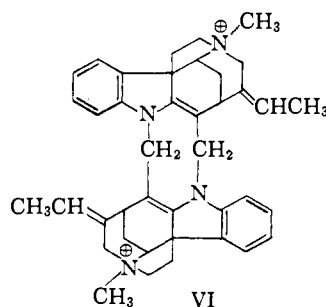
The evidence in support of des-C-curarine-I as the product of a single Hofmann degradation can be summarized as follows. The composition of des-C-curarine-I chloride is in accord with the molecular formula $\text{C}_{40}\text{H}_{43-45}\text{ON}_4\text{Cl}$. On paper electrophoresis using a buffer of pH 6.8, the comparative mobilities of C-curarine-I chloride, des-C-curarine-I chloride and the octahydro base IV were in the ratio of 1:0.76:0.00, just as would be expected in comparing a monoquaternary salt with the corresponding diquaternary salt and the ditertiary base. The infrared spectrum of V showed absorption bands indicative of a terminal methylene group (11.13μ), a vinyl group (10.08 and 10.87μ) and a trisubstituted double bond (12.10μ). In support of these conclusions from the spectrum, oxidation of the des-base with osmium tetroxide, sodium chlorate and then with periodic acid¹¹ yielded both formaldehyde and acetaldehyde. Treatment of des-C-curarine-I with methyl iodide gave a crystalline diquaternary salt whose $-\text{N}-\text{CH}_3$ content was markedly higher than that of C-curarine-I chloride. To show that no other structural change had occurred and as final proof of partial structure V, des-C-curarine-I hydroxide was subjected to a second Hofmann degradation and the product was shown to be identical in all respects with the ditertiary ether base obtained previously from C-curarine-I.⁶

The formation of des-C-curarine-I provides unequivocal evidence for certain structural features of the C-curarine-I molecule. First of all, these findings offer proof, quite independent of that previously given,⁷ that the correct formulation of C-curarine-I is that of a C_{40} and not a C_{20} -alkaloid. Secondly, the hypothesis that the conversion of C-curarine-I to C-curarine-III on acid treatment involves the cleavage of a C_{40} -alkaloid to give a C_{20} -fragment^{2,12} can now be tested. For, by an extension of this hypothesis, it would be predicted that a similar acid treatment of des-C-curarine-I should yield C-curarine-III plus a tertiary base fraction corresponding to the second half of C-curarine-I. This has been found to be true. The mixture resulting from treating des-C-curarine-I with concd. hydrochloric acid contained both quaternary and tertiary amines and the presence of C-curarine-III in the quaternary fraction readily was established. Thus, this acid degradation of des-C-curarine-I provides conclusive evidence that C-curarine-III is a C_{20} -alkaloid.¹³

(12) H. Fritz and Th. Wieland, *Ann.*, **611**, 277 (1958).

(13) During the preparation of this manuscript, the publication of W. von Philipsborn, H. Meyer, H. Schmid and P. Karrer (*Helv. Chim.*

Probably the chief importance of the discovery of des-C-curarine-I lies in the fact that it makes it possible to distinguish between the two halves of the C-curarine-I molecule and thus the prospect is opened that points of structural interest can be examined in one-half of the molecule independently of the other. Attempts to capitalize on this differentiation are being pursued. The overriding question, of course, is whether C-curarine-I has a symmetrical structure or, at least, whether the two C_{20} -fragments are structurally alike. Although it has been generally assumed that this was true, there is as yet no clear basis for a decision. Bernauer, Schmid and Karrer¹⁴ have demonstrated that photochemical oxidation of C-dihydrotoxiciferine gives C-curarine-I. Further, in a very recent paper,¹⁵ they have proposed structure VI for this molecule, although as yet the experimental basis for this proposal has not been published.^{15a}



Whether or not C-dihydrotoxiciferine has structure VI probably will need to await further study. However, the present findings would suggest that a completely symmetrical structure such as this is not appropriate for C-curarine-I. The isolation of des-C-curarine-I is explained most easily by assuming that the Hofmann elimination occurs more readily at one quaternary nitrogen than the other. Of course, a possible solution of this point would be the correlation of structure of C-curarine-III with that of a tertiary base produced in the acid cleavage of des-C-curarine-I. This approach is being followed.

Experimental¹⁶

Emde Degradation of C-Curarine-I.—The following procedure has been found to give reproducible results. A mixture of 11 mg. of Adams catalyst and 7.2 ml. of a 0.01 *N* potassium hydroxide solution (prepared by dissolving the calculated quantity of analytical reagent potassium hydroxide in freshly-distilled 95% ethanol) in a new 35-ml. Pyrex flask was stirred magnetically using a Teflon coated magnet for 10 hr. in an atmosphere of hydrogen. Then, 11 mg. of C-curarine-I chloride in a Teflon cylinder was added and stirring was continued for 4 days. The hydrogen uptake

Acta, **41**, 1257 (1958)) was received. Their report contains independent evidence that C-curarine-III chloride has the molecular formula $\text{C}_{20}\text{H}_{29}\text{ON}_2\text{Cl}$.

(14) K. Bernauer, H. Schmid and P. Karrer, *ibid.*, **40**, 1999 (1957).

(15) K. Bernauer, H. Schmid and P. Karrer, *ibid.*, **41**, 1408 (1958).

(15a) Since the submission of this manuscript, K. Bernauer, F. Berlage, W. von Philipsborn, H. Schmid and P. Karrer have described the conversion of Wieland-Gumlich aldehyde to caracurine-V (*Helv. Chim. Acta*, **41**, 2293 (1958)) and the further conversion of caracurine-V to C-dihydrotoxiciferine (*ibid.*, **42**, 201 (1959)). These transformations provide good evidence that C-dihydrotoxiciferine has structure VI.

(16) Analyses by Mr. W. Manser, Miss A. Smith and the Micro Tech Laboratories. Infrared spectra were obtained using a Perkin-Elmer infrared spectrophotometer, model 21. Ultraviolet spectra were taken using a Cary recording spectrophotometer, model 11 MS.

corresponded to the theoretical. Water then was added, the catalyst was removed and the solution was concentrated *in vacuo*. Extraction of the residue with ether followed by concentration of the ethereal solution gave 8 mg. of a crystalline solid. This, after recrystallization from an ether-ethanol mixture, gave 7 mg. of white crystals, m.p. 182–184°. In some runs, the resulting crystals melted at 151–153°. Both forms of the crystals have the same infrared spectrum in solution and the interconversion of the two crystalline forms by the proper seeding experiments demonstrates that these are polymorphic forms. The ultraviolet absorption spectrum of the Emde product in alcohol showed maxima at 209, 258 and 290 μ , which were only slightly altered by addition of acid to 209, 260 and 290 μ (shoulder). Hydrogenation of a sample of the Emde product gave an oil whose infrared spectrum was identical with that of octahydro base.⁶

Anal. Calcd. for $C_{40}H_{48}ON_4$: C, 80.23; H, 7.74; N, 9.36. Calcd. for $C_{40}H_{48}ON_4 \cdot Cl \cdot H_2O$: C, 79.96; H, 8.05; N, 9.33. Found: C, 80.24, 80.54; H, 7.74, 7.84; N, 9.61, 9.47.

The dimethiodide of the Emde product was prepared by dissolving 10 mg. of the Emde product in a solution of 0.5 ml. of benzene, 0.5 ml. of alcohol and 1 ml. of methyl iodide and allowing the mixture to stand in the dark for 3 days. The crystalline dimethiodide, m.p. 195–200°, was collected and, after recrystallization from acetone-methanol, gave white plates, m.p. 210–211°.

Anal. Calcd. for $C_{42}H_{52}ON_4I_2 \cdot 4H_2O$: C, 52.85; H, 6.29. Found: C, 53.30; H, 6.24.

Osmium Tetroxide-Periodate Oxidation of the Emde Methochloride.—A solution of 21 mg. of the dimethiodide of the Emde base was converted to the corresponding chloride by passage over an ion exchange column (Dowex-2, chloride). The crystals, m.p. 203–205°, resulting on concentration of the ethanol eluate, were dissolved in 3 ml. of water and treated with 1.4 mg. of osmium tetroxide and 56 mg. of sodium metaperiodate. After the mixture had been stirred for 22 hr. at room temperature, it was heated on a steam-bath under a nitrogen stream leading on exit into 2,4-dinitrophenylhydrazine reagent. There separated 5.7 mg. (46%) of the 2,4-dinitrophenylhydrazone of formaldehyde, identified by comparative paper chromatography.¹⁷ A weak spot indicating acetaldehyde, probably due to double bond isomerization, was noted. Oxidation of C-curarine-III in a similar manner gave only acetaldehyde, isolated and identified through its 2,4-dinitrophenylhydrazone, in 32% yield.

Des-C-curarine-I Chloride. (a) **Standardized Procedure.**—A solution of 103 mg. of C-curarine-I chloride in 10 ml. of ethanol was passed over an ion exchange resin (Amberlite I.R.A.-400, hydroxide) to convert it to the corresponding quaternary hydroxide. To the eluate there was now added a solution of 40 mg. of C-curarine-I chloride in 50 ml. of absolute ethanol and the resulting solution then was boiled under reflux for 12 hr. under an atmosphere of nitrogen. The solution was concentrated under reduced pressure and the residue was heated on a steam-bath for 30 min. After addition of 20 ml. of water, the milky suspension first was extracted with ether and then with chloroform. Concentration of the ether extract gave 4 mg. of crystals, whose infrared spectrum was identical with that of the ditertiary ether base first described by Wieland, Pistor and Bähr.⁶ The aqueous solution was passed over an ion exchange column (Dowex-2, chloride) and, on concentration of the eluate, 45 mg. of crystalline C-curarine-I chloride was recovered. Concentration of the chloroform extract gave 96 mg. of a colorless sirup which was dissolved in ethanol and passed over an ion exchange column (Dowex 2, chloride). The resulting eluate was basic and contained chloride ion. On concentration, it gave a crystalline residue which, after recrystallization from methanol-diisopropyl ether, yielded 83 mg. of white crystals, m.p. >350°. Its ultraviolet absorption spectrum in alcohol showed maxima at 258 ($\log \epsilon$ 4.37) and 294 μ ($\log \epsilon$ 4.06). In the infrared it showed absorption at 10.08 and 10.87 ($-\text{CH}=\text{CH}_2$), 11.13 ($>\text{C}=\text{CH}_2$) and 12.10 μ ($-\text{C}=\text{CH}-$). The relative mobilities of C-curarine-I chloride, des-C-curarine-I chloride and octahydro base were compared by paper electrophoresis using a phosphate buffer (pH 6.8) and found to be 1:0.76:0.00. A similar comparison by partition chromatography

on paper using 1-butanol saturated with water as the moving phase in a descending chromatogram showed the ratio of R_f values to be 0.2:0.65:0.82. The color reactions of des-C-curarine-I were very similar to those of C-curarine-I.

Anal. Calcd. for $C_{40}H_{48}ON_4Cl \cdot H_2O$: C, 73.99; H, 6.99; N, 8.63; Cl, 5.46; N-CH₃ (2), 4.65; C-CH₃ (1), 2.32. Calcd. for $C_{40}H_{48}ON_4Cl \cdot H_2O$: C, 73.76; H, 7.28; N, 8.60; Cl, 5.44; N-CH₃ (2), 4.62; C-CH₃ (1), 2.31. Found: C, 73.31; H, 7.06; N, 8.67; Cl, 5.77; N-CH₃, 5.14; C-CH₃, 2.20.

The des-C-curarine-I methiodipicrate was prepared by dissolving 93 mg. of des-C-curarine-I chloride in 1.5 ml. of methyl iodide and allowing the solution to stand overnight at room temperature in the dark. The white solid, which had separated, was dissolved by addition of a few drops of methanol and the solution was allowed to stand an additional two hours. After removal of the methanol and excess methyl iodide *in vacuo*, the residue was dissolved in 5 ml. of water, the slightly turbid solution was filtered, and a saturated aqueous solution of picric acid then was added dropwise to the clear solution. The solid picrate, which separated, was collected and, after recrystallization from an acetone-water mixture, gave 117 mg. of fine yellow needles, m.p. 267–268°.

Anal. Calcd. for $C_{41}H_{48}ON_4 \cdot 2(C_6H_3O_7N_3)$: C, 59.54; H, 4.90; N, 13.10. Found: C, 59.63; H, 5.21; N, 12.83.

The des-C-curarine-I methiodiiodide was prepared by dissolving 6.25 mg. of des-C-curarine-I methiodipicrate in methanol and passing it over an ion exchange resin (Dowex-2, iodide). Removal of the solvent from the eluate gave 53 mg. of a solid which, after recrystallization from a methanol-diisopropyl ether mixture, gave white needles, m.p. >300°.

Anal. Calcd. for $C_{41}H_{48}ON_4I_2 \cdot 3H_2O$: C, 53.49; H, 5.91; N, 6.09; N-CH₃(3), 4.90. Found: C, 53.56; H, 5.50; N, 6.05; N-CH₃, 5.55.

(b) **By the Emde Procedure.**—A mixture of 123 mg. of Adams catalyst in 20 ml. of a 0.5 N solution of ethanolic potassium hydroxide was stirred magnetically with a Teflon coated stirrer in a polyethylene flask under an atmosphere of hydrogen for 1 day. The hydrogen atmosphere was replaced by nitrogen, 41.5 mg. of C-curarine-I chloride was added and the solution was stirred an additional 12 days at 30°. After the addition of water, the catalyst was removed and the solution was concentrated. The residue was taken up in water giving a milky suspension which was extracted first with ether and then with chloroform. Concentration of the ether extract gave 22 mg. of a colorless gum. The residue from the chloroform extract weighed 21 mg. and this was converted to crystalline des-C-curarine-I chloride by the ion exchange procedure described in (a).

Conversion of Des-C-curarine-I to Ditertiary Ether Base.—A solution of 11 mg. of des-C-curarine-I chloride in ethanol was passed over an ion exchange column (Amberlite I.R.A.-400, hydroxide) and the eluate was boiled under reflux under a nitrogen atmosphere for 17 hr. The solution was then concentrated and the residue was heated on a steam-bath for 10 min. An ether-water mixture then was added with shaking to dissolve the residue. After the ether layer was separated, it was concentrated to give 8 mg. of a crystalline residue. It was shown to be identical with the ditertiary ether base of Wieland, Pistor and Bähr⁶ by a comparison of their ultraviolet and infrared spectra. Also, the two bases showed the same color reactions. Finally, the sample of ditertiary ether base obtained from des-C-curarine-I was converted to the corresponding dimethiodide and this was shown to be identical in all respects with a sample of the dimethiodide prepared from an authentic specimen of the ditertiary ether base. The dimethiodide of the ditertiary ether base was obtained as white crystals, m.p. >300°, after recrystallization from a methanol-diisopropyl ether mixture.

Anal. Calcd. for $C_{42}H_{52}ON_4I_2 \cdot 4H_2O$: C, 53.06; H, 5.94; N, 5.89. Found: C, 53.09; H, 5.76; N, 6.29.

Oxidation of Des-C-curarine-I Chloride with Osmium Tetroxide-Sodium Chlorate.—A sample of 29.8 mg. of the crystalline des-C-curarine-I dimethiodipicrate was dissolved in 10 ml. of a 1:1 acetone-methanol mixture and passed over an ion exchange resin (Dowex 2, chloride). Concentration of the eluate gave 21.6 mg. of a solid which was oxidized directly following the general procedure described

(17) F. E. Huelin and B. H. Kennett, *Chemistry & Industry*, 715 (1956).

by Th. Wieland, Fritz and Hasspacher.¹¹ To a solution of 21.6 mg. of the quaternary chloride in 3 ml. of water there was added 35 mg. of sodium chlorate and one crystal of osmium tetroxide and the resulting solution was heated at 70° in a sealed tube for 90 hr. The solution was then transferred to a distilling flask and 40 mg. of periodic acid was added. The flask was then heated using a nitrogen stream for ebullition and leading the exit gases into a trap containing 2,4-dinitrophenyl hydrazine dissolved in 2 *N* hydrochloric acid. After the bulk of the water had been distilled, the contents of the trap were extracted with chloroform. After the chloroform extract had been dried over sodium sulfate, it was concentrated to give 11 mg. of a solid. This was filtered, then taken up in chloroform, and chromatographed over a 4:1 mixture of Bentonite and Celite. From the ethanol-chloroform eluate fractions there was isolated two crystalline dinitrophenylhydrazones. The first of these, weighing 0.9 mg. (14%), was shown to be the 2,4-dinitrophenylhydrazone of acetaldehyde by comparative paper chromatography using a heptane-methanol mixture.¹⁷ The second fraction weighed 1.9 mg. (16%) and was identified as the 2,4-dinitrophenylhydrazone of formaldehyde by a similar comparative paper chromatogram.

Degradation of Des-C-curarine-I with Acid to Give C-Curarine-III.—A solution of 15.6 mg. of des-C-curarine-I chloride in 2 ml. of concd. hydrochloric acid was allowed to stand in the dark at room temperature for 2 days. It first became red-brown and then, eventually, yellow-brown. After removal of the hydrochloric acid *in vacuo*, the residue was taken up in water-saturated 1-butanol and chromatographed over powdered cellulose (Solka-Floc, BW-40).

By their fluorescence in ultraviolet light, six separate compounds could be detected on the column. The first of these moved with the solvent front and showed the behavior of a tertiary base. The third component weighed 5.2 mg. (33%) and had an ultraviolet absorption spectrum in agreement with that of C-curarine-III. It was purified further by a second chromatogram over powdered cellulose using a methyl ethyl ketone-methanol-water mixture (solvent C) to give 2.1 mg. of pure material. This was shown to be identical with an authentic sample of C-curarine-III by the following experiments. Comparative paper chromatograms using two different solvents—1-butanol and the solvent C (methyl ethyl ketone-methanol-water)—showed both to have identical behavior. Paper electrophoresis experiments both using 5% acetic acid and using a phosphate buffer (pH 6.8) showed no differences in behavior of the two compounds. Finally, the ultraviolet absorption spectra of the two samples were identical and both showed the same shift with base characteristic of C-curarine-III.

From the first fraction which moved with the solvent front there was isolated a solid residue. This was dissolved in water and made basic with ammonia. Extraction of the aqueous solution with chloroform gave 4.5 mg. of a solid which was taken up in solvent C and chromatographed over powdered cellulose. A compound showing pale-blue fluorescence moved with the solvent front. This showed only a slight movement on paper electrophoresis using either 5% acetic acid or a phosphate buffer (pH 6.8) and is presumed to be a tertiary base derived from the second half of des-C-curarine-I.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

Syntheses of Thermochromic Ethylenes. A Study of the Relationship between Constitution and Thermochromism

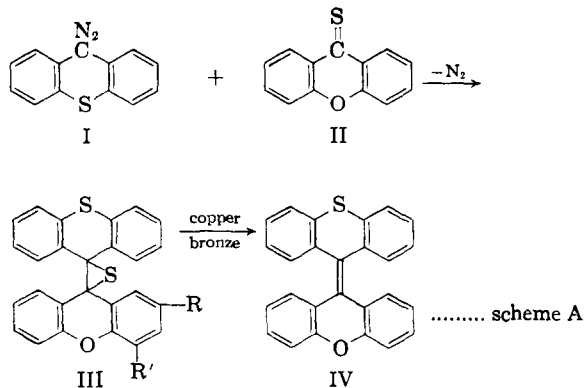
BY ALEXANDER SCHÖNBERG AND MAHMOUD MOHAMED SIDKY

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A number of tetraarylethylenes were prepared by the ethylene sulfide method: the action of diaryldiazomethanes on diaryl thioketones yielded ethylene sulfides from which tetraarylethylenes were obtained by elimination of sulfur. Monothiodixanthylene (IV) shows thermochromic changes (colorless \rightleftharpoons deep green) at higher temperatures than dixanthylene (IV, S to be replaced by O). 9-(9-Fluorenylidene)-xanthene (VIIIa) is deep violet in color (non-thermochromic) in contrast to the yellow sulfur analog VIIIb, which is strongly thermochromic (yellow \rightleftharpoons malachite green); the green (thermochromic) form is believed to correspond to the violet form of (VIIIa). The relationship between thermochromic and adsorption colors of spiropyrans (comp. XIII) and dixanthylens (comp. IV, O = S) is discussed.

In order to increase our knowledge of the relationship between thermochromic properties and constitution of tetraarylethylenes and thus to gain a better understanding of thermochromism, we have synthesized a number of new ethylenes, some of which showed strong thermochromic properties.

Preparation of Ethylenes by the Ethylene Sulfide Method.—Monothiodixanthylene(9-(thiaxon-



thene-10-ylidene)-xanthene) (IV) was obtained according to scheme A. Similarly dithiodixanthylene (IV, O = S) was prepared from diazothioxanthene (I) and thioxanthione (Vb).

The action of thioxanthione (Vb) on diazothioxanthene (I) yielded III (replace O by S; R = R' = H); using I and 2-methylxanthione (V, A = O, R = CH₃, R' = H) or 4-methylxanthione (V, A = O, R = H, R' = CH₃), the ethylene sulfide derivatives III (R = CH₃, R' = H) and III (R = H, R' = CH₃) were obtained, respectively.

By reactions similar to scheme A, xanthione (Va) and 9-diazofluorene (VI) yielded 9-(9-fluorenylidene)-xanthene (VIIIa), whereas 10-(9-fluorenylidene)-thioxanthene (VIIIb) was obtained¹ from thioxanthione (Vb) and 9-diazofluorene. Derivatives of VII also were prepared, e.g., by the action of 9-diazofluorene on 2-methylxanthione (Va, R = CH₃, R' = H) and on 4-methylxanthione (Va, R = H, R' = CH₃).

(1) It should be noted that in xanthenes the oxygen atoms have number 10, whereas the sulfur atoms in thioxanthenes have the number 5.