benzenesulfonate and sodium benzenesulfinate by comparison of its infrared spectrum with that of an authentic mixture.

Reaction of α-cyanobenzyl benzenesulfonate with sodium ethoxide (2:1). A solution of 5.5 g. (0.02 mole) of α-cyanobenzyl benzenesulfonate in 20 ml. of ethanol containing 0.23 g. (0.01 mole) of sodium was allowed to stand at room temperature for 3 hr. The solid which had separated was then collected by filtration to give 1.7 g. of sodium benzenesulfonate, identical with an authentic sample. Evaporation of the filtrate under reduced pressure and distillation of the liquid residue gave 1.35 g. (97%) of ethyl benzoate, b.p. 210–212°. The residue from the distillation was dissolved in water and the *p*H adjusted to 4 with hydrochloric acid. Filtration then gave 1.0 g. (39%) of α-cyanobenzyl phenyl sulfone, m.p. 148–150°, identical with an authentic sample.[4]

PRINCETON, N. J.

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DEPARTMENT RESEARCH DIVISION, ABBOTT LABORATORIES]

Nitrosation and Diazonium Salt Coupling of Amadori Products

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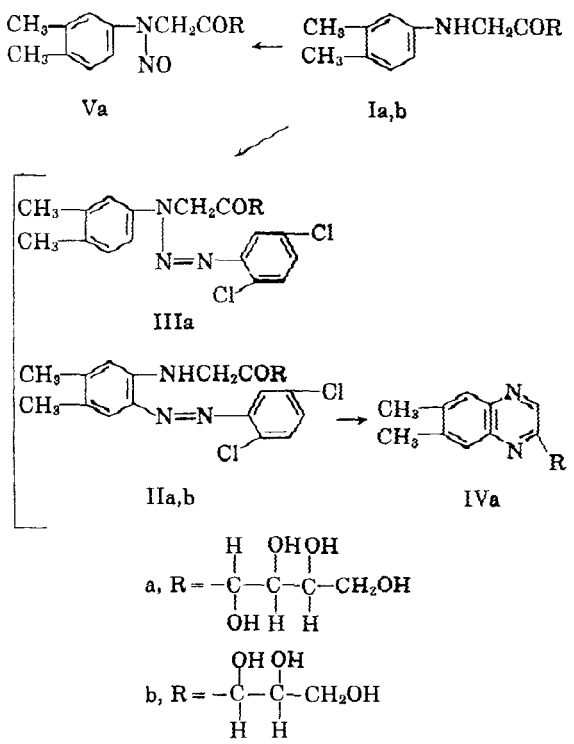
Whereas nitrosation of the aminodeoxyfructose derivative Ia occurs at the nitrogen atom, coupling with diazotized 2,5-dichloroaniline in aqueous acid solution takes place at the nitrogen and ring-carbon atoms. Coupling of the deoxypentulose derivative Ib occurs entirely at the ring-carbon atom. Attempts to convert the azo compounds IIa and IIb to analogs of riboflavin have failed. The structures of these Amadori products are discussed.

The present work was undertaken in an attempt to prepare an analog of riboflavin containing a 1-deoxy-D-erythropentulose side-chain in place of the normal D-ribityl group. It has been suggested[1] that this "dehydroriboflavin" may function as a biological precursor of the natural vitamin. This article describes unsuccessful efforts to synthesize it.

The 1-deoxy-D-fructose derivative Ia, in contrast to the structurally more pertinent Ib, is readily isolable.[1,2] Therefore, Ia was selected as a model. Coupling of Ia with diazotized 2,5-dichloroaniline[3] in aqueous acid solution gave two isomeric products: the yellow triazene IIIa and the red azo compound IIa, readily separated by fractional crystallization from 95% ethanol. The solubility, optical rotatory, and ultraviolet and infrared spectral properties of the triazene IIIa are quite similar to those recently reported by Kuhn, Krüger, and Seeliger[4] for a series of analogous compounds. However, under the basic conditions (pyridine-methanol) of their coupling reactions only the yellow triazenes were formed. Under the acidic conditions used in the present work, formation of the red azo compound IIa appeared to preponderate. Although it is much more soluble in ethanol than IIIa, IIa could be isolated readily in analytically pure form. Paper-strip chromatographic analysis demonstrated the absence in it of any of the yellow isomer (see Experimental).

Reductive cleavage of the azo group in IIa followed by condensation with alloxan gave no product possessing the properties of the desired isoalloxazine. This failure to react intermolecularly is accounted for by a predominant tendency of the intermediate *o*-phenylenediamine to cyclize to the quinoxaline IVa, identical with an authentic specimen prepared by treating 4,5-dimethyl-*o*-phenylenediamine with D-fructose, according to the method of Ohle.[5] Thus, little more was learned than that the preferred point of attack of the diazonium ion was at the symmetrical position of the benzene ring. This much was expected.[6]



(1) F. Weygand, *Ber.*, **73**, 1259 (1940).

(2) R. Kuhn and L. Birkofer, *Ber.*, **71**, 621 (1938).

(3) Preliminary experiments with a number of diazotized anilines demonstrated a clear superiority of this diazonium salt as regards yields and ease of purification of products.

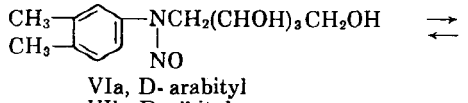
(4) R. Kuhn, G. Krüger, and A. Seeliger, *Ann.*, **628**, 240 (1959).

(5) H. Ohle, *Ber.*, **67**, 155 (1934).

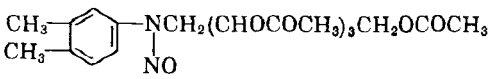
In order to minimize intramolecular cyclization, the azo compound IIa was treated directly with barbituric acid according to the method of Tishler and co-workers.[6] In this reaction barbituric acid serves both as reducing agent and reactant. However, under a variety of conditions, only dark amorphous products which possessed none of the light absorption and fluorescence characteristics of the isoalloxazine ring system were obtained.[7]

The Amadori product Ib, obtained from 3,4-xylidine and D-arabinose, cannot be isolated in crystalline form.[1] Nevertheless, an acidic aqueous solution of it, treated with diazotized 2,5-dichloroaniline, gave an azo compound IIb, which could be isolated and characterized (see Experimental). In this case, the azo compound appeared to be unaccompanied by any of the yellow isomeric triazene IIIb. However, in common with the fructose derivative IIa, all efforts to convert the pentulose analog IIb to an isoalloxazine failed. No attempts were made to isolate the quinoxaline IVb which, very likely, formed in many of these reactions.

As was to be expected, nitrosation of the Amadori product Ia occurred on the nitrogen atom to give Va. The position of the nitroso group was indicated by its infrared absorption spectrum (see Experimental) and by analogy to the products VIa and VIb obtained by nitrosation of the corresponding xylidine derivatives. The infrared spectra of VIa and VIb both indicate the presence of a nitrosamine rather than a C-nitroso group. Furthermore, by reductive cleavage of the nitroso group in VIa, and by conversion of VIa to its tetraacetate VIIa, which could be reconverted to VIa by mild methanolysis, it was proved that in VIa, at least, the nitroso group is on the xylidine nitrogen atom.



VIa, D-arabityl
VIb, D-ribityl



VIIa

Structure of Amadori products. There is no doubt about the ketose structure of Amadori rearrangement products.[8] Furthermore, recent spectral and chemical evidence indicates that many Amadori products of the hexulose series exist as hemiketals,[9] preferably of the pyranose form.[10] When the pyranose form is unattainable, as in the pentulose series, the acyclic ketone structure is favored over the alternative furanose ring system.[4] However, exceptions to this rule have been noted[4,11] wherein a few Amadori products of the hexulose series appear to prefer the acyclic form, at least in the solid state (*i.e.*, their infrared absorption spectra in potassium bromide show strong carbonyl absorption).

In the present work, the starting material Ia is the only compound possessing an infrared absorption spectrum shown by Micheel[9a,c] to be characteristic of many Amadori products [i.e., no carbonyl absorption, and the presence of a sharp band at 3570 cm.$^{-1}$ (2.80 μ) assigned to the hemiketal hydroxyl group]. All of the other hexulose derivatives, IIa, IIIa, and Va show strong carbonyl absorption in the infrared (potassium bromide) and no sharp peak at 3570 cm.$^{-1}$ In this they resemble the pentulose derivative IIb which, as expected,[4] also exhibits carbonyl absorption.[12]

As has been found[4,11] with other exceptions of this type, the triazene IIIa exhibits mutarotation in pyridine solution indicating that, in the dissolved state, a ring-chain equilibrium must exist. Similar behavior on the part of the nitroso compound Va could not be detected. What little optical activity it possessed in pyridine solution remained quite constant.

EXPERIMENTAL[13]

1-Deoxy-1-[6'-(2",5"-dichlorophenylazo)-3',4'-xylidino]-D-fructose (IIa) and *1-deoxy-1-[N-(2",5"-dichlorophenylazo)-3',4'-xylidino]-D-fructose* (IIIa). To an ice cold solution of 8.4 g. (0.052 mole) of 2,5-dichloroaniline in 50 ml. of water containing 15 ml. of concd. hydrochloric acid, was added, portion-wise, a solution of 4.5 g. (0.069 mole) of sodium nitrite in 25 ml. of water. The temperature was maintained below 10° during the diazotization. After stirring for 3 hr. in an ice bath, excess sulfamic acid was added to decompose excess nitrous acid, and the diazonium salt solution was filtered, diluted to a volume of 150 ml. with cold water, and added all at once to a stirred ice cold solution of 12.3 g. (0.044 mole) of 1-deoxy-1-(3',4'-xylidino)-D-fructose (Ia)[1] in 70 ml. of water containing 4 ml. of concd. hydrochloric acid. After stirring in an ice bath for 2 hr., the reaction mixture was treated dropwise over a period of 0.25 hr. with a solution of 25 g. of sodium acetate in 50 ml. of water. After being stirred overnight in a refrigerated room (4–5°), the mixture was filtered by suction (the *p*H of the filtrate was 2.1) and the product (mixture of IIa and IIIa) was washed well with water. Drying gave 20.1 g. of dark red powder, m.p. 90–105°.

(6) Compare, M. Tishler, K. Pfister, R. D. Babson, K. Ladenburg, and A. J. Fleming, *J. Am. Chem. Soc.*, **69**, 1487 (1947).

(7) The failure to form the isoalloxazine ring system in these reactions casts grave doubt on some of the claims made by J. Kamlet in U. S. Pat. **2,406,774**, Sept. 3, 1946.

(8) J. E. Hodge, *Advances in Carbohydrate Chemistry*, Vol. 10, Academic Press, Inc., New York, 1955, p. 199.

(9) (a) F. Micheel and B. Schleppinghoff, *Chem. Ber.*, **89**, 1702 (1956). (b) G. Huber, O. Schier, and J. Druey, *Helv. Chim. Acta*, **43**, 713 (1960). (c) F. Micheel and V. Hühne, *Chem. Ber.*, **93**, 2383 (1960).

(10) R. Kuhn and G. Krüger, *Ann.*, **618**, 82 (1958).

(11) F. Weygand, H. Simon, and R. von Ardenne, *Ber.*, **92**, 3117 (1959).

(12) It is interesting to note that, of a series of triazenes of type IIIa prepared by Kuhn and Krüger,[4] the only hexulose that shows carbonyl absorption in the infrared was one which, like IIIa, contains a 2,5-dichlorophenylazo group.

(13) Melting points are not corrected.

The two components of this mixture were readily separated by fractional crystallization from 95% ethanol. From the insoluble portion was obtained 5.9 g. of orange powder, m.p. 175–180°. One recrystallization from dioxane gave the triazene IIIa as a canary-yellow powder, m.p. 186–187° dec., $[\alpha]_D$ −27.5° (*c* 0.1034 in pyridine) changing to, and remaining constant at +56.5° in a period of 20 hr., log $\epsilon_{shoulder}$ 4.090 (247 mμ), log ϵ_{min} 3.550 (272 mμ), log ϵ_{max} 4.220 (358 mμ) in 95% ethanol.

Anal. Calcd. for $C_{20}H_{22}Cl_2N_4O_5$: C, 52.66; H, 5.08; N, 9.21; Cl, 15.55. Found: C, 52.82; H, 5.22; N, 9.36; Cl, 15.72.

This compound reduces methylene blue in alkaline solution and its infrared spectrum (potassium bromide pellet) shows carbonyl absorption at 5.74 μ (1740 cm.$^{-1}$), but none at 2.80 μ (3570 cm.$^{-1}$).[9a]

From the soluble fraction, on concentration and cooling, was obtained 4.57 g. of crude azo compound IIa as a deep-red powder, m.p. 139–142°. For analysis, it was recrystallized several times from *i*-propyl alcohol to give a bright-crimson crystalline powder, m.p. 145–146° (dec.), log $\epsilon_{shoulder}$ 4.199 (235 mμ), log ϵ_{min} 3.680 (290 mμ), log ϵ_{max} 4.179 (338 mμ), log ϵ_{min} 3.497 (400 mμ), and log ϵ_{max} 3.931 (490 mμ) in 95% ethanol.

Anal. Calcd. for $C_{20}H_{22}Cl_2N_4O_5$: C, 52.66; H, 5.08; N, 9.21. Found: C. 52.50; H, 5.07; N, 9.01. The infrared spectrum (potassium bromide) shows carbonyl absorption at 5.78 μ (1730 cm.$^{-1}$) but none at 2.80 μ (3570 cm.$^{-1}$).[9a] The virtual absence, in this sample, of any of the isomeric triazene IIIa was proved by a paper strip chromatogram using 95% ethanol as a developing solvent. The red azo compound moved with the solvent front and left no yellow color at the origin. Under similar conditions it was found that the yellow triazene IIIa remained at the origin.

1-Deoxy-1-[6′-(2″,5″-dichlorophenylazo)-3′,4′-xylidino]-D-erythropentulose (IIb). A mixture of 10 g. of D-arabinose, 8 g. of 3,4-xylidine,[14] and 0.5 g. of benzoic acid was pulverized, treated with 3 ml. of water, and heated in a nitrogen atmosphere for 3 min. at 90–95°. The reaction mixture was cooled in an ice bath, and then was stirred vigorously for 10 min. at room temperature with a solution of 5 ml. of concd. hydrochloric acid in 100 ml. of water. Benzene (100 ml.) was then added, and stirring was continued for another 15 min. The separated aqueous layer was filtered through a layer of charcoal, cooled in ice, and treated with a cold solution of 3.5 g. of sodium hydroxide in 10 ml. of water. After extraction with 100 ml. of benzene in two portions, the cold aqueous solution was treated with a cold solution of 5 ml. of concd. hydrochloric acid in 10 ml. of water and filtered once more through charcoal. The mixture, diluted to 250 ml., was cooled in ice and treated with stirring with a cold diazonium salt solution prepared, as described above, from 2.43 g. of 2,5-dichloroaniline. After stirring in an ice bath for 1 hr., 5 g. of solid sodium acetate was added, stirring was continued for another hour, and 10 g. more sodium acetate was added. Stirring was then continued overnight in a melting ice bath. The red product was filtered off at the water pump (the *p*H of the filtrate was 4.5) and dried in a vacuum oven at 50°. There was obtained 5.12 g. of crude product, m.p. 90–98°. Three recrystallizations from 95% ethanol gave 1.43 g. of pure IIb, as a red powder, m.p. 119–121° dec., log $\epsilon_{shoulder}$ 4.176 (242 mμ), log ϵ_{min} 3.774 (280 mμ), log ϵ_{max} 4.104 (350 mμ), log ϵ_{min} 3.377 (430 mμ), log ϵ_{max} 3.542 (490 mμ) in 95% ethanol.

Anal. Calcd. for $C_{19}H_{21}Cl_2N_3O_4$: C, 53.55; H, 4.97; N, 9.86. Found: C, 53.33, 53.24; H, 4.83, 4.95; N, 9.76.

This compound rapidly reduces methylene blue in dilute alkaline solution and its infrared spectrum (potassium bromide) shows ketonic carbonyl absorption at 5.76 μ (1736 cm.$^{-1}$), but none at 2.80 μ (3570 cm.$^{-1}$).[9a]

The absence in this material of any of the isomeric triazene analogous to IIIa was established by paper strip chromatography in the same manner as is described above for IIIa. The red azo compound moved with the solvent front and left no color at the origin.

6,7-Dimethyl-2-(D-arabo-tetrahydroxybutyl)quinoxaline (IVa). A. *From 4,5-dimethyl-o-phenylenediamine.* A mixture of 7.2 g. of D-fructose and 5.5 g. of 4,5-dimethyl-*o*-phenylenediamine[15] in 100 ml. of water containing 4 ml. of glacial acetic acid was heated on the steam bath for 1.5 hr., filtered hot through a layer of charcoal, and refrigerated overnight. The crystallized product was collected at the filter and dried. It weighed 1.89 g., m.p. 191–194° dec. One recrystallization from ethanol gave 1.69 g. of pure quinoxaline IVa, m.p. 198–200° dec., log ϵ_{min} 4.140 (228 mμ), log ϵ_{max} 4.465 (242 mμ), log ϵ_{min} 3.179 (270 mμ), log ϵ_{max} 3.945 (324 mμ) in 95% ethanol $[\alpha]_D$ −165° (*c* 0.717 in pyridine).

Anal. Calcd. for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52. Found: C, 60.55; H, 6.46.

B. *From the azo compound* IIa. A solution of 5.4 g. of the azo derivative IIa, m.p. 143–145°, in 300 ml. of 95% ethanol containing 4 drops of glacial acetic acid was hydrogenated at room temperature and 20 lb. pressure for 0.25 hr. Then 0.5 g. of 10% platinized charcoal was added, and hydrogenation was continued for 1 hr. after which 0.5 g. of pre-reduced Adam's catalyst was added. In two more hours, hydrogenation appeared to be complete. The catalyst was removed by filtration, and the filtrate was allowed to stand overnight. A small quantity of precipitate was removed by filtration through a layer of charcoal, and the light-red filtrate was concentrated to dryness in *vacuo*. Trituration of the residual solid with ether, followed by filtration and drying, gave 2.5 g. of crude product, m.p. 160–165°. Three recrystallizations from 95% ethanol gave 0.4 g., of pure quinoxaline IVa, m.p. 199–200°, $[\alpha]_D$ −166° (*c* 0.650 in pyridine).

Anal. Calcd. for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52. Found: C, 60.65; H, 6.62. A mixed melting point with the authentic sample (procedure A) gave no depression and the infrared spectra (mineral oil mull) of the two samples were qualitatively identical.

1-Deoxy-1-(N-nitroso-3′-4′-xylidino)-D-fructose (Va). A solution of 2.8 g. (0.01 mole) of Ia in 100 ml. of a 2:1 ethanol-water mixture was cooled to 20° and treated with 11 ml. of 1*N* hydrochloric acid. The pink solution was cooled further to 10°, and, with stirring, was treated dropwise with a cold solution of 0.75 g. of sodium nitrite in 5 ml. of water. After a positive test for the presence of nitrous acid was no longer observed (potassium iodide starch paper), 1 ml. of 2*N* sodium hydroxide solution was added, and the reaction mixture was distilled under reduced pressure to a volume of about 10 ml. After refrigeration overnight, the crystallized product was removed at the suction filter and dried. There was obtained 2.55 g. (82%) of Va, m.p. 138–140° dec. For analysis, a sample was recrystallized once from 2-butanone to give fine needles, m.p. 139–140° dec., $[\alpha]_D$ + 6.4° (*c* 0.547 in pyridine; no detectable change in rotation in 24 hr.).

Anal. Calcd. for $C_{14}H_{20}N_2O_6$: C, 53.84; H, 6.45; N, 8.96 Found: C, 53.97; H, 6.37; N, 8.71. This compound reduces both methylene blue and *o*-dinitrobenzene in alkaline solution. Unlike the nitroso-derivatives described below, this one is more soluble in both water and ethanol than is the starting material Ia. Its infrared absorption spectrum (potassium bromide) shows strong carbonyl absorption at 5.80 μ (1724 cm.$^{-1}$), but none at 2.80 μ (3570 cm.$^{-1}$). Furthermore, the presence of several strong bands between 6.6 and 7.0 μ (1500–1430 cm.$^{-1}$: the region assigned[16] to >N—NO absorption) and their absence in the 6.25–6.67 μ region (1600–1500 cm.$^{-1}$: the typical C—NO absorption[16]) support the nitrosamine structure Va.

1-Deoxy-1-(N-nitroso-3′,4′-xylidino)-D-arabitol (VIa). Nitrosation of 2 g. of 1-deoxy-1-(3′,4′-xylidino)-D-arabitol,[1] dissolved in 200 ml. of water containing 4 ml. of concd.

(14) H. E. Zaugg, *J. Am. Chem. Soc.*, **67**, 1861 (1945).

(15) E. Noelting and G. Thesmar, *Ber.*, **35**, 628 (1902).

(16) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen and Co., Ltd., London, 1958, p. 298.

hydrochloric acid, was accomplished by adding a solution of 0.70 g. of sodium nitrite in 20 ml. of water, and allowing the reaction mixture to stand for 2 hr. at room temperature. Filtration and drying gave a 95% yield of VIa, m.p. 169–170° dec. Recrystallization from ethanol gave straw-colored needles of the same melting point $[\alpha]_D$ −81.4° (*c* 1.72 in pyridine).

Anal. Calcd. for $C_{18}H_{20}N_2O_8$: C, 54.92; H, 7.09; N, 9.85. Found: C, 54.89; H, 6.98; N, 9.95.

That nitrosation had occurred on nitrogen rather than carbon was indicated by the following reductive cleavage reaction: About 100 mg. of the nitroso compound VIa was suspended in 10 ml. of dry ethanol containing a few granules of tin. The suspension was saturated with anhydrous hydrogen chloride, a few drops of water were added and the mixture was heated on the steam bath for 0.5 hr. On cooling, shiny white platelets of a tin salt crystallized. These were collected at the filter, unchanged tin granules were separated mechanically, and the salt was dissolved in water. Neutralization with a saturated sodium bicarbonate solution gave a white precipitate which was removed by filtration and dried. It proved, by m.p. and mixed m.p. (138–139°) to be the starting 1-deoxy-1-(3′,4′-xylidino)-D-arabitol.

1-Deoxy-1-(N-nitroso-3′,4′-xylidino)-D-arabitol tetraacetate (VIIa). A mixture of 2.6 g. of VIa and 8 ml. of dry pyridine was treated with 5.8 ml. of acetic anhydride, and warmed on the steam bath for 0.25 hr. after homogeneity occurred. After standing at room temperature for 2 hr., the solution was poured into 100 ml. of ice water containing 4 ml. of concd. hydrochloric acid. After standing at room temperature for several hours with occasional trituration, the yellow oil solidified and was collected at the filter. Drying gave 4.00 g. (97%) of VIIa, m.p. 70–72.° For analysis, a sample was recrystallized from 95% ethanol to give elongated prisms, m.p. 73–74°, $[\alpha]_D$ + 67.2° (*c* 1.80 in pyridine).

Anal. Calcd. for $C_{21}H_{28}N_2O_{12}$: C, 55.74; H, 6.24; N, 6.19. Found: C, 55.80; H, 6.53; N, 6.03.

As with Va the absence of prominent absorption bands in the 1600–1500 cm.$^{-1}$ region of the infrared absorption spectrum of VIIa (7% solution in chloroform) provides further support for the assigned *N*-nitroso structure.

The absence of a replaceable hydrogen on the nitrogen atom of VIa (and VIIa) was further demonstrated by dissolving a sample of VIIa in methanol, which had previously been saturated with potassium carbonate. Even without heating the solution, solvolysis of the acetate groups occurred rapidly to give a good yield of nitroso-compound VIa, m.p. and mixed m.p. 169–170° dec. It is extremely unlikely than an aniline *N*-acetyl group would solvolyze this readily. Hence, all four acetyl groups must be on oxygen, and the nitrogen atom in VIa must carry the nitroso group; otherwise it would have been acetylated under the above conditions.

1-Deoxy-1-(N-nitroso-3′,4′-xylidino)-D-ribitol (VIb). Nitrosation of 2 g. of 1-deoxy-1-(3′,4′-xylidino)-D-ribitol dissolved in 10 ml. of water containing 2 ml. of concd. hydrochloric acid in the above manner gave 1.82 g. (82%) of VIb, m.p. 133–135. Two recrystallizations from ethanol raised the m.p. to 138–139°, $[\alpha]_D$ +44.6 (*c* 1.68 in pyridine).

Anal. Calcd. for $C_{13}H_{20}N_2O_5$: C, 54.92; H, 7.09; N, 9.85. Found: C, 54.77; H, 7.25; N, 9.73. The infrared spectrum (potassium bromide) is consistent with the assigned nitrosamine structure.

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NORTH CHICAGO, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HAVERFORD COLLEGE, AND THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Preparation of Substituted 1-Picryl-2,2-diphenylhydrazyl Free Radicals[1]

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Received January 9, 1961

The preparation of a series of 1-picryl-2,2-diphenylhydrazyl free radicals substituted in the *para-* positions of the two benzene rings by —OCH_3, —CH_3, —F, —Cl, —Br, —$COOCH_3$, —NO_2, or —C_6H_5 groups is described. Some limitations in the conventional preparative sequence used for 1-picryl-2,2-diphenylhydrazyl (DPPH) are revealed in this series of compounds. Two new reagents, nitrosyl chloride for *N*-nitrosation of diarylamines, and *N*-picrylpyridinium chloride for picrylation of 1,1-diarylhydrazines, offer advantages at these stages of the preparative sequence. Some alternative methods which involve substitution reactions with various compounds of that sequence have also been developed.

The comparison of properties of structurally similar molecules which differ only by the substitution of groups with known effects on electron distribution has been a powerful tool in the investigation of organic compounds. This technique has seen very little application to the "stable" free radicals because of difficulties in the preparation and handling of the necessary compounds. These difficulties are well known in the case of the triarylmethyl radicals, which react with oxygen, disproportionate, and dimerize extensively. Members of the series of *para-* substituted 2,6-di-*t*-butylphenoxy[4] radicals also are unstable in air, and dimerize at the *para* carbon atoms. A reasonably complete series of stable substituted triarylaminium salt[5]

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(2) A portion of this material was abstracted from a thesis submitted by A. F. D'Adamo, Jr., to the Graduate School of Rutgers University in partial fulfillment of the requirements for the Ph.D. degree, September 1954.

(3) Inquiries should be addressed to this author at Haverford College.

(4) See the series of papers by E. Müller and co-workers. Paper XII; E. Müller, A. Rieker, K. Ley, R. Mayer, and K. Scheffler, *Ber.*, 92, 2278 (1959).

(5) R. I. Walter, *J. Am. Chem. Soc.*, 77, 5999 (1955).