(reported[12] 145°); a mixture m.p. with the 139–140° sample from hydrogenolysis melted at 141–143°. The amide of the synthetic acid melted at 122–123° and there was no depression of melting point when mixed with the amide from hydrogenolysis, m.p. 121–122°.

Metalation of Phenoxathiin 10-Oxide.—A solution of 0.32 mole of *n*-butyllithium in ether was added (one-half hour) to a suspension of 21.6 g. (0.10 mole) of phenoxathiin 10-oxide[13] in ether. The mixture was stirred and cooled in a Dry Ice–acetone-bath held at −20° during the addition and for an additional five hours. The bath was removed and stirring continued for an additional hour as the mixture came to room temperature. Carbonation and work-up of the mixture in the usual manner gave 5.4 g. of carboxylic acid melting at 221–222° (crystallized from methanol).

Anal. Calcd. for $C_{13}H_8O_3S$: C, 63.92; H, 3.30; neut. equiv., 244. Found: C, 63.92, 64.03; H, 3.46, 3.37; neut. equiv., 248.

While the analyses indicated the product to be a phenoxathiincarboxylic acid rather than the sulfoxide, further confirmation of this was obtained by treating the acid in glacial acetic acid with zinc dust under conditions which allow reduction of sulfoxides to sulfides.[14] The material was not affected.

The 1-phenoxathiincarboxylic acid (0.5 g.) was oxidized by 30% hydrogen peroxide in glacial acetic acid solution. The yield of product was 0.34 g. (60%) melting at 228–229°. A mixture melting point with 1-phenoxathiincarboxylic acid 10,10-dioxide, m.p. 228–229°, showed no depression.

Methyl 1-Phenoxathiincarboxylate.—The methyl ester was prepared by the diazomethane treatment described earlier. It melted, after crystallization from ethanol, at 95–96°.

Anal. Calcd. for $C_{14}H_{10}O_3S$: C, 65.10; H, 3.90. Found: C, 65.13, 65.17; H, 3.92, 3.92.

The corresponding hydrazide prepared in 89% yield, melted at 197–198°.

Anal. Calcd. for $C_{13}H_{10}H_2O_2S$: N, 10.85. Found: N, 10.81, 10.82.

Synthesis of 3-Phenoxathiincarboxylic Acid.—Four grams (0.016 mole) of 2,2′-dihydroxydiphenyl disulfide[15] and 8.0 g. of 4-chloro-3,5-dinitrobenzoic acid were condensed[5] to give 2.0 g. (22%) of 1-nitro-3-phenoxathiincarboxylic acid, m.p. 260–262°. One gram (0.003 mole) of the nitro compound was reduced with hydrazine and Raney nickel.[16] The resulting amine, m.p. 248–249°, was diazotized and treated with 50% hypophosphorous acid in the usual manner[17] to give 0.2 g. (24% based on the nitro-acid) of 3-phenoxathiincarboxylic acid, m.p. 223–224°; reported[5] m.p. 223°. A mixture melting point between this acid and the sample, m.p. 221–222°, from the metalation of phenoxathiin 10-oxide showed a depression of about 40°.

Methyl 4-Phenoxathiincarboxylate.—Phenoxathiin was metalated with *n*-butyllithium according to the procedure of Gilman and co-workers.[3] The 4-phenoxathiincarboxylic acid obtained was converted in 76% yield to the methyl ester with diazomethane. The ester boiled at 183–187° at 1 mm. pressure.

Anal. Calcd. for $C_{14}H_{10}O_3S$: C, 65.10; H, 3.90. Found: C, 65.12; H, 4.14.

The hydrazide melted at 127–128°.

Anal. Calcd. for $C_{13}H_{10}N_2O_2S$: N, 10.85. Found: N, 10.99.

Hydrazide of 4-Phenoxathiincarboxylic Acid 10,10-Dioxide.—Oxidation of 4-phenoxathiincarboxylic acid with 30% hydrogen peroxide gave the sulfone, m.p. 189–190°; reported[3] m.p. 183–184°. This was esterified with diazomethane to yield the ester, m.p. 123–124°, reported[3] m.p. 124°. The ester was converted to the hydrazide (m.p. 260°) in 57% yield.

Anal. Calcd. for $C_{13}H_{10}N_2O_4S$: N, 9.65. Found: N, 9.67.

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[12] G. Lock and F. H. Kempter, *Monatsh.*, **67**, 24 (1935).

[13] Provided through the courtesy of the Dow Chemical Co.

[14] R. Connor in H. Gilman, editor, "Organic Chemistry—An Advanced Treatise," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 872.

[15] Bios Laboratories, New York.

[16] D. Balcom and A. Furst, This Journal, **75**, 4334 (1953).

[17] N. Kornblum in R. Adams, editor, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 262.

KNOXVILLE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ANTIOCH COLLEGE]

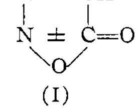
The Preparation of Substituted Hydrazines. I. Alkylhydrazines *via* Alkylsydnones[1]

BY JOSEPH FUGGER, JACK M. TIEN AND I. MOYER HUNSBERGER[2]

RECEIVED SEPTEMBER 25, 1954

The conversion of an alkylamine to an alkylhydrazine *via* the corresponding N-alkylglycine, N-nitroso-N-alkylglycine and N-alkysydnone is shown to constitute an acceptable preparative method in the case of benzylhydrazine, *n*-butylhydrazine and *n*-hexylhydrazine. The infrared spectra of N-benzylsydnone, N-(*n*-butyl)-sydnone and N-(*n*-hexyl)-sydnone are presented.

The sydnones I, a very interesting class of compounds first reported in 1935,[3] were not studied very intensively until 1946 and thereafter.[4] The American literature is virtually devoid of any reference to these unusual compounds, for which no single classical valence-bond formula can be written. The ± symbol is used to indicate the *meso*-ionic nature of the sydnones.[4d,i]


(I)

Sydnones are prepared readily by treatment of an N-substituted-N-nitrosoglycine with acetic anhydride. Alkaline hydrolysis of the sydnone regenerates the nitrosoglycine, whereas hydrolysis in di-

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[1] This work was sponsored by the Air Forces under Contract No. AF 33(038)-22909, Supplemental Agreement Nos. S1 (53-134) and S2 (53-1063).

[2] To whom inquiries regarding this article should be sent.

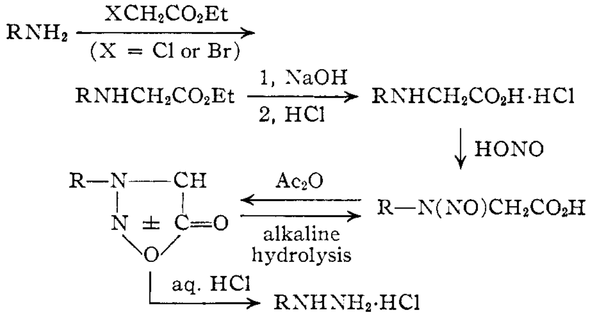
[3] J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, 899 (1935).

[4] (a) J. C. Earl, *Nature*, **158**, 910 (1946); (b) R. A. Eade and J. C. Earl, *J. Chem. Soc.*, 591 (1946); (c) W. Baker and W. D. Ollis, *Nature*, **158**, 703 (1946); (d) W. Baker, W. D. Ollis, V. D. Poole, J. A. Barltrop, R. A. W. Hill and L. E. Sutton, *ibid.*, **160**, 366 (1947); (e) J. Kenner and K. Mackay, *ibid.*, **158**, 909 (1946); **160**, 465 (1947); (f) J. C. Earl, E. M. W. Leake and R. J. W. LeFevre, *J. Chem. Soc.*, 2269 (1948); (g) R. A. Eade and J. C. Earl, *ibid.*, 2307 (1948); (h) R. A. W. Hill and L. E. Sutton, *J. chim. phys.*, **46**, 244 (1949); *J. Chem. Soc.*, 746 (1949); 1482 (1953); (i) W. Baker, W. D. Ollis and V. D. Poole, *ibid.*, 307 (1949); (j) J. C. Earl, R. J. W. LeFevre and I. R. Wilson, *ibid.*, S103 (1949); (k) W. Baker, W. D. Ollis and V. D. Poole, *ibid.*, 1542 (1950); (l) J. C. Earl, R. J. W. LeFevre, A. G. Pulford and A. Walsh, *ibid.*, 2207 (1951); (m) J. C. Earl, *Chemistry & Industry*, 746, 1284 (1953); (n) D. L. Hammick and A. M. Roe, *ibid.*, 900 (1953); (o) D. L. Hammick, A. M. Roe and D. J. Voaden, *ibid.*, 251 (1954); (p) S. Kruger, *ibid.*, 465 (1954).

lute hydrochloric acid readily produces the corresponding hydrazine (*cf.* diagram below). Although most of the work on sydnones has focused on synthesis and proof of structure, Eade and Earl[4b] did state that the stability of the sydnones and their ease of hydrolysis to hydrazines recommend them for use as reagents for characterizing carbonyl compounds.

The stability of the sydnone ring does not appear to depend to any significant extent on the nature of R. Thus, N-cycloalkyl-, N-aralkyl- and N-arylsydnones have been prepared, and all are quite stable.[5] Furthermore, all these sydnones easily hydrolyze to the corresponding monosubstituted hydrazines. Very recently condensed-ring sydnones[4o,p] have been reported in which adjacent carbon and nitrogen atoms of the sydnone ring also are part of another ring.

It thus would appear that the process diagrammed below constitutes an extremely general method capable of converting virtually any primary amine to the corresponding monosubstituted hydrazine. The N-substituted glycines required as intermediates are prepared readily by condensation of the amine with ethyl chloro- or bromoacetate followed by saponification of the resulting ester.



R = cycloalkyl, aralkyl and aryl in previous work
R = alkyl (n-C_4H_9 and n-C_6H_{13}) in present work

This method of preparing arylhydrazines obviously is not as convenient as the conventional method, which proceeds from the amine *via* reduction of the diazonium salt. However, since benzylamine cannot be diazotized, the preparation of benzylhydrazine *via* N-benzylsydnone would appear to be a satisfactory practical route. Thus, Eade and Earl[4e] reported the conversion of the ethyl ester of N-benzylglycine to N-benzylsydnone in 34% over-all yield, but they did not hydrolyze the sydnone. Baker, Ollis and Poole[4i,k] reported the conversion of benzylamine *via* the Strecker process to the glycine and thence to the nitrosoglycine in 57% over-all yield. Dehydration to the sydnone and hydrolysis of the sydnone proceeded in 94 and 59% yield, respectively. Hence, their over-all yield for converting benzylamine to benzylhydrazine hydrochloride was 32%.

The conversion of benzylamine to benzylhydrazine now has been studied in some detail in our laboratory. We have prepared the ethyl ester of N-benzylglycine according to King and McMillan[6] by heating 2 moles of benzylamine with 1 mole of ethyl chloroacetate in benzene solution. The crude ester, without purification, was saponified to produce a 50% yield[7] of pure N-benzylglycine hydrochloride. This glycine was converted to the pure nitroso compound in 73% yield and thence to the pure sydnone in 53% yield. Acid hydrolysis then afforded pure benzylhydrazine hydrochloride in 44% yield (8.5% over-all yield).[7]

The utility of this synthesis was increased by demonstrating that it can be performed without purifying any of the intermediates. Under these conditions the over-all yield of crude benzylhydrazine hydrochloride was 36%[7] and of the twice-recrystallized hydrochloride was 13%.[7] This is the only experiment in the benzyl series which is described in the Experimental part. In another experiment crude N-benzylglycine hydrochloride was converted to the pure sydnone in 54% over-all yield. Although these yields very likely are not the highest obtainable, they are satisfactory from a preparative standpoint. The pure N-benzylsydnone was essentially unchanged after storage for over one year in a brown bottle.

Our next interest in the sydnone process stemmed from its possible use as a general method for preparing alkylhydrazines. Although the higher monoalkylhydrazines have been prepared by interaction of the alkyl halide and hydrazine,[8] this method requires the use of sealed tubes and simultaneously produces unsymmetrical dialkylhydrazines. No good general method for preparing monoalkylhydrazines below hexyl was available until 1949, when Gever and Hayes[9] demonstrated that the lower alkylhydrazines (ethyl through pentyl), and by inference the higher, can be prepared in satisfactory yield by reaction of the alkylamine with hydroxylamine-O-sulfonic acid in the presence of alkali or of a large excess of the amine. Very recently the lower monoalkylhydrazines have been prepared[10] in good yield by a modified Raschig synthesis, which involves reaction of an excess of alkylamine with chloramine in the presence of alkali.

We have now extended the scope of the sydnone synthesis to include the preparation of n-butylhydrazine and n-hexylhydrazine.

The preparation of the N-alkylsydnones proceeds best if much less acetic anhydride is used than was used in most cases previously reported.[4b,i] Heating of the N-nitroso-N-alkylglycines for about three hours on the steam-bath sufficed for the dehydration. The N-(n-butyl)- and N-(n-hexyl)-sydnones are the first alkylsydnones to be reported. Both are stable oils which may be distilled at low pressure without decomposition.

Less acid was used in the hydrolysis of the N-alkylsydnones than generally was used in earlier work.[4b,i] The alkylhydrazine hydrochlorides, which were prepared first, formed as long transparent needles which appeared to be very hygroscopic and unstable. In the atmosphere the crystals disappeared in about 15 minutes and left only oily spots on the filter paper. In an evacuated

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[5] However, it has been reported[4d] that N-cyclohexylsydnone slowly decomposes in benzene solution at 25°.

[6] J. A. King and F. H. McMillan, This Journal, **72**, 1236 (1950).

[7] Based on ethyl chloroacetate.

[8] O. Westphal, *Ber.*, **74**, 759 (1941).

[9] G. Gever and K. Hayes, *J. Org. Chem.*, **14**, 813 (1949).

[10] L. F. Audrieth and L. H. Diamond, This Journal, **76**, 4869 (1954).

desiccator over phosphorus pentoxide and potassium hydroxide well-formed crystals lost their shape in about seven hours, but they kept somewhat better in a nitrogen atmosphere. Suspended in concentrated hydrochloric acid in a refrigerator, they kept several months without any apparent change. These characteristics rendered reproducible melting points of the hydrochlorides nearly impossible to obtain. Hence, these hydrazines were characterized and stored as their hydrogen oxalates.

Excellent over-all yields of the alkylhydrazines have been obtained without purifying any of the intermediates. However, since N-(*n*-butyl)-glycine hydrochloride was the only intermediate previously characterized, all intermediates in the two syntheses were purified and analyzed. When no intermediates were isolated, large-scale preparations of *n*-butylhydrazine hydrogen oxalate and *n*-hexylhydrazine hydrogen oxalate afforded over-all yields[11] of 23 and 61%, respectively, while the hydrochlorides were obtained in over-all yields[11] of 38 and 42%, respectively. Without doubt the sydnone process represents an excellent preparative route to the little-studied alkylhydrazines.

Infrared spectra have been published[4l] for only three sydnones, and these included only the 5–15 μ region. Figure 1 presents the spectra of the three sydnones studied in this investigation. What probably are the sydnone carbonyl bands appear at 1768 (butylsydnone), 1768 (hexylsydnone) and 1761 cm.$^{-1}$ (benzylsydnone). These frequencies compare closely with the 1766, 1756 and 1752 cm.$^{-1}$ values listed[4l] for N-(2-naphthyl)-, C-bromo-N-phenyl- and N-phenylsydnone, respectively. The butyl- and hexylsydnones also showed weak but definite bands at 3533 and 3521 cm.$^{-1}$, respectively. Probably these are OH bands arising from the presence of a small amount of nitrosoglycine. In freshly distilled samples these bands were weak (as shown in Fig. 1). However, in samples which had been standing for a longer period of time[12] these bands were much more intense. No similar band was given by benzylsydnone. However freshly recrystallized benzylsydnone gave two very weak bands at 3460 and 3333 cm.$^{-1}$, which also may arise from slight hydrolysis of the sydnone. It is believed that the strong sharp bands at 3185 (butyl), 3194 (hexyl), and 3140 cm.$^{-1}$ (benzyl) are attributable to the unique CH of the sydnone ring.

At present we are engaged in the preparation of a sydnone in which the R group is a heterocyclic residue.

Experimental[13]

Benzylhydrazine Hydrochloride.—A solution of 122 g. (1.00 mole) of ethyl chloroacetate[14] and 214 g. (2.00 moles) of benzylamine[14] in 1 liter of benzene was stirred five hours under reflux. The white benzylamine hydrochloride was filtered off and the filtrate distilled at reduced pressure to leave 154 g. of the **ethyl ester of N-benzylglycine** as a yellow oil which was filtered to remove additional amine hydrochloride. The crude ester was added dropwise, with stirring, during 15 minutes to a boiling solution of 63.6 g. (1.59 moles) of sodium hydroxide in 300 ml. of water. After refluxing for 45 minutes the yellow solution was extracted with two 100-ml. portions of ether and the ether extracts discarded. The alkaline solution was acidified (ice-bath) to *p*H 2 with concentrated hydrochloric acid. The white suspension of N-benzylglycine was treated at 0–2°, with stirring, over 0.5 hour with 55.2 g. (0.800 mole) of sodium nitrite in 100 ml. of cold water. After 2 hours of stirring in the cold the suspension again was brought to *p*H 2 with concentrated hydrochloric acid. After refrigeration for one hour the yellow-white suspension was filtered and the precipitate vacuum-dried over potassium hydroxide to yield 139 g. of crude N-nitroso-N-benzylglycine. This was heated for 5 hours with stirring on a steam-bath with 685 ml. (7.26 moles) of acetic anhydride. The resulting dark red solution was filtered free of some yellow solid and the solvent removed at reduced pressure to yield 115 g. of crude **N-benzylsydnone** as a red-brown oily residue which solidified in an ice-bath on scratching. This sydnone was heated for 4.5 hours on a steam-bath with 1 liter of 1:1 hydrochloric acid. The sydnone gradually dissolved, and carbon dioxide was evolved slowly but continually. The red solution was filtered hot through fluted paper of high porosity in order to remove some brown tar and the clear filtrate concentrated under reduced pressure to less than 100 ml. Filtration then afforded 56.8 g. (36%[7]) of crude **benzylhydrazine hydrochloride** as a yellow-white solid. Two recrystallizations from boiling ethanol afforded 14.6 g. of hydrochloride, m.p. 108–110.5° (lit. m.p.'s 105–107[4i], 110°[15]), plus another 6.1 g., m.p. 108–110.5°, from the concentrated filtrate, the total yield being 20.7 g. (13%[7]).

Anal. Calcd. for $C_7H_{11}N_2Cl$: neut. equiv., 159. Found: neut. equiv., 156.

N-(*n*-Butyl)-glycine Hydrochloride.—A solution of 68 ml. (0.60 mole) of ethyl bromoacetate[14] in 100 ml. of benzene was added (heat evolved) portionwise with swirling and cooling (tap water) to 120 ml. (1.20 moles) of *n*-butylamine[14] in 300 ml. of benzene. The mixture was refluxed for 2 hours on a steam-bath, cooled, and 59 g. of the amine hydrobromide filtered off and washed with 80 ml. of benzene. The filtrate, after concentration at reduced pressure until

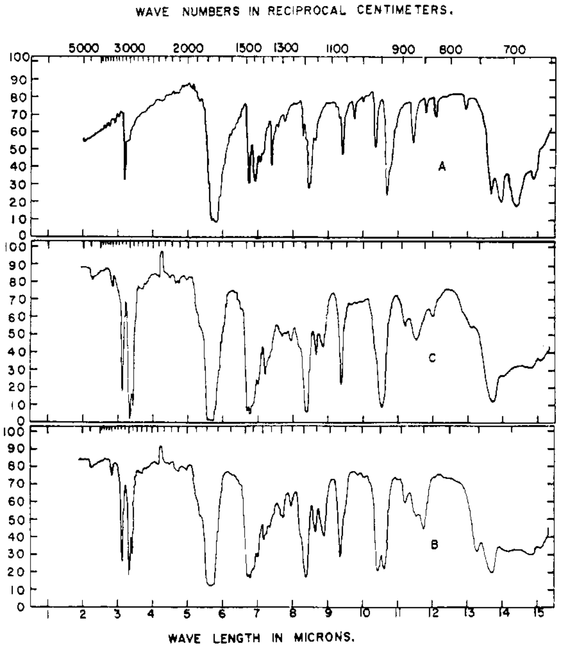

Fig. 1.—Infrared spectra of the sydnones: curve A, N-benzylsydnone (0.5% in KBr disc); curve C, N-(*n*-hexyl)-sydnone (0.022 mm. cell); curve B, N-(*n*-butyl)-sydnone (0.022 mm. cell).

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[11] Based on ethyl bromoacetate.

[12] These spectra were determined free of charge by Samuel P. Sadtler and Son, Inc., Philadelphia 2, Penna.

[13] All m.p.'s are uncorrected. All neutral equivalent determinations were performed in water or aqueous alcohol using congo red–thymol blue mixed indicator (Chicago Apparatus Co.), whose *p*H range is 7.5–9.5 on the alkaline side.

[14] Eastman Kodak Co., White Label Grade.

[15] A. Wohl and C. Oesterlin, *Ber.*, **33**, 2736 (1900).

white fumes appeared, left a residue of glycine ester which was refluxed for 25 minutes with 28 g. (0.70 mole) of sodium hydroxide in 120 ml. of water. The cooled alkaline solution was extracted with 200-ml. portions of ether until the strong amine odor virtually disappeared from the extract. The aqueous layer was acidified (ice-bath) to *p*H 2 with concentrated hydrochloric acid. By consecutive refrigeration and concentration of the acidified aqueous liquor a total of 68.9 g.[16] (68%) of crude N-(*n*-butyl)-glycine hydrochloride was obtained as snow-white needles and plates.

Further purification was accomplished by recrystallization from either hydrochloric or acetic acid. Thus, 1 g. of the crude hydrochloride was dissolved in 10 ml. of concentrated hydrochloric acid by warming slightly on a steam-bath. Any precipitated sodium chloride was filtered out and the filtrate allowed to cool in a refrigerator. Three repetitions of this process produced the pure hydrochloride, m.p. 204–205°. Alternately, 1 g. of crude hydrochloride was dissolved in 20 ml. of glacial acetic acid heated on a steam-bath. The small solid particles were separated from the clear solution by filtration or decantation. Crystallization occurred on standing at room temperature. One repetition of this process afforded pure hydrochloride as show-white flakes, m.p. 204–205°.[17]

Anal. Calcd. for $C_6H_{14}O_2NCl$: Cl, 21.16. Found[18]: Cl, 21.1, 21.3 and 21.6.

Our first preparation of N-(*n*-butyl)-glycine hydrochloride required a painstaking isolation procedure because, on acidification of the solution of the sodium salt of the glycine, sodium chloride separated before the glycine hydrochloride. Later it was found that most of the sodium chloride can be precipitated from the acid solution containing the glycine hydrochloride merely by adding acetone.[19] Refrigeration of the filtrate then permitted the glycine hydrochloride to crystallize before any more sodium chloride separated. However, the desired glycine hydrochloride also can be made to crystallize before the sodium chloride by the simple expedient, described above, of using no more than a slight excess over the theoretical quantity of alkali in the saponification.

N-(*n*-Hexyl)-glycine Hydrochloride.—Exactly the same procedure as above was used on the same molar quantities of reagents. However, less heat was evolved on mixing the *n*-hexylamine[14] and ethyl bromoacetate. Also, the alkaline solution of the glycine was swirled (ice-bath) as 90 ml. of concentrated hydrochloric acid and 100 g. of chopped ice were introduced slowly from a separatory funnel. Immediately 81.0 g. of crude N-(*n*-hexyl)-glycine hydrochloride separated as tiny yellowish-white flakes. Refrigeration of the mother liquor afforded a second fraction of 4.8 g., the total yield being 85.8 g. (73%).

No trouble was experienced with sodium chloride precipitating before the glycine hydrochloride. However, if the amount of alkali used in the saponification was slightly less than theoretical, the glycine hydrochloride separated as a paste which was extremely difficult to filter. Acidification with dilute hydrochloric acid rendered the hydrochloride easier to filter than when concentrated acid was used.

Further purification was accomplished by fractional recrystallization from dilute hydrochloric acid. Thus, 1 g. of the crude hydrochloride was dissolved in 10 ml. of water and precipitated by adding 1 ml. of concentrated hydrochloric acid.[20] Three repetitions of this process afforded large snow-white flakes of the pure hydrochloride, m.p. 210–217°. Alternately, 1 g. of crude hydrochloride was recrystallized from 20 ml. of 1:1 methanol–acetone or from 40 ml. of glacial acetic acid as described for the butyl analog.

Anal. Calcd. for $C_8H_{18}O_2NCl$: Cl, 18.12. Found[18]: Cl, 18.0, 18.4.

N-Nitroso-N-(*n*-butyl)-glycine.—N-(*n*-Butyl)-glycine hydrochloride (78.0 g., 0.464 mole) in 300 ml. of water was treated over 0.5 hour at −4 to −5° with 37.5 g. (0.543 mole) of sodium nitrite in 100 ml. of water. After stirring the mixture for 2 hours, the bottom layer of oily nitroso compound was drawn off. By dissolving this material in ether, drying over magnesium sulfate, and evaporating the filtered ether 62.0 g. (83.6%) of crude nitroso compound was obtained as a yellow granular powder. Crystallization of 8.0 g. of this material from a small amount of ether afforded 4.53 g. of nitroso compound as nearly white granules, m.p. 60–62°. Further crystallization from aqueous alcohol or from ether–petroleum ether gave well-formed long snow-white flakes, m.p. 61–62°.

Anal.[21] Calcd. for $C_6H_{12}O_3N_2$: C, 44.98; H, 7.55; N, 17.49; neut. equiv., 160. Found: C, 45.14; H, 7.58; N, 16.95, 16.94; neut. equiv., 162, 161.

N-Nitroso-N-(*n*-hexyl)-glycine.—An alkaline solution of N-(*n*-hexyl)-glycine, prepared as before from 0.60 mole of ethyl bromoacetate, was cooled and treated (stirring) with 49.7 g. (0.720 mole) of sodium nitrite in 100 ml. of water in one portion, followed dropwise over 1.25 hours by 90 ml. of concentrated hydrochloric acid diluted with 50 g. of ice. After stirring for another hour the *p*H was adjusted to 2.0 by adding more concentrated hydrochloric acid. The top layer of brown oil on standing yielded 74.8 g. (66.3%[11]) of crude N-nitroso-N-(*n*-hexyl)-glycine as a yellow granular powder. This compound crystallized from ether much more readily than the butyl analog and yielded snow-white flakes, m.p. 78–79°. Further crystallization from aqueous alcohol or petroleum ether–ether produced well-formed long white flakes, m.p. 79–80°.

Anal.[22] Calcd. for $C_8H_{16}O_3N_2$: C, 51.05; H, 8.57; N, 14.89; neut. equiv., 188. Found: C, 51.28; H, 8.54; N, 14.82; neut. equiv., 184, 186.

The preparation of the N-alkyl-N-nitrosoglycines proceeds best by use of a slight excess of sodium nitrite. The nitrite may be added to a solution of the glycine hydrochloride (as in the butyl series) or to an alkaline solution of the glycine (as in the hexyl series). Neither nitroso compound kept well. On standing, the snow-white flakes became pale yellow. The melting points of these compounds varied from day to day. Neutral equivalents and combustion analyses had to be performed on freshly-prepared samples.[23]

N-(*n*-Butyl)-sydnone.—A solution of 40 g. (0.25 mole) of crude N-nitroso-N-(*n*-butyl)-glycine in 236 ml. (2.5 moles) of acetic anhydride was heated on the steam-bath for 3 hr. and then kept at room temperature for 1 day. Removal of excess acetic anhydride at reduced pressure left 33 g. (93%) of the oily sydnone. Distillation of 8.0 g. of this sample afforded 4.5 g. (52%) of the pure sydnone as a pale-yellow oil, b.p. 165–167° at 2 mm.

Anal.[21] Calcd. for $C_6H_{10}O_2N_2$: C, 50.67; H, 7.09; N, 19.70. Found: C, 50.55; H, 7.47; N, 19.58.

Nearly identical results were obtained when 0.362 mole of nitroso compound was heated for 3 hours with only 1.09 moles of acetic anhydride.

The over-all yield of once-distilled sydnone was 29%[11] when no intermediates were isolated. The pure sydnone was obtained in 15% yield[11] when the intermediates were isolated and purified.

N-(*n*-Hexyl)-sydnone.—The crude yellow-white N-nitroso-N-(*n*-hexyl)-glycine, prepared from 0.20 mole of ethyl bromoacetate, was taken up in ether and the extract dried over sodium sulfate. To the dried ether was added 190 ml. (2.0 moles) of acetic anhydride. After 1 day at room temperature the ether was removed (steam-bath) and the residual oily mixture refluxed for 3 hours. Removal of acetic anhydride at reduced pressure left a viscous clear brown oil which, after drying *in vacuo* over potassium hydroxide and phosphorus pentoxide, weighed 23 g. Distillation through an 18-cm. Vigreux column produced 18 g.

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[16] Five fractions (26.0, 3.5, 14.5, 19.7 and 5.2 g.) were obtained, the first two by successive refrigeration and the last three by concentration of the liquor. The 5.2-g. fraction separated after some sodium chloride had been filtered from the hot concentrated solution.

[17] While this work was in progress, F. Basolo and Y. T. Chen [THIS JOURNAL, **76**, 953 (1954)] published a preparation of this compound, m.p. 204–205°, in 70% yield. The earlier literature contains no reference to this hydrochloride, but W. Cocker and J. O. Harris [*J. Chem. Soc.*, 1290 (1940)] prepared the free base, m.p. 192°.

[18] Analyses for chlorine were performed gravimetrically in our laboratories.

[19] The N-(*n*-butyl)-glycine hydrochloride will not dissolve in pure acetone, but it is soluble in solvent-grade acetone, water in the latter presumably being responsible.

[20] This did not cause any sodium chloride to precipitate.

[21] Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.

[22] Analysis by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[23] In this connection it should be recalled that Eade and Earl (ref. 4b) reported that certain N-nitroso-N-arylglycines were sensitive to sunlight.

(53%[11]) of sydnone, b.p. 170–176° at 0.43 mm. Redistillation of 6.0 g. of this sample afforded 4.0 g. of pure sydnone, b.p. 141–143° at 0.09 mm.

Anal.[21] Calcd. for $C_8H_{14}O_2N_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 57.10; H, 8.69; N, 16.21.

A 93% yield (based on nitrosoglycine) of crude sydnone (not distilled) was obtained by dissolving (heat evolved) 0.334 mole of the nitrosoglycine in 1.14 moles of warm acetic anhydride, letting the brown mixture stand overnight, and then heating it for 2 hours on a steam-bath.

***n*-Butylhydrazine Hydrochloride.** (**a**).—The crude sydnone (40.5 g., 0.286 mole) was mixed (heat evolved) with 80 ml. of concentrated hydrochloric acid and heated for 2 hours on a steam-bath. The mixture was cooled to room temperature, treated with an additional 20 ml. of concentrated hydrochloric acid, and refrigerated overnight. Since no crystallization had occurred, hydrogen chloride was introduced until crystals began to deposit. Further refrigeration produced a granular light-brown cake which was filtered and washed with 1:1 methanol–ether to yield 22 g. of nearly-white transparent needles. Even in an evacuated desiccator these needles soon became opaque. They were stored under concentrated hydrochloric acid, but they could not be recovered completely merely by filtration.

The above mother liquor was decolorized with Norit A and saturated with hydrogen chloride, during which time the temperature was kept below 0° to prevent the color from returning. Since no crystals had formed after several days in a refrigerator, the mixture was neutralized with solid sodium carbonate, extracted with two 300-ml. portions of ether, and the combined extracts dried over potassium carbonate. Passage of hydrogen chloride through part of this ethereal extract precipitated 2.5 g. of hydrochloride salt as a white powder. The remainder of the ether extract was treated with oxalic acid in alcohol (as described below) to yield 1.0 g. of oxalate salt (equivalent to 0.7 g. of hydrochloride); total yield of hydrochloride, 25.2 g. (71% based on sydnone, 38% based on ethyl bromoacetate).

(**b**).—In another experiment 4.4 g. (0.031 mole) of the distilled sydnone was heated with 30 ml. of concentrated hydrochloric acid for 2.5 hours, 10 ml. more acid being added to the yellow solution after 2 hours. Saturation of the cooled solution with hydrogen chloride yielded 3.1 g. (79%) of *n*-butylhydrazine hydrochloride as thin white plates, m.p. 149–154°.

This hydrochloride (3.0 g.) was treated with 15 ml. of 25% aqueous sodium carbonate and the alkaline mixture extracted three times with 50-ml. portions of ether. Distillation afforded 1.0 g. of the presumed ***n*-butylhydrazine**, b.p. 82–85° at 20 mm., as a colorless liquid with an odor similar to *n*-butylamine.

From this free base 0.9 g. of *n*-butylhydrazine hydrochloride was obtained as white plates, m.p. 150–153°.

***n*-Hexylhydrazine Hydrochloride.**—To 40.7 g. (0.239 mole) of crude N-(*n*-hexyl)-sydnone 80 ml. of concentrated hydrochloric acid was added (no heat evolved) and the mixture heated 2 hours on a steam-bath, 30 ml. more acid being added before the mixture was refrigerated. The resulting dark brown cake was dissolved in about 150 ml. of water, and the solution, after heating for a few minutes on the steam-bath with about 5 g. of Norit, was filtered while hot. On cooling, the filtrate deposited 19.8 g. of fine transparent needles of the *n*-hexylhydrazine hydrochloride. From the mother liquor 18.0 g. of oxalate salt (equivalent to 13.3 g. of hydrochloride) was obtained as described below; total yield of hydrochloride, 33.1 g. (90% based on sydnone, 42% based on ethyl bromoacetate).

***n*-Hexylhydrazine Hydrogen Oxalate.**—The alkaline solution of the sodium salt of N-(*n*-hexyl)-glycine, prepared as before from 0.60 mole of ethyl bromoacetate (except that 75 g. of amine hydrobromide was obtained), was kept below 0° while 37.2 g. (0.54 mole) of sodium nitrite in 120 ml. of water was added in one portion, followed over a 30-minute period by 100 ml. of concentrated hydrochloric acid containing 50 g. of cracked ice. After about *p*H 6 the acid was added dropwise. The cooling bath having been removed, the mixture was stirred for 1 hour and then extracted with two 300-ml. portions of ether. Evaporation of the ether left 88.7 g. (78.6%, based on ethyl bromoacetate) of crude nitrosoglycine, 83.7 g. (0.445 mole) of which was heated on a steam-bath for about 2 hours with 126 ml. (1.33 moles) of acetic anhydride. The original light amber solution turned dark brown in about 5 minutes. Removal of excess acetic anhydride at reduced pressure left 81.5 g. of crude sydnone, 64 g. of which was heated for 2 hr. on a steam-bath with 110 ml. of concentrated hydrochloric acid. The cooled (ice-bath) mixture was neutralized with 25% sodium hydroxide, saturated with potassium carbonate, and extracted eight times[24] with 300-ml. portions of ether. The combined extracts were dried over potassium carbonate and run into a solution of 76 g. (0.84 mole) of anhydrous oxalic acid in 400 ml. of 95% ethanol. The thin paste which formed immediately turned to a jelly on aging overnight. The yellowish solid was filtered off and dried to yield 55.5 g. (77% base on nitrosoglycine, 61% based on ethyl bromoacetate) of crude *n*-hexylhydrazine hydrogen oxalate.

The crude oxalate (1.0 g.) was recrystallized from 25 ml. of hot methanol–ethanol (9:1) to yield 410 mg. of fluffy flakes, m.p. 171–172°. This material (94 mg.) was recrystallized by letting its solution in 5 ml. of hot methanol evaporate slowly at room temperature in an open container to yield 64 mg. of large white needles, m.p. 173–173.5°. The twice recrystallized material was dissolved in 5 ml. of hot methanol–ethanol (4:1). The filtered solution was poured into a sintered glass funnel of medium porosity. In about an hour the mother liquor passed through, leaving in the funnel 26 mg. of pure hydrogen oxalate as transparent needles, m.p. 174.5–175.5°.

Anal. Calcd. for $C_8H_{18}N_2O_4$: C, 46.6; H, 8.7; N, 13.59; neut. equiv., 103. Found: C, 46.9[25]; H, 8.6[25]; N, 13.6,[25] 13.74[21]; neut. equiv.,[26] 104, 104, 108, 105, 108.

N-Hexylhydrazine has been characterized only as the free base, b.p. 80–81° at 14 mm.,[8] which was obtained in 26% yield from the alkyl halide.

N-Butylhydrazine Hydrogen Oxalate.—This preparation was the same as for the hexyl analog except that the crystalline hydrazine hydrochloride first was prepared and from it the oxalate. Thus, the filtered white hydrochloride was dissolved in 150–200 ml. of water, neutralized (ice-bath) by portionwise addition of 30% sodium hydroxide and saturated with solid potassium carbonate. Three extractions with 200-ml. portions of ether sufficed to remove all hydrazine. The combined extracts were dried over potassium carbonate and added to a solution of 54 g. (0.60 mole) of anhydrous oxalic acid in 320 ml. of 95% ethanol, whereupon a thin white paste formed immediately.[27] On setting aside overnight, the precipitate became more granular and was filtered in about 10 minutes to yield 18.5 g. of crude oxalate. From the mother liquor of the original hydrochloride an additional 6.3 g. of oxalate was obtained in the same manner; total yield of crude hydrogen oxalate, 24.8 g. (23%, based on ethyl bromoacetate). If the oxalate was prepared without first forming the hydrochloride, the oxalate was obtained as a gelatinous paste which was virtually impossible to filter. No similar trouble was experienced in the hexyl series.

The crude hydrogen oxalate (1 g.) was recrystallized from 60 ml. of hot methanol–ethanol (9:1) to yield 420 mg. of pure oxalate as fine snow-white needles. This material (180 mg.) was recrystallized from 20 ml. of the same solvent mixture to yield 144 mg. of white needles, m.p. 164–165°. Further recrystallization did not alter the m.p.

Somewhat unexpected is the fact that *n*-butylhydrazine appears to have been reported only as its hydrogen oxalate, m.p. 165°,[9] and very recently as its hydrogen sulfate.[10] The last compound was prepared[10] in 68% yield, based on chloramine, while the oxalate was prepared[9] in 60% yield, based on hydroxylamine-O-sulfonic acid. Westphal[8] prepared a mixture of mono- and dibutylhydrazine, b.p. 45–95° at 11 mm., by a sealed-tube reaction, but he did not separate the mixture.

Acknowledgments.—The authors take pleasure in thanking Dr. H. V. Knorr of the Kettering

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[24] Three to four extractions suffice if the aqueous solution is completely saturated with potassium carbonate.

[25] Analysis by New York University Microchemical Laboratory.

[26] The end-points in the titrations were a bit uncertain (within a drop or two of the 0.01 *N* base used) because the color change occurred gradually.

[27] Gever and Hayes (ref. 9) prepared this oxalate by mixing an ethereal solution of the hydrazine with an aqueous solution of oxalic acid dihydrate, steaming to dryness, and recrystallizing the product from SDA #30 alcohol.

Foundation, Yellow Springs, Ohio, for determining the infrared spectra with a double-beam Perkin–Elmer instrument. We also are grateful to Professor T. S. Ma of the New York University Microchemical Laboratory for performing some of the combustion analyses. Mr. Gilbert Farfel assisted with some of the preparative work on benzylhydrazine.

YELLOW SPRINGS, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF LYMAN CHALKLEY]

Hydrophilic Dye Cyanides. I. Ethyl Green and Xylene Blue Cyanides

BY LYMAN CHALKLEY

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The addition of a hydrophilic group (quaternary ammonium or sulfonic acid) to an aminotriphenylmethane dye cyanide produces substances that are photosensitive in aqueous solution. The preparation is described of ethyl green cyanide (I), xylene blue VS cyanide (II) and xylene blue AS cyanide (III).

The photosensitive system composed of the cyanide of a basic triphenylmethane dye and alcohol[1] is of theoretical interest and has found practical applications in actinometry.[2] When alcoholic solutions of certain triphenylmethane dye cyanides, which are initially colorless, are exposed to ultraviolet light they take on the color of the dye, the end effect being the ionization of the dye cyanide

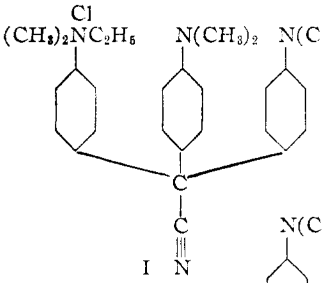
$$\underset{\text{(colorless)}}{Ar_3C{-}CN} \xrightarrow{\text{Light}} \underset{\text{(colored)}}{Ar_3C^+ + CN^-} \qquad (1)$$

The alcohol plays an essential role in the photochemical reaction. Without it, or some substance that can perform an equivalent photoactivating function, the dye cyanide does not undergo the characteristic reaction. Water can act as a photoactivator if the dye cyanide contains a hydrophilic group.[3] The two dye cyanides of this type examined by Lifschitz yield dyes, phenolphthalein and benzaurine, of somewhat limited utility for actinometry and other practical applications.

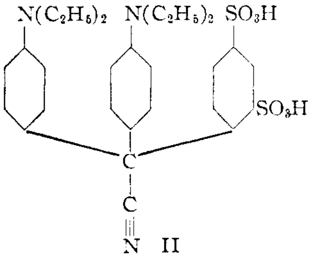
An objective of the present work is to provide new dye cyanides through which to extend the study of the fundamental photochemical reaction, and which may have practical advantages in actinometry over the dye cyanides used in the past. The first goal, and that toward which this paper is entirely directed, is the preparation of hydrophilic cyanides of the aminotriphenylmethane dyes, none of which have been found in the literature. The author hopes later to present studies of photochemical properties, which will be mentioned in the present paper only very briefly and qualitatively.

Salt forming groups, quaternary ammonium and sulfonic acid, were used to confer hydrophilic properties on aminotriphenylmethane dye cyanides. The compounds whose preparation is described are ethyl green cyanide (I), xylene blue VS cyanide (II), and xylene blue AS cyanide (III).

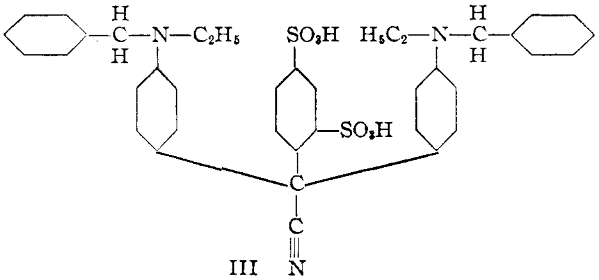
Ethyl green cyanide was prepared by the conventional reaction of the dye with sodium cyanide at room temperature.



I



II



III

The xylene blue dyes, on the other hand, did not react readily with sodium cyanide at room temperature. Solutions of these dyes containing excess sodium cyanide were examined colorimetrically. After 48 hours at 25° they had not lost 2% of their optical density, indicating that the reaction at room temperature is very slow if it proceeds at all. When solutions of the dyes and sodium cyanide were boiled, hydrogen cyanide was lost by hydrolysis and evaporation, and the dyes underwent an alkaline hydrolysis of an amino group like that described by the Erdmanns[4] for Patent Blue V. However, it was found that if the dye were heated with sodium cyanide solution in a pressure bottle a good yield of dye cyanide could be obtained.

Photosensitivity.—Aqueous solutions of the new dye cyanides were all colored by exposure to ultraviolet light. The ethyl green cyanide solution behaved photochemically much like an alcoholic

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(1) J. Lifschitz, *Ber.*, **52B**, 1919 (1919); J. Lifschitz and L. C. Joffe, *Z. physik. Chem.*, **97**, 426 (1921).

(2) (a) W. Frankenburger, R. Robl and W. Zimmermann, U. S. Patent 1,845,835 (Feb. 16, 1932); (b) L. Harris, J. Kaminsky and R. G. Simard, THIS JOURNAL, **57**, 1151 (1935); (c) L. Harris and J. Kaminsky, *ibid.*, **57**, 1154 (1935); (d) J. G. Calvert and H. J. L. Rechen, *ibid.*, **74**, 2101 (1952); (e) L. Chalkley, *J. Opt. Soc. Am.*, **42**, 387 (1952).

(3) J. Lifschitz, *Ber.*, **58B**, 2434 (1925).

(4) E. and H. Erdmann, *Ann.*, **294**, 376 (1897).