outlined above, 0.50 g (1.76 mmoles) of diphenylketene-*p*-tolylimine in chloroform solution was treated with a chloroform solution of 0.84 g (5.6 mmoles) of peroxybenzoic acid and 10.5 g (0.175 mmole) of glacial acetic acid. N-(*p*-Tolyl)-α-acetoxydiphenylacetamide, 0.20 g (32%), had a melting point of 195–196° after two crystallizations from acetone–petroleum ether, the mixture melting point with authentic material (see below) was not depressed, and the infrared spectra were superimposable.

Anal. Calcd for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.89. Found: C, 77.10; H, 6.12.

Reaction of Diphenylketene-*p*-tolylimine and Peroxyacetic Acid.—To 0.50 g (1.76 mmoles) of diphenylketene-*p*-tolylimine in 25 ml of chloroform was added 4 ml of commercial (Becco "40%") peroxyacetic acid, containing approximately 1.5 g (21 mmoles) of peroxy acid. The reaction mixture was treated in the same manner as in the reaction with peroxybenzoic acid, resulting in the isolation of a 24% yield of N-(*p*-tolyl)-α-acetoxydiphenylacetamide.

If the reaction were carried out in ether as a solvent in place of chloroform, N-(*p*-tolyl)diphenylacetamide (0.39 g, 74%) was the only amide isolated.

Chromatography of the residual oil remaining after removal of α-acetoxyamide and evaporation of the solvent, as above, again yielded benzophenone and di-*p*-tolylformamidine. An intermediate benzene eluate, however, also produced N-(*p*-tolyl)-diphenylacetamide in 33% yield. This was presumably due to the action of the large amount of acetic acid contained in the Becco reagent.

N-(*p*-Tolyl)-α-benzoxydiphenylacetamide.—To a solution of 3.3 g (0.01 mole) of N-(*p*-tolyl)-α-chlorodiphenylacetamide[27] and 2.4 g (0.02 mole) of benzoic acid in 50 ml of dry benzene was added 2.8 g (0.01 mole) of silver carbonate. The flask was protected from the light; the contents were vigorously stirred for 24 hr at room temperature. The benzene was filtered several times, extracted with dilute aqueous sodium carbonate, washed with water, dried over sodium sulfate, and concentrated to a few milliliters. Addition of petroleum ether precipitated crystals of N-(*p*-tolyl)-α-benzoxydiphenylacetamide, 3.6 g (86%), mp 163–164°, after one crystallization from ethanol.

N-(*p*-Tolyl)-α-acetoxydiphenylacetamide.—To a solution of 3.3 g (0.01 mole) of N-(*p*-tolyl)-α-chlorodiphenylacetamide in 50 ml of dry benzene was added 3.34 g (0.02 mole) of silver acetate. The flask was protected from the light; the contents were vigorously stirred for 24 hr at room temperature. The benzene was filtered several times, washed repeatedly with dilute ammonium hydroxide and water, and dried over sodium sulfate. Concentration and dilution with petroleum ether caused crystallization of N-(*p*-tolyl)-α-acetoxydiphenylacetamide, 3.2 g (90%), mp 195–196°, after one crystallization from ethanol.

Reaction of Diphenylketene-*p*-tolylimine and Peroxybenzoic Acid in Methanol—To a solution of 0.5 g (1.76 mmoles) of diphenylketene-*p*-tolylimine in 50 ml of methanol was added 0.42 g (2.8 mmoles) of peroxybenzoic acid. The mixture was swirled until solution was complete and allowed to stand at room temperature for 24 hr. Methanol was removed under reduced pressure, and the residue was taken up in a minimum of chloroform. This was extracted with dilute sodium bicarbonate, washed with water, dried, diluted with petroleum ether, and chilled. Crystals were obtained which could be separated into two fractions on fractional crystallization from ethanol to yield N-(*p*-tolyl)-α-methoxydiphenylacetamide[22] (55 mg, 9.5%) and N-(*p*-tolyl)diphenylacetamide (42 mg, 8.0%).

Acknowledgment.—The authors are indebted to the Chemistry Department of Wayne State University for facilities and materials used in a portion of this work. In particular, we are grateful to Professor Calvin L. Stevens of that department for the use of his resources and for the informative discussions relating to this project in which he was kind enough to engage with us.

Reactions of 2,2-Dicyano-3,3-bis(trifluoromethyl)oxirane with Thiocarbonyl Compounds[1]

W. J. MIDDLETON

Contribution No. 1219 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware

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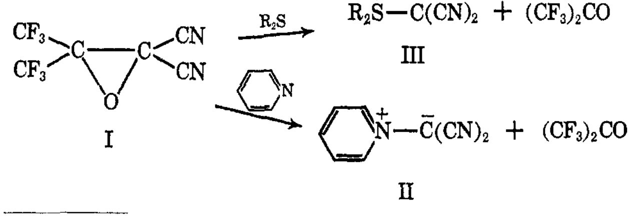
2,2-Dicyano-3,3-bis(trifluoromethyl)oxirane reacts with thioureas by transferring a dicyanomethylene group to the sulfur atom to give stable methylenesulfonium ylides. The oxirane reacts with other thioamides to give either thiazoles or dicyanoethylenes.

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene undergoes many reactions similar to those of tetracyanoethylene.[2] One example is epoxidation, for 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane (I) can be prepared by oxidation of the ethylene with peracetic acid. This epoxide, like the epoxide of tetracyanoethylene,[3] reacts with pyridine to transfer a dicyanomethylene group to the nitrogen atom to give the dicyanomethylide II. Dicyanomethylene groups can also be transferred from both tetracyanoethylene oxide and I to the sulfur atom in alkyl sulfides to give stable sulfur ylides (III).[4]



We have now extended this investigation of dicyanomethylene transfer to the reaction of dicyanoethylene epoxides with certain thiocarbonyl compounds, including thioureas, thioamides, and a trithiocarbonate. For these studies, we have used the epoxide I instead of tetracyanoethylene oxide, for we found that reactions of I with thiocarbonyl compounds were much cleaner than reactions of tetracyanoethylene oxide with the same compounds. This is probably because carbonyl cyanide, the by-product from reactions of tetracyanoethylene oxide, undergoes secondary reactions causing tar formation, whereas hexafluoroacetone, the by-product from I, is much less reactive than carbonyl cyanide.

Three general types of reactions between I and thiocarbonyl compounds have been observed. They are (1) direct transfer of the dicyanomethylene group to

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[1] Portions of this paper were presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill, Sept 1964.

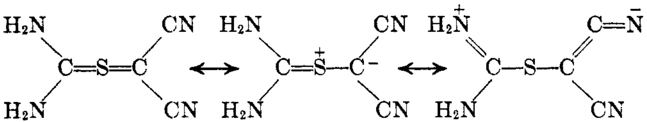
[2] W. J. Middleton, *J. Org. Chem.*, **30**, 1402 (1965).

[3] W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2032 (1963); **87**, 3651 (1965).

[4] W. J. Middleton, E. L. Buhle, J. G. McNally, Jr., and M. Zanger, *J. Org. Chem.*, **30**, 2384 (1965).

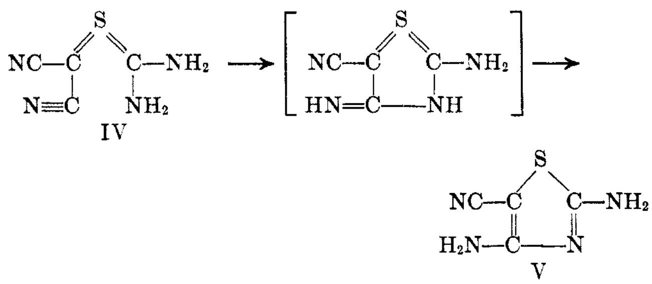
the sulfur atom to give an ylide, (2) transfer of a dicyanomethylene group and subsequent cyclization to give a thiazole, and (3) replacement of the sulfur with a dicyanomethylene group to give a dicyanoethylene.

Ylides.—A solution of thiourea in alcohol reacts rapidly and exothermically with I to give (diaminomethylene)sulfonium dicyanomethylide (IV) in high yield. This product can best be represented by a number of resonance forms, of which IVa, IVb, and IVc are examples. It seems likely that the compound owes its unusual stability to the fact that both the positive and negative charge in the dipolar resonance forms can be delocalized over a number of atoms. The presence of a doublet in the infrared spectrum of IV at the very long wavelength of 4.58 and 4.67 μ confirms the presence of a $C(CN)_2^-$ group and is consistent with the spectra of other dicyanomethylides.[4]


IVa IVb IVc

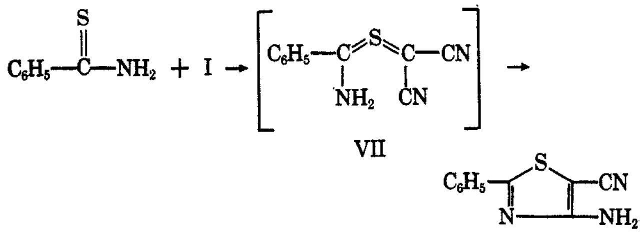
Other thioureas, such as N,N,N′,N′-tetramethylthiourea and N,N′-ethylenethiourea react with I to give similar ylides. Both IV and the ylide derived from ethylenethiourea are stable indefinitely at room temperature but decompose at their melting points. The ylide prepared from tetramethylthiourea decomposes in a few hours when stored at room temperature.

Thiazoles.—The ylide IV undergoes a facile cyclization reaction when heated in water to give the thiazole V. As would be expected, the thiazole V is considerably more stable than the isomeric ylide (IV). The thiazole structure was confirmed by ultraviolet, infrared, and elemental analysis.


IV

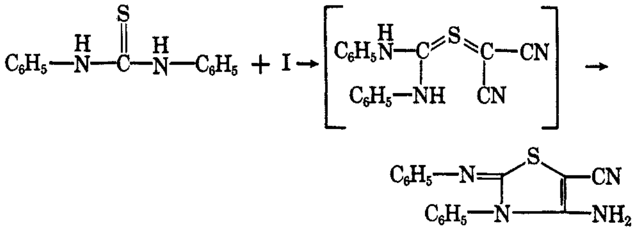
V

Thiobenzamide reacts with I to give a thiazole (VI) directly without the intermediate isolation of an ylide (VII). The intermediate ylide VII, if it is formed, is apparently less stable than the corresponding ylide IV. This may be due to less stabilization of a positive charge by a phenyl group than by an amino group. With a proportionally larger accumulation of positive charge on the amino group in intermediate VII, cyclization would occur more readily.

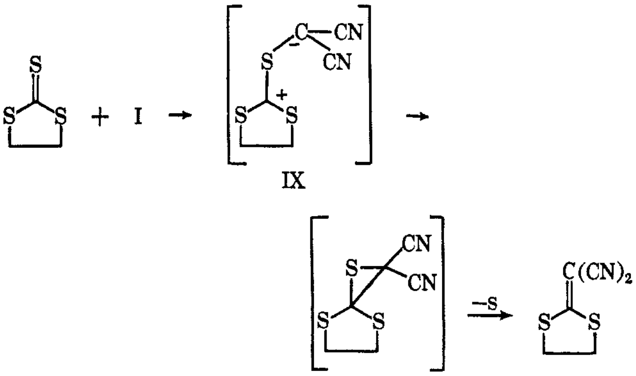

VII

VI

Cyclization also occurs with the reaction of I with *s*-diphenylthiourea. In this case, tautomerization of the resulting heterocycle (VIII) to the fully aromatic thiazole is prohibited by the phenyl substituent in the 3 position of the ring.


VIII

Dicyanoethylenes.—In all of the examples discussed thus far, both of the groups attached to the carbon of the thiocarbonyl group have been amino or aromatic. Both of these groups tend to stabilize a positive charge, and therefore stabilize the ylide first formed by reaction with I. We have found that certain thiocarbonyl compounds that contain methyl or thio groups attached directly to the thiocarbonyl group react with I to replace the sulfur atom with a dicyanomethylene group. For example, ethylene trithiocarbonate reacts to give XI with elimination of elemental sulfur. Similarly, thioacetamide and thioacetanilide react with I to give 2-amino-1,1-dicyanopropene and 2-phenylamino-1,1-dicyanopropene, respectively. Formation of these products can be explained by postulating that the first step of the reaction is attachment of the dicyanomethylene to the sulfur atom to give an ylide (*e.g.*, IX). Since the positive charge would be stabilized less by a methyl or thio group than by an amino or aromatic group, a greater accumulation of positive charge would be found on the carbon atom. Such a situation might lead to charge neutralization by collapse to a three-membered ring containing sulfur (*e.g.*, X). Such negatively substituted episulfides are known to lose sulfur readily to give olefins.[5]


IX

X XI

Experimental Section

2,2-Dicyano-3,3-bis(trifluoromethyl)oxirane.[6]—1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene, 42.8 g (0.2 mole), was added

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[5] D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 21 (1951); W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, **30**, 1378 (1965).

[6] W. J. Middleton, U. S. Patent 3,194,819 (1965).

dropwise to a flask containing 40 g (0.21 mole) of 40% peracetic acid, stirred, and cooled in an ice bath. The rate of addition was adjusted so that the temperature did not rise above 50°. A few milliliters of mercaptoacetic acid was then added until no further exothermic reaction occurred. The reaction mixture was distilled, and the fraction that boiled between 75 and 98° was collected. Redistillation through a 14-in. spinning-band column gave 35.5 g of 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane as a colorless liquid, bp 96°, that solidified to a colorless solid, mp 46–47°. The F^{19} nmr spectrum at 56.4 Mc showed a single band at +2.37 ppm relative to 1,2-difluorotetrachloroethane as an external reference.

Anal. Calcd for $C_6F_6N_2O$: C, 31.32; F, 49.55; N, 12.18. Found: C, 31.21; F, 49.34; N, 12.02.

N-Dicyanomethylenepyridine.—A solution of 0.79 g (0.01 mole) of pyridine in 10 ml of ether was added dropwise to a cooled solution of 2.3 g (0.01 mole) of 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane in 15 ml of ether. A vigorous, exothermic reaction occurred. The yellow precipitate that formed was collected on a filter and recrystallized from alcohol to give 1.25 g of N-dicyanomethylenepyridine as light yellow needles, mp 245–246°. The sample was identified by its infrared spectrum, which was identical with that of an authentic sample.[3]

Hydrolysis of 2,2-Dicyano-3,3-bis(trifluoromethyl)oxirane.—A mixture of 2,3 g (0.01 mole) of 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane, 30 ml of water, and 10 ml of 10% sodium hydroxide solution was stirred together for 5 min at room temperature, and the suspended white solid that formed was collected on a filter and washed with water. Recrystallization from alcohol gave 1.01 g of 2,2-dicarbamoyl-3,3-bis(trifluoromethyl)oxirane as colorless needles, mp 273–274°. The infrared spectrum showed bands at 2.94, 3.04, 3.12, and 6.15 for NH_2 and 5.86 and 5.93 μ for $CONH_2$.

Anal. Calcd for $C_6H_4F_6N_2O_3$: C, 27.07; H, 1.52; F, 42.85; N, 10.52. Found: C, 27.28; H, 1.63; F, 42.63; N, 10.73.

(Diaminomethylene)sulfonium Dicyanomethylide.[7]—A mixture of 15 ml of ethyl alcohol, 0.76 g (0.01 mole) of thiourea, and 2.3 g (0.01 mole) of 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane was stirred at room temperature until solution was complete. An exothermic reaction occurred, and the reaction mixture was warmed spontaneously to 50°. Ether (100 ml) was added, and the precipitate that formed was collected on a filter and washed with ether. Recrystallization from alcohol–ether gave 1.1 g (79%) of (diaminomethylene)sulfonium dicyanomethylide as colorless prisms, mp 114–115° dec (black). The infrared spectrum showed bands at 2.94, 3.05, and 3.19 for NH_2 and 4.65 and 4.57 μ for conjugated CN. The ultraviolet spectrum showed λ_{max}^{EtOH} 277 mμ (ϵ 728).

Anal. Calcd for $C_4H_4N_4S$: C, 34.28; H, 2.88; N, 39.98; S, 22.87. Found: C, 34.44; H, 3.30; N, 39.43; S, 22.36.

S-Dicyanomethylene-2-imidazolidinethione.—2,2-Dicyano-3,3-bis(trifluoromethyl)oxirane (12.5 g, 0.05 mole), was added portionwise to a stirred suspension of 5.01 g (0.05 mole) of finely powdered 2-imidazolidinethione in 200 ml of ethanol. An exothermic reaction ensued, and the reaction mixture was warmed spontaneously to 47°. The reaction mixture was stirred for 2 hr, and the suspended solid was collected on a filter and washed thoroughly with alcohol. There was obtained 7.8 g (80%) of crude S-dicyanomethylene-2-imidazolidinethione as near-white crystals, mp 170–175° dec (black). A sample was recrystallized from a large volume of alcohol for analysis.

Anal. Calcd for $C_6H_6N_4S$: C, 43.36; H, 3.65; N, 33.71; S, 19.28. Found: C, 43.56; H, 3.71; N, 33.88; S, 18.74.

The infrared spectrum contains a broad band at 3.15 for NH, 3.42 for saturated CH, and 4.58 and 4.67 μ for conjugated CN.

The product was soluble in dilute, aqueous sodium hydroxide and was precipitated unchanged from this solution with dilute hydrochloric acid.

[Bis(dimethylamino)methylene]sulfonium Dicyanomethylide.—Tetramethylthiourea (2.64 g, 0.02 mole) was added portionwise to a stirred solution of 4.6 g (0.02 mole) of 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane in 10 ml of methanol cooled in an ice bath. An exothermic reaction ensued, and the solution became yellow as the thiourea dissolved. The solution was cooled to −40°, and the solid that separated was collected on a filter to give 3.65 g (80%) of crude crystalline product. Recrystallization from methanol, keeping the temperature below 30°, gave 2.93 g of [bis(dimethylamino)methylene]sulfonium dicyanomethylide as colorless plates.

The melting point is about 70°, with decomposition, when heated rapidly. The product can be stored at −78° but decomposes when stored at room temperature for a few days. The infrared spectrum had bands at 4.62 and 4.70 μ for conjugated CN.

Anal. Calcd for $C_8H_{12}N_4S_2$: C, 43.08; H, 5.31; N, 24.55; S, 28.10. Found: C, 42.58; H, 5.38; N, 24.59; S, 28.20.

2,4-Diamino-5-cyanothiazole.—Diaminomethylenesulfonium dicyanomethylide (4.0 g) was dissolved in 20 ml of hot water, and the solution was heated to reflux for 1 hr. Decolorizing charcoal (5 g) was added to the hot black solution, and the reaction mixture was filtered. The filtrate was cooled, and the needles that separated were collected on a filter and recrystallized from water. There was obtained 1.9 g of 2,4-diamino-5-cyanothiazole as colorless needles, mp 190–192°. The infrared spectrum had bands at 3.04 and 3.13 for NH_2, 4.59 for CN, and 6.50 and 6.57 μ for the thiazole ring. The ultraviolet spectrum showed λ_{max}^{EtOH} 302 mμ (ϵ 9700) and 224 mμ (ϵ 17,100).

Anal. Calcd for $C_4H_4N_4S$: C, 34.28; H, 2.88; N, 39.98; S, 22.87. Found: C, 34.50; H, 2.88; N, 40.09; S, 23.30.

4-Amino-5-cyano-2-phenylthiazole.—2,2-Dicyano-3,3-bis(trifluoromethyl)oxirane, 1.15 g (0.005 mole), was dissolved in a solution of 0.62 g (0.005 mole) of thiobenzamide in 15 ml of ether. A vigorous evolution of gas occurred, and a light yellow precipitate formed. The reaction mixture was cooled to −50°, and the precipitate was collected on a filter and washed with cold ether. Recrystallization from alcohol gave 0.9 g of 4-amino-5-cyano-2-phenylthiazole as light yellow crystals, mp 196–201°. The infrared spectrum showed bands at 2.99, 3.03, and 3.12 for NH_2, and 4.57 μ for CN.

Anal. Calcd for $C_{10}H_7N_3S$: N, 20.88; S, 15.93. Found: N, 20.58; S, 15.49.

4-Amino-5-cyano-3-phenyl-2-phenylimino-4-thiazoline.—*s*-Diphenylthiourea (2.28 g, 0.01 mole), was dissolved in a solution of 2,3 g (0.01 mole) of 2,2-dicyano-3,3-bis(trifluoromethyl)-oxirane in 10 ml of methanol. An exothermic reaction occurred. The precipitate that formed when the mixture was cooled to 0° was collected on a filter and washed with cold methanol. Recrystallization from ethanol gave 2.3 g of 4-amino-5-cyano-3-phenyl-2-phenylimino-4-thiazoline as colorless prisms, mp 194–196°. The infrared spectrum had bands at 2.93, 3.03, 3.12 and 3.15 for NH_2, 4.53 for CN, and 6.15, 6.30, and 6.70 μ for NH_2, C=C, and C=N.

Anal. Calcd for $C_{16}H_{12}N_4S$: C, 65.73; H, 4.14; N, 19.17; S, 10.97. Found: C, 66.09; H, 4.37; N, 19.37; S, 10.95.

2-Amino-1,1-dicyanopropene.—A solution of 1.15 g (0.005 mole) of 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane in 10 ml of ether was added dropwise to a suspension of 0.38 g (0.005 mole) of thioacetamide in 15 ml of ether. A vigorous evolution of gas occurred, and a yellow precipitate formed. The precipitate was collected on a filter, washed with ether, and recrystallized from water to give 0.21 g of 2-amino-1,1-dicyanopropene as colorless prisms, mp 228°. The proton nmr spectrum in deuterioacetone showed a singlet at τ 7.75 (CH_3) and a very broad resonance at about 2.4 (NH_2). The infrared spectrum had bands at 2.99, 3.02, 4.50, 4.53, 5.95, and 6.42 μ.

Anal. Calcd for $C_5H_5N_3$: C, 56.06; H, 4.71; N, 39.28. Found: C, 56.31; H, 4.81; N, 39.32.

2-Phenylamino-1,1-dicyanopropene.—A solution of 1.15 g (0.005 mole) of 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane in 10 ml of ether was added dropwise to a clear, filtered solution of 0.76 g (0.005 mole) of thioacetanilide in 20 ml of ether. A vigorous evolution of gas occurred, and a light tan solid precipitated. The precipitate was collected on a filter and washed with ether to give 0.15 g of 2-phenylamino-1,1-dicyanopropene as light tan crystals, mp 194–195°.[8] The infrared spectrum contained bands at 3.09 for NH and at 4.54 and 4.59 μ for CN. The proton nmr spectrum in deuterioacetone showed absorptions at τ 7.73 (CH_3), 2.52 (C_6H_5), and −1.0 (NH).

Anal. Calcd for $C_{11}H_9N_3$: C, 72.03; H, 4.85; N, 22.94; mol wt, 183.2. Found: C, 72.11; H, 4.96; N, 22.64; mol wt, 182.

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[7] W. J. Middleton, U. S. Patent, 3,185,700 (1965).

[8] This melting point does not correspond to the melting point of 92° given by German patent 834,104 (1952) for the same compound prepared by a different method.

2-Dicyanomethylene-1,3-dithiolane.—Ethylene trithiocarbonate (0.68 g, 0.005 mole) and 1.15 g (0.005 mole) of 2,2-dicyano-3,3-bis(trifluoromethylene)oxirane were dissolved in 15 ml of ether, and the solution was allowed to remain at room temperature overnight. The yellow solid that precipitated was collected on a filter and washed with ether. Recrystallization from alcohol gave 0.59 g of 2-dicyanomethylene-1,3-dithiolane as colorless plates, mp 202-203°. The infrared spectrum agreed with that of an authentic sample prepared by another method.[9]

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[9] R. Gompper and W. Toepfl, *Ber.*, **95**, 2861 (1962).

Linear Indanthrone and Related Phenazines[1]

EDWARD LEETE,[2a] OLUCHUKWU EKECHUKWU, AND PETER DELVIGS[2b]

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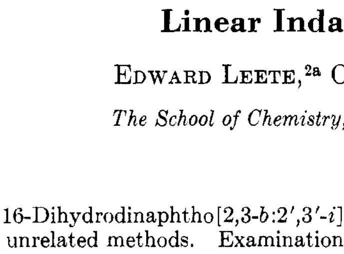
Received June 24, 1966

7,16-Dihydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine-5,9,14,18-tetrone (linear indanthrone) has been prepared by two unrelated methods. Examination of the properties of this substance and its derivatives indicates that the previously described syntheses of linear indanthrone have not afforded authentic material. Naphtho[2,3-*b*]phenazine and several of its derivatives which are similar chemically and physically to linear indanthrone are described.

Indanthrone (1), which was discovered by Bohn[3] in 1901, is an important blue vat dye, and its chemistry has been extensively investigated.[4] However when we started our work little was known about the linear isomer of indanthrone, 7,16-dihydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine-5,9,14,18-tetrone (2), and we consider that the reported syntheses[5] of this compound have not yielded authentic material. Schiedt[5a] claimed to have obtained 2 by the reaction of formamide with hystazarinquinone (anthracene-2,3,9,10-tetrone) at 130°. The product was obtained as dark brown rods from quinoline, melting above 400°. A correct nitrogen analysis was reported, but no other properties were described. Attempts to repeat this reaction have been unsuccessful.[5c] Clark reported the synthesis of 2 by heating 2-amino-3-bromoanthraquinone with potassium carbonate, and also by the condensation of 2,3-diaminoanthraquinone with either 2,3-dibromoanthraquinone or hystazarinquinone.[5c] The linear indanthrone was reported to be a reddish brown compound which could not be crystallized from any organic solvent. Unsatisfactory analyses for carbon content were attributed to the hygroscopic nature of the product. No derivatives of the linear indanthrone were described.



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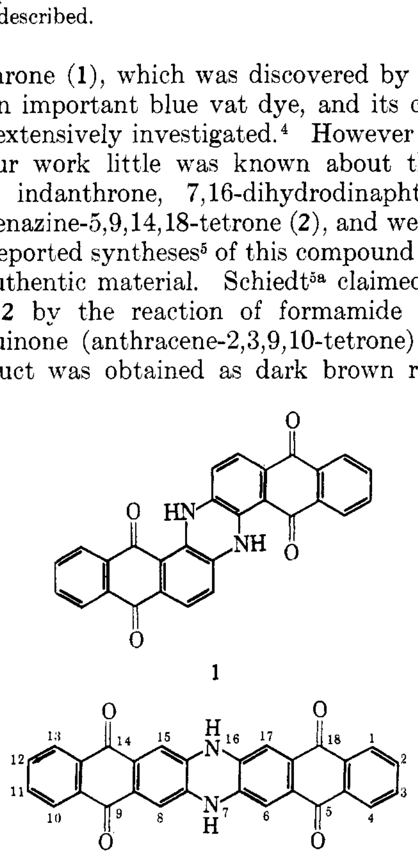

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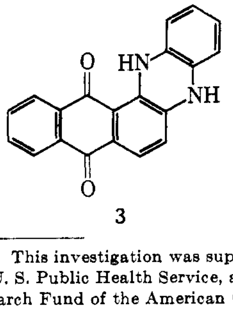

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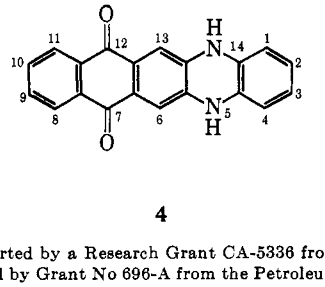

4

5,14-Dihydronaphtho[2,3-*a*]phenazine-8,13-dione (3) is a blue substance having properties very similar to indanthrone.[6] Thus, as a preliminary to the unambiguous synthesis of linear indanthrone, we prepared 5,14-dihydronaphtho[2,3-*b*]phenazine-7,12-dione (4) since we anticipated that this compound would resemble the linear indanthrone 2 in its physical and chemical properties.[7] 2-Bromo-3-nitroanthraquinone[8] was condensed with *o*-nitroaniline in boiling *o*-dichlorobenzene in the presence of lead oxide and cupric acetate affording the orange 2-(*o*-nitroanilino)-3-nitroanthraquinone (5). Reduction of this compound with sodium sulfide in ethanol afforded a mixture of the green dihydrophenazine 4 and 2-(*o*-aminoanilino)-3-aminoanthraquinone (6). Oxidation of compound 6 with ferric chloride in hydrochloric acid yielded the yellow naphtho[2,3-*b*]phenazine-7,12-dione (7). A small yield of the phenazine 7 was also obtained by reaction of 2,3-diaminoanthraquinone with *o*-benzoquinone in warm acetic acid. A much better yield of the 1,2,3,4-tetrachloro derivative of 7 was obtained by reaction of 2,3-diaminoanthraquinone with the more stable 3,4,5,6-tetrachloro-*o*-benzoquinone. Treatment of the phenazine 7 with an alkaline solution of sodium hydrosulfite afforded a reddish brown vat, which on oxidation with air yielded the green dihydrophenazine 4. The phenazine 7 was also obtained by oxidation of 5,14-dihydro-

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[2] (a) Alfred P. Sloan Foundation Fellow, 1963–1966; (b) National Science Foundation Predoctoral Fellow, 1962–1963.

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