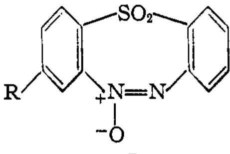
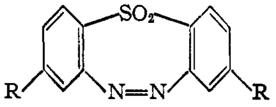
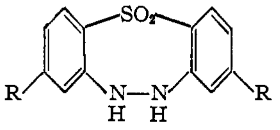
pound (II) which in turn was oxidized with peracetic acid to the azoxy compound I. The hydrazo compound III, or any of its higher oxidation products, could be catalytically hydrogenated or chemically reduced to di-(2-amino-4-trifluoromethylphenyl) sulfone.



I



II



III

(R = CF$_3$)

It is of interest to note that I and II are thermally quite stable and that they do not show any tendency to lose nitrogen or its oxides at their respective melting points (above 250°) and to produce thereby derivatives of dibenzothiophene. The hydrazo compound, on the other hand, is unstable and decomposes at its melting point (*ca.* 136°) rather violently. The instability of III is not necessarily due to the presence of a seven-membered ring since even simple compounds such as hydrazobenzene are known to decompose on heating.[3]

Experimental[4]

Di-(2-nitro-4-trifluoromethylphenyl) Sulfide. (A).—Potassium ethyl xanthate, 120 g., was added to a mixture of 158 g. of *m*-nitro-*p*-trifluoromethylchlorobenzene and 350 cc. of ethanol. After the initial vigorous reaction subsided the mixture was refluxed for two days. The precipitate was washed and crystallized from acetic acid to give a 40% yield of the desired sulfide, m.p. 146°.

(B).—A solution of 50.5 g. of sodium thiosulfate in 200 cc. of water was added dropwise to a vigorously stirred solution of 45 g. of 4-chloro-3-nitrobenzotrifluoride in 350 cc. of ethanol while the mixture was maintained at constant reflux. After an additional reflux period of six hours the sulfide was filtered, washed with water and ethanol. There was obtained a 61% yield of crude product m.p. 144°.

Anal. Calcd. for $C_{14}H_6O_4N_2SF_6$: C, 40.78; H, 1.47. Found: C, 40.92; H, 1.62.

Di-(2-nitro-4-trifluoromethylphenyl) Sulfone.—The sulfide, 151 g., was dissolved in 1 l. of glacial acetic acid and 50 g. of chromic anhydride was added slowly to the hot solution. The mixture was refluxed for 8 hours, poured on ice and the crude product m.p. 153–155° (86%) was crystallized from acetic acid to a constant melting point of 167–168°.

Anal. Calcd. for $C_{14}H_6O_2N_2SF_6$: C, 37.85; H, 1.36. Found: C, 38.11; H, 1.44.

The Hydrogenation of Di-(2-nitro-4-trifluoromethylphenyl) Sulfone.—A solution of 27 g. of the sulfone in 250 cc. of dioxane was hydrogenated in the presence of Raney nickel[5] until the pressure dropped 22 lb. from the initial pressure of 62.5 lb. The solution was filtered and concentrated and 14.5 g. of the hydrazo compound III separated as a white solid, m.p. 136–137°. This solid was crystallized from benzene and treated with charcoal but on exposure to air it turned yellowish and melted with violent decomposition. In spite of several attempts it could not be preserved in an analytically pure state.

Anal. Calcd. for $C_{14}H_8O_2N_2SF_6$: C, 43.98; H, 2.19. Found: C, 41.69; H, 2.41.

The filtrate from the hydrogenation mixture on further concentration yielded 1 g. of yellow azo compound II, m.p. 247–248° on crystallization from ispropyl alcohol.

Anal. Calcd. for $C_{14}H_6O_2N_2F_6$: C, 44.21; H, 1.59. Found: C, 43.70; H, 2.23.

The hydrazo compound III was also obtained in 37% yield by hydrogenating 5 g. of the sulfone in 200 cc. of isopropyl alcohol (pressure drop from 62.5 to 58.8 lb.).

The azoxy compound I was obtained when a solution of 2 g. of the sulfone in 300 cc. of isopropyl alcohol was hydrogenated in the presence of Raney nickel at atmospheric pressure until 2.8 moles of hydrogen were absorbed. The product (*ca.* 1 g.) on crystallization from isopropyl alcohol gave white crystals, m.p. 267–268°.

Anal. Calcd. for $C_{14}H_6O_3N_2SF_6$: C, 42.42; H, 1.53. Found: C, 42.65; H, 1.93.

Di-(2-amino-4-trifluoromethylphenyl) Sulfone.—The nitro sulfone, 20 g., was dissolved in 250 cc. of benzene and to the stirred solution there was added 100 cc. of water and 20 g. of iron powder. Hydrochloric acid, 2.5 cc. of 20% solution, was added in small portions to the heated mixture and stirring was continued for three hours. The hot mixture was filtered rapidly and from the benzene layer on concentration and cooling there was obtained a 5-g. yield of pure product, m.p. 133–136° after crystallization from benzene.

Anal. Calcd. for $C_{14}H_{10}O_2N_2SF_6$: C, 43.75; H, 2.62. Found: C, 43.77; H, 2.87.

The diamine, 1 g., was also obtained when 2 g. of the azo compound II was hydrogenated in the presence of Raney nickel. The hydrogenation was carried out under 62 lb. of hydrogen pressure and required 24 hours.

The Oxidation of II to I.—The azo compound II, 1 g., was dissolved in 20 cc. of glacial acetic acid and the solution was refluxed with 20 cc. of 40% peracetic acid until the yellow coloration faded. The mixture was poured on ice and upon crystallization from isopropyl alcohol there was isolated 0.7 g. of azoxy compound I, m.p. 267°.

The Oxidation of III to II.—Air was passed into an alcoholic solution of 3 g. of the hydrazo compound III containing a few drops of dilute alkali. After two hours the red solution was concentrated and cooled and there were obtained yellow crystals of the azo compound. After crystallization there was isolated 1.5 g. of product m.p. 247–248° identical with the product obtained from the hydrogenation of the dinitro sulfone.

Acknowledgment.—We wish to thank the Hooker Electrochemical Company for a generous supply of *m*-nitro-*p*-chlorobenzotrifluoride, and the Becco Sales Corporation for the gift of peracetic acid.

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Dispiro(5.1.5.1)tetradecane[1]

BY H. M. WALBORSKY AND E. R. BUCHMAN

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Simple dispirane hydrocarbons have not previously been reported. A representative member of this class, dispiro(5.1.5.1)tetradecane (I), was prepared utilizing as starting material dispiro(5.1.5.1)tetradecan-7,14-dione (II) (formed by dimerization of pentamethyleneketene), which was available through the researches of J. R. Johnson and C. M. Hill.[2]

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[3] N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Oxford University Press, New York, N. Y., 1942, p. 384.

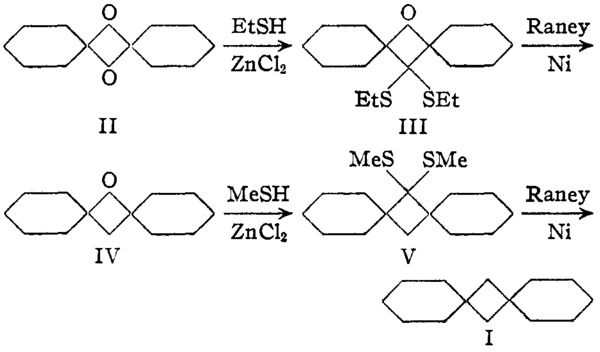
[4] The melting points are uncorrected. All microanalyses by Mr. George Stragand, University of Pittsburgh.

[5] The catalyst was prepared according to the directions of Covert and Adkins (THIS JOURNAL, **54**, 4116 (1932)), and the dioxane was purified as described by Vogel in "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., p. 175.

[1] Presented before the Division of Organic Chemistry, American Chemical Society, at the Philadelphia Meeting, April, 1950. This research received support from the Office of Naval Research.

[2] C. M. Hill, Doctoral thesis, Cornell University, 1941.

Although cyclobutan-1,3-diones (ketoketene dimers) possessing the structural features of II have been intensively studied,[3] at the time of this investigation it had not been found possible to convert them to the corresponding cyclobutanes.[4] The conversion, in the case of II, was carried out making use of a method developed for carbonyl reduction by Wolfrom and Karabinos.[5] The steps in the synthesis (outlined in the Chart) were realized without difficulty. Noteworthy is the fact that only one carbonyl function[6] in II is reactive toward mercaptans.



Experimental[7]

Dispiro(5.1.5.1)tetradecan-7,14-dione (II).[2]—Hexahydrobenzoyl chloride (140 g., 0.96 mole) and 1 liter of dry benzene were introduced into a three-necked flask equipped with stirrer, condenser and dropping funnel. An atmosphere of dry nitrogen was maintained in the reaction vessel; dry triethylamine (165 g., 1.6 moles) was slowly added with stirring. Stirring was continued and the reaction mixture was refluxed overnight. The triethylamine hydrochloride was filtered off and washed with benzene. The combined filtrates were washed with dilute hydrochloric acid and with water. Solvent was removed by distillation and the residue was recrystallized from petroleum ether–ethanol; yield 56 g. (53%) of II, m.p. 164–165° (lit.[2] m.p. 164–165°). The 2,4-dinitrophenylhydrazone of II was obtained as a difficultly soluble yellow solid, m.p. 267–268°.

14,14-Di-(ethylmercapto)-dispiro(5.1.5.1)tetradecan-7-one (III).—Freshly fused zinc chloride (1.8 g.), anhydrous sodium sulfate (1.5 g.) and II (6 g., 0.027 mole) were placed in a stoppered flask together with an excess of ethyl mercaptan (*ca.* 20 g.). The mixture was placed in the ice-chest overnight, then allowed to stand at room temperature for 24 hours and finally poured into a separatory funnel containing ice-water and ether. The ether layer was separated, washed well with 10% aqueous sodium hydroxide solution and dried. Solvent was distilled off and the residue (7.5 g., 84% yield) was recrystallized from ethanol, m.p. 57.5–58.3°.

Anal. Calcd. for $C_{18}H_{30}OS_2$: C, 66.2; H, 9.3; S, 19.6. Found: C, 66.1; H, 9.4; S, 19.2.

In a like manner II reacted with excess of methyl mercaptan in a sealed tube at room temperature. The product, the methylmercapto analog[8] of III, was recrystallized from ethanol, m.p. 110.5–110.8°, analysis for $C_{16}H_{26}OS_2$.

Dispiro(5.1.5.1)tetradecan-7-one (IV).—A mixture of 345 g. of Raney nickel, 750 ml. of ethanol and 15 g. (0.046 mole) of III was refluxed for 48 hours. The solid was separated by centrifugation and washed with hot ethanol. Solvent was distilled *in vacuo* from the combined alcoholic solutions; from the residue was obtained 7 g. (73% yield) of IV. After recrystallization from acetonitrile, IV melted at 89–90.5° and had an odor resembling that of citrus fruit.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.5; H, 10.7. Found: C, 81.3; H, 10.8.

The 2,4-dinitrophenylhydrazone of IV was crystallized from ethanol–acetonitrile, m.p. 181–182°, analysis for $C_{20}H_{26}N_4O_4$.

7,7-Di-(methylmercapto)-dispiro(5.1.5.1)tetradecane (V).—Zinc chloride (5 g.) was fused in a glass bomb tube and was allowed to solidify on the walls of the tube. While the tube was cooled in a Dry Ice–acetone-bath, there were added 5 g. of anhydrous sodium sulfate, 9 g. (0.0436 mole) of IV and 50 g. of methyl mercaptan. The tube was sealed, shaken and allowed to stand for 48 hours at room temperature. Excess mercaptan was allowed to distil off and the residue in the tube was taken up in ice-water–ether. The ether solution was washed with sodium hydroxide solution and worked up as usual, yield 6 g. (48%) of V, which, after recrystallization from ethanol (or acetonitrile), melted at 83.5–84.5°.

Anal. Calcd. for $C_{16}H_{28}S_2$: C, 67.5; H, 9.9. Found: C, 67.5; H, 10.0.

Dispiro(5.1.5.1)tetradecane (I).—Freshly prepared Raney nickel (180 g.), ethanol (500 ml.) and V (6 g., 0.021 mole) were placed in a flask and refluxed for 30 hours. The Raney nickel was centrifuged off and washed with hot ethanol. The alcoholic solutions were combined, diluted with water and extracted with petroleum ether (b.p. 60–70°). The extract was distilled through a column to remove solvent and the residue was distilled from a Claisen flask; yield 0.69 g. (17%) of I, b.p. 175–190° at 110 mm. Redistillation over sodium gave material with the following constants: b.p. 131° at 10 mm., m.p. 10°, $n^{26.8}$D 1.4735, $d^{26.54}$ 0.872.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.4; H, 12.6. Found: C, 87.5; H, 12.6.

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[3] H. Staudinger, "Die Ketene," F. Enke, Stuttgart, 1912; W. E. Hanford and J. C. Sauer, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 108.

[4] More recently it has been shown that this type of reduction may be accomplished by the Wolff–Kishner method *via* the disemicarbazone; see H. L. Herzog and E. R. Buchman, *J. Org. Chem.*, **16**, 99 (1951).

[5] M. L. Wolfrom and J. V. Karabinos, THIS JOURNAL, **66**, 909 (1944).

[6] *Cf.* T. Posner, *Ber.*, **33**, 2983 (1900); **35**, 493 (1902).

[7] Melting points are uncorrected; analyses by Dr. A. Elek, Los Angeles.

[8] II combines with trimethylene mercaptan in one to one molar ratio to give a similar derivative, m.p. 112.5–113°; see H. M. Walborsky, Ph.D. thesis, The Ohio State University, 1949.

Diffusion of Polymer Mixtures

BY GUY B. TAYLOR AND F. T. WALL

RECEIVED JULY 15, 1953

This note describes an investigation of the simultaneous diffusion of two or more substances, such as unfractionated polymers, by the experimental method of Wall, Grieger and Childers.[1]

The method consists of saturating a thin porous porcelain plate (frit) with a solution, then following its change in weight with time when it is submerged in a large volume of pure solvent while hanging by a fine wire from one arm of an analytical balance. The method employs the same principle for the actual diffusion as that of Aten and Dreve[2] except that these authors determined the quantity diffused by analytical methods.

The integrated diffusion equation in suitable form for our conditions can be written

$$(W_t - W_\infty) = \frac{16AL(d_2 - d_1)}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-(2n+1)^2\pi^2Dt}{4L^2}\right] \qquad (1)$$

where W_t is the observed weight at time t, W_∞ the weight at infinite time, A the effective area of one face of the plate, L half its effective thickness, n all integers to infinity, and D the diffusion coefficient. The term $(d_2 - d_1)$ is the difference between the density of the original solution and

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[1] F. T. Wall, P. F. Grieger and C. W. Childers, THIS JOURNAL, **74**, 3562 (1952).

[2] A. H. W. Aten and J. V. Dreve, *Trans. Faraday Soc.*, **44**, 202 (1948).