The crude product (1.3 g.), on recrystallization from ethanol–water, yielded 520 mg. as the first crop and about half again as much from the mother liquors. The total yield of such material (m.p. 264–266° dec.), which was of reasonable purity, amounted to 10–14%.

Anal. Calcd. for $C_9H_{15}Br_2NO$: C, 34.50; H, 4.78. Found: C, 34.67; H, 4.81.

Elimination Studies with 2(β)-Bromotropinone Methobromide.—When the salt was treated with sodium bicarbonate at 85° for 56 hours, a 7% spectral yield of tropone formed. The reaction conditions were the same as those used for hydroxytropinone methiodide, except that the concentration of reactants was approximately five times as great.

When sodium carbonate was substituted for sodium bicarbonate, the yield rose to about 20%. This optimum yield was obtained after about 14 hours.

In the sodium hydroxide-induced eliminations, a 34.3-mg. sample of the quaternary salt was dissolved in 10 ml. of water, and 0.66 ml. of 0.033 *N* base was added. After 5 minutes on a boiling water-bath, the spectral yield was 22–25%; longer periods of heating caused a diminution in the yield.

The best results were obtained through the use of sodium bicarbonate and trimethylamine as a pair of reagent bases. Thirty-one milligrams of the quaternary salt, dissolved in 0.5 ml. of water, was mixed with 120 mg. of bicarbonate and 2.5 ml. of a 50% solution of trimethylamine in water. After being heated for 4 hours at 83°, the reaction mixture, on the basis of spectral analysis, contained about a 60% yield of tropone. Further investigation of this technique showed that higher concentration of reactants, omission of the bicarbonate, or a large excess of bicarbonate led to decreased yields. Isolation of tropone as the picrate proceeded along lines described earlier in this account.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Base-catalyzed Rearrangement of 2-Nitrobenzenesulfenanilide

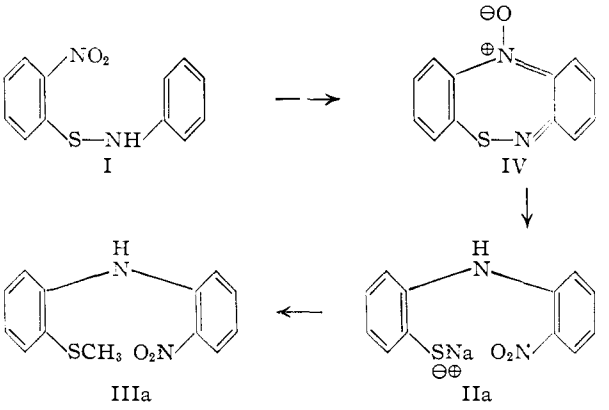
BY M. P. CAVA AND C. E. BLAKE[1]

RECEIVED JUNE 29, 1956

The rearrangement of 2-nitrobenzenesulfenanilide by sodium hydroxide does not yield the sodium salt of 2-mercapto-2′-nitrodiphenylamine, as previously claimed. The product actually formed is sodium azobenzene-2-sulfinate, converted by methyl iodide to 2-methylsulfonylazobenzene. Confirmation of these structures is shown by a number of transformation reactions and by an independent synthesis of 2-methylsulfonylazobenzene.

It has been reported by Moore and Johnson[2] that 2-nitrobenzenesulfenanilide (I) is transformed by boiling alcoholic sodium hydroxide into an orange sodium salt $C_{12}H_9N_2O_2SNa$ (II). Methylation of this salt with methyl iodide gave a neutral orange compound $C_{13}H_{12}N_2O_2S$, m.p. 97–98° (III). Compound III was assigned the structure 2-thiomethyl-2′-nitrodiphenylamine (IIIa), since it was identical both in elementary composition and in melting point[3] with a substance of known structure IIIa prepared by a different route by Evans and Smiles.[4] The original sodium salt II was then assumed to be the sodium salt of 2-mercapto-2′-nitrodiphenylamine (IIa).

The exact course of the alkaline rearrangement of 2-nitrobenzenesulfenanilide, not previously commented upon, seemed to us rather difficult to explain by simple and logical mechanistic steps. A possible path was one involving seven-membered heterocyclic intermediates such as IV. This hypothesis predicts that the nitro group in the methylated product IIIa is derived from the sulfenamide nitrogen of the starting material I,[5] a prediction which could be checked by using N^{15}-labeled starting material and systematically degrading the methylated rearrangement product.



As the first stage in the stepwise degradation of the thiomethyl ether IIIa, reduction of the nitro group of IIIa to a primary amino group was desired. An excellent reagent for this type of reduction is ethanolic hydrazine containing a trace of Raney nickel.[6] In a model experiment this reagent reduced *o*-nitrodiphenylamine to *o*-aminodiphenylamine in 82% yield. Reduction of the methylated rearrangement product III occurred readily to give an almost quantitative yield of a colorless reduction product V, m.p. 124–125°. Analysis of V showed it had the formula $C_{13}H_{14}O_2N_2S$, a structure in which two hydrogens had been gained but in which *no oxygens had been lost.* The reduction, therefore, could not have involved the conversion of a nitro group to a primary amino group. The reduction product V was insoluble in cold dilute hydrochloric acid, but dissolved in the acid when heated. After neutralization of the acid solution there was obtained a new compound VI, m.p. 163–164°, which was isomeric with V. Since a cold acid solution of VI reacted with sodium nitrite, followed by alkaline β-naphthol to give a red precipitate, VI was evidently a primary aromatic amine. Acetylation of VI by acetic anhydride in pyridine gave a diacetyl

(1) From the M.S. Dissertation of C. E. Blake, The Ohio State University, 1956.

(2) M. L. Moore and T. B. Johnson, THIS JOURNAL, **57**, 2235 (1935).

(3) No mixed melting point was reported.

(4) W. J. Evans and S. Smiles, *J. Chem. Soc.*, 187 (1935).

(5) For a detailed discussion of this argument, see ref. 1.

(6) D. Balcom and A. Furst, THIS JOURNAL, **75**, 4334 (1953).

derivative VII, $C_{17}H_{18}O_4N_2S$, m.p, 276–278°, indicating the presence of two readily acylable amino groups. Neither of these was likely to be a diphenylamine function, since under similar acetylation conditions *o*-aminodiphenylamine gave the known monoacetyl derivative in which only the more basic primary amino group is acetylated.

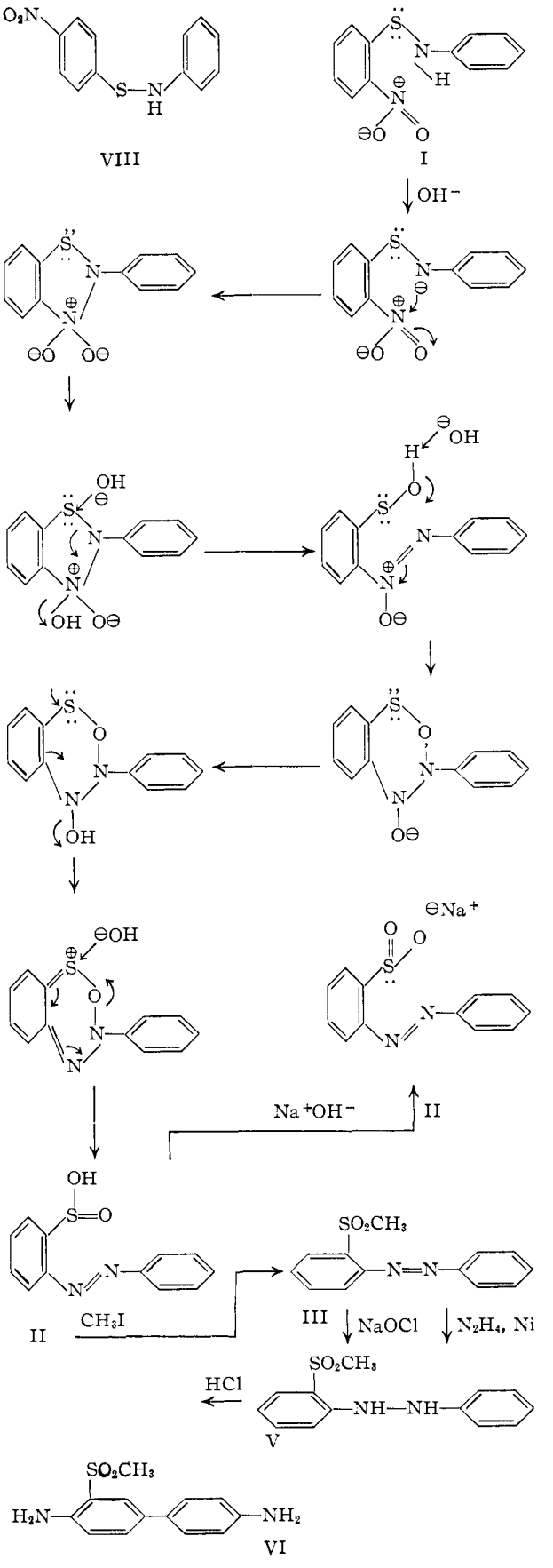
The infrared spectrum of *o*-nitrobenzenesulfenanilide (I) showed the presence of the expected nitro group bands at 6.32 and 7.42 μ.[7,8] The spectrum of the methylated rearrangement product III did not show these bands, but showed two new strong bands at 7.59 and 8.68 μ, *characteristic of a sulfone group.*[7] The spectra of the further transformation products V, VI and VII exhibited the same sulfone bands,

If III is a methyl sulfone, the empirical composition of III is consistent with its formulation as a methylsulfonylazobenzene. The colorless reduction product V must then be the corresponding hydrazobenzene derivative. This hypothesis is in full accord with the ready oxidation of V back to III with sodium hypochlorite solution. The isomerization of V by acid to the diamine VI is then simply a benzidine rearrangement.

Since *p*-nitrobenzenesulfenanilide (VIII) is not rearranged by base,[4] a cyclic rearrangement mechanism involving the *o*-nitro group best explains the conversion of *o*-nitrobenzenesulfenanilide (I) to the sodium salt II, then formulated as sodium azobenzene-2-sulfinate. The methylation of II to 2-methylsulfonylazobenzene (III) and the further transformations of III are then unexceptional processes.

Confirmation of the structure of III was obtained by an independent synthesis. 2-Nitrothioanisole (IX) was oxidized by peracetic acid to 2-methylsulfonylnitrobenzene (X). Reduction of X with iron powder gave 2-methylsulfonylaniline (XI), m.p, 53.5–54.5°. This amine has been reported previously as melting at 90–92°[9] and at 65–66°[10]; we have been unable to repeat either of the two earlier preparations. Reaction of XI with thionyl chloride gave 2-methylsulfonylthionylaniline (XII) which was directly treated with excess phenylhydroxylamine, according to the general azobenzene synthesis of Michaelis and Petou.[11] After chromatography on alumina there was obtained in 25% yield, 2-methylsulfonylazobenzene, m.p. 95.5–96.5°, *identical in all respects* with the methylated rearrangement product III.

Recently sodium azobenzene-2-sulfinate (II) has been prepared by a sequence of reactions[12] totally unrelated to those described in this paper. It has been reported[12,13] that hydrobromic acid transforms II, in part, to the stable azobenzene-2-sulfenyl bromide (XIII), characterized further by reaction with aqueous potassium cyanide to give 2-thio-



(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

(8) M. L. Moore and T. B. Johnson, THIS JOURNAL, **58**, 1961 (1936).

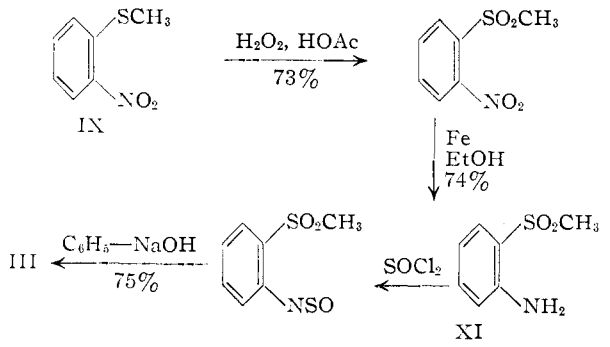
(9) M. Claasz, *Ber.*, **45**, 1022 (1912).

(10) P. Brand, *ibid.*, **42**, 3466 (1909).

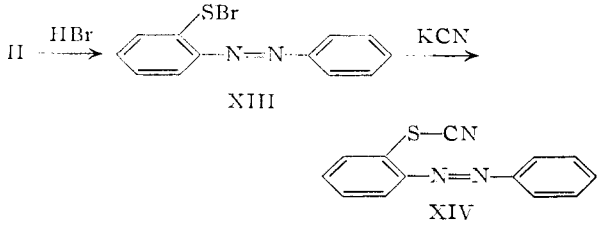
(11) A. Michaelis and K. Petou, *ibid.*, **31**, 988 (1898).

(12) A. Burawoy and C. E. Vellins, *J. Chem. Soc.*, 93 (1954).

(13) A. Burawoy, F. Liversedge and C. E. Vellins, *ibid.*, 4486 (1954).



cyanoazobenzene (XIV). We have been able to convert the orange sodium salt from the basic rearrangement of I into XIII and XIV, thus further confirming its identity as II.



Experimental[14]

2-Nitrobenzenesulfenanilide (I).—This compound was prepared in 81% yield from aniline and 2-nitrobenzenesulfenyl chloride[15] according to the procedure of Zincke and Farr.[16] Recrystallization from cyclohexane gave large red-brown clusters, m.p. 94–95.5° (lit.[16] 94°).

The infrared spectrum in chloroform exhibited high intensity bands at 6.20, 6.59, 6.65, 7.42, 7.60 and 7.76 μ; low intensity bands at 6.32, 6.84, 7.20, 9.03, 11.06, 11.75 and 14.57 μ.

Rearrangement of 2-Nitrobenzenesulfenanilide (I).—This reaction was carried out according to the directions of Moore and Johnson.[2] The 2-nitrobenzenesulfenanilide (10.5 g.) was added to alcohol (25 ml.) containing 20% aqueous sodium hydroxide (5 ml.) and refluxed for six hours. After cooling, the solution was then diluted to twice its volume with water and upon chilling in an ice-bath sodium azobenzene-2-sulfinate was obtained as an orange-red crystalline mass. The mother liquor on concentration yielded a further quantity of the same material. The sodium salt was washed with anhydrous ether (50 ml.). After drying, 11 g. (97%) of glistening orange crystals (II) remained.

Methylation of the Rearrangement Product.—The sodium salt II from the above operation (6 g.) was dissolved in absolute ethanol (30 ml.) and refluxed for four hours with an excess of methyl iodide (7.4 ml.). The solution was then diluted with water (100 ml.), when with rubbing of the container dark red crystals separated. After one recrystallization from alcohol–water, 4.7 g. (81%) of 2-methylsulfonylazobenzene (III) was obtained as orange-red needles, m.p. 95.5–96.5° (lit.[2] 97–98°).

The infrared spectrum in chloroform exhibited high intensity bands at 7.59, 8.68 and 10.41 μ; low intensity bands at 3.23, 6.25, 6.66, 6.80, 6.95, 8.89, 9.36 and 14.62 μ.

2-Methylsulfonylhydrazobenzene (V).—To a boiling solution of 2-methylsulfonylazobenzene (2.0 g.) and anhydrous hydrazine (2.0 ml.) in alcohol (25 ml.) was added a catalytic amount of Raney nickel. This mixture was refluxed until the characteristic orange color disappeared (*ca.* 1–2 hours), then filtered hot and the filtrate cooled to 50°. Water (25 ml.) was then added which precipitated the white hydrazobenzene-2-methylsulfone. One recrystallization from alcohol–water yielded 1.95 g. (98%) of needles, m.p. 124–125°.

Anal. Calcd. for $C_{13}H_{14}O_2N_2S$: C, 59.52; H, 5.38; N, 10.68; S, 12.22. Found: C, 59.58; H, 5.38; N, 10.44; S, 12.25.

The infrared spectrum in chloroform exhibited high intensity bands at 6.19, 6.63, 6.82, 7.56, 7.71, 8.77 and 10.42 μ; low intensity bands at 2.97, 3.25, 7.06, 7.88, 9.40 and 14.50 μ.

4,4′-Diamino-3-methylsulfonylbiphenyl (VI).—2-Methylsulfonylhydrazobenzene (0.5 g.) was dissolved in hot 20% hydrochloric acid (25 ml.). The solution was cooled and made basic with 20% sodium hydroxide, when white 4,4′-diamino-3-methylsulfonylbiphenyl separated. After one recrystallization from alcohol–water 0.48 g. (94%) of white plates, m.p. 163–164°, was obtained. These became discolored on standing in the air.

Anal. Calcd. for $C_{13}H_{14}O_2N_2S$: C, 59.52; H, 5.38; N, 10.68; S, 12.23; Found: C, 59.60; H, 5.35; N, 10.58; S, 12.39.

The infrared spectrum in chloroform exhibited high intensity bands at 6.15, 6.71, 7.70, 8.80, 10.45 and 12.22 μ; low intensity bands at 3.00, 7.15 and 15.10 μ.

4,4′-Diacetamido-3-methylsulfonylbiphenyl (VII).—To a solution of 4,4′-diamino-3-methylsulfonylbiphenyl (0.085 g.) in pyridine (2 ml.) was added acetic anhydride (0.1 ml.). The solution was warmed for one hour on the steam-bath, then cooled and poured into ice and dilute hydrochloric acid. The mixture was filtered and, after one recrystallization from 95% ethanol, 0.080 g. (72%) of 4,4′-diacetamido-3-methylsulfonylbiphenyl was obtained as fine white needles, m.p. 276–278°.

Anal. Calcd. for $C_{17}H_{18}O_4N_2S$: C, 58.94; H, 5.24; N, 8.09; S, 9.26. Found: C, 59.16; H, 4.73; N, 8.11; S, 9.28.

Oxidation of 2-Methylsulfonylhydrazobenzene (V).—To a solution of V (0.9 g.) in alcohol (20 ml.) was added slowly 5.25% sodium hypochlorite (20 ml.). The solution was refluxed over steam for one hour, then cooled. The mixture was diluted with water (100 ml.) and extracted with ether. The extract was dried with anhydrous magnesium sulfate, concentrated to a small volume and purified by chromatography on alumina. The orange phase was collected, evaporated to dryness and, after one recrystallization from alcohol–water, 0.6 g. (67%) of 2-methylsulfonylbenzene, m.p. 92–95°, was obtained. A mixed melting point with the material obtained from the previous basic rearrangement and subsequent methylation was 92–95°.

2-Nitrothioanisole (IX).—To a boiling suspension in alcohol (20 ml.) of 2,2′-dinitrodiphenyldisulfide (5 g.) was added an aqueous solution of hydrated sodium sulfide (2 g.) and sodium hydroxide (1.4 g.). This mixture was refluxed until all of the disulfide was dissolved, then cooled, diluted tenfold with water and filtered. The filtrate was made strongly alkaline with sodium hydroxide (5 g.) and methyl sulfate (8 ml.) was added slowly, when 2-nitrothioanisole separated. After filtering and one recrystallization from alcohol–water, 1.5 g. (27%) of lemon-yellow plates, m.p. 61.5–62°, was obtained. Brand[10] reported m.p. 85–87°; however, Claasz[9] reported m.p. 58–60° in addition to analytical confirmation for $C_7H_7O_2NS$. The results of the present work seem to be in agreement with the latter results.

2-Methylsulfonylnitrobenzene (X).—To a boiling solution in glacial acetic acid (10 ml.) of 2-nitrothioanisole (1.5 g.) was added slowly 30% hydrogen peroxide (4 ml.). The solution was then heated for two hours over steam. Upon cooling and diluting with water (15 ml.), X separated. After recrystallization from alcohol–water, 1.3 g. (73%) of white plates, m.p. 105–106° (lit.[9] 105–106°), was obtained.

2-Methylsulfonylaniline (XI).—To a solution in 50% ethanol (50 ml.) of X (2.0 g.) was added iron powder (5 g.) and a few drops of 10% hydrochloric acid. This mixture was refluxed for 24 hours, then cooled and filtered. After concentration, the solution was saturated with sodium chloride and extracted with chloroform. The extract was dried with anhydrous magnesium sulfate, filtered and evaporated to dryness. After one recrystallization from benzene–petroleum ether (b.p. 30–60°) 1.5 g. (81%) of the amine XI was obtained as transparent prisms, m.p. 53.5–54.5° (lit.[9] 90–92°, 65–66°[10]).

Anal. Calcd. for $C_7H_9O_2NS$: C, 49.10; H, 5.30; N, 8.18; S, 18.73. Found: C, 48.89; H, 5.59; N, 8.13; S, 18.53.

(14) All melting points are corrected. Analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

(15) We should like to thank the Monsanto Chemical Co. for a generous supply of 2-nitrobenzenesulfenyl chloride.

(16) T. Zincke and F. Farr, *Ann.*, **391**, 79 (1912).

2-Methylsulfonylthionylaniline (XII).—To a solution in anhydrous benzene (10 ml.) of XI (0.4 g.) was added thionyl chloride (0.2 ml.) when a precipitate of amine hydrochloride separated immediately. The mixture was refluxed on the steam-bath for ten hours, when all of the amine hydrochloride was dissolved. The solvent was removed under vacuum, then petroleum ether (b.p. 30–60°) was added and removed under vacuum. This treatment was repeated until the odor of thionyl chloride had disappeared. The remaining yellow-brown solid was not removed for classification, but was used immediately in the next step.

Reaction of 2-Methylsulfonylthionylaniline with Phenylhydroxylamine.—To a solution of phenylhydroxylamine (0.6 g.) in benzene containing granular anhydrous sodium sulfate (2.5 g.) was added dropwise to a solution in benzene of the thionylamine XII prepared in the previous step. After standing four hours, the mixture was filtered, the filtrate concentrated and then chromatographed on alumina. The orange phase was collected and evaporated to dryness. After recrystallization from alcohol, 0.15 g. (25%) of 2-methylsulfonylazobenzene, m.p. 95.5–96.5°, was obtained. A mixed melting point with the methylated rearrangement product III prepared previously was 95.5–96.6° and the infrared spectra of both samples in chloroform were identical.

Anal. Calcd. for $C_{13}H_{12}O_2N_2S$: C, 59.98; H, 4.65; N, 10.77; S, 12.32. Found: C, 59.43; H, 4.68; N, 10.53; S, 10.01, 8.02.

The irregular sulfur analysis may have been due to a loss of sulfur dioxide during the analysis.

Azobenzene-2-sulfenyl Bromide (XIII).—To a solution of the base rearrangement product II (0.245 g.) in glacial acetic acid (4 ml.) was added 40% hydrobromic acid (3 ml.). The mixture was boiled for ten minutes, cooled, diluted with water (50 ml.), and extracted with chloroform. The extract was evaporated to dryness, leaving an orange-brown solid. After recrystallization from ethanol 0.12 g. (45%) of azobenzene-2-sulfenyl bromide was obtained as yellow needles, m.p. 222.5–224.5° (lit.[12] 223–224°).

Anal. Calcd. for $C_{12}H_9N_2SBr$: C, 49.16; H, 3.09; N, 9.56; S, 10.94; Br, 27.26. Found: C, 49.12; H, 3.28; N, 9.39; S, 10.67; Br, 27.42.

2-Thiocyanoazobenzene (XIV).—To a solution of azobenzene-2-sulfenyl bromide (0.1 g.) in water (20 ml.) was added slowly an aqueous solution of potassium cyanide (0.2 g.). Immediately an orange precipitate of XIV separated. The mixture was extracted with chloroform and the extract evaporated to dryness. The residue was recrystallized from petroleum ether (b.p. 30–60°), giving 0.07 g. (86%) of orange needles, m.p. 99–101° (lit.[13] 99–100°).

COLUMBUS, OHIO

COMMUNICATIONS TO THE EDITOR

THE *CIS* ADDITION OF DIBROMOCARBENE AND METHYLENE TO *CIS*- AND *TRANS*-BUTENE

Sir:

With the discovery of the addition to olefins of dichloro- and dibromocarbene to give 1,1-dihalocyclopropane derivatives[1] and of methylene to give cyclopropane derivatives,[2,3] it became important to one's understanding of the mechanism and the synthetic usefulness to determine the stereochemical characteristics of the additions. In a recent paper,[4] Skell and Garner have found that the general bromoform reaction of Doering and Hoffmann with *cis*- and *trans*-2-butene is stereospecific, although the stereochemistry remains unknown due to the failure to elucidate the structure of the products. Our results confirm the stereospecificity reported by Skell and Garner, and establish the stereochemistry to be *cis*, in the additions of both dibromocarbene and methylene.

From the reaction of *cis*- and *trans*-butene, each of 99% purity, with bromoform and potassium *t*-butoxide, *cis*-[5] and *trans*-[6] 1,1-dibromo-2,3-dimethylcyclopropanes, respectively, are obtained. Intercontamination is estimated not to exceed 1% by gas chromatographic analysis (Perkin–Elmer Model 154, Column "A," 10 lb., He, 145°). Reduction with sodium and methanol in tetrahydrofuran affords *cis*-[7] and *trans*-[8] 1,2-dimethylcyclopropanes, respectively, having infrared spectra identical with those of authentic samples[9] and showing less than 1% intercontamination. The configurations of *cis*- and *trans*-1,2-dimethylcyclopropane have been assigned by Baudrenghien[10] using the Auwers–Skita rule, quite valid here where the rigid ring system allows unequivocal assignment of the lower dipole moment and therefore lower boiling point to the *trans*-isomer. Accordingly the two dibromodimethylcyclopropanes have the configurations assigned above. The exclusively *cis* mode of addition makes available a two-step method for the preparation of cyclopropane derivatives having the same configurations as those of the olefins from which they are derived. Mechanistically the *cis* addition is inconsistent with initial addition of the tribromomethide ion and supports the direct addition of dibromocarbene to the olefin without benefit of intermediates. The electron demands of the transition state are being determined by competition experiments and variation in the olefin structure.

When *cis*- and *trans*-butene are irradiated with diazomethane[3] and the products are examined gas chromatographically and infrared spectroscopically, no isomerization of the starting olefins can be detected. At −75 and −5°, respectively, *cis*-butene leads to *cis*-1,2-dimethylcyclopropane containing less than 1% of other C_5 products, whereas *trans*-butene leads to *trans*-1,2-dimethylcyclopropane (27 and 35%), *trans*-pentene-2 (59 and 46%) and 2-methylbutene-2 (14 and 19%). Despite the extraordinary reactivity and general lack of discrimination usually shown by methylene,[3] in both

(1) W. von E. Doering and A. K. Hoffmann, THIS JOURNAL, **76**, 6162 (1954).

(2) Cf. ref. 1, footnote 10.

(3) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, THIS JOURNAL, **78**, 3224 (1956).

(4) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956).

(5) B.p. 85.5° at 50 mm.; m.p. −53°; $n^{30}D$ 1.5150; d^{30}_4 1.7513; C, 26.45; H, 3.61; Br, 70.17; 2.24 D.

(6) B.p. 81.8° at 50 mm.; m.p. −32.5°; $n^{30}D$ 1.5074; d^{30}_4 1.7298; C, 26.42; H, 3.72; Br, 69.99; 2.24 D.

(7) B.p. 37.0°; $n^{20}D$ 1.3856 (reported[9] b.p. 37.03°; $n^{20}D$ 1.3830).

(8) B.p. 28.2°; $n^{20}D$ 1.3701 (reported[9] b.p. 28.20°; $n^{20}D$ 1.3710).

(9) R. G. Kelso, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **77**, 1751 (1955), who very kindly furnished infrared spectra of authentic samples.

(10) J. Baudrenghien, *Bull. soc. chim. Belg.*, **38**, 172 (1929).