The methylation of this flavone with dimethyl sulfate and potassium carbonate yielded a pentamethyl ether which melted at 158–159° (reported[19] 156–157°).

Anal. Calcd. for $C_{20}H_{20}O_7$: C, 64.50; H, 5.41. Found: C, 64.42; H, 5.49.

The melting point of a mixture of this sample and an authentic sample of morin pentamethyl ether was 158.5–160°.

NEW BRUNSWICK, N. J.

(19) T. J. Haley and M. Bassin, *J. Am. Pharm. Assoc.*, **40**, 111 (1951).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY]

Friedel–Crafts Reaction of 1-Benzenesulfonyl-2-bromomethylethyleneimine and Benzene[1]

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1-Benzenesulfonyl-2-bromomethylethyleneimine (I) reacts with benzene in the presence of aluminum chloride to give 3,3-diphenyl-1-benzenesulfonamidopropane (X). Possible reaction paths are considered. The following are shown not to be intermediates: 1-bromo-2-benzenesulfonamido-3-phenylpropane (II), 1,3-diphenyl-2-benzenesulfonamidopropane (III), 1-benzenesulfonyl-2-benzylethyleneimine (IV) and N-(cinnamyl)-benzenesulfonamide (VI).

Interest in the chemistry of 1-benzenesulfonyl-2-bromomethylethyleneimine (I)[2] prompted trial of the Friedel–Crafts reaction of 1-benzenesulfonyl-2-bromomethylethyleneimine (I) with benzene. The present paper is concerned with the structure and the mode of formation of the reaction product, $C_{21}H_{21}NO_2S$, a solid melting at 128–129°. This material was obtained in only moderate yield when benzene was the solvent and when 1.5 moles of aluminum chloride was used. No other pure product could be isolated, nor could the yield be improved by varying conditions. Treatment of the material with sodium and isoamyl alcohol[3] or with lithium aluminum hydride effected removal of a benzenesulfonyl grouping. A better method, however, was hydrolytic cleavage using concentrated hydrochloric acid at 160°. The resulting amine could be handled conveniently as the hydrochloride ($C_{15}H_{17}N\cdot HCl$) or as the ammonium carbamate ($C_{15}H_{16}NCOO^{-}\cdot C_{15}H_{17}\overset{+}{N}H$).[4] The latter derivative formed readily by simply exposing the oily amine to the air. The original Friedel–Crafts product could be regenerated by treating the amine with benzenesulfonyl chloride.

The coincidence in melting points of our amine hydrochloride with that reported for the hydrochloride of 3,3-diphenyl-1-aminopropane[5,6] was the lead that helped us establish the structures of our products. Preparation of 3,3-diphenyl-1-aminopropane (by lithium aluminum hydride reduction of the amide of β,β-diphenylpropionic acid[7]) and direct comparisons of hydrochlorides, carbamates and benzenesulfonyl derivatives left no doubt that the amine obtained from the Friedel–Crafts product was 3,3-diphenyl-1-aminopropane, and that the Friedel–Crafts product itself was 3,3-diphenyl-1-benzenesulfonamidopropane (X).[8]

The accompanying formulations define several possible sequences for conversion of the ethyleneimine I to the product X. Test of some of these reaction paths was made by exposing intermediates to the action of aluminum chloride in benzene solvent under conditions comparable to those used in the original reaction. No 3,3-diphenyl-1-benzenesulfonamidopropane (X) was obtained when such experiments were carried out with compounds II, III, IV, and VI. The benzenesulfonamido derivative of cinnamylamine (VI)[9] furnished only benzenesulfonamide. 1-Bromo-2-benzenesulfonamido-3-phenylpropane (II)[10] was largely recovered, as was 1,3-diphenyl-2-benzenesulfonamidopropane (III).[11] 1-Benzenesulfonyl-2-benzylethyleneimine (IV)[10] gave rise to an intractable oil. Three reaction paths remain untested, *viz.*, I via compounds VI and VIII to X,[12] I via IX to V and by isomerization to X, and I via XI to X. Intermediate XI is of special interest in that a four membered ring compound is derived from a three membered ring compound in a manner at least formally analogous to the generation of cyclobutyl compounds from the cyclopropylmethyl cation.[13] Further work is planned.

Experimental[14]

3,3-Diphenyl-1-benzenesulfonamidopropane (X) from 1-Benzenesulfonyl-2-bromomethylethyleneimine (I).—A mix-

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(1) Abstracted from the thesis submitted by John C. Rockett to the Graduate School of Boston University in partial fulfillment of the requirements for the degree of Master of Arts, 1951.

(2) *Cf.* W. J. Gensler, THIS JOURNAL, **70**, 1843 (1948).

(3) C. C. Howard and W. Marckwald, *Ber.*, **32**, 2031 (1899).

(4) *Cf.* M. Frankel and E. Katchalski, THIS JOURNAL, **65**, 1670 (1943); E. Katchalski, C. Berliner-Klibanski and A. Berger, *ibid.*, **73**, 1829 (1951).

(5) S. K. Freeman, W. F. Ringk and P. E. Spoerri, *ibid.*, **69**, 858 (1947).

(6) D. W. Adamson, *J. Chem. Soc.*, 144S (1949).

(7) D. Vorländer, E. Rack and W. Leister, *Ber.*, **56**, 1131 (1923).

(8) A feature that was misleading in that it indicated absence of the $-SO_2NH-$ grouping in the Friedel–Crafts product was its insolubility in aqueous alkali. However, once the structure was established we were left with no choice but to accept this property as a peculiarity of the molecule. Subsequently we determined that 1,3-diphenyl-2-benzenesulfonamidopropane (III) was likewise insoluble in aqueous alkali. Other alkali-insoluble benzenesulfonyl derivatives of primary amines have been reported (*cf.* W. H. Carothers and G. A. Jones, THIS JOURNAL, **47**, 3051 (1925); W. H. Carothers, C. F. Bickford and G. S. Hurwitz, *ibid.*, **49**, 2908 (1927).

(9) T. Posner, *Ber.*, **26**, 1856 (1893).

(10) W. J. Gensler and J. C. Rockett, THIS JOURNAL, **74**, 4451 (1952).

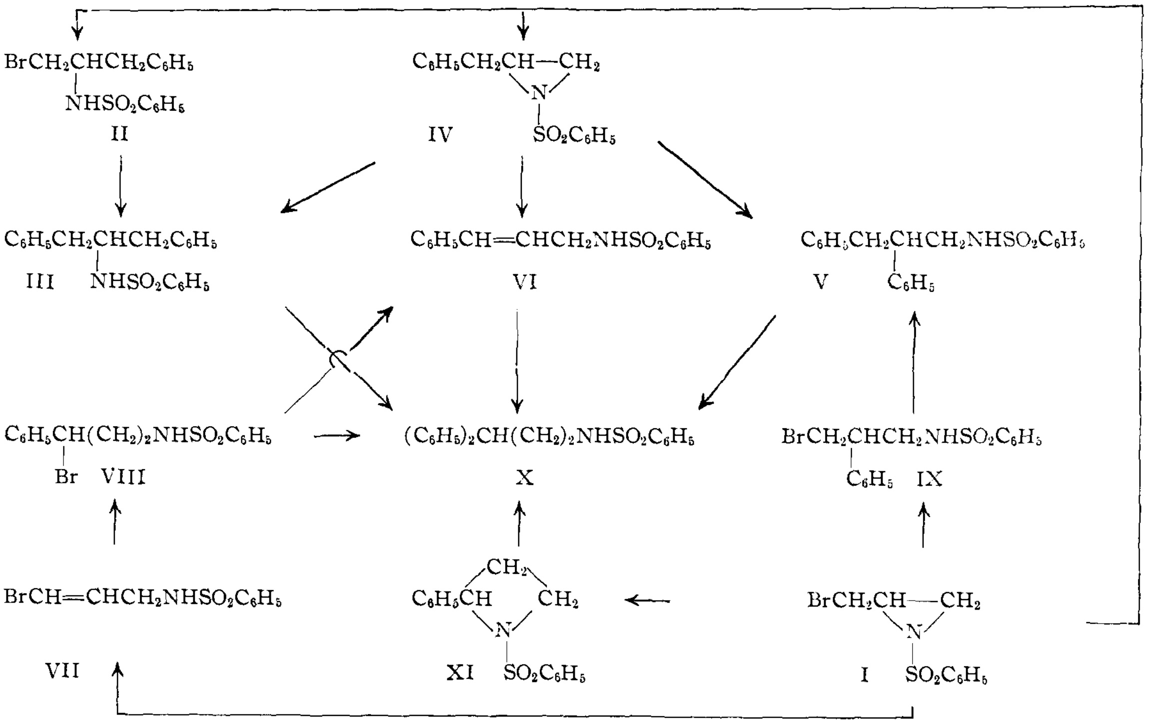
(11) C. F. Koelsch, *ibid.*, **67**, 1718 (1945).

(12) Several unsuccessful attempts have been made in these laboratories to synthesize N-(bromoallyl)-benzenesulfonamide (VII).

(13) Compare J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 3542 (1951), and references therein.

(14) Melting points are uncorrected. Analyses were carried out by Carol K. Fitz, Ph.D., 115 Lexington Avenue, Needham Heights 94, Mass.

CHART I



ture of 7.04 g. (0.026 mole) of 1-benzenesulfonyl-2-bromomethylethyleneimine (I),[2] 100 ml. (1.14 moles) of dry benzene, and 5.1 g. (0.038 mole) of aluminum chloride was stirred at reflux temperature for three hours. The amber colored reaction mixture was poured over 200 g. of ice-water and 25 ml. of concentrated hydrochloric acid. The acid mixture was extracted thoroughly with ether, and the ether was washed with water, dried over magnesium sulfate, and concentrated to a volume of approximately 20 ml. On cooling (ice bath) a solution of the resulting viscous oil in 30 ml. of alcohol, a precipitate was obtained, which was removed by filtration. The filtrate on standing in the refrigerator overnight deposited more of the solid. The combined precipitates weighed 3.4 g. and melted at 124–130°. Crystallization from ethanol afforded 2.7 g. (30%) of 3,3-diphenyl-1-benzenesulfonamidopropane (X), with m.p. 128–129°.

Anal. Calcd. for $C_{21}H_{21}NO_2S$: C, 71.77; H, 6.02; N, 3.99. Found: C, 72.1; H, 6.1; N, 3.8.

The compound was soluble in acetone and acetic acid, but was insoluble in dilute aqueous sodium hydroxide solution. The melting point of this compound admixed with authentic material was 128–129°.

When only 10 molar per cent., or when an equimolar amount of aluminum chloride was used in the Friedel-Crafts reaction, no crystalline material other than starting material could be obtained. Increasing the amount of aluminum chloride to two moles resulted in a crystalline product (31%) recognized as benzenesulfonamide. Reaction with two moles of benzene and one mole of aluminum chloride in nitrobenzene solvent at 100° furnished only starting material (63% recovery).

Cleavage of 3,3-Diphenyl-1-benzenesulfonamidopropane (X) to 3,3-Diphenyl-1-aminopropane.—A sealed tube containing 3.36 g. (0.0094 mole) of the Friedel-Crafts product X and 10 ml. of concentrated hydrochloric acid was heated at 160° for two hours. Crude amine hydrochloride was obtained by filtering the cooled reaction mixture. Crystallization from absolute ethanol afforded 1.41 g. (61%) of white crystalline 3,3-diphenyl-1-aminopropane hydrochloride, m.p. 218–219.5°. The melting point of a mixture of this material with authentic 3,3-diphenyl-1-aminopropane hydrochloride (m.p. 218–219°) was 218–219°.

Treatment of the amine hydrochloride with benzenesulfonyl chloride and alkali, in a manner similar to that described below for the preparation of the authentic derivative, regenerated the original material, m.p., 128–129°. The mixed melting point with the Friedel-Crafts product was 128–129.5°.

Attempted hydrolysis by boiling compound X for one day with sulfuric acid in aqueous alcohol or with concentrated hydrochloric acid gave only starting material. Application of the sodium-amyl alcohol reductive cleavage of Howard and Marckwald[3] furnished small amounts of amine (0.4%) as well as much starting material (80%). Treatment of the Friedel-Crafts product X with lithium aluminum hydride in boiling tetrahydrofuran gave only a trace of the amine and mainly starting material. The same reaction in boiling dioxane led to amine in 10% and starting material in 70% yield; and in boiling dibutyl ether (b.p. 141–143°) to amine in 16% and starting material in 38% yield.[15] In these reduction experiments the amine product was conveniently isolated as the carbamate by allowing the oily amine to stand in the air. The white solid that formed melted at 85–86° and was analytically pure.

Anal. Calcd. for $C_{31}H_{34}N_2O_2$: C, 79.9; H, 7.3. Found: C, 79.7; H, 7.5.

The melting point was unchanged when this solid was mixed with the carbamate from authentic 3,3-diphenyl-1-aminopropane.

Derivatives of Authentic 3,3-Diphenyl-1-aminopropane.—Pure β,β-diphenylpropionic acid, m.p. 151–152°, was prepared in 75% yield by following the directions of Vorländer, Rack and Leister.[7] The corresponding amide was formed by allowing 5.0 g. (0.022 mole) of the acid in 5.0 g. (0.042 mole) of thionyl chloride to stand overnight. Excess thionyl chloride was removed under water-pump vacuum, the residual oil was diluted with 15 ml. of dry benzene, and the solution was added slowly to concentrated aqueous ammonium hydroxide in excess. The solid was collected and

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(15) At the time these experiments were performed two reports [C. S. Marvel and P. D. Caesar, THIS JOURNAL, **72**, 1033 (1950); J. Strating and H. J. Backer, *Rec. trav. chim.*, **69**, 638 (1950)] indicated that such reductive cleavages with lithium aluminum hydride were not practical, while a third report [L. Field and F. A. Grunwald, *J. Org. Chem.*, **16**, 946 (1951)] mentioned the production of diethylamine (?) from the lithium aluminum hydride reduction of N,N-diethylbenzenesulfonamide. Since then the action of lithium aluminum hydride on sulfonamides has attracted further attention: [D. Klamann, *Monatsh.* **84**, 651 (1953); *cf.* A. Mustafa, *J. Chem. Soc.*, 2435 (1952); P. Karrer and K. Ehrhardt, *Helv. Chim. Acta*, **34**, 2202 (1951)].

was crystallized from benzene to give 3.7 g. (76%) of β,β-diphenylpropionamide, m.p. 123–124°.[16] The amide (3.0 g. or 0.013 mole) was treated with 1.5 g. (0.039 mole) of lithium aluminum hydride in 100 ml. of boiling ether for three hours.[17] Sodium hydroxide (50 ml. of a 40% aqueous solution) was added carefully, and the mixture was extracted thoroughly with ether. The ether extract was washed with water and dried over magnesium sulfate. The hydrochloride precipitated when dry hydrogen chloride was introduced into the filtered ether solution. Crystallization from absolute ethanol furnished 1.07 g. (32%) of pure 3,3-diphenyl-1-aminopropane hydrochloride, m.p. 218–219°.[18]

The carbamate was prepared by mixing 0.2 g. of the above hydrochloride with 5 ml. of 40% sodium hydroxide solution, and extracting the alkaline mixture with ether. The ether was washed with a small portion of water, and was dried over magnesium sulfate. After removal of all solvent, the residual colorless oil was left open to the air. Solid crystalline carbamate, m.p. 85–86°, formed rapidly.[19]

The benzenesulfonyl derivative of 3,3-diphenyl-1-aminopropane (*i.e.*, compound X) was formed by vigorously stirring a mixture of 0.1 g. of authentic hydrochloride in 10 ml. of 20% sodium hydroxide solution with a ten-fold excess of benzenesulfonyl chloride for thirty minutes at room temperature. The solids were collected, washed and pressed on the funnel and, after drying in the air, were crystallized from 3 ml. of absolute alcohol. 3,3-Diphenyl-1-benzenesulfonamidopropane, m.p. 128–129°, was obtained in 64% yield.

1,3-Diphenyl-2-benzenesulfonamidopropane (III).—1,3-Diphenyl-2-aminopropane was prepared in 71% yield from dibenzyl ketone by the Leuckart method essentially according to the directions of Koelsch.[11] A mixture of 10 g. (0.047 mole) of this amine, 8.8 g. (0.050 mole) of benzenesulfonyl chloride, and 50 ml. of 30% aqueous sodium hydroxide was stirred vigorously. After a few minutes the reaction flask was cooled in an ice-bath. Filtration afforded 16.1 g. (97%) of material melting at 107.5–108°. Further crystallizations did not change the melting point of the 1,3-diphenyl-2-benzenesulfonamidopropane.

Anal. Calcd. for $C_{21}H_{21}NO_2S$: C, 71.77; H, 6.02. Found: C, 71.5; H, 6.1.

N-(Cinnamyl)-benzenesulfonamide (VI).—Cinnamylamine was prepared by a modification of Posner's method[9] based on the work of Sheehan and Bolhofer.[20]

A mixture of 5.69 g. (0.037 mole) of cinnamyl chloride and 7.40 g. (0.040 mole) of potassium phthalimide in 40 ml. of dimethylformamide was stirred for one hour. The temperature rose to 38° during the first ten minutes of the reaction and then dropped slowly to 25°. Chloroform (40 ml.) was added and the mixture was poured into 100 ml. of water. The aqueous phase was separated and was extracted with two 10 ml. portions of chloroform. The combined chloroform extracts, after washing with 20 ml. of 0.2 *N* sodium hydroxide solution and 20 ml. of water, was dried over sodium sulfate. All chloroform was removed, and the residual material was triturated with 40 ml. of ether. N-(Cinnamyl)-phthalimide, m.p. 153–153.5°, was obtained in 85% yield.

The phthalimide (4.00 g. or 0.015 mole) was allowed to react for one hour with 1.8 ml. of 85% aqueous hydrazine (0.03 mole) in 50 ml. of boiling methanol. Concentrated hydrochloric acid (25 ml.) was added to the cooled reaction mixture, and reflux was continued for one-half hour. The reaction mixture was cooled to 0°, filtered, and the filtrate concentrated to a volume of 40 ml. Cooling this solution in an ice-bath for two hours precipitated the cinnamylamine hydrochloride, which was collected and was crystallized from absolute alcohol to give 1.84 g. (72%) of product, m.p. 209–219°.

The benzenesulfonamide derivative was prepared by vigorously shaking 0.5 g. (0.0029 mole) of cinnamylamine hydrochloride with concentrated aqueous sodium hydroxide and 2 ml. of benzenesulfonyl chloride. The crystals deposited from the cooled mixture were collected and crystallized from 3 ml. of ethyl alcohol. Analytically pure N-(cinnamyl)-benzenesulfonamide (0.71 g. or 89%) melting at 89–90° was obtained.

Anal. Calcd. for $C_{15}H_{15}NO_2S$: C, 65.90; H, 5.53. Found: C, 65.7; H, 5.5.

Test of Possible Intermediates in the Reaction Leading to 3,3-Diphenyl-1-benzenesulfonamidopropane (X).—When the postulated intermediates were treated with aluminum chloride in benzene solution under conditions comparable to those used with 1-benzenesulfonyl-2-bromomethylethyleneimine (I), the following results were obtained. 1,3-Diphenyl-2-benzenesulfonamidopropane (III) yielded only starting material (72%), with melting point and mixed melting point 107–108°. 1-Benzenesulfonyl-2-benzylethyleneimine (IV)[10] gave a heavy viscous oil that could not be crystallized from ethanol, benzene, carbon tetrachloride, acetone, or ether. N-(Cinnamyl)-benzenesulfonamide (VI) afforded benzenesulfonamide (40%) as the only crystalline product. 1-Bromo-2-benzenesulfonamido-3-phenylpropane (II)[10] gave starting material (75%) that melted alone or admixed with authentic material at 22–23°.

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[16] Previously reported melting at 124–125°, 125–126°, and 127° (S. Rajagopalan, *Proc. Indian Acad. Sci.*, **14A**, 126 (1941) [*C. A.*, **36**, 1604 (1942)]; J. F. Eijkman, *Chemisch Weekblad*, **5**, 655 [*Chem. Zentr.*, **79II**, 1100 (1908)]; E. P. Kohler and M. Reimer, *Am. Chem. J.*, **33**, 333 (1905).)

[17] *Cf.* W. G. Brown in Adams' "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469.

[18] Previously reported melting at 216–218°[6] and 217.5–218.5°.[5]

[19] Freeman, Ringk and Spoerri[5] reported that 3,3-diphenyl-1-aminopropane rapidly absorbs carbon dioxide from the air to form a solid "carbonate." No melting point was given.

[20] J. C. Sheehan and W. A. Bolhofer, THIS JOURNAL, **72**, 2786 (1950).