1.62 [$(CH_3)_2C{=}C$], 1.80 (—CH—), a multiplet centered at 2.27 ($—CH_2—$ and $—CH_2C{=}C—$), 3.30, 3.40 (C=C—CH—CO—), and 3.60 p.p.m. ($—OCH_3$).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.20; H, 10.15.

Methyl *trans*-pulegenate, isolated by v.p.c., showed $n^{22}D$ 1.4636; λ_{max} 3.42, 5.80, 6.93, 7.02, 7.32, 7.50, 7.70, 8.00, 8.13, 8.72, 9.20, 9.90, and 13.50 μ; and n.m.r. signals at 0.98, 1.08 ($CH_3—CH—$), 1.58, 1.66 [$(CH_3)_2C{=}C—$], 1.92 (—CH—), a multiplet centered at 2.30 ($—CH_2—$ and $—C{=}C—CH_2—$), 2.90 (—C=C—CH—CO—), and 3.60 p.p.m. ($—OCH_3$).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.93; H, 10.32.

***cis*- and *trans*-Pulegenic Acids.**—To a heated and well-stirred solution of 60 g. of potassium hydroxide in 700 ml. of water was added dropwise 400 ml. of the petroleum ether solution of pulegone dibromide obtained above. The petroleum ether was distilled from the reaction as the addition proceeded. After the addition was complete and the hydrocarbon had distilled, the mixture was heated for 4–5 hr. The undissolved organic material floated to the top of the mixture after 2.5 hr. After cooling and extracting the mixture with ether, the alkaline solution was acidified with dilute hydrochloric acid and extracted with ether. The ether solution was dried and distilled to give 13.86 g. (26%) of the pulegenic acids, b.p. 80–104° (0.70 mm.), $n^{25}D$ 1.4776. Ethereal diazomethane converted the acids into the corresponding methyl esters; gas chromatographic analysis of the esters indicated the presence of 47% of the *cis* isomer and 53% of the *trans* isomer.

In another experiment the pulegone dibromide was freed of solvent before its addition to aqueous alkali. In this instance a 36% yield of pulegenic acids was obtained. The composition of the acid was essentially identical with that of the acid described above.

Ethyl *cis*- and *trans*-Pulegenates.—A dried petroleum ether solution of pulegone dibromide, prepared from 20.0 g. of (+)-pulegone, was added dropwise to a heated and stirred solution of sodium ethoxide (from 9.5 g. of sodium) in 200 ml. of carefully dried ethanol. As the addition proceeded the petroleum ether was distilled from the reaction mixture. After the addition was complete and the hydrocarbon had been distilled, the mixture was kept at reflux for 2 hr. The mixture was cooled and poured rapidly into 300 ml. of 10% hydrochloric acid. The heavy oil which separated was taken up with ether and the aqueous phase was thoroughly extracted with ether. The combined ether extracts were washed successively with water, sodium bicarbonate solution, and water and finally dried. Distillation gave after a forerun of pulegone, b.p. 54–56° (0.60–0.65 mm.), 13.74 g. (64%) of the ethyl pulegenates, b.p. 56–62° (0.60–0.65 mm.), $n^{23.5}D$ 1.4674. Gas chromatographic analysis indicated the presence of 26% of the *cis* isomer and 74% of the *trans* isomer.

Ethyl *cis*-pulegenate, isolated by v.p.c., displayed $n^{23}D$ 1.4634; λ_{max} 3.42, 5.82, 6.91, 7.35, 7.51, 7.79, 8.02, 8.55, 8.80, 9.00, 9.18, 9.55, 9.75, 10.55, and 11.25 μ; and n.m.r. signals at 0.96, 1.06 ($CH_3—CH—$), 1.15, 1.25, 1.35 ($CH_3—CH_2—$), 1.68 ($(CH_3)_2C{=}C—$), a multiplet centered at 1.86 (—CH—) and 2.28 ($—CH_2—$, $—C{=}C—CH_2—$), a doublet centered at 3.35 (—C=C—CH—CO), and a quartet centered at 4.15 ($O—CH_2—CH_3$) p.p.m.

Ethyl *trans*-pulegenate, isolated by v.p.c., exhibited $n^{23}D$ 1.4594; λ_{max} 3.42, 5.82, 6.95, 7.38, 7.55, 7.72, 8.02, 8.15, 8.58, 8.90, 9.20, 9.70 μ; and n.m.r. signals at 0.98, 1.09 ($CH_3—CH—$), a triplet centered at 1.22 ($CH_3—CH_2—$), 1.62, 1.70 ($(CH_3)_2C{=}C—$), multiplets at 1.96 ($—CH—CH_3$), 2.39 ($—CH_2—$, $—CH_2—C{=}C—$), 2.93 (—C=C—CH—CO—), and a quartet centered at 4.16 p.p.m. ($O—CH_2—CH_3$).

Hydrolysis of Ethyl *cis*- and *trans*-Pulegenates.—The following describes the typical conditions employed for the hydrolysis of methyl and ethyl pulegenates. To a solution of 1.00 g. (5.1 mmole) of the ethyl esters in 5 ml. of absolute ethanol was added 0.241 g. (4.3 mmoles) of potassium hydroxide in 2 ml. of water. The resulting solution was kept at reflux for 3 hr. After dilution with water the solution was extracted with ether to remove neutral products. The alkaline solution was acidified with dilute hydrochloric acid and the mixture was extracted with ether. The acid was converted into the corresponding methyl ester with ethereal diazomethane. Gas chromatographic analysis indicated the exclusive presence of methyl *trans*-pulegenate.

Acknowledgment.—This work was supported in part by a grant from the Purdue Research Foundation.

Basic Cleavages of Arylsulfonamides[1]

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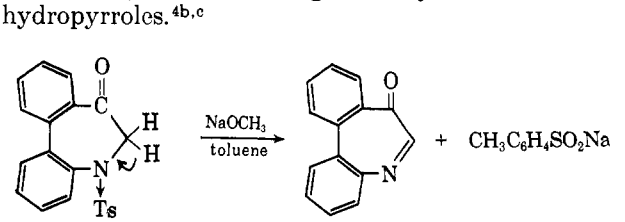
A novel, indirect, basic cleavage of arylsulfonamides of secondary amines has been studied. It appears to take place quite generally if the base which is used is strong enough to remove α-hydrogen. The reaction mechanism involves the formation of a >C=N— linkage and an arylsulfinate anion.

The basic cleavage of sulfonamides, in contrast with carboxamides, is a difficult reaction. Only in recent years have a few moderately useful methods of basic cleavage been devised.[3] Arylsulfonamides of some secondary amines have been successfully cleaved with sodium isoamoxide at 150–200°.[3b] The proposed mechanism involved a direct attack of the base at the sulfur atom with the replacement of the amino group.

No example of basic cleavage using metal amides has been reported but aminolysis of sulfonamides at 150–220° has been studied and successfully applied in some cases.[3c]

More recently several examples of a new type of basic cleavage of sulfonamides has been reported.[4] Proctor[4a] prepared a dibenzo derivative of azatropone in the following manner. Pyrrole derivatives have been prepared by similar cleavages of tosyl derivatives of dihydropyrroles.[4b,c]



The objectives of the present investigation were (1) to determine the nature and applicability of this

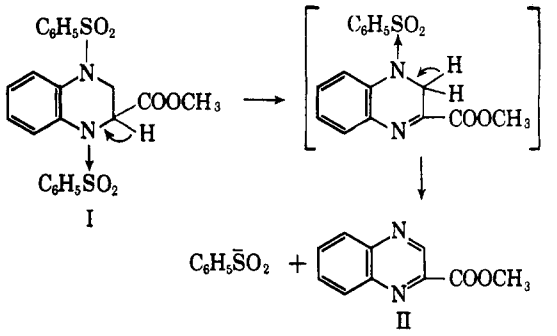
(1) This work is part of a thesis submitted by E. Negishi in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(2) Harrison Fellow, 1962–1963.

(3) (a) Y. Takata, *J. Pharm. Soc. Japan*, **71**, 1471 (1951); D. Klamann and H. Bertsch, *Ber.*, **91**, 1688 (1958). (b) D. Klamann and H. Bertsch, *ibid.*, **212**, 1427 (1958). (c) D. Klamann and G. Hofbauer, *Ann.*, **581**, 182 (1953); D. Klamann and E. Fabienke, *Ber.*, **92**, 712 (1959).

(4) (a) G. R. Proctor, *Chem. Ind.* (London), 408 (1960); (b) A. V. Robertson, J. E. Francis, and B. Witkop, *J. Am. Chem. Soc.*, **84**, 1079 (1962); (c) A. H. Jackson, G. W. Kenner, and W. G. Terry, *Tetrahedron Letters*, **No. 20**, 921 (1962).

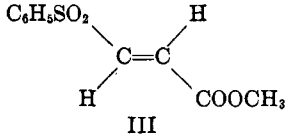
new mode of cleavage; and (2) to clarify the relationship between the new indirect cleavage and the conventional direct cleavage. The first compound selected for study was methyl 1,4-dibenzenesulfonyl-1,2,3,4-tetrahydro-2-quinoxalinecarboxylate (I) which was prepared from N,N′-dibenzenesulfonyl-*o*-phenylenediamine and methyl 2,3-dibromopropionate in the presence of sodium methoxide. When compound I was refluxed in tetrahydrofuran with 2 equiv. of sodium hydride, II was obtained in 72% yield. The mecha-



I II

nism is assumed to be stepwise, as shown above, and the —N=C< group formed in the first step activates the adjacent hydrogen atoms in the second step. The identity of II, as methyl 2-quinoxalinecarboxylate, was established through infrared, melting point determinations, and derivatives. The infrared spectrum of the sodium benzenesulfinate which was formed was identical with that of an authentic sample.

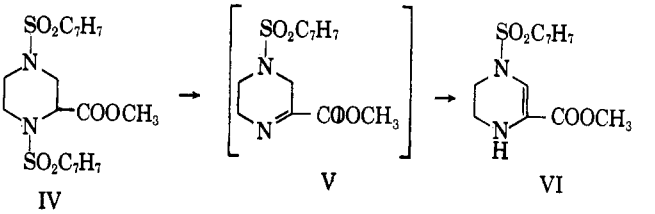
An interesting by-product was obtained from the filtrate from I (yield 9%) which contained no nitrogen. Analyses indicated the compound to be a methyl benzenesulfonylacrylate which was probably formed from methyl 2,3-dibromopropionate and sodium benzenesulfinate. The infrared spectrum indicated the presence of the ester grouping and the benzenesulfonyl grouping. A strong absorption band was found at 965 cm.$^{-1}$. This has been shown to be due to two hydrogen atoms out of plane at a double bond. Rasmussen and Brattain have shown that this band appears only with *trans* double bonds.[5] Thus, the compound is best represented as III. The ultraviolet spectrum



III

showed the presence of an α,β-unsaturated ester and the n.m.r. spectrum was in agreement with the above conclusions. The same product (III) was obtained by treating methyl 2,3-dibromopropionate with sodium benzenesulfinate in the presence of sodium methoxide.

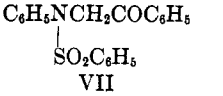
In view of the results of the reaction of I with sodium hydride, it was expected that methyl 1,4-bis(*p*-toluenesulfonyl)-2-piperazinecarboxylate (IV) would form methyl 5,6-dihydropyrazinoate under similar conditions. The latter would be expected to be spontaneously oxidized to methyl pyrazinoate. Compound IV was prepared by a base-catalyzed condensation of N,N′-bis-(*p*-toluenesulfonyl)ethylenediamine with methyl 2,3-dibromopropionate. However when IV was treated with 3 equiv. of sodium hydride, the expected product was not obtained. The product proved to be methyl 4-(*p*-toluenesulfonyl)-1,4,5,6-tetrahydropyrazinoate (VI). An attempt to isolate compound V, using only 1 equiv. of sodium hydride, was unsuccessful.



IV V VI

The reaction with methyl 1,4-bis(*p*-toluenesulfonyl)-2-piperazinecarboxylate suggests that aromatization is not the only driving force in the cleavage reaction under investigation. Moreover, it suggests an interesting synthetic possibility, namely, a selective cleavage of sulfonamide groups.

Another objective of this investigation was to determine whether the ring structure assumed any significance in this reaction. In order to test this point, N-benzenesulfonyl-2-anilinoacetophenone (VII) was prepared. When VII was treated in tetrahydrofuran with



VII

1 equiv. of sodium hydride, three products were obtained. The first one, obtained in almost quantitative yield proved to be sodium benzenesulfinate. From the filtrate a yellow product (VIII), m.p. 218–220°, was obtained in excellent yield as well as a very small amount of another yellow compound (IX), m.p. 152–

IX

153°. The analyses of both products were consistent with the composition of the expected phenyliminoacetophenone (IX). The infrared spectrum of the compound, m.p. 152–153°, also supported this structure.

The main product, VIII, melting at 218–220°, showed the same elemental analysis as IX but molecular weight measurements showed it to be dimeric and IX to be monomeric. A few methylenimine derivatives occur as dimers in place of the more usual trimers or higher polymers. They have been formulated as 1,3-diazacyclobutane derivatives (uretidines).[6] Compound VIII does not appear to be a simple uretidine but its structure cannot be specified at present.[7]

Paterson and Proctor[8] treated N-(*p*-toluenesulfonyl)-2-anilinoacetophenone with sodium ethoxide and obtained a product melting at 210° which was isomerized by palladized charcoal to an isomer melting at 145°. They assumed the two to be isomeric phenyliminoacetophenones although no further details were given.

It would appear at this point that the indirect desulfonylation cleavage takes place whether or not the nitrogen atom of the sulfonamide group is incorporated

(5) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131, 135 (1947).

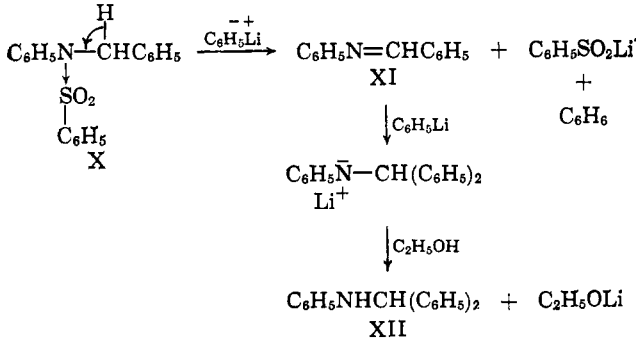
(6) C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, **123**, 2745 (1923).

(7) Proof of structure of the dimer has turned out to be a formidable and lengthy problem. A separate investigation is underway with a series of alkyl- and arylaminoacetophenones to solve the nature of the dimerization.

(8) W. Paterson and G. R. Proctor, *Proc. Chem. Soc.*, 248 (1961).

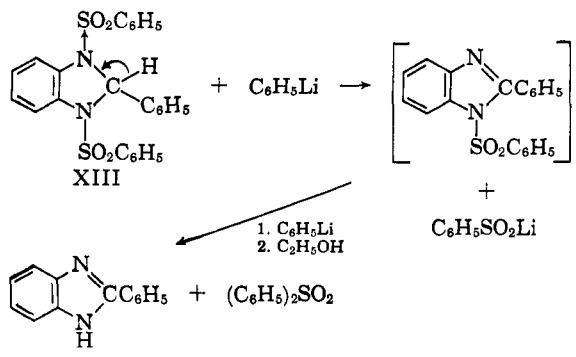
in a ring as long as the α-hydrogen is sufficiently active.

It was of interest to know whether N-benzyl-N-phenylbenzenesulfonamide (X), in which the α-hydrogens are only weakly activated by the adjacent benzene ring, will undergo the indirect cleavage with bases. When X, in tetrahydrofuran solution, was treated with an excess of phenyllithium in benzene and ether, a vigorous reaction occurred and the mixture became quite dark. The hydrochloride of N,1,1-triphenylmethylamine was isolated from the mixture in almost quantitative yield. The infrared spectra of the free base and of an authentic sample were identical. The reaction was repeated using only 1 equiv. of phenyllithium. Ethanol was added to the yellow solution at the end of the reaction. The following products were isolated: N-benzylideneaniline (XI, 20%), N,1,1-triphenylmethylamine (XII, 25%), and unused starting material. The formation of XI and XII is strong evidence for the following mechanism. Since 2 equiv. of phenyllithium are consumed it is obvious why starting material is recovered when only 1 equiv. of phenyllithium is added.

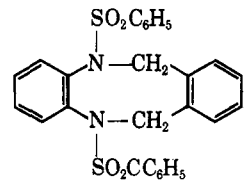


It is interesting to note that when 1-benzenesulfonylpiperidine was treated with sodium hydride, the starting material was recovered almost quantitatively. When treated with phenyllithium, however, small amounts of piperidine and moderate amounts (21%) of 1-phenylpiperidine were isolated. In this case the methylene groups adjacent to the nitrogen are not active enough for the indirect cleavage to take place.

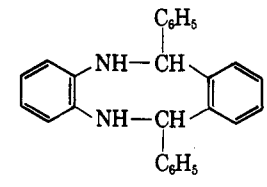
The ease with which acyl groups are released from N-acylbenzimidazoles is well known. In connection with this study it appeared of interest to examine the behavior of 1,3-dibenzenesulfonyl-2-phenyl-1,2-dihydrobenzimidazole (XIII) with phenyllithium. As was expected, 2-phenylbenzimidazole was an end product of this reaction. This product was the result of an indirect cleavage and a direct cleavage. Both the sulfinate and diphenyl sulfone were identified as end products of this reaction. The starting compound for this reaction (XIII) was easily prepared from N,N′-dibenzenesulfonyl-*o*-phenylenediamine and α,α-dichlorotoluene in dimethylformamide solution with sodium methoxide as catalyst.



Another interesting benzenesulfonyl derivative, because of its similarity to X, was 5,12-dibenzenesulfonyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*][1,4]diazocine (XIV). The latter was readily prepared from N,N′-dibenzenesulfonyl-*o*-phenylenediamine and α,α'-dibromo-*o*-xylene in the presence of potassium hydroxide. Compound XIV gave 6,11-diphenyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*][1,4]diazocine (XV), when treated with excess of phenyllithium. Compound XV was isolated as its dihydrochloride. From the mode of reaction



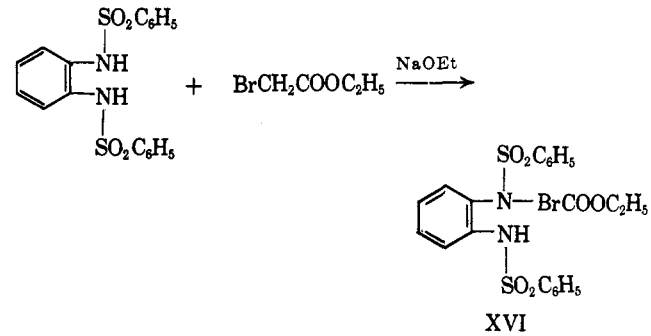
XIV



XV

which X underwent with phenyllithium and the analyses and infrared spectrum of the final product (XV) the structure assigned to XV appears to be the correct one. This procedure opens the way for the syntheses of a number of 6,11-disubstituted-5,6,11,12-tetrahydrodibenzo[*b*,*f*][1,4]diazocines.

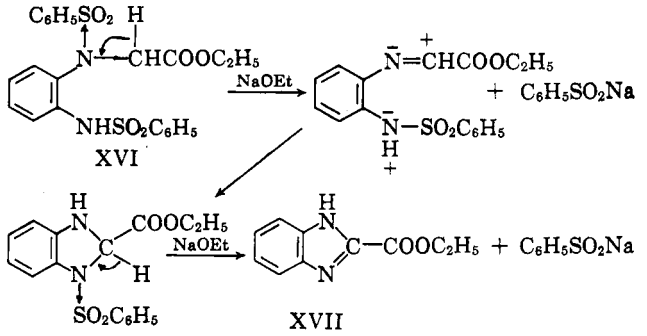
A final reaction was carried out by treating N,N′-dibenzenesulfonyl-*o*-phenylenediamine with ethyl bromoacetate and 2 equiv. of sodium ethoxide. The expected reaction to form 1,4-dibenzenesulfonyl-3,4-dihydro-2-(1H)-quinoxalinone and/or 1-benzenesulfonyl-2(1H)-quinoxalinone did not take place. The main product was N,N′-dibenzenesulfonyl-N-ethoxycarbonylmethyl-*o*-phenylenediamine (XVI). A small amount of



XVI

ethyl 2-benzimidazolecarboxylate was isolated from the filtrate from XVI. This compound was identified by analyses and comparison with an authentic sample prepared by the method of Copeland and Day.[9] When compound XVI was treated with 2 equiv. of sodium ethoxide, a 47% yield of ethyl 2-benzimidazolecarboxylate (XVII) was obtained. The following mechanism accounts for the formation of the benzimidazole derivative, XVII.

(9) R. A. B. Copeland and A. R. Day, *J. Am. Chem. Soc.*, **65**, 1072 (1943).



Experimental

N,N'-Dibenzenesulfonyl-*o*-phenylenediamine was prepared by the procedure of Stetter.[10] The product melted[11] at 190–192° after recrystallization from acetone (lit.[11] m.p. 186°).

Methyl 1,4-Dibenzenesulfonyl-1,2,3,4-tetrahydro-2-quinoxalinecarboxylate (I).—N,N'-Dibenzenesulfonyl-*o*-phenylenediamine (46.7 g., 0.12 mole) was suspended in 250 ml. of dry methanol and 13 g. (0.24 mole) of sodium methoxide was added with stirring. After stirring for 1 hr., 29.6 g. (0.12 mole) of methyl 2,3-dibromopropionate[12] was added and the mixture was refluxed overnight with stirring. The methanol was almost completely evaporated and 100 ml. of dry actone was added with stirring. The sodium bromide was removed by filtration, the acetone was removed from the filtrate until precipitation started at the boiling temperature, and then half of the remaining solvent was further removed. On cooling, 14.5 g. (31%) of starting material separated. The filtrate was further evaporated. Addition of ether gave 28.6 g. of I. It was recrystallized from methanol: yield 48%; m.p. 119–121°; ν_{max}^{KBr} 1747 (s) (C=O ester), 1350 (s) (SO_2N), 1230 (s), and 1160 (s) (SO_2N) cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{20}N_2O_6S_2$: C, 55.87; H, 4.27; N, 5.93; S, 13.47. Found: C, 55.78; H, 4.49; N, 5.92; S, 13.67.

The filtrate from I was evaporated to dryness and the residue was extracted with ligroin. Partial evaporation of the ligroin gave another 5% of I and further evaporation gave methyl 2-quinoxalinecarboxylate (II) which was recrystallized from ligroin, yield 8%, m.p. 112–113°. II was identified by the methods used in the next experiment.

The above experiment was repeated since we were curious as to why better yields of I were not obtained. On this repeat experiment about the same amount of compound I was obtained. The addition of more ether to the filtrate from I made possible the isolation of a more soluble fraction: yield 9%; m.p. 99–101°; ν_{max}^{KBr} 1720 (s) (C=O, α,β), 1615 (w), 1320 (s), 1310 (s), 1300 (s), 1235 (s), 1165 (s), 1150 (s) (sulfone), and 965 (s) (CH=CH *trans*) cm.$^{-1}$; $\lambda_{max}^{ethanol}$ 205 and 234 mμ (ϵ_{max} 12,300 and 9350).

Anal. Calcd. for $C_{10}H_{10}O_4S$: C, 53.08; H, 4.46; S, 14.17. Found: C, 53.02; H, 4.49; S, 14.21.

These data strongly indicate the compound to be *trans*-methyl β-benzenesulfonylacrylate (III).

III was also obtained in small amounts, along with other products, when a methanol solution of methyl 2,3-dibromopropionate, sodium benzenesulfinate, and a small amount of sodium methoxide was refluxed for several hours. No effort was made to determine the optimum conditions nor to determine the nature or other products present.

Methyl 2-Quinoxalinecarboxylate (II).—Methyl 1,4-dibenzenesulfonyl-1,2,3,4-tetrahydro-2-quinoxalinecarboxylate (4.72 g., 0.01 mole) was dissolved in 50 ml. of dry tetrahydrofuran. To this solution was added 1.01 g. (0.021 mole) of sodium hydride in a nitrogen atmosphere. The reaction mixture was gradually warmed and finally refluxed for 10 hr. After cooling, the sodium benzene sulfinate was removed by filtration, yield 75%. An aqueous solution of the salt decolorized potassium permanganate solution and an infrared spectrum of the solid (phase KBr) was identical with that of an authentic sample of sodium benzenesulfinate.

The filtrate from the sodium benzenesulfinate was evaporated at 50° under reduced pressure. The brown residue was recrystallized from ligroin, yield 72%, m.p. 111–112°.[13] The infrared spectrum of II was identical with that obtained from an authentic sample and a mixture melting point determination showed no depression. The melting point of the hydrazide was 211–212°.[14]

Methyl 1,4-Bis(*p*-toluenesulfonyl)-2-piperazinecarboxylate (IV).—N,N'-Bis(*p*-toluenesulfonyl)ethylenediamine[15] (14.72 g., 0.04 mole) and 0.08 mole of potassium hydroxide were dissolved in 50 ml. of methanol. To this solution 9.84 g. (0.04 mole) of methyl 2,3-dibromopropionate was added dropwise. After the exothermic reactions had subsided, the mixture was refluxed for 3 hr. The methanol was removed *in vacuo*. The residue was washed with ether and recrystallized from 1:1 methanol–acetone: yield 67%; m.p. 174–176.5°; ν_{max}^{KBr} 1730 (s) (COO), 1340 (s) (SO_2N), and 1160 (s) (SO_2N) cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{24}N_2O_6S_2$: C, 53.08; H, 5.35; N, 6.19; S, 14.17. Found: C, 53.46; H, 5.11; N, 6.02; S, 14.43.

Methyl 4-(*p*-Toluenesulfonyl)-1,4,5,6-tetrahydropyrazinoate (VI).—Methyl 1,4-bis(*p*-toluenesulfonyl)-2-piperazinecarboxylate (4 g., 0.012 mole) was incompletely dissolved in 80 ml. of dry tetrahydrofuran. To this mixture was added 0.865 g. (0.036 mole) of sodium hydride under nitrogen. The mixture was warmed to 50° until smooth gas evolution set in. Heating was suspended until the exothermic reaction had subsided. The mixture was then refluxed for 3 hr. Red mercuric oxide (1 g.) was then added and refluxing continued for 2 hr. After filtering, the filtrate was dried over anhydrous magnesium sulfate, filtered, and evaporated to a sirup which solidified on standing. The product was recrystallized from ether and obtained as pale yellow needles: yield 49%; m.p. 92–93°; ν_{max}^{KBr} 3415 (s) (NH), 3392 (s) 3123 (w), 2950 (m), 2860 (m), 1695 (s) (COO^-), 1625 (m) (C=C), 1345 (s) (SO_2N), 1290 (s) (COO^-), and 1155 (s) (SO_2N) cm.$^{-1}$; λ_{max}^{THF} 238, 270, and 308 mμ (ϵ_{max} 6720, 6820, and 1580) (shows the presence of α,β-unsaturated grouping).

Anal. Calcd. for $C_{13}H_{16}N_2O_4S$: C, 52.69; H, 5.44; N, 9.45; S, 10.82. Found: C, 52.56; H, 5.49; N, 9.31; S, 10.98.

N-Benzenesulfonyl-2-anilinoacetophenone (VII).—2-Anilinoacetophenone[16] (5.28 g., 0.025 mole) was dissolved in 75 ml. of dry pyridine. While stirring, 4.42 g. (0.025 mole) of benzenesulfonyl chloride was added. The mixture was stirred for 2 hr. and allowed to stand overnight. The pyridine was removed *in vacuo* at 40–50° and 15% hydrochloric acid was added to the residue until it was acid to congo red. The precipitate was removed by filtration, washed with water, dried, and recrystallized from ethanol, yield 8.5 g. (quantitative), m.p. 129–130°.

Anal. Calcd. for $C_{20}H_{17}NO_3S$: C, 68.35; H, 4.88; N, 3.99; S, 9.12. Found: C, 68.25; H, 4.86; N, 3.99; S, 9.29.

Reaction of N-Benzenesulfonyl-2-anilinoacetophenone (VII) with Sodium Hydride.—VII (7.02 g., 0.02 mole) was dissolved in 100 ml. of dry tetrahydro furan. While stirring the solution and passing in nitrogen, 1 g.(0.02 mole) of sodium hydride was added. The mixture was stirred for 30 min. at room temperature and then for 2 hr. at 50–60°. Ethanol (5 ml.) was added, the mixture was filtered, and the precipitate was washed with tetrahydrofuran. This product decolorized dilute potassium permanganate solution and its infrared spectrum (in KBr) was identical with that of an authentic sample of sodium benzenesulfinate.

The filtrate was evaporated and the residue was recrystallized from ethanol and ethyl acetate. The product was obtained as yellow crystals: yield 50%; m.p. 218–220° (VIII); ν_{max}^{KBr} 3345 (s), 1660 (m), 1590 (s), 1490 (s), and 1220 (s) cm.$^{-1}$; λ_{max}^{THF} 250, 292, and 353 mμ (ϵ_{max} 23,700, 9820, and 8620).

Anal. Calcd. for $C_{28}H_{22}N_2O_2$: C, 80.36; H, 5.30; N, 6.69; mol. wt., 418. Found: C, 80.08; H, 5.37; N, 6.56; mol. wt., 424.

Evaporation of the filtrate from the above recrystallization yielded a yellow residue which was extracted with ethanol. A small amount of yellow solid (phenyliminoacetophenone IX) was obtained from this extract: yield 2–3%; m.p. 152–153°; ν_{max}^{KBr} 1670 (s) (C=O conj.), 1624 (m) (C=N), 1590 (m), 1580 (m), 1480 (m), 1447 (m), 1250 (m), 1240 (m), 873 (m), 760 (m), 745 (m), 690 (m), and 600 (m) cm.$^{-1}$; $\lambda_{max}^{ethanol}$ 206, 220, and 254 mμ (ϵ_{max} 18,100, 14,300, and 15,000).

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Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69; mol. wt., 209. Found: C, 80.32; H, 5.41; N, 6.58; mol. wt., 204.

N-Benzyl-N-phenylbenzenesulfonamide (X).—The benzenesulfonylation of N,1-diphenylmethylamine was carried out in pyridine solution and the product was recrystallized from ethanol, m.p. 119° (lit.[17] m.p. 119).

Reaction of X with Excess Phenyllithium.—X (3.23 g., 0.01 mole) was dissolved in 30 ml. of dry tetrahydrofuran. Twelve milliliters of a 1.78 *M* phenyllithium solution in benzene–ether (0.021 mole) was added under a nitrogen atmosphere and with stirring. When the exothermic reaction was over, another 15 ml. (0.026 mole) of phenyllithium was added. Another exothermic reaction occurred and the solution became quite dark. Stirring was continued for 5 hr. at room temperature. Ethanol (5 ml.) was added to the cold solution to destroy any phenyllithium remaining. The solvent was removed on a steam bath and the residue was extracted with benzene. After drying, the benzene was evaporated leaving a yellow oil. The oil was dissolved in dry ether and saturated ethanolic hydrogen chloride was added to precipitate the hydrochloride of N,1,1-triphenylmethylamine (XII). The hydrochloride was recrystallized from 95% ethanol, yield 95%, m.p. 201–204° (lit.[18] 199°). The identity of XII with an authentic sample of the hydrochloride was demonstrated by their identical infrared spectra as well as by mixture melting measurements which showed no depression: ν_{max}^{KBr} 3050 (m), 2910 (m), 2850 (m), 2700 (broad), and 2510 (m) cm.$^{-1}$.

Anal. Calcd. for $C_{31}H_{28}ClN$: C, 77.14; H, 6.13; Cl, 11.99; N, 4.74. Found: C, 77.26; H, 6.35; Cl, 11.76; N, 14.58.

In a second experiment, the yellow oil from the benzene extract was distilled, b.p. ~170° at 1.5 mm. The infrared spectrum of this substance was identical with that of an authentic sample prepared from N-benzylideneaniline and phenyllithium.

Reaction of X with Phenyllithium.—X (9.69 g., 0.03 mole) was dissolved in 100 ml. of dry tetrahydrofuran. While stirring and passing in nitrogen, 17 ml. (0.03 mole, 1 equiv.) of 1.78 *M* phenyllithium in benzene–ether was added. After stirring overnight, 5 ml. of ethanol was added and the mixture was filtered. The precipitate, 3.3 g., decolorized dilute potassium permanganate solution and probably consisted chiefly of lithium sulfinate.

The filtrate was evaporated to give an oil mixed with some solid. The solid was removed by filtration and recrystallized from ethanol (1.5 g.). This proved to be starting material from melting point and mixture melting point data and from its infrared spectrum.

The remaining oil, filtrate from above, was distilled *in vacuo* yielding two fractions. The first one distilled at 110–120° (1.5 mm.) and soon solidified to yellow crystals, m.p. 52–53°. Mixture melting point measurements, with an authentic sample, showed no depression and infrared spectra of the product and an authentic sample of N-benzylidene showed them to be identical.

The second fraction distilled at 160–180° (1.5 mm.) and weighed 1.95 g. (25%). The infrared spectrum of this sample was identical with that from an authentic sample of N,1,1-triphenylmethylamine (XII) prepared from N-benzylideneaniline and phenyllithium.

Reaction of 1-Benzenesulfonylpiperidine with Sodium Hydride.—1-Benzenesulfonylpiperidine (4.5 g., 0.02 mole) was dissolved in 50 ml. of bis(2-ethoxyethyl) ether. While stirring in a nitrogen atmosphere, 1 g. (0.02 mole) of sodium hydride was added. The mixture was heated at 100° for 5 hr. The solvent was removed by distillation. After the careful addition of water, the solid residue was removed and washed with water, dilute hydrochloric acid, and water. After drying, the product melted at 93–94°.[19] A mixture melting point determination with 1-benzenesulfonylpiperidine proved it to be recovered starting material (recovery 92%).

Reaction of 1-Benzenesulfonylpiperidine with Phenyllithium.—1-Benzenesulfonylpiperidine (9.0 g., 0.04 mole) was dissolved in 100 ml. of dry tetrahydrofuran. Sixty milliliters (0.107 mole) of 1.78 *M* phenyllithium in benzene–ether was added in a nitrogen atmosphere with stirring. Stirring was continued overnight. Ethanol (12 ml.) was added carefully with stirring to the cold solution. Hydrochloric acid was then added until the aqueous layer remained acid to congo red. The aqueous layer was evaporated to dryness. The residue was covered with water and a slight excess of 30% sodium hydroxide solution was added. The basic layer was extracted with ether and the ether extract was dried over anhydrous magnesium sulfate. After removing the ether, the residual oil was fractionally distilled. A small fraction boiling at 80–110° contained a small amount of piperidine which was isolated as its picrate, m.p. 152–153°. A mixture melting point determination with an authentic sample showed no depression.

A higher boiling fraction, 86° (5 mm.), weighed 1.31 g. (21%). This product proved to be largely 1-phenylpiperidine, picrate m.p. 146–147° (lit. m.p. 145–146°). Almost a quantitative yield of the hydrochloride was obtained by passing dry hydrogen chloride into a carbon tetrachloride solution of the base. It was recrystallized from ethanol–ether, m.p. 210–211°.

Anal. Calcd. for $C_{11}H_{16}ClN$: C, 66.82; H, 8.16; Cl, 17.93; N, 7.09. Found: C, 66.62; H, 8.13; Cl, 17.96; N, 7.12.

1,3-Dibenzenesulfonyl-2-phenyl-1,2-dihydrobenzimidazole (XIII).—N,N′-Dibenzenesulfonyl-*o*-phenylenediamine (7.76 g., 0.02 mole) was dissolved in 50 ml. of dry dimethylformamide and 2.16 g. (0.04 mole) of sodium methoxide was added. The methanol thus formed was removed at 100° under reduced pressure. α,α-Dichlorotoluene (3.54 g., 0.022 mole) was then added dropwise at room temperature. Stirring was continued overnight and finally for 1 hr. at 100°. The dimethylformamide was removed *in vacuo*. The residue was dissolved in a small amount of acetone; water was added to precipitate the product. It was recrystallized from 95% ethanol: yield, 91%, m.p. 167–170°, ν_{max}^{KBr} 1360 (s) (SO_2N) and 1160 (s) (SO_2N) cm.$^{-1}$.

Anal. Calcd. for $C_{25}H_{20}N_2O_4S_2$: C, 63.00; H, 4.23; N, 5.88; S, 13.46. Found: C, 63.17; H, 4.34; N, 5.76; S, 13.32.

Reaction of XIII with Phenyllithium.—XIII (2.38 g., 0.005 mole) was dissolved in 40 ml. of dry tetrahydrofuran. While stirring in a stream of nitrogen, 10 ml. of 1.93 *M* phenyllithium in benzene–ether was added and the mixture was stirred for 5 hr. The solvent was evaporated and the residue was extracted with acetone. The extract was evaporated; the residue was washed with a little ligroin and recrystallized from 50% ethanol; yield of 2-phenylbenzimidazole was 77%, m.p. 286–287°. The infrared spectrum was identical with that of an authentic sample. Mixture melting point determinations showed no depression.

5,12-Dibenzenesulfonyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*][1,4]diazocine, (XIV).—N,N′-Dibenzenesulfonyl-*o*-phenylenediamine (38.8 g., 0.1 mole) was suspended in 300 ml. of water and 0.2 mole of potassium hydroxide was added. To this mixture was added 26.4 g. (0.1 mole) of α,α'-dibromo-*o*-xylene in 100 ml. of benzene, with stirring. Stirring was continued for 1 hr. and then the mixture was refluxed for 8 hr. with stirring. The benzene and part of the water were removed *in vacuo*. The precipitate was removed and recrystallized from acetone: yield 90%, m.p. 176–180°, ν_{max}^{KBr} 1343 (s) (SO_2N) and 1157 (s) (SO_2N) cm.$^{-1}$.

Anal. Calcd. for $C_{26}H_{22}N_2O_4S_2$: C, 63.65; H, 4.52; N, 5.71; S, 13.07. Found: C, 63.74; H, 4.70; N, 5.41; S, 13.29.

Reaction of XIV with Phenyllithium to Form 6,11-Diphenyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*][1,4]diazocine (XV).—XIV (4.90 g., 0.01 mole) was dissolved in 100 ml. of dry tetrahydrofuran. While stirring, in a stream of nitrogen, 45 ml. (0.08 mole) of 1.78 *M* phenyllithium in benzene–ether was added. An exothermic reaction took place. The mixture was stirred for 3 days. Ethanol (6 ml.) was slowly added and the solvent was then removed under reduced pressure. The residue was extracted with benzene. The benzene was evaporated, the residue was taken up in dry ethanol, and the solution was saturated with dry hydrogen chloride. Long treatment with hydrogen chloride is necessary. The alcohol was evaporated leaving 3 g. of yellow solid which was recrystallized from acetone and dried at 100° *in vacuo*, m.p. 268–272°, ν^{KBr} series between 3000 and 2200, 1610 (s), 1563 (s), 1480 (m), 1443 (s), 1300 (m), 1145 (m), 740 (s), 688 (s), and 600 (s) cm.$^{-1}$. The product proved to be the dihydrochloride of XV.

Anal. Calcd. for $C_{26}H_{24}Cl_2N_2$: C, 71.72; H, 5.56; Cl, 16.29; N, 6.43. Found: C, 71.92; H, 5.77; Cl, 15.91; N, 6.64.

Attempts to isolate the pure free base have so far been unsuccessful.

Reaction of N,N′-Dibenzenesulfonyl-*o*-phenylenediamine with Ethyl Bromoacetate and Sodium Methoxide.—N,N′-Dibenzenesulfonyl-*o*-phenylenediamine (7.76 g., 0.02 mole) and 2.2 g. (0.041 mole) of sodium methoxide were added to 70 ml. of dry ethanol. After adding 3.34 g. (0.02 mole) of ethyl bromoacetate, the reaction mixture was heated on a steam bath in a pressure

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bottle for 8 hr. After cooling, the precipitate was removed, washed with water, dried, and recrystallized from ethanol–acetone. The product, N,N′-dibenzenesulfonyl-N-ethoxycarbonylmethyl-*o*-phenylenediamine (XVI), was obtained in 63.2% yield, m.p. 186–188°; ν_{max}^{KBr} 3220 (m), 1733 (s) (COO), 1343 (s) (SO_2N), 1200 (s), and 1160 (s) (SO_2N) cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{22}N_2O_6S_2$: C, 55.68; H, 4.67; N, 5.90; S, 13.51. Found: C, 55.70; H, 4.72; N, 5.76; S, 13.82.

The filtrate from above was evaporated to dryness and the residue was recrystallized from acetone to give a small amount of ethyl 2-benzimidazolecarboxylate. It was then recrystallized from acetone and ligroin, m.p. 225–226° dec.

Anal. Calcd. for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.03; H, 5.16; N, 14.62.

The infrared spectrum was identical with that of a sample prepared by the method of Copeland and Day.[9]

Conversion of N,N′-Dibenzenesulfonyl-N-ethoxycarbonylmethyl-*o*-phenylenediamine (XVI) to Ethyl 2-Benzimidazolecarboxylate (XVII).—XVI (2.37 g.) was suspended in 50 ml. of dry tetrahydrofuran. Sodium (0.5 g.) was dissolved in 25 ml. of dry ethanol and added to the above mixture. Everything went into solution. This solution was heated at 100° in a pressure bottle for 1 day. On cooling, 1 g. of material precipitated which has not been identified up to now. The filtrate was evaporated to dryness and the residue was extracted with acetone. The residue proved to be sodium sulfinate. The acetone extract was then evaporated and the residue was extracted with a mixture of acetone and ligroin and filtered. Evaporation of the filtrate gave XVII. It was recrystallized from acetone–ligroin, yield 0.45 g. (47%), m.p. 224–225° dec. Comparison of its melting point and infrared spectra with that of an authentic sample established its identity.

Reactions Catalyzed By Potassium Fluoride. IV. The Reaction of N-Chlorobenzamide with Potassium Fluoride

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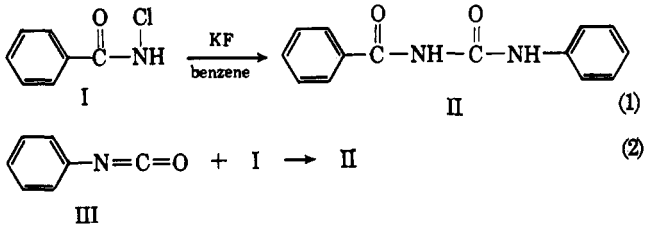
Potassium fluoride has been shown to convert N-chlorobenzamide into N-benzoyl-N′-phenylurea. Initial proton abstraction by the fluoride followed by a Hofmann-type rearrangement gives phenyl isocyanate. Addition of a second mole of the amide to the isocyanate with subsequent hydrolysis yields the product.

Potassium fluoride has been reported to catalyze several reactions. These include the decarboxylation of adipic and 2,2,5,5-tetramethyladipic acids to the corresponding cyclopentanones,[2] the synthesis of 1,-2,3,4,5,6-hexaphenylpentalene through the Michael addition of 1,2,3-triphenyl-1,3-cyclopentadiene to 1,-2,3-triphenyl-2-propen-1-one,[3] the decarboxylation of certain acids,[4] and various Knoevenagel reactions.[5–7] In addition, a preliminary communication[8] reported that anhydrous potassium fluoride functions as a base in the Hofmann reaction converting N-chlorobenzamide to phenyl isocyanate. This paper describes the mechanism of that reaction and the subsequent formation of N-benzoyl-N′-phenylurea.

When dry N-chlorobenzamide (I) was refluxed in dry benzene with anhydrous potassium fluoride, N-benzoyl-N′-phenylurea (II) was obtained in high yield. The amount of II formed was found to depend upon the concentration of potassium fluoride, 2 equiv. of I reacting with 1 equiv. of the fluoride. Severe etching of the reaction flask was noted indicating the formation of hydrogen fluoride. This is in contrast with the results obtained in the Knoevenagel reaction where it was shown[6] that an equimolar amount of the catalyst was not necessary although a practical lower limit to the concentration that could be used was reached. In this reaction, potassium fluoride presumably abstracts a proton from the active methylene-containing compound with subsequent protonation of the condensed anion to form the alcohol. With N-chlorobenzamide, however, abstraction of the proton by the fluoride results in formation of hydrogen fluoride and potassium chloride. The calculated amount of the chloride was realized from an alkali extract of the reaction mixture. Alternatively, II was obtained in high yield when equimolar amounts of I and phenyl isocyanate were reacted. No reaction occurred when benzamide was refluxed in benzene with potassium fluoride.[9]



These observations were taken as evidence for an initial Hofmann rearrangement of 1 mole of N-chlorobenzamide (I) to form the isocyanate. Addition of the second mole of N-chlorobenzamide to phenyl isocyanate followed by hydrolysis yields the product (II). However, on the basis of these considerations, two mechanisms can account for the formation of III. In order to differentiate between reactions 3 and 4, N-chloro-N-methylbenzamide (IV) and potassium fluoride were refluxed in benzene. The fluoride and unchanged IV were recovered quantitatively. Also, when cesium fluoride, which was shown to be a more effective catalyst in the

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