hydroxide[25] and the other with Bial's orcinol reagent.[26] Three ketose bands were detected. Two of these were close to each other and were situated in the 1,3-dihydroxy-2-propanone region; the third was in the region usually occupied by hexoses. The similar bands from the four chromatograms were combined and eluted. Fraction A, the effluent from the slowest band, on concentrating to dryness, weighed 0.7 g. This sirupy material was identified as containing 4-C-(hydroxymethyl)-DL-*glycero*-pentulose (dendroketose)[15] from its similarity in behavior to the product prepared by the action of dilute alkali on compound I. The dendroketose from the two sources showed similar chromatographic behavior, and both gave a gray color with the orcinol spray.

5,7-O-Ethylidene-D-*manno*-heptulose (III).—The material in fraction *B*, which reacted with the orcinol spray to give a blue-green color, weighed 4.2 g. on drying. Compound III crystallized from methanol; weight 0.41 g., m.p. 200.5–201.5°, $[\alpha]^{20}D$ +4.4° (*c* 3, water). No mutarotation was observed.

Anal. Calcd. for $C_9H_{16}O_7$: C, 45.8; H, 6.8. Found: C, 45.6; H, 6.8.

A solution of 0.05 g. of compound III in 2 ml. of water containing 0.5 ml. of Amberlite IR-120(H^+) was agitated with a gentle stream of nitrogen and hydrolyzed by heating for 0.5 hr. in a boiling water bath. On removal of the resin, D-*manno*-heptulose[16] was obtained; it was identified by its infrared spectrum,[27] m.p. 151–152°, mixed m.p. with authentic material 151–152°, and $[\alpha]^{20}D$ +29°. Compound III and the parent sugar were found to produce a green color in the orcinol test, in accordance with observations by Richtmyer.[28]

D-*gluco*-**Heptulose** (IV).—The mother liquor (from which III had crystallized) was hydrolyzed as described above and, from the hydrolyzate, was crystallized 1.025 g. of compound IV,[18] identified by its infrared spectrum, m.p. 171–174°, mixed m.p. 171–174°, $[\alpha]^{20}D$ +67.6°, and a blue color[26] with the orcinol reagent.

5,7-O-Ethylidene-α-D-*altro*-heptulose (V).—A sirupy residue resulted on concentrating the effluent from band *C;* wt. 1.9 g. Crystalline compound V, wt. 0.98 g., was obtained from a 2-propanol solution of the material, m.p. 149–151°, $[\alpha]^{20}D$ +55° (*c* 1; water), $[\alpha]^{20}D$ +50° (1 min.) → +40° (7 min.; *c* 1; methanol). From the mutarotation in methanol, an α-D configuration is assigned to the crystalline acetal.

Anal. Calcd. for $C_9H_{16}O_7$: C, 45.8; H, 6.8. Found: C, 45.7; H, 6.9.

A sample (0.05 g.) of compound V, on hydrolysis as described above, yielded 2,7-anhydro-D-*altro*-heptulose hydrate,[20] which was identified by its infrared spectrum,[27] m.p. 99–101°, mixed m.p. with authentic material 99–101°, and $[\alpha]^{20}D$ −134°.

All melting points are uncorrected.

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2-Chloro-3-dimethylamino-6-phenylsulfonylphenyllithium

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By the metalation of 3-chloro-4-dimethylaminodiphenyl sulfone (I) using *n*-butyllithium, 3-chloro-4-dimethylamino-6 phenylsulfonylphenyllithium (II) was prepared. At temperatures higher than −10°, II eliminates lithium chloride forming 3-dimethylamino-6-phenylsulfonylbenzyne (III). This intermediate reacts readily with furan yielding 5-dimethylamino-8-phenylsulfonyl-1,4-dihydronaphthalene 1,4-endoxide (V). The consumption of the organolithium compound II with time was used to measure the rate of formation of III. The elimination of lithium chloride by II was shown to be a first-order process.

An elimination-addition mechanism has been discussed to explain reactions of *o*-halophenyllithium compounds proceeding through a dehydrobenzene[2] intermediate.[3] It has been shown that *o*-halophenyllithium compounds can be prepared and are stable at temperatures ranging from −60 to −110°.[4] For example, *o*-chlorophenyllithium is stable at −90°. We hoped to modify the properties of both the halophenyllithium compounds and the short-lived benzyne intermediate by the introduction of the dimethylamino and the phenylsulfonyl groups at positions 3 and 6. These groups were chosen because of their respective mesomeric and inductive effects. The expected stabilization of this 3,6-disubstituted *o*-chlorophenyllithium compound was observed.

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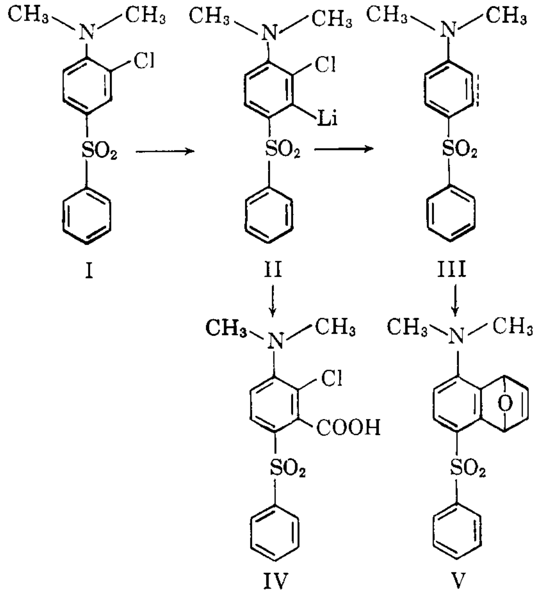
(2) The authors feel that dehydrobenzene is a more general name than benzyne, because the name benzyne implies the presence of a triple bond in the symmetrical intermediate. Experimental evidence is not available to substantiate this implication. For the sake of conformity with the current usage of this journal, we shall use the term benzyne to mean dehydrobenzene.

(3) For the reviews of the field see G. Wittig, *Naturwissenschaften*, **30**, 696 (1942); G. Wittig, *Angew. Chem.*, **69**, 245 (1957); E. F. Jenny, M. C. Caserio, and J. D. Roberts, *Experientia*, **14**, 349 (1958); R. Huisgen in H. Zeiss, "Organometallic Chemistry," Reinhold Publishing Corp., New York, 1960, pp. 36–87.

(4) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **79**, 2625 (1957); *ibid.*, **78**, 2217 (1956); H. Gilman and T. S. Soddy, *J. Org. Chem.*, **22**, 1715 (1957).

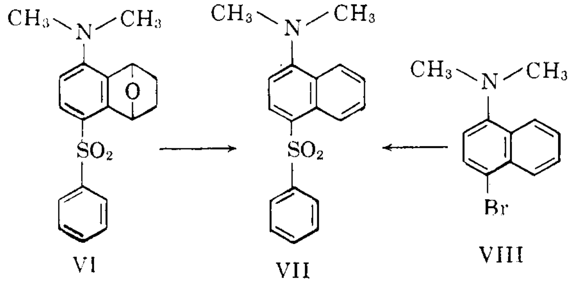
Results

3-Chloro-4-dimethylaminodiphenyl sulfone (I) was metalated rapidly and completely at −80° with *n*-butyllithium yielding 3-chloro-4-dimethylamino-6-phenylsulfonylphenyllithium (II). When II was treated with freshly crushed carbon dioxide at temperatures below −60°, 3-chloro-4-dimethylaminodiphenyl sulfone-2-carboxylic acid (IV, 83–90%) was formed. Regardless of whether carboxylation was carried out shortly after the addition of butyllithium or twenty-four hours later, the results were the same as long as a temperature below −60° was maintained throughout.



Upon warming an ether solution of II gradually to room temperature in the presence of furan (1.0–6.0 moles), 5-dimethylamino-8-phenylsulfonyl-1,4-dihydronaphthalene 1,4-endoxide (V) was secured in 50–61% yields. With a somewhat larger excess of furan (12.0 moles), yields were only slightly increased (68%).

In order to confirm the structure of V, hydrogenation was carried out over palladium to form 5-dimethylamino-8-phenylsulfonyl-1,2,3,4-tetrahydronaphthalene 1,4-endoxide (VI). This endoxide was converted to 1-dimethylamino-4-phenylsulfonylnaphthalene (VII) by heating with hydrochloric acid in acetic anhydride on the steam bath.[5]



For an alternate synthesis of VII, 1-dimethylamino-4-lithionaphthalene was prepared from 1-bromo-4-dimethylaminonaphthalene[6] (VIII) by halogen-metal interconversion using *n*-butyllithium. Upon treatment of this intermediate with benzenesulfonyl fluoride,[7] 1-dimethylamino-4-phenylsulfonylnaphthalene was obtained. This sample of VII was identical with that obtained from endoxide VI as evidenced by mixture melting point and infrared spectra comparison.

In order to determine the temperature at which II eliminated lithium chloride to form III, the extent of reaction was followed as the temperature of the system was elevated. The number of equivalents of organolithium reagent present at the indicated temperatures was determined after hydrolysis with water by titration using 0.1000 *N* hydrochloric acid. The data of Table I were obtained by pipetting aliquots (1.0 ml. ± 0.15 ml.) of a reaction mixture (0.10 *N*) and titrating to the phenolphthalein end point. In six titrations which were obtained between −65 and −10°, the standard deviation was 0.90 mmole of RLi (II) or ±9.1%. The data of Table I were interpreted to indicate that the elimination of lithium chloride from II was proceeding with a measureable rate at 0°.

TABLE I

Time, min.	*T*, °C.	Mmoles II	Mmoles consumed	% Reaction
0	−65	9.88	...	...
294	− 9	9.87	0.01	0.1
320	0.0	6.85	3.03	30.6
353	+21.0	5.53	4.35	44.0
∞	+25.0	0.15	9.73	98.5

Preliminary kinetic studies using the acidimetric titration method for a reaction indicate that the half-life of II is about seven minutes (k_1 = 0.094 min.$^{-1}$).[8] The data of Table II were secured at 0°. In order to check this result, four runs similar to

TABLE II

Time, min.	(II), mole/l.
0	0.1835
9.0	.0420
10.0	.0360
19.0	.0206
21.0	.0156
28.0	.0066
30.0	.0056

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(5) These are more strenuous reaction conditions than were required to effect removal of the oxygen atom in 1,2,3,4-tetrahydronaphthalene 1,4-endoxide [G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956)].

(6) H. R. Snyder and F. W. Wyman, *J. Am. Chem. Soc.*, **70**, 234 (1948).

(7) G. Kobrich, *Ber.*, **92**, 2981 (1959).

(8) The extent of reaction with time was followed by acidimetric titration of the amount of II remaining (using 5.0-ml. aliquots). The data of Table II were obtained using 20.7 mmoles of I and 22.0 mmoles of *n*-butyllithium. When the logarithm of the organolithium concentration minus a correction for excess butyllithium and non-organometallic bases was plotted against time, a linear relationship was secured.

that in Table II were conducted in the presence of furan (5.0 ml., 0.0674 mole). Reaction was terminated at different times by adding excess carbon dioxide. The results are shown in Table III. A plot of the logarithm of per cent IV was linear with time; the slope was determined and a value for k_1 of 0.064 min.$^{-1}$ was found ($t_{1/2}$ = 10.9 min.)

TABLE III

Mmoles, I	% IV	% V	Time, min.
5.115	65.9	17.9	5.0
5.094	57.3	32.3	15.0
5.077	30.1	41.9	26.0
5.084	12.5	56.3	39.0

Discussion

The data indicate that the elimination of lithium chloride from *o*-chlorophenyllithium compounds is a first-order process. Secondly, the temperature at which this process occurs has been sharply modified by the dimethylamino and phenylsulfonyl substituents. The increased acidity of the proton at position two in 3-chloro-4-dimethylaminodiphenyl sulfone (I) is believed to be caused by the presence of the phenylsulfonyl group in the *ortho* position.

Recently, *o*-bromo-N,N-dimethylaniline was studied in the lithium piperidide–piperidine system.[9] The conclusion drawn from this work was that the metalation step prior to lithium halide elimination is the rate-determining step. This conclusion is based upon the assumption that the lithium halide elimination from the substituted *o*-halophenyllithium compounds is an extremely rapid process. This assumption—that elimination is not rate determining at +20°—is probably valid in the lithium piperidide–piperidine system.

Although efforts were made to trap all of the intermediate III as the endoxide V with various concentrations of furan, III undergoes competitive side reactions. One of these side reactions was emphasized in the absence of furan to yield a crystalline product which is believed to be a dimer of III. The reactions of III form the nucleus for continued investigations in this laboratory.

Experimental

Throughout this study freshly prepared solutions of *n*-butyllithium in ether (1.2–1.3 *N*) were used. All operations were carried out in a dry, oxygen-free nitrogen atmosphere. Infrared spectra of IV and V were obtained in matching 0.30-cm. cells with a Perkin-Elmer Model 21 double beam apparatus. The endoxide absorption of V at 10.03 μ was measured at various concentrations from 0.025 *M* to 0.10 *M*. Slight deviation from linearity was observed at concentrations greater than 0.138 *M* (absorbance = 1.02). The carbonyl absorption at 5.75 μ of the acid IV was studied over the concentration range 0.0222 to 0.0457 *M*. No difficulty was experienced in analyzing mixtures of IV and V.

The data of Table III were obtained using the chloro sulfone (0.00509 mole I), ether (75.0 ml.), furan (5.0 ml., 0.0674 mole, freshly distilled from sodium), and *n*-butyllithium (4.15 ml., 0.00510 mole). After reaction was ended with carbon dioxide, hydrolysis was accomplished with water. Solid endoxide (V contaminated with IV) was separated from the water and ether phases, dried, and weighed. This solid was dissolved in chloroform and was analyzed by infrared spectroscopy using the endoxide and carbonyl absorptions as described above. The aqueous and ether phases were separated and the latter was dried over sodium sulfate. The ether was replaced with chloroform and the samples were analyzed by infrared spectroscopy as described. Endoxide, V, was present in the ether phase in amounts ranging from 10–15% based on the amount of starting material. Chloro acid (IV) was present in percentages from 2.8–4.4. The bulk of the chloro acid was isolated after acidification of the aqueous phase. Since the chloro acid is slightly hygroscopic, it was dried *in vacuo* before its identity was checked by melting point and neutralization equivalent.

3-Chloro-4-dimethylaminodiphenyl Sulfone.—In a 1-l. three-necked flask equipped with a stirrer were placed 4-dimethylaminodiphenyl sulfone[10] (65.2 g., 0.250 mole), a crystal of ferric chloride, and dry chloroform (600 ml.). To this system, maintained at 0°, was added chlorine (20.8 g., 0.294 mole) which had previously been dissolved in chloroform (250 ml.) at −80°. This solution became colorless after 1 hr. of stirring at 0°; after 3 hr., the chloroform solution was shaken twice with 100-ml. portions of water. Phases were separated and chloroform was replaced with methanol (200 ml.). Crystallization of 3-chloro-4-dimethylaminodiphenyl sulfone (53.3 g., 71.0%, m.p. 65.0–65.8°) occurred slowly at room temperature during several days. Recrystallization from methanol yielded a purified product, m.p. 65.8–66.0°.

Anal. Calcd. for $C_{14}H_{14}ClNO_2S$: C, 56.85; H, 4.77; Cl, 11.99; N, 4.73. Found: C, 56.55; H, 4.78; Cl, 12.19; N, 5.46.

3-Chloro-4,4-dimethylaminodiphenylsulfone-2-carboxylic Acid.—In a nitrogen-filled Schlenk tube were placed 3-chloro-4-dimethylaminodiphenylsulfone (2.980 g., 0.0101 mole) and absolute ether (100 ml.). To this solution maintained at −80° was added *n*-butyllithium (8.90 ml., 0.0111 mole). The solution became yellow immediately and a white precipitate was noticed after a short time. The tube was sealed in a nitrogen atmosphere and was maintained at −80° for 24.0 hr. The tube was opened under dry nitrogen and freshly crushed carbon dioxide was added. Hydrolysis was accomplished with water, the phases were separated, and the aqueous phase was warmed gently to expell excess carbon dioxide and ether. Following careful acidification with hydrochloric acid, 2.980 g. of the acid IV was isolated, m.p. 165–170°. After purification by recrystallization from water (65 mg. per 100 ml.) or a water–methanol pair (10:1), 2.82 g. of purified acid was obtained, m.p. 172–173.0°. An analytical sample was obtained after one additional recrystallization from water, m.p. 173.2–174.0°.

Anal. Calcd. for $C_{15}H_{14}ClNO_4S$: C, 53.02; H, 4.15; Cl, 10.43; N, 4.12; S, 9.44. Found: C, 52.80; H, 4.23; Cl, 10.52; N, 4.27; S, 9.38.

Neut. equiv.: Calcd: 339.8. Found 338.0, 339.1.

An analogous run having excess furan present (4.0 ml., 0.055 mole) yielded 2.85 g. (83.2%) of acid IV, m.p. 171.0–173.0°, after a reaction time of 1.25 hr. Neither 4-dimethylaminodiphenyl sulfone-3-carboxylic acid (the product one would expect if halogen-metal interconversion had occurred) nor the endoxide V could be isolated.

5-Dimethylamino-8-phenylsulfonyl-1,4-dihydronaphthalene 1,4-Endoxide.—In a three-necked flask equipped with stirrer were placed 3-chloro-4,4-dimethylaminodiphenyl-

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[9] R. Huisgen, W. Mack, K. Herbig, N. Ott, and E. Anneser, *Ber.*, **93**, 412 (1960).

[10] Prepared by the method of A. Gebauer-Fullneg, *Ber.*, **61**, 1307 (1928), in 63% yield using chlorobenzene as solvent.

sulfone (6.053 g., 0.02045 mole), furan (16.3 g. 0.248 mole, freshly distilled from sodium), and absolute tetrahydrofuran[11] (50 ml.). The resulting solution was cooled to −65° and *n*-butyllithium (21.2 ml., 0.254 mole) was added dropwise during 15 min. The resulting pale yellow solution was stirred with gradual warming to room temperature. Hydrolysis of the reaction mixture was accomplished with a saturated ammonium chloride solution. 5-Dimethylamino-8-phenylsulfonyl-1,4-dihydronaphthalene 1,4-endoxide (3.248 g., 48.7%, m.p. 166–170°) was separated from the ether and aqueous phases. The ether was separated from the aqueous phase and the solvent was replaced with methanol yielding additional crude endoxide (1.250 g., 18.6%, m.p. 165–170°). Recrystallization of these materials from methanol yielded a purified product (3.73 g., m.p. 172.5–174.0°).

Anal. Calcd. for $C_{18}H_{17}O_3NS$: C, 66.03; H, 5.23; N, 4.28; Found: C, 66.32; H, 5.39; N, 4.30.

5-Dimethylamino-8-phenylsulfonyl-1,2,3,4-tetrahydronaphthalene 1,4-Endoxide.—Palladium oxide (0.2073 g., 0.00168 mole) in 25 ml. of methanol was reduced with hydrogen in a conventional glass hydrogenation vessel (250 ml. volume). To this freshly prepared catalyst-suspension was added 5-dimethylamino-8-phenylsulfonyl-1,4-dihydronaphthalene 1,4-endoxide (0.5260 g., 0.00161 mole) in 25 ml. of methanol. During 35 min., 40.3 ml. of hydrogen was consumed at 29° and 761 mm. (0.00 156 mole, 97.5% of theory). The catalyst was removed by filtration and was extracted with boiling methanol. Concentration of the methanol solution was followed by crystallization of 5-dimethylamino-8-phenylsulfonyl-1,2,3,4-tetrahydronaphthalene 1,4-endoxide (0.470 g., 0.00144 mole, 89.5%, m.p. 171.4–172.2°). A mixed melting point with the starting material was undepressed! The infrared spectrum, however, was noticeably different having a strong absorption at 2980-cm.$^{-1}$ characteristic for alicyclic carbon-hydrogen bond stretching motions.

Anal. Calcd. for $C_{18}H_{19}O_3NS$: C, 65.63; H, 5.81; N, 4.25; S, 9.73. Found: C, 65.90; H, 5.70; N, 4.23; S, 9.58.

1-Dimethylamino-4-phenylsulfonylnaphthalene.—A mixture of 5-dimethylamino-8-phenylsulfonyl-1,2,3,4-tetrahydronaphthalene 1,4-endoxide (0.1708 g., 0.000516 mole), acetic anhydride (5.0 ml.), and concentrated hydrochloric acid (1.0 ml.) was heated on the steam bath for 16.5 hr. Neutralization was accomplished with excess 2 *N* ammonium hydroxide (55 ml.); the organic materials were extracted with ether and separated from the aqueous phase. Replacement of the ether with methanol was followed by crystallization of 1,1-dimethylamino-4-phenylsulfonylnaphthalene (0.1321 g., 82.1 %, m.p. 149–153°). Three further recrystallizations from methanol raised the m.p. to 157.2–158.2°.

For structure proof, 1-dimethylamino-4-phenylsulfonylnaphthalene (VII) was synthesized from 1-bromo-4-dimethylaminonaphthalene[6] (VIII). In a three-necked flask equipped with a stirrer were placed a solution of 1-bromo-4-dimethylaminonaphthalene[6] (8.80 g., 0.0352 mole) in absolute diethyl ether (25 ml.) To this solution maintained at −65° was added *n*-butyllithium (37.8 ml., 0.0363 mole) during 30 min. This new solution was added dropwise during 12 min. to a cold solution (−70°) of benzenesulfonyl fluoride[12] (5.42 g., 0.0351 mole) in ether (25 ml.). The resulting reaction mixture was stirred for 2 hr. at −70°, warmed to room temperature during 2 hr., and then hydrolyzed with water (50 ml.). Excess ether was used to dissolve the organic reaction products; phases were separated and the ether phase was dried over sodium sulfate. After concentration to a volume of 50 ml., the ether solution deposited two different kinds of crystals: (a) rhombohedrons, m.p. 154–157° and (b) monoclinic prisms, m.p. 135–138°. These materials were separated mechanically. Purified 1,1-dimethylamino-4-phenylsulfonylnaphthalene (1.755 g., 16.0 %, m.p. 157.5–158.5°) was isolated after three recrystallizations of the former compound from methanol. A mixed melting point of this material with the sulfone obtained by cleavage of water from 5,5-dimethylamino-8-phenylsulfonyl-1,2,3,4-tetrahydronaphthalene 1,4-endoxide (VI) was undepressed. The infrared spectra of these two compounds were superimposable.

Anal. Calcd. for $C_{18}H_{17}NO_2S$: C, 69.42; H, 5.50; N, 4.50; S, 10.30. Found: C, 69.65; H, 5.52; N, 4.28; S, 10.19.

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(11) The results were the same in diethyl ether as in THF.

(12) W. Davies and J. H. Dick, *J. Chem. Soc.*, 2104 (1931).