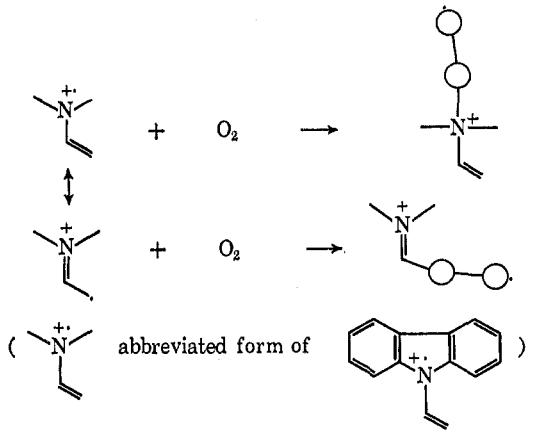
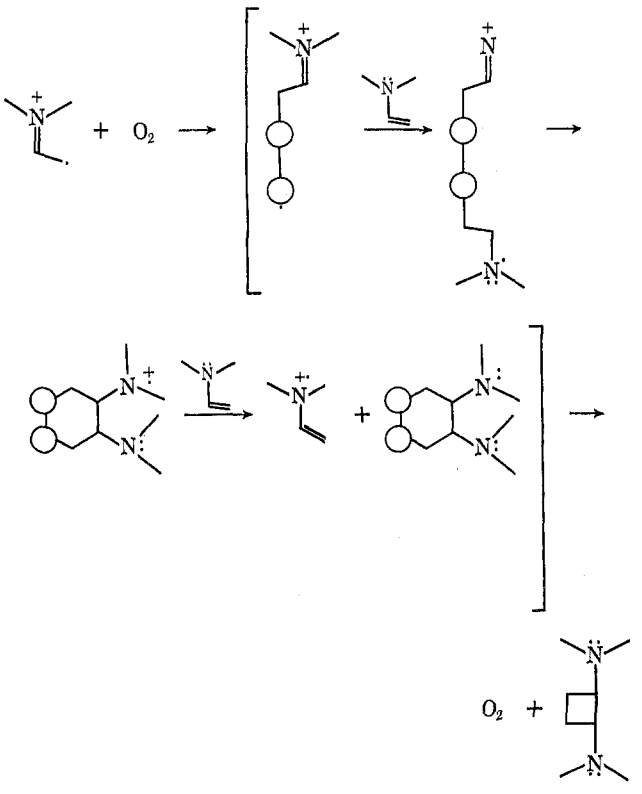
tion of either a nitrogen peroxy radical, which is practically unknown, or the carbon peroxy radical.



The formation of carbon peroxy radical will eventually suppress the competitive reactions, namely, the hydrolysis of the N-vinyl group and the chain reaction of N-vinylcarbazole polymerization. It is also plausible that the carbon peroxy radical will add to the carbon–carbon unsaturation, which will lead to the formation of the six-membered ring peroxide intermediate and eventually to the final product.



The mechanism proposed is purely conjectural, since the isolation of the cyclic oxygen-containing intermediate was not fruitful and the detection of singlet oxygen was not carried out. However, the fact that no dimer formed when oxygen was excluded lends credence to the direct participation of molecular oxygen in the dimer formation.

Experimental Section[9]

Formation and Identification of the Dimer.—To a solution of 1 g (5.0×10^{-3} mol) of N-vinylcarbazole (Matheson Coleman and Bell), mp 67°, in 100 ml of 9:1 methanol–water, 0.02 g (5×10^{-5} mol) of ferric nitrate (Mallinckrodt), $Fe(NO_3)_3 \cdot 9H_2O$, was added. The mixture was stirred at room temperature in open air and a white precipitate gradually appeared. At the end of 4 hr the solid was collected. The yield was 0.25 g (*ca.* 25%): mp 189–192° (recrystallization from 1:1 ethanol–acetone raised the melting point to 191–193°); nmr δ_{TMS} 7–8.2 (16 H, aromatic), 6.26 (2 H, NCH), and 2.4–3.2 (4 H, methylene).

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25; mol wt, 386.5. Found: C, 86.74; H, 5.80; N, 7.31; mol wt, 373 (Rast method, Nagy), 386 (mass spectrum).

All data correspond to the reported dimer, *trans*-1,2-dicarbazylcyclobutane.[10] Concentration of the filtrate by evaporation afforded 0.2 g of another white solid, which was identified as carbazole by melting point and by comparison of their infrared spectra. The mother liquid furnished acetaldehyde in *ca.* 20% yield based on the isolation of acetaldehyde 2,4-dinitrophenylhydrazone, mp 146–147° (lit.[11] mp 148°).

In other runs under identical conditions except with a gentle stream of oxygen, the yield of the dimer was 37–40% of the theoretical; the yield was not altered when the reaction was carried out at −10° instead of at room temperature. Efforts to detect the presence of peroxide intermediate in both cases failed. Under a stream of nitrogen only a trace amount of the dimer was obtained. The rest of the products were qualitatively identified as carbazole, acetaldehyde, and perhaps some low molecular weight poly-N-vinylcarbazole.

Increasing the amount of ferric nitrate up to tenfold in other runs did not substantially affect the corresponding yield of the dimer in the presence of either an oxygen or a nitrogen atmosphere.

Parallel experiments were carried out between N-vinylcarbazole and hydrogen peroxide. In a typical run, 2.25 ml (5.7×10^{-5} mol) of 0.06% hydrogen peroxide (Baker Analyzed reagent, 3% diluted to 0.06% with water) was added to a solution of 1 g (5.0×10^{-3} mol) of N-vinylcarbazole in 100 ml of 9:1 methanol–water solution. The solution was stirred at room temperature for 4 hr under a stream of (a) oxygen and (b) nitrogen and (c) in open air.

The experiments were worked up essentially in the same manner as in the previous ones. The yield of the dimer was *ca.* 10% in a, 0% in b, and *ca.* 3% in c. Change of the amount of hydrogen peroxide in each case did not alter the yield of the dimer to an appreciable degree.

Registry No.—*trans*-1,2-Dicarbazylcyclobutane, 1484-96-4.

(9) Elementary analysis was performed by M. S. Nagy, Massachusetts Institute of Technology. Melting points are not corrected. The nmr spectrum was recorded by using a Varian A-60 spectrometer from A. D. Little Analytical Laboratories. The mass spectrum was done by using a A.E.I. MS9 mass spectrometer with the generous help from Dr. G. Dudek, Harvard University.

(10) L. P. Ellinger, J. Fenney, and A. Ledwith, *Monatsh. Chem.*, **96**, 131 (1965).

(11) G. R. Clemo and W. H. Perkin, Jr., *J. Chem. Soc.*, **125**, 1804 (1924).

Sodium Arylsulfonates from Phenols

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Direct sulfonation of aromatic compounds often yields mixtures of isomeric sulfonic acids which are difficult to separate; however, sulfur-containing compounds of other types can be prepared free of isomers. Many can be oxidized to sulfonic acids.[1] The recently

(1) E. E. Gilbert, "Sulfonation and Related Reactions," Interscience Publishers, New York, N. Y., 1965, p 201.

TABLE I
O-ARYL AND S-ARYL DIMETHYLTHIOCARBAMATES

Dimethylthiocarbamate	Mp, °C	Formula	Registry No.	Calcd, % N	Calcd, % S	Found, % N	Found, % S
O-Phenyl	Liquid	$C_9H_{11}NOS$	16241-04-6	7.73	17.69		
S-Phenyl	47–48	Same	7304-68-9			7.81	17.72
O-2,6-Dimethylphenyl	84–85	$C_{11}H_{15}NOS$	16241-12-6	6.69	15.32	6.68	15.24
S-2,6-Dimethylphenyl	42.5–43.5	Same	16241-13-7			6.71	15.19
O-2,6-Diisopropylphenyl	152.5–154	$C_{15}H_{23}NOS$	24010-73-9	5.28	12.08	5.34	12.02
S-2,6-Diisopropylphenyl	106.5–109	Same	24010-52-4			5.43	12.18

TABLE II
SODIUM ARYLSULFONATES

Aryl group	Yield, %	Formula	Registry No.	Calcd, % S	Calcd, % Na	Found, % S	Found, % Na
Benzene	63.5	$C_6H_5SO_3Na$	515-42-4	17.80	12.76	17.74	12.67
2,6-Dimethylbenzene	55.3	$C_8H_9SO_3Na$	24010-54-6	15.39	11.04	15.21	11.04
2,6-Diisopropylbenzene	57.7	$C_{12}H_{17}SO_3Na$	24010-55-7	12.13	8.70	12.24	8.80

TABLE III
DERIVATIVES OF ARYLSULFONIC ACIDS

	Sulfonamide					S-Benzylthiuronium salt				
		Calcd, %		Found, %			Calcd, %		Found, %	
Aryl group	Mp, °C	N	S	N	S	Mp, °C	N	S	N	S
Benzene	151–152[a]	8.91	20.40	8.63	20.44	147–148[b]	8.63	19.77	8.74	19.97
2,6-Dimethylbenzene[c]	114–115	7.56	17.31	7.65	17.09	160–161	7.95	18.19	7.86	17.96
2,6-Diisopropylbenzene[d]	125–126	5.80	13.28	5.58	13.10	200–201	6.85	15.69	6.88	15.84

[a] Lit. value, 150–150.5°: E. H. Huntress and J. S. Autenrieth, *J. Amer. Chem. Soc.*, **63**, 3446 (1941). [b] Lit. value, 147.5–148.5°: E. Chambers and G. W. Watt, *J. Org. Chem.*, **6**, 376 (1941). [c] Registry no.: for sulfonamide, 24010-56-8; for S-benzylthiuronium salt, 24010-58-0. [d] Registry no: for sulfonamide, 24010-57-9; for S-benzylthiuronium salt, 24010-59-1.

described Newman–Kwart rearrangement of O-aryl dimethylthiocarbamates to S-aryl dimethylthiocarbamates makes possible conversion of phenols into organic sulfur compounds with sulfur attached to the aromatic ring.[2] We now show these compounds capable of being oxidized to arylsulfonic acids. The overall scheme is illustrated below.

$$ArOH \longrightarrow ArOCSN(CH_3)_2 \xrightarrow{\Delta} ArSCON(CH_3)_2 \xrightarrow{[O]} ArSO_3H$$

Sodium benzenesulfonate, sodium 2,6-dimethylbenzenesulfonate, and sodium 2,6-diisopropylbenzenesulfonate were prepared to illustrate the method. Correct melting points for benzenesulfonamide and S-benzylthiuronium benzenesulfonate confirm that benzenesulfonic acid is produced by oxidizing S-phenyl dimethylthiocarbamate. Preparing sodium 2,6-dimethylbenzenesulfonate and sodium 2,6-diisopropylbenzenesulfonate shows that compounds not readily available by other procedures can be synthesized easily. Preparation of the latter demonstrates that hindered sodium arylsulfonates can be made.

The O-aryl and the S-aryl dimethylthiocarbamates were prepared by the method described by Newman and Karnes.[2] Melting points and elemental analyses of these compounds are given in Table I. Since O-phenyl dimethylthiocarbamate is a liquid, purification by recrystallization is not possible, and, since it is thermally unstable, distilling would lead to rearrangement. Physical constants are, therefore, not available for the compound.

Oxidation of the S-aryl compounds to the arylsulfonic acids was accomplished using 30% hydrogen peroxide as the oxidizing agent and formic acid as the solvent. A similar procedure was used by Yoder for oxidizing isothiuronium derivatives of steroids.[3] After the oxidation reaction was complete, formic acid was removed. The arylsulfonic acid was taken up in water, and the pH was adjusted to 9 using 1 *N* sodium hydroxide solution. Water was removed by evaporating, and sodium arylsulfonate remained. Base must be added during evaporation of the water to ensure removal of dimethylamine resulting from incomplete oxidation. Products were purified by recrystallizing until further purification produced no change in infrared spectrum. Yields and results of elemental analyses are shown in Table II. In order to characterize the sodium arylsulfonates, S-benzylthiuronium derivatives and arylsulfonamides were prepared. Melting points of the derivatives of sodium benzenesulfonate agree with those reported in the literature. Elemental analyses of derivatives of the other sulfonates are satisfactory. These are given in Table III.

Work reported here demonstrates that hydroxyl groups of phenols can be replaced by sulfonate groups even in the case of phenols as hindered as 2,6-diisopropylphenol. Since many techniques are available for preparing variously substituted phenols, the procedure reported here makes possible the synthesis of a wide variety of sulfonic acids free of isomeric impurities.

Experimental Section

Melting points were taken using a capillary melting point apparatus and are corrected. Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn. Phenol was Baker Analyzed; 2,6-dimethylphenol and 2,6-diisopropylphenol were obtained from Aldrich Chemical Co.

Preparation of Sodium 2,6-Diisopropylbenzenesulfonate.—To a 2000-ml, round-bottom flask was added a solution of 63.2 g

(2) M. S. Newman and H. A. Karnes, *J. Org. Chem.*, **31**, 3980 (1966).

(3) L. Yoder, *ibid.*, **20**, 1317 (1955).

(0.238 mol) of S-2,6-diisopropylphenyl dimethylthiocarbamate in 1000 ml of formic acid. The solution was stirred with a magnetic stirrer as 365 ml of 30% hydrogen peroxide was added dropwise. The mixture was stirred overnight. Formic acid was removed under vacuum using a rotary evaporator. The 2,6-diisopropylbenzenesulfonic acid was taken up in water, and the pH was adjusted to 9 using 1 *N* NaOH solution. The water was removed by evaporating on a steam bath. The pH was checked periodically during the evaporation and was maintained at 9 by adding 1 *N* NaOH solution. Sodium 2,6-diisopropylbenzenesulfonate was recrystallized several times by being dissolved in water and precipitated by saturating the solution with NaCl at the boiling point. The white crystalline product was dried in an 80° vacuum oven. A yield of 36.3 g (0.137 mol, 57.7%) of product was obtained.

The Acid-Catalyzed Nitramine Rearrangement. V. The Effect of Isotopic Replacement of Aromatic Ring Hydrogens[1-3]

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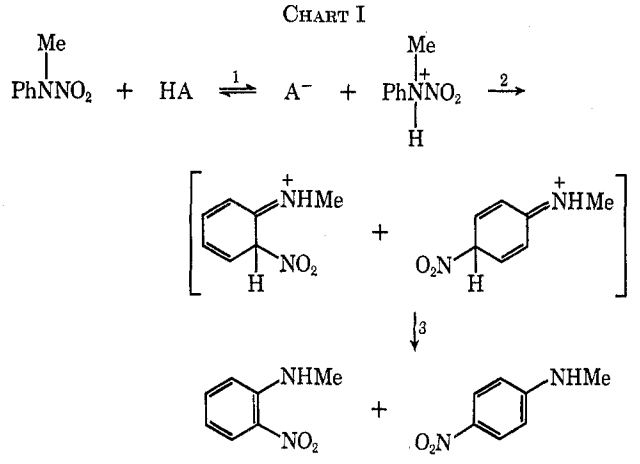
The detection of specific acid catalysis for the aromatic nitramine rearrangement[1b] showed that the rate-determining process in this reaction followed the protonation step. The observed substituent effects[1c] suggested that the breaking of the amine–nitro group bond (Chart I, step 2) was rate limiting. To substantiate this latter assignment, it was desirable to rule out proton loss (step 3) as being significant in rate or product determination. This was accomplished by examining the reactivity of nitramines in which the aromatic hydrogens were replaced by deuterium or tritium atoms.

CHART I



Rates and product distributions were determined for N-nitro-N-methylaniline and N-nitro-N-methylaniline-2,6-d_2 and for N-nitro-N-methyl-*p*-toluidine and N-nitro-N-methyl-*p*-toluidine-2-*t*. The results are listed in Table I. It is obvious that deuterium or tritium substitution at the migration terminus did not affect either the rate of rearrangement or the distribution of products.

TABLE I

EFFECT OF ISOTOPIC REPLACEMENT OF AROMATIC-RING HYDROGENS ON THE AROMATIC NITRAMINE REARRANGEMENT

Compd	10^3k, sec^{-1}	*ortho*,[c] %	*para*,[d] %
N-Nitro-N-methylaniline[a]	1.63 ± 0.04	47.9 ± 1.4	29.3 ± 0.1
N-Nitro-N-methylaniline-2,6-d_2[a]	1.66 ± 0.07	47.8 ± 1.0	29.9 ± 0.5
		% 2-H[e]	% 2-t[f]
N-Nitro-N-methyl-*p*-toluidine[b]	2.65 ± 0.03	100	...
N-Nitro-N-methyl-*p*-toluidine-2-*t*[b]	2.69 ± 0.03	48 ± 2	52 ± 2

[a] Rearrangement was carried out at 40.0° in 0.511 *M* aqueous $HClO_4$ containing 0.500 *M* $NaClO_4$. [b] Rearrangement was carried out at 20.0° in 0.204 *M* aqueous $HClO_4$ containing 0.807 *M* $NaClO_4$. [c] Per cent of 2-nitro-N-methylaniline in the product. [d] Per cent of 4-nitro-N-methylaniline in the product. [e] Per cent of 2-nitro-N-methyl-*p*-toluidine in the nitrated product. [f] Per cent of 2-nitro-N-methyl-*p*-toluidine-2-*t*-in the nitrated product.

These results demonstrate that proton loss (step 3) is not involved in determining the rate of the overall reaction and that, in fact, proton loss must be a relatively fast, facile, low activation energy step in comparison with other changes that occur in the forward progress of the reaction. The first of these points is proved by the finding that the rate of appearance of product was not at all affected by isotopic substitution. If the activation energy of step 3 was of significant magnitude, then the pentadienimine cation intermediate should accumulate and the rate of product formation should be determined by its decomposition. Since its breakdown depends on the scission of a carbon–hydrogen bond, the process should be slowed if a C–D bond replaces the original C–H bond, and the rate of production of nitroanilines from normal and deuterated nitramines should have been different. This result also supports the finding of specific acid catalysis in the nitramine rearrangement, since rate-limiting proton loss (step 3) would have led to general acid catalysis.

It has been suggested that an *ortho* pentadienimine cation intermediate intervenes between the protonated nitramine and the *para* pentadienimine cation[4,5] (Chart II). If the rearrangement follows such a pathway and step 2 is rate determining, then no rate effect of isotopic substitution would be observed. However, if step 4 was reversible or similar in rate to step 5, deuteration of the 2,6 positions of N-nitro-N-methylaniline should lead to a higher proportion of *p*-nitro-N-methylaniline in the product, since C–D bonds are hard to break and step 5 would be retarded. Alter-

(1) Previous papers in this series: (a) W. N. White, D. Lazdins, and H. S. White, *J. Amer. Chem. Soc.*, **86**, 1517 (1964); (b) W. N. White, C. Hathaway, and D. Huston, *J. Org. Chem.*, **35**, 737 (1970); (c) W. N. White and J. R. Klink, *J. Org. Chem.*, **35**, 965 (1970).

(2) Part of this work has been reported in preliminary form: W. N. White, J. R. Klink, D. Lazdins, C. Hathaway, J. T. Golden, and H. S. White, *J. Amer. Chem. Soc.*, **83**, 2024 (1961).

(3) This work was supported by Grants G-7345 and GP-1970 from the National Science Foundation.

(4) S. Brownstein, C. A. Bunton, and E. D. Hughes, *J. Chem. Soc.*, 4534 (1958).

(5) M. J. S. Dewar in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 306–313.