shown to be 1-chlorodibenzothiophene, rather than the 3-isomer by the method of mixed melting points with an authentic sample of 1-chlorodibenzothiophene.[4]

3-Chloro-2-benzamidodibenzothiophene.—Into a 500-ml. round-bottomed, three-necked flask, equipped with a mechanical stirrer and reflux condenser fitted with an acid trap, were placed 5.0 g. (0.0165 mole) of 2-benzamidodibenzothiophene[5] and 200 ml. of chloroform. To the reaction mixture were then added 2.3 g. (0.017 mole) of sulfuryl chloride, dissolved in 30 ml. of chloroform, and a small crystal of iodine. The reaction mixture was heated at reflux for a period of 3 hr. and the solvent was stripped from the residue. Crystallization from methyl Cellosolve gave 3.7 g. (67.5%) of material which melted at 211–212°. The infrared spectrum of this compound was almost identical with that of 2-benzamido-3-bromodibenzothiophene.

Anal. Calcd. for $C_{19}H_{12}ClNOS$: S, 9.49. Found: S, 9.35.

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The Aminolysis of N-Nitrotoluenesulfonamides[1]

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In connection with other investigations we have observed an extremely facile cleavage of the sulfonamide linkage. Substituted N-nitrotoluenesulfonamides are readily aminolyzed by secondary amines at room temperature to produce primary nitramines and the corresponding disubstituted toluene amide. This reaction has proved to be a general

$$p\text{-}CH_3C_6H_4SO_2\underset{\displaystyle NO_2}{\underset{|}{N}}R + R_2'NH \longrightarrow p\text{-}CH_3C_6H_4SO_2NR_2' + RNHNO_2$$

one for the preparation of mono- and dialkylcarbinyl nitramines. The reactions were carried out in acetonitrile as a solvent and piperidine was used most generally as the aminolytic agent. The experimental results are summarized in Table I. The nitrotoluenesulfonamides were prepared by the method of Gillibrand and Lamberton.[2]

TABLE I

CONVERSION OF TOLUENESULFONAMIDES TO PRIMARY NITRAMINES

Toluenesulfonamide	Yield, % of N-nitrotoluenesulfonamide	Yield,[a] % nitramine
n-Butyl	92	81
s-Butyl	54	86
n-Amyl	81	90
Isoamyl	95	96
n-Hexyl	84	86

[a] Based on N-nitrotoluenesulfonamide.

This rapid and nearly quantitative cleavage of the sulfur–nitrogen bond is remarkable in view of the resistance toward alkaline hydrolysis exhibited by sulfonamides as a class. A recent review has pointed out that there appear to be no examples of alkaline hydrolysis of sulfonamides involving, as a first step, breaking of the sulfur–nitrogen bond.[3] Hydrolysis of these compounds is universally carried out under strongly acid conditions at elevated temperatures. Indeed the resistance of sulfonamides to bases prompted our investigation of nitrosulfonamides as alkaline nitrating agents. It was thought that nucleophilic attack might possibly occur at the nitro group rather than at the sulfonyl group producing a secondary nitramine (eq. 1).

$$R_2'NH + p\text{-}CH_3C_6H_4SO_2\underset{\displaystyle NO_2}{\underset{|}{N}}R \longrightarrow R_2'NNO_2 + p\text{-}CH_3C_6H_4SO_2NHR \quad (1)$$

It is possible that the direction of cleavage is controlled by the stability of the leaving group. Attack on the sulfonyl group produces the resonance-stabilized nitramine anion whereas attack at the nitro group would yield a sulfonamide ion stabilized by the interaction of adjacent opposite charges and d-orbital resonance.[4] The nitramine anion is probably the more stable species, as it has been demonstrated that the nitromethane anion is more stable than a sulfonylmethyl anion.[5] In the case under study here the nitrogen analogs of these two species are involved

Carbon[6]	Nitrogen
$RSO_2CH_2^-$	RSO_2NR^-
$CH_2{=}NO_2^-$	$RN{=}NO_2^-$

Whatever the cause, the reaction must be initiated by nucleophilic attack at the sulfonyl group and probably involves expansion of the sulfur octet. Another example of this reaction is known. Gillibrand and Lamberton[2] have reported the hydrolysis of N-nitrotoluenesulfonamides by boiling caustic. The comparative slowness of their method was probably due to the insolubility of the nitramides in water.

This reaction could not be applied to the preparation of trialkylcarbinylnitramines as the corresponding N-nitrotoluenesulfonamides could not be prepared. The tosyl derivatives of *t*-carbinamines cleaved very readily in the acidic nitration medium to produce toluenesulfonamide and, presumably, the tertiary carbonium ion. Only the amide and various nitration and degradation products of the olefins corresponding to the carbonium ion were obtained. A similar acid-catalyzed solvolysis of tertiary toluenesulfonamides has been reported recently.[6]

Experimental[7]

Toluenesulfonamides.—The following sulfonamides were prepared in the manner described by Shriner and Fuson:[8]

(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) M. I. Gillibrand and A. H. Lamberton, *J. Chem. Soc.*, 1883 (1949).

(3) H. R. Snyder and R. E. Heckert, THIS JOURNAL, **74**, 2006 (1952).

(4) W. von E. Doering and L. K. Levy, *ibid.*, **77**, 509 (1955), *et seq.*

(5) R. G. Pearson, D. H. Anderson and L. L. Alt, *ibid.*, **77**, 527 (1955).

(6) R. H. Wiley, C. C. Ketterer and S. F. Reed, *ibid.*, **76**, 4996 (1954).

(7) We are indebted to Miss Annie Smelley for the microcombustion data.

(8) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, Ed. 3, p. 178.

N-*sec*-butyl-, m.p. 61.5–62.5° (lit.[8] m.p. 55°); **N-*n*-butyl**, m.p. 40–42° (lit.[8] m.p. 43°); **N-isoamyl**, b.p. 152° (0.3 mm.), n^{20}D 1.5181 (lit.[9] b.p. 178° (1 mm.), n^{25}D 1.5171); **N-*n*-hexyl**, m.p. 60–62° (lit.[10] m.p. 62°).

N-*n*-Amyltoluenesulfonamide.—The same procedure[8] was followed. From 29.6 g. (0.34 mole) of *n*-amylamine and 57.2 g. (0.3 mole) of *p*-toluenesulfonyl chloride there was obtained, upon distillation, 66.3 g. (92%) of the desired amide, b.p. 158° (0.2 mm.), n^{20}D 1.5206. This material has been reported as an unpurified oil.[10]

Anal. Calcd. for $C_{12}H_{19}NO_2S$: C, 59.72; H, 7.93. Found: C, 59.63; H, 7.43.

N-*t*-Butyltoluenesulfonamide.—This amide was prepared by the method of Wiley.[6] From 36.5 g. (0.5 mole) of *t*-butylamine and 95.3 g. (0.5 mole) of *p*-toluenesulfonyl chloride in 250 ml. of pyridine there was obtained 69.9 g. (62%) of the desired amide, m.p. 115–115.5° (recrystallized from ethanol).

Anal. Calcd. for $C_{11}H_{17}NO_2S$: C, 58.12; H, 7.54; N, 6.16. Found: C, 58.01; H, 7.66; N, 6.25.

N-*t*-Octyltoluenesulfonamide.—The same method was used as for the preparation of the *t*-butyl derivative. From 64.5 g. (0.5 mole) of *t*-octylamine and 95.3 g. (0.5 mole) of *p*-toluenesulfonyl chloride in 250 ml. of pyridine there was obtained 108.6 g. (76%) of the sulfonamide, m.p. 134.5–135.5° (from ethanol).

Anal. Calcd. for $C_{15}H_{25}NO_2S$: C, 63.56; H, 8.89; N, 4.95. Found: C, 64.05; H, 8.67; N, 5.01.

N-Nitro-N-*sec*-butyltoluenesulfonamide.—The general method described by Gillibrand and Lamberton[2] for the preparation of N-nitro-N-methyltoluenesulfonamide was followed exactly. From 55.3 g. (0.243 mole) of N-*sec*-butyltoluenesulfonamide there was obtained 34.9 g. (54%) of the nitramide, m.p. 73.5–74° (from ethanol).

Anal. Calcd. for $C_{11}H_{16}N_2O_4S$: C, 48.51; H, 5.92; N, 10.29. Found: C, 48.19; H, 5.44; N, 11.08.

N-Nitro-N-*n*-amyltoluenesulfonamide.—Following the general method, from 66.3 g. (0.27 mole) of N-*n*-amyltoluenesulfonamide there was obtained 63.9 g. (81%) of the N-nitro derivative, m.p. 51.5–52° (from ethanol).

Anal. Calcd. for $C_{12}H_{18}N_2O_4S$: C, 50.33; H, 6.34. Found: C, 50.40; H, 6.34.

N-Nitro-N-isoamyltoluenesulfonamide.—From 45 g. (0.19 mole) of N-isoamyltoluenesulfonamide there was obtained 50.8 g. (95%) of the nitramide. This compound proved to be an oil that could not be induced to crystallize. Since its infrared spectrum contained a band at 1565 cm.$^{-1}$ similar to that present in the spectra of the other nitramides, and the NH bands of the starting material had disappeared, there seemed to be no doubt of the compound's identity. No efforts were made to distil this material for analysis.

N-Nitro-N-*n*-hexyltoluenesulfonamide.—From 60 g. (0.25 mole) of N-*n*-hexyltoluenesulfonamide there was obtained 57.5 g. (84%) of the N-nitro derivative as an oil. It could be recrystallized from ethanol by chilling the solution to −20°, m.p. 28–29°.

Anal. Calcd. for $C_{13}H_{21}NO_2S$: C, 52.94; H, 6.91; N, 9.22. Found: C, 52.33; H, 6.08; N, 9.39.

Preparation of Primary Nitramines.—The following general procedure was followed for the aminolysis of the nitrotoluenesulfonamides. To a solution of 10 g. of the nitramide in 35 ml. of acetonitrile was added 10 g. of piperidine with stirring at 5–10°. The reaction was noticeably exothermic. After addition, the mixture was stirred under reflux with no apparent change for 30 minutes and then poured into 100 ml. of 10% sodium hydroxide solution. N-Tosylpiperidine precipitated and was collected on a filter. The filtrate was acidified and extracted with ether. The dried extracts were concentrated and distilled to obtain the nitramine.

***n*-Amylnitramine.**—Following the general procedure described above, there was obtained 4.5 g. (92%) of *n*-amylnitramine, b.p. 60–62° (0.02 mm.), n^{20}D 1.4611.

Anal. Calcd. for $C_5H_{12}N_2O_2$: C, 45.43; H, 9.16; N, 21.20. Found: C, 46.09; H, 9.44; N, 20.86.

Isoamylnitramine.—Following the general procedure, there was obtained 4.4 g. (90%) of isoamylnitramine, b.p. 62–64° (0.02 mm.), n^{20}D 1.4594. This nitramine has previously been reported as an unpurified oil.[11]

Anal. Calcd. for $C_5H_{12}N_2O_2$: C, 45.43; H, 9.16; N, 21.20. Found: C, 45.72; H, 9.38; N, 21.02.

(9) J. B. Wright and R. C. Elderfield, *J. Org. Chem.*, **11**, 111 (1946).

(10) L. Demeny, *Rec. trav. chim.*, **50**, 51 (1931).

(11) A. Berg, *Ann. chim.*, [7] **3**, 357 (1894).

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The Reactions of Mesitoyl Nitrate and Other Hindered Acyl Nitrates with Nucleophilic Reagents[1]

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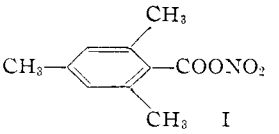
In connection with a general study of alkaline nitration, the reactions of mesitoyl nitrate (I), pivalyl nitrate (II) and diethylacetyl nitrate (III) with various nucleophiles have been investigated.

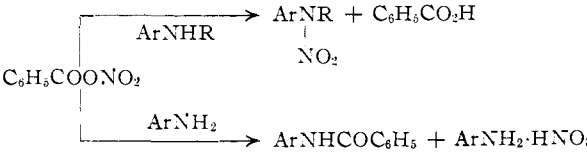


I

$(CH_3)_3CCOONO_2$ II

$(C_2H_5)_2CHCOONO_2$ III

Previous studies of acyl nitrates as alkaline nitrating agents have been limited to the reaction of benzoyl nitrate with amines. Francis[2] reported that benzoyl nitrate reacted with secondary aromatic amines to produce the nitramine, but with primary amines only the amide was produced. These results were confirmed and extended by Butler[3] who showed that aliphatic amines are acylated exclusively. Benzoyl nitrate also has been studied in the nitration of aromatic substances but this reaction is apparently due to the generation of nitrogen pentoxide,[4] and appears to be quite different from the amine nitration. It was thought that an acyl nitrate having greater steric requirements in the vicinity of the carbonyl group would be more desirable as an alkaline nitrating agent. Thus mesitoyl nitrate[5] (I) was selected for investigation.



It has been found that mesitoyl nitrate (I) reacts with secondary aliphatic amines to form the corresponding nitramines in 40–60% yields. The reaction proceeded most readily with the highly branched amines. Cyclic amines such as piperidine were nitrated but also underwent acylation leading to difficultly separable mixtures of the amide and nitram-

(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) F. E. Francis, *J. Chem. Soc.*, **89**, 1 (1906); *Ber.*, **39**, 3798 (1906).

(3) T. H. Butler, *ibid.*, **39**, 3804 (1906).

(4) V. Gold, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2467 (1950).

(5) After the completion of this investigation a report appeared of the preparation of mesitoyl nitrate by H. Burton and P. F. G. Praill [*J. Chem. Soc.*, 729 (1955)]. Their method of preparation was essentially the same as ours, but their interest was in the compound's acylating ability rather than its nitrating ability.