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.

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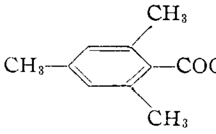
In connection with a general study of alkaline nitration, the reactions of mesitoyl nitrate (I), pivalyl nitrate (II) and diethylacetyl nitrate (III) with various nucleophiles have been investigated.



I

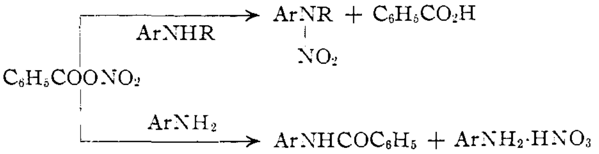
$(CH_3)_3CCOONO_2$

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-

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[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.

ine. At the beginning of this study isolation of the pure nitramines was made difficult by the presence of mesitoic anhydride in the reaction mixtures.

$$\text{MesCOONO}_2 + \text{R}_2\text{NH} \longrightarrow \text{MesCOOH} + \text{R}_2\text{NNO}_2$$

Mes = 2,4,6-trimethylphenyl

This material was very difficult to separate since it is quite resistant to hydrolysis.[6] Its separation from the nitramine was effected by treating the mixture with trifluoroacetic anhydride followed by quenching in sodium hydroxide solution. Presumably mesitoic anhydride is converted to the mixed anhydride IV which is very readily hydrolyzed to the acid salt.

$$(\text{MesCO})_2\text{O} + (\text{CF}_3\text{CO})_2\text{O} \longrightarrow \underset{\text{IV}}{\text{MesCOOCOCF}_3} \xrightarrow{\text{NaOH}} \text{MesCOONa}$$

The presence of the anhydride was not surprising in view of Francis' report that benzoic anhydride was always produced in the preparation of benzoyl nitrate.[2] The anhydride is probably produced by attack of the mesityloxocarbonium ion (V) on mesitoyl nitrate. The carbonium ion is generated by the removal of the halogen by silver nitrate. Other possible modes of anhydride formation have been discussed.[5]

$$\underset{\text{V}}{\text{MesCO}^+} + \text{MesCOONO}_2 \longrightarrow (\text{MesCO})_2\text{O} + \text{NO}_2^+$$

While secondary amines attacked mesitoyl nitrate almost exclusively at the nitro group, primary amines reacted at the carbonyl group, thus producing amides. The only example in which a primary amine was nitrated with mesitoyl nitrate was that of *t*-butylamine. Thus it appears that mesitoyl nitrate is an extremely discriminating reagent. Rigid steric requirements in the structure of the attacking nucleophile must be met before nitration supersedes acylation. This behavior of mesitoyl nitrate is quite different from that of other compounds containing the mesitoyl group.[7] For examples, ketones and esters of the mesitylene series are attacked only by the smallest reagents, *i.e.*, hydrogen and the methyl Grignard reagent. Mesitoyl chloride, the most reactive of this group of compounds, does not discriminate on the basis of steric requirements as its reactions probably involve prior ionization. For instance, it reacts with both primary and secondary amines.[8]

This same steric requirement extends to alcohols also. While mesitoyl nitrate reacted readily with alcohols, the mesitoic acid esters were the major products although the nitrate esters were produced in small amounts. When *t*-butyl alcohol was examined in this reaction, a small amount of *t*-butyl nitrate was obtained. It is presumed that this material was the major product of the reaction as no *t*-butyl mesitoate was isolated. It is probable that most of this nitrate ester was lost by its solvolysis during the work-up of the reaction mixture.

It was apparent that the steric hindrance offered by the *o*-methyl groups was not sufficient to prevent reaction at the carbonyl group of mesitoyl nitrate. In the hope that other hindered compounds would be more effective for nitration, pivalyl nitrate (II) and diethylacetyl nitrate (III) were examined briefly. It was thought that the latter might have enhanced nitrating power due to its higher six number.[9] Both reagents were prepared from the corresponding acyl chloride and silver nitrate in either acetonitrile or ether. Pivalyl nitrate[10] converted octyl alcohol to octyl nitrate in 49% yield and diethylacetyl nitrate effected the same conversion in 75% yield. The nitration of amines was also attempted with these reagents but in every case the products isolated were the N-substituted amides and the amine nitrate, *i.e.*, acylation rather than nitration was observed. It is interesting to note, however, that with the highly hindered diisopropylamine, a low yield of the nitramine was obtained using diethylacetyl nitrate.

Experimental[11]

Reaction of Mesitoyl Nitrate with Secondary Amines. Di-*n*-propylamine.—An ethereal solution of mesitoyl nitrate was prepared in the following manner. A solution of 18.3 g. (0.1 mole) of mesitoyl chloride in 20 ml. of dry ether was added slowly at 0–10° to a slurry of 20.4 g. (0.12 mole) of anhydrous silver nitrate in 50 ml. of dry ether. This mixture was stirred at ice-bath temperatures for an hour. At this point it was ready for use. If desired the precipitated silver chloride could be removed by filtration. However, its presence did not appear to affect the reaction. One attempt was made to isolate mesitoyl nitrate. A violent fume-off occurred as the solvent was being evaporated.

The mesitoyl nitrate solution was cooled to −20° and 20.2 g. (0.2 mole) of di-*n*-propylamine was added within three minutes. The resulting mixture was stirred for five minutes and then filtered. The filtrate was washed with water, 10% hydrochloric acid, water and finally exhaustively with 10% sodium hydroxide solution. The ethereal solution was dried over anhydrous magnesium sulfate and concentrated to yield 14.4 g. of a mushy residue. Trifluoroacetic anhydride (24 g.) was added to the residue and this mixture was warmed at 30° for an hour. It was then poured into water, made basic and extracted with ether. After drying the ether extracts were concentrated and distilled *in vacuo* to yield 8.1 g. (56%) of di-*n*-propylnitramine, b.p. 46–48° (0.06 mm.), $n^{20}\text{D}$ 1.4560 (lit.[12] b.p. 103–104° (10 mm.), $n^{20}\text{D}$ 1.4559).

Diisopropylamine.—The general procedure described above was followed exactly. From 18.3 g. (0.1 mole) of mesitoyl chloride, 20.4 g. (0.12 mole) of silver nitrate and 20.4 g. (0.2 mole) of diisopropylamine there was obtained 5.8 g. (40%) of **diisopropylnitramine**, m.p. 106–109° (lit.[13] m.p. 108–108.5°).

Reaction of Mesitoyl Nitrate with Primary Amines. *n*-Butylamine.—The ethereal solution of mesitoyl nitrate was prepared in the same manner. At −20°, 14.6 g. (0.2 mole) of *n*-butylamine was added rapidly. The mixture was stirred for five minutes and filtered. The filtrate was washed with water and 10% hydrochloric acid, and then it was extracted exhaustively with 10% sodium hydroxide solution.

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(6) R. C. Fuson, J. Corse and N. Rabjohn, THIS JOURNAL, **63**, 2852 (1941).

(7) The remote possibility that the acylation reagent in all these reactions may have been mesitoic anhydride rather than mesitoyl nitrate was eliminated by examining the reaction of *n*-butylamine and mesitoic anhydride between −20 and 100°. There was no *n*-butylmesitamide formed over this temperature range, and mesitoic anhydride was recovered quantitatively.

(8) R. G. Kadesch, THIS JOURNAL, **64**, 726 (1942).

(9) M. S. Newman, *ibid.*, **72**, 4783 (1950).

(10) The reactions with this reagent were carried out by Mr. Angelo S. Pagano.

(11) We are indebted to Miss Annie Smelley for the microcombustion data and to Dr. Keith S. McCallum for infrared interpretations.

(12) W. R. Kingdon and G. F Wright, THIS JOURNAL, **72**, 1030 (1950).

(13) W. J. Chute, F. E. Dunn, J. C. McKenzie, G. S. Meyers, G. N. R. Smart, J. W. Suggitt and G. F Wright, *Can. J. Research*, **26B**, 114 (1948).

Upon acidification of these alkaline extracts mesitoic acid precipitated but no butylnitramine was found.

The organic extracts were dried and concentrated to yield 9.1 g. of a white solid whose infrared spectrum indicated that it was a mixture of an amide and an anhydride. By recrystallization from ligroin there was obtained 3.2 g. (15%) of N-*n*-butylmesitamide, m.p. 83–87° (lit.[14] m.p. 88.5–89°). The melting point was not depressed upon admixture with an authentic sample.

Cyclohexylamine.—The same procedure as that for *n*-butylamine was followed. Again no nitramine could be found in the reaction mixture. By fractional crystallization of the crude amide–anhydride mixture 6.1 g. (25%) of **N-cyclohexylmesitamide** was obtained. Recrystallization from ethanol yielded an analytical sample, m.p. 171–172°.

Anal. Calcd. for $C_{16}H_{23}NO$: C, 78.37; H, 9.39; N, 5.71. Found: C, 77.72; H, 9.17; N, 5.73.

***t*-Butylamine.**—The general procedure employed for *n*-butylamine was used. In this case alkaline extraction of the reaction mixture yielded a mixture of mesitoic acid and *t*-butylnitramine. Distillation of this mixture yielded 2.3 g. (20%) of pure ***t*-butylnitramine**, m.p. 41–42.5° (lit.[15] m.p. 38°).

Reaction of Mesitoyl Nitrate with *n*-Hexyl Alcohol.—The following procedure is typical of those used with alcohols. The mesitoyl nitrate was prepared in exactly the same manner as described above. The ethereal solution of mesitoyl nitrate was cooled to −20° and 10.2 g. (0.1 mole) of *n*-hexyl alcohol was added rapidly. The mixture was stirred for 15 minutes, then poured on ice, made basic and filtered. The filtrate was transferred to a separatory funnel and the organic layer was separated and dried. Removal of the solvent left an oily solid. This material was slurried with silica in methylene chloride to remove any unreacted alcohol. The eluate was concentrated and treated with trifluoroacetic anhydride to remove the mesitoic anhydride. The remainder of the mixture was fractionated to yield 1.8 g. (12%) of ***n*-hexyl nitrate**, b.p. 86–88° (10 mm.), $n^{25}D$ 1.4172 (lit.[16] b.p. 46° (1 mm.), $n^{24.5}D$ 1.4180), and 6.9 g. (28%) *n*-hexyl mesitoate, b.p. 79–80° (0.2 mm.), $n^{20}D$ 1.4927.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.72; H, 8.60.

[14] N. J. Leonard and E. W. Nommenson, THIS JOURNAL, **71**, 2808 (1949).

[15] J. Barrott, I. N. Denton and A. H. Lamberton, *J. Chem. Soc.*, 1998 (1953).

[16] L. M. Soffer, E. W. Parrotta and J. DiDomenico, THIS JOURNAL, **74**, 5301 (1952).

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The Reaction of Triethyl Phosphite with a Dialkyl Disulfide

BY HERBERT I. JACOBSON, RONALD G. HARVEY AND ELWOOD V. JENSEN

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Trialkyl phosphites, such as triethyl phosphite, are nucleophilic reagents which react readily with alkyl halides to form the dialkyl esters of the corresponding phosphonic acids (II).[1] This reaction is believed to involve displacement of the halogen substituent by the triethyl phosphite to form a phosphonium compound (I) which, on attack by the halide ion, eliminates ethyl halide to form the phosphonate.

$$P(OEt)_3 + RX \longrightarrow \underset{\text{I}}{\left[R\overset{\oplus}{P}(OEt)_3\overset{\ominus}{X}\right]} \longrightarrow \underset{\text{II}}{RPO(OEt)_2} + EtX$$

Recently it has been found that trialkyl phosphites react with alkyl *p*-toluenesulfonate esters[2] and with quaternary salts of Mannich bases[3] to produce the corresponding phosphonate esters, with bromine to yield dialkyl phosphobromidates[4] and with alkyl sulfenyl chlorides to produce trialkyl monothiophosphate esters.[5] Although the mechanisms of these latter reactions have not been established with certainty, the formation of the observed products in each case is consistent with a mechanism similar to that of the Arbuzov reaction, involving a nucleophilic displacement of the substituent group by the triethyl phosphite moiety coupled with the cleavage of the ethoxy linkage by the displaced anionic species.

If such a mechanism is indeed common to the reaction of trialkyl phosphites with such a variety of substances as alkyl halides, sulfonate esters, Mannich base salts, bromine and sulfenyl halides, it is reasonable to expect that other linkages, which are either polarized or polarizable, might undergo a similar type of reaction with triethyl phosphite, provided the group displaced is capable of cleaving the ethoxy bond. A grouping likely to possess these properties is the disulfide linkage which is known to undergo nucleophilic cleavage with great ease, especially by sulfhydryl anions.[6] Accordingly, the reaction of triethyl phosphite with diethyl disulfide was investigated and found to produce triethyl monothiophosphate (III) and diethyl sulfide (IV) in excellent yield. This phenomenon

$$P(OEt)_3 + EtSSEt \longrightarrow \begin{bmatrix} EtS^{\ominus} \\ EtS\overset{\oplus}{P}(OEt)_3 \end{bmatrix} \longrightarrow \underset{\text{III}}{EtSPO(OEt)_2} + \underset{\text{IV}}{EtSEt}$$

provides additional suggestive evidence for a common mechanism of the Arbuzov type in the reaction of trialkyl phosphites with a variety of compounds as well as affording a convenient preparative method for monothiophosphate esters of type III.

Experimental

A mixture of 12.2 g. (0.10 mole) of diethyl disulfide (Eastman Kodak Co.) and 41.5 g. (0.25 mole) of redistilled triethyl phosphite[7] was distilled at atmospheric pressure through a 30-in. Fenske column with take off at such a rate that the distillate temperature remained at 90–92°. In about 10 hours there was collected a practically quantitative yield of diethyl sulfide (IV), b.p. 90°, $n^{25}D$ 1.4401, m.p. of sulfone derivative 70.8–71.2°, reported b.p. 93°,[8] $n^{20}D$ 1.4423,[8] m.p. of sulfone[9] 72°. After removal of the excess triethyl phosphite at reduced pressure, triethyl monothiophosphate (III) was collected at 105–110° (10 mm.), $n^{25}D$ 1.4540; 15.2 g., 77%. Redistillation of this product through the column yielded the analytical sample, b.p. 110°

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[1] A. E. Arbuzov, *J. Russ. Phys. Chem. Soc.*, **38**, 687 (1906); G. M. Kosolapoff in R. Adams, "Organic Reactions," Vol. 6, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 273.

[2] T. C. Myers, S. Preis and E. V. Jensen, THIS JOURNAL, **76**, 4172 (1954).

[3] T. C. Myers, R. G. Harvey and E. V. Jensen, *ibid.*, **77**, 3101 (1955).

[4] W. Gerrard and G. J. Jeacocke, *J. Chem. Soc.*, 3647 (1954).

[5] D. C. Morrison, THIS JOURNAL, **77**, 181 (1955).

[6] T. Bersin and J. Steudel, *Ber.*, **71**, 1015 (1938).

[7] Generously donated by the Monsanto Chemical Co. and the Virginia–Carolina Co.

[8] R. Nasini, *Ber.*, **15**, 2878 (1882).

[9] W. Strecker and R. Spitaler, *ibid.*, **59**, 1754 (1926).