and 0.3 g. of sodium carbonate in 20 ml. of water, bromine (0.18 ml.) was added dropwise with vigorous stirring. The precipitate was filtered, washed with water and recrystallized from ethyl acetate to give 0.33 g. (84%) of the bromolactone, m.p. 165–170° dec. (lit.[6] m.p. 180° dec.).

Anal. Calcd. for $C_{15}H_{21}O_4Br$: C, 52.18; H, 6.13; Br, 23.15. Found: C, 52.37; H, 6.24; Br, 23.40.

Preparation of ψ-Santonin (I) from Bromolactone (V).—The bromolactone (0.4 g.), prepared as above, was heated with 4 ml. of 2,4,6-collidine and 2 ml. of toluene at 140° for 3 hours. The cooled solution was poured into water, extracted with chloroform and the organic layer washed with dilute acid, bicarbonate solution and dried. Decolorization of the solution with Norit and evaporation of the solvent yielded a solid which upon recrystallization from benzene–chloroform gave 0.18 g. (59%) of ψ-santonin, m.p. and mixed m.p. with authentic material, 189.8–190.8°, $[\alpha]^{25}D$ −161.0° (*c* 0.41, EtOH). The ultraviolet and infrared spectra of the product were identical with those of ψ-santonin.

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.38; H, 7.77.

1-Keto-7-hydroxy-$\Delta^{5(10)}$-santenic Acid (IV).—Hydrogenation of ψ-santonin according to the method of Clemo and Cocker[12] and recrystallization from methanol gave 82% of the product, m.p. 191.0–193.4°, $[\alpha]^{26}D$ −3.3° (*c* 1.01, EtOH), $[\alpha]^{25}D$ −6.6° (*c* 0.635, HOAc). Clemo and Cocker[12] report a m.p. 188–189° but a $[\alpha]^{20}D$ −239 (*c* 0.96 HOAc) which we have never obtained.

The methyl ester was prepared with diazomethane and recrystallized from ether–hexane, m.p. 76.8–78.7°, $[\alpha]^{25}D$ +5.6° (*c* 1.6, EtOH) (lit.[12] m.p. 77°). The ester upon reaction with acetic anhydride and a drop of pyridine in the warm for 2 hours followed by evaporation of the reagents and washing of the residue with acid, base and water yielded the crystalline acetate ester. The material was recrystallized from ether–hexane and then sublimed, m.p. 105.8–106.3°.

Anal. Calcd. for $C_{18}H_{26}O_5$: C, 67.06; H, 8.13. Found: C, 67.04; H, 8.06.

(12) G. R. Clemo and W. Cocker, *J. Chem. Soc.*, 30 (1946).

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, NAVAL ORDNANCE TEST STATION]

The Synthesis of Secondary Nitramines by the Nitrolysis of N,N-Disubstituted Amides

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The nitrolysis of N,N-disubstituted amides in trifluoroacetic anhydride has been further investigated. When the substituents are *n*-alkyl groups, the nitrolysis of acetamides, methanesulfonamides and benzenesulfonamides gives almost quantitative yields of the corresponding secondary nitramines. The nitrolysis, however, is retarded easily both by steric hindrance from the N-alkyl groups and by electronegative substituents.

The nitrolysis of N,N-disubstituted amides has long been known as a possible route for the synthesis of secondary nitramines.[1] In fact, Franchimont[2] obtained the first known nitramine by the nitrolysis of *unsym*-dimethylurea. Such nitrolyses usually were carried out in what was described as "absolute" or "fuming" nitric acid and gave the nitramines in very poor yield if at all. Thus acetamides, oxamides, sulfonamides, carbamates and ureas generally failed to give the nitramines if substituted with other than N,N-dimethyl, piperazino or morpholino groups. Prior to the very recent and elegant Emmons nitrosamine oxidation method[3] the only useful laboratory method for the preparation of secondary nitramines was Wright's[4] chloride-catalyzed nitration of secondary amines. The latter method, although of quite general applicability, frequently involves undesirable side reactions and may be very slow in certain cases.

It was shown previously[5] that a series of N,N-disubstituted formamides were nitrolyzed readily to the secondary nitramines in trifluoroacetic anhydride. These reactions were very rapid even at 0° and the nitramines were obtained essentially in quantitative yield. Neither starting amide nor nitrosamine by-product was detected. Because of the utility of a method for the synthesis of secondary nitramines which involves only the preparation of easily obtainable amide intermediates, this nitrolysis has been studied further with a number of amides in which both the N-alkyl substituents and the acyl moieties have been varied (Table I).

TABLE I

THE NITROLYSIS OF VARIOUS TYPES OF N,N-DISUBSTITUTED AMIDES IN TRIFLUOROACETIC ANHYDRIDE

Amide	Yields, % Nitramine	Nitrosamine[a]	Recovd. amide
N,N-Diethylacetamide	81	0	..
N,N-Di-*n*-propylacetamide	93	..	0
N,N-Di-*n*-butylacetamide	82	0	0
N,N-Di-*n*-hexylacetamide	95	..	..
N,N-Di-*n*-heptylacetamide	98	..	..
N,N-Diethylmethanesulfonamide	94	0	0
N,N-Di-*n*-butylmethanesulfonamide	87	0	0
N,N-Di-*n*-butylbenzenesulfonamide	78	0	..
N,N′-Diformylpiperazine	45	..	..
N,N′-Diformylpiperazine[b]	0	..	0
2,6-Diformyl-2,6-diaza-4-oxaheptane	0	..	..
N,N-Diisopropylformamide[c]	0	..	68
N,N-Dicyclohexylformamide[c]	0	..	51
N,N-Diisobutylacetamide	4	..	81
N,N-Diisobutylacetamide[d]	15	..	..
N,N-Di-*n*-butyltrichloroacetamide	0	0	91
N,N-Di-β-cyanoethylacetamide	0	..	79
Ethyl N,N-diethylcarbamate	0	..	0
Ethyl N,N-di-*n*-butylcarbamate	0	0	0
N,N-Diethylurea	18	..	0

[a] The yields are indicated only in cases where the nitrosamine could be isolated either by distillation or by extraction with concentrated hydrochloric acid. [b] Reaction carried out in acetic anhydride. [c] Reaction time two hours at 0°. [d] Reaction time four hours at 20°.

(1) Review article by H. J. Backer, *Sammlung Chem. und Chem. Tech. Vortrage*, **18**, 359 (1912); see also A. H. Lamberton, *Quart. Revs.*, Vol. V, No. 1 (1951).

(2) A. P. N. Franchimont, *Rec. trav. chim.*, **2**, 121 (1883).

(3) W. D. Emmons, THIS JOURNAL, **76**, 3468 (1954).

(4) W. J. Chute, K. G. Herring, L. E. Toombs and G. F. Wright, *Can. J. Research*, **26B**, 89 (1948).

(5) J. H. Robson, THIS JOURNAL, **77**, 107 (1955).

Amides containing the following straight chain alkyl groups, when associated with the acyl groups listed below, were nitrolyzed in almost quantitative yield in trifluoroacetic anhydride: ethyl, *n*-propyl, *n*-butyl, *n*-hexyl and *n*-heptyl. The acyl groups found to be nitrolyzed successfully were formyl,[5] acetyl, methanesulfonyl and benzenesulfonyl. Only one example of a benzenesulfonamide was examined since the secondary reactions involving nitration of the aromatic ring, although not appreciably lowering the nitramine yield, vitiated the usefulness of the primary reaction. This would also be true of N-aryl substituents. It is pertinent that nitrosamine by-product formation was not observed, since nitrosamines usually are encountered in amine nitrations and frequently are difficult to separate from the corresponding nitramines.

The low yields obtained from N,N′-diformylpiperazine (45% in trifluoroacetic and 0% in acetic anhydride) probably were due to loss *via* water solubility of dinitropiperazine, since Van Dorp[6] has reported that N,N′-dibenzenesulfonylpiperazine was nitrolyzed quantitatively in absolute nitric acid even without solvent. The nitrolysis of 2,6-diformyl-2,6-diaza-4-oxaheptane was accompanied by the evolution of nitrogen oxides and probably involved degradation of the oxa linkage.

The reaction was found to be particularly susceptible to steric hindrance. Thus N,N-diisopropylformamide and N,N-dicyclohexylformamide gave none of the corresponding nitramines even after extended reaction times, and substantial amounts of the amides were recovered. N,N-Diisobutylacetamide, which is considerably less hindered, did give a very low yield (4%) of the nitramine; under more drastic reaction conditions this yield was raised to 15%. N,N-Diisobutylacetamide and diisobutylnitramine have been incorrectly described in the prior literature. This error has been corrected in the Experimental section of this paper.

Electronegative substituents on the acyl group effectively stopped the reaction. Di-*n*-butyltrichloroacetamide was recovered quantitatively. This effect was observed previously by Franchimont[7] who demonstrated that dimethyltrichloroacetamide was unchanged under conditions that gave a 24% yield of nitramine with dimethylacetamide. A similar effect was noted when the N-alkyl groups were cyano-substituted; thus N,N-di-β-cyanoethylacetamide failed to give the nitramine even though the cyano groups are separated from the amino nitrogen by two methylene groups. This effect of electronegative substitution, either in the acyl or in the amino portions of the amides, may be explained on the basis of the previously suggested mechanism of amide nitrolysis,[5] where an attack of nitronium ion (NO_2^+) on the amide was postulated according to equations 1 and 2

$$2HNO_3 + (CF_3CO)_2O \longrightarrow NO_2^+NO_3^- + 2CF_3COOH \quad (1)$$

$$NO_2^+ + \begin{matrix} R \\ \diagdown \\ :N\text{—}Ac \\ \diagup \\ R \end{matrix} \longrightarrow O_2N\text{—}\begin{matrix} R \\ \diagup \\ N \\ \diagdown \\ R \end{matrix} + Ac^+ \quad (2)$$

Due to an effective electron withdrawal and consequent reduction of electron density at the amino nitrogen when negatively substituted, the ease of electrophilic displacement of the acylium group would be decreased. Further evidence in support of this mechanism is adduced from the fact that the reaction is readily hindered by bulky N-alkyl groups as would be expected in an electrophilic displacement on the amino nitrogen.

Two other general types of amides, ureas and carbamates, were examined. N,N-Di-*n*-butylurea gave the nitramine in very poor yield. The two N,N-dialkylcarbamates, although failing to nitrolyze to the nitramines, showed an unusual behavior; the only products isolated (72% in one case) were the N-alkylcarbamates. Reactions in which one of the alkyl groups is replaced by a nitro group rather than a hydrogen have been reported previously for N,N-dialkylcarbamates and sulfonamides.[8] However no such reaction has been noted where the major product is the monoalkylcarbamate.

Direct nitration of piperidine in trifluoroacetic anhydride was attempted unsuccessfully; only piperidine was recovered. Inclusion of catalytic amounts of zinc chloride in this medium also failed to yield any nitropiperidine, although chloride catalysis in acetic anhydride has been reported[4] to produce this nitramine in 58% yield. An alternative nitrolysis procedue also was tried without success. Piperidine was added to a formic acid–trifluoroacetic anhydride solution to allow mixed anhydride formylation *in situ* prior to addition of nitric acid. Although an unexamined reaction occurred in the formylation step, no nitramine was obtained.

The interesting observation was made during this study that many water-soluble N,N-dialkylamides formed water-insoluble adducts with trifluoroacetic acid. For example the formamides and acetamides of diethylamine, diisopropylamine di-*n*-propylamine and piperidine formed insoluble oils when one mole equivalent of trifluoroacetic acid was added to their dilute aqueous solutions. Treatment of these adducts with solid potassium carbonate allowed recovery of the original amide. The trifluoroacetic acid content of these adducts was found to be widely variable as determined by base titration to a phenolphthalein end-point. Although they could be distilled over a very narrow (1–2°) temperature range, successive fractions over the range showed large decreases in acid content. Since their solutions in absolute ethanol were strongly conducting, these adducts appeared to be salts of the weakly basic amides with a surprising insolubility in water. Perchloric acid also formed similar water-insoluble adducts while sulfuric and hydrochloric acids did not.

Experimental[9]

Except where indicated, the nitrolyses were performed according to the method given below for N,N-di-*n*-butylacetamide. In most cases the nitramines were known compounds, readily isolated and purified by distillation; otherwise their isolation and/or characterization is described.

(6) W. H. Van Dorp, *Rec. trav. chim.*, **28**, 68 (1908).

(7) A. P. N. Franchimont, *ibid.*, **2**, 336 (1883); A. P. N. Franchimont and E. A. Klobbie, *ibid.*, **6**, 234 (1887).

(8) A. P. N. Franchimont and E. A. Klobbie, *ibid.*, **8**, 283 (1889); **5**, 274 (1886).

(9) All melting and boiling points are reported uncorrected.

N,N'-Diformylpiperazine.—One hundred grams (0.515 mole) of piperazine hydrate was added to 98 cc. (2.17 moles) of 98% formic acid and the solution refluxed 30 minutes. Distillation at 1 mm. then gave a fraction boiling at 170–175° which solidified upon cooling. Recrystallization from absolute ethanol gave 62.2 g. (85%) of the diamide, m.p. 127.5–128.5°, insoluble in ether, acetone or benzene but very soluble in water.

Anal. Calcd. for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N, 19.71. Found: C, 50.9, 50.7; H, 6.63, 6.62; N, 19.7, 20.0.

N,N-Di-*n*-hexylacetamide.—This compound was prepared by the reaction of distilled di-*n*-hexylamine with excess acetic anhydride. Distillation gave 72% of the amide, b.p. 106–107° (7.6 mm.), $n^{25}D$ 1.4506.

Anal. Calcd. for $C_{14}H_{29}NO$: C, 73.93; H, 12.88; N, 6.16. Found: C, 74.6; H, 12.8; N, 5.82.

N,N-Di-*n*-heptylacetamide was prepared in 93% yield by the same method used for the previous compound, b.p. 147.9–148.2° (1.0 mm.), $n^{25}D$ 1.4526.

Anal. Calcd. for $C_{16}H_{33}NO$: C, 75.23; H, 13.02; N, 5.48. Found: C, 74.9; H, 12.9; N, 5.18.

N,N-Di-*n*-butyltrichloroacetamide.—To a solution of 52.8 g. (0.29 mole) of trichloroacetyl chloride in 100 cc. of benzene was added 75.0 g. (0.58 mole) of distilled di-*n*-butylamine. After removing the amine hydrochloride by filtration, the filtrate was distilled to yield 66.0 g. (83%) of the amide, b.p. 121–122° (1 mm.). An analytical sample was obtained by a second fractionation, $n^{25}D$ 1.4824.

Anal. Calcd. for $C_{10}H_{18}NOCl_3$: C, 43.73; H, 6.61; N, 5.10. Found: C, 43.5; H, 6.49; N, 4.97.

N,N-Di-β-cyanoethylacetamide was prepared in 67% yield by the method described for N,N-di-*n*-hexylacetamide b.p. 210–212° (1.0 mm.), $n^{25}D$ 1.4837, soluble in water, insoluble in ether.

Anal. Calcd. for $C_8H_{11}N_3O$: C, 58.20; H, 6.67; N, 25.41. Found: C, 58.2; H, 6.64; N, 25.8.

N,N-Dialkylmethanesulfonamides.—Both the diethyl and di-*n*-butyl derivatives of methanesulfonamide have been reported by Marvel, *et al.*,[10] but only as unidentified oils which gave the correct amines upon hydrolysis. Therefore they are more fully characterized below.

N,N-Diethylmethanesulfonamide was water insoluble and boiled at 102.3–103.0° (5.6 mm.), $n^{25}D$ 1.4461.

Anal. Calcd. for $C_5H_{13}NO_2S$: C, 39.71; H, 8.66. Found: C, 39.9; H, 8.59.

N,N-Di-*n*-butylmethanesulfonamide was water insoluble and boiled at 106–108° (1 mm.), $n^{25}D$ 1.4503.

Anal. Calcd. for $C_9H_{21}NO_2S$: C, 52.13; H, 10.21; N, 6.76. Found: C, 52.3; H, 10.8; N, 6.64.

2,6-Diformyl-2,6-diaza-4-oxaheptane.—A suspension of 18.7 g. (0.59 mole) of 95% paraformaldehyde, 70.0 g. (1.18 moles) of N-methylformamide (prepared by the method of D'Alelio[11]) and 1.0 cc. of concentrated hydrochloric acid was held at 115° for 18 hours. Distillation at 100° and 0.1 mm. left a residue which partially crystallized upon cooling. Three recrystallizations from methyl isobutyl ketone (1 cc./g.) gave 30.0 g. (64%) of product, m.p. 64.5–66.0°, which was soluble in water but insoluble in hexane and carbon tetrachloride. The crystal density, determined by the flotation method, was 1.301 at 25°. Based on this density, X-ray unit cell data indicated a molecular weight of 157, while theory required 160.

Anal. Calcd. for $C_6H_{12}N_2O_3$: C, 44.98; H, 7.50; N, 17.50. Found: C, 45.09, 45.55; H, 7.50, 7.42; N, 17.7, 17.8.

Ethyl N,N-Dialkylcarbamates.—The monobutyl-, diethyl- and dibutylcarbamates were prepared by the general method of Hartman.[12] The ethyl N,N-di-*n*-butylcarbamate boils at 109–110° (11 mm.), $n^{20}D$ 1.4327.

Anal. Calcd. for $C_{11}H_{23}NO_2$: C, 65.7; H, 11.4; N, 6.97. Found: C, 66.1; H, 11.4; N, 6.88.

The Reaction of N,N-Diisopropylformamide and Trifluoroacetic Acid.—To a solution of 12.9 g. (0.10 mole) of the amide in 75 cc. of water was added 8.43 cc. (0.11 mole) of trifluoroacetic acid. There was a considerable evolution of heat and a lower oil layer formed immediately. Separation and filtration to remove suspended water gave 18.9 g. of clear oil, an 85% yield based on a 1:1 adduct of amide and acid. Titration of this oil with standard base to a phenolphthalein end-point gave a neutral equivalent of 293 (required neut. equiv. for a 1:1 adduct is 243). This oil was treated with excess potassium carbonate and the residual oil extracted with ether; distillation of the ethereal extract gave 7.69 g. (64.5%) of N,N-diisopropylformamide, b.p. 96–97° (26 mm.), $n^{25}D$ 1.4350. Since the oil is partially water soluble this recovery of amide was low. One drop of the oil in 200 cc. of absolute ethanol gave a strongly conducting solution.

In a second experiment, the amide–acid adduct was distilled through a Vigreux column and the product, boiling over the range 94–96° (9.2 mm.), was collected in several fractions. These fractions had neutral equivalents ranging from 272 to 554, indicating that a loss of acid occurred during distillation even though the entire amount of material distilled at a nearly constant temperature.

The Reaction of N,N-diisobutylacetamide and Trifluoroacetic Acid.—When a suspension of this amide in water was treated with trifluoroacetic acid as described above, an 89.5% yield (based on a 1:1 adduct) of oil was obtained, b.p. 87–88° (1.0 mm.), neutral equivalent 334 (required for a 1:1 adduct 285). This oil also gave a conducting ethanol solution and its treatment with potassium carbonate allowed a 91% recovery of the starting amide.

In a second experiment the amide–acid adduct, after distillation at 88° and 1.0 mm., had a neutral equivalent of 370. Assuming it to contain only amide and acid, its composition was calculated to be 69.2% di-*i*-butylacetamide and 30.8% trifluoroacetic acid.

Anal. Calcd. for the above mixture: C, 55.0; H, 8.80; N, 5.76. Found: C, 54.7; H, 8.89; N, 6.13.

The Nitrolysis of N,N-Di-*n*-butylacetamide.—To 80 cc. (0.58 mole) of trifluoroacetic anhydride, cooled to 5°, was added 5 cc. of absolute (98–100%) water-white nitric acid. After a short induction period, reaction was evidenced by heat evolution, and 11.8 cc. of nitric acid (total 0.40 mole) was added dropwise at 0–5°. This solution was maintained at −5° to −10° while 17.1 g. (0.10 mole) of N,N-di-*n*-butylacetamide (prepared by the method of Sowa,[13] was added dropwise. After stirring 20 minutes at −5° the solution was rapidly reduced to *ca.* half volume by distillation at −10° and 20 mm., and the residue poured onto 50 g. of ice. After making the two-phase solution basic with 50% potassium hydroxide, the oil phase was extracted with ether, dried over magnesium sulfate and distilled to give di-*n*-butylnitramine, b.p. 123–124° (8–9 mm.), $n^{25}D$ 1.4556 (literature values[14] b.p. 127–130° (11 mm.), $n^{25}D$ 1.4557). This product, weighing 14.2 g. (82%), was shown to contain no starting amide or di-*n*-butylnitrosamine since its extraction with concentrated hydrochloric acid gave no acid-soluble material upon neutralization of the aqueous extract.

The Nitrolysis of N,N'-Diformylpiperazine. A. With Acetic Anhydride.—A mixture of 30 cc. (0.31 mole) of purified acetic anhydride and 10 cc. (0.17 mole) of glacial acetic acid was cooled to −10° and 14.4 cc. (0.34 mole) of absolute nitric acid added at that temperature. To this solution was added 4.9 g. (0.034 mole) of diformylpiperazine. After two hours at 25°, the suspension was filtered to give 7.7 g. of crystalline solid, m.p. 85–90°, which was entirely water soluble. No dinitropiperazine was formed, as shown by this water solubility of the crude product. Repeated recrystallizations from ethyl acetate and ethanol gave only one product, 4.2 g. (60%) of piperazine nitrate trihydrate, m.p. 240° dec. The same compound was prepared by treating a saturated aqueous solution of piperazine hexahydrate with excess concentrated nitric acid. Cooling and filtering yielded the mononitrate salt whose melting point, 241° dec., was not depressed by admixture with the above product. Its neutral equivalent was 203 (calcd. 203).

B. With Trifluoroacetic Anhydride.—This reaction was run by the method used for N,N-di-*n*-butylacetamide.

(10) C. S. Marvel, M. D. Helfrick and J. P. Belsley, THIS JOURNAL, **51**, 1272 (1929).

(11) G. F. D'Alelio and E. E. Reed, *ibid.*, **59**, 109 (1939).

(12) W. W. Hartman and M. R. Brethen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 278.

(13) F. J. Sowa and J. A. Nieuwland, THIS JOURNAL, **59**, 1202 (1937).

(14) W. J. Chute, *et al.*, *Can. J. Research*, **26B**, 114 (1948).

After removal of about 50% of the volatile solvents at 35 mm. and −5°, the reaction mixture was poured into 200 cc. of ice-water and filtered to give 4.14 g. (45%) of product, m.p. 207–212°. The recrystallization from methyl ethyl ketone (50 cc./g.) gave the dinitramine melting of 215–216° (literature value[6] m.p. 215°).

Nitrolysis of 2,6-Diformyl-2,6-diaza-4-oxaheptane.—This nitrolysis was made in the same manner as described for N,N-di-*n*-butylacetamide. Considerable gassing and the evolution of nitrogen oxides was observed during addition of the amide to the nitric acid–trifluoroacetic anhydride mixture. No water-insoluble product was formed and continuous ether extraction of the basic aqueous solution of the reaction mixture gave only a trace (0.1 g.) of an oil which was not identified.

Di-*n*-hexylnitramine.—This compound was prepared by the nitrolysis of N,N-di-*n*-hexylacetamide according to the above procedure (see N,N-di-*n*-butylacetamide) in 95% crude yield, m.p. 3–6°, b.p. 107–108° (0.4 mm.). A second distillation raised the m.p. to 6–7°, $n^{25}D$ 1.4587.

Anal. Calcd. for $C_{12}H_{26}N_2O_2$: C, 65.41; H, 11.89; N, 12.72. Found: C, 64.8; H, 11.9; N, 12.49.

Di-*n*-heptylnitramine was prepared by the nitrolysis of N,N-di-*n*-heptylacetamide according to the above procedure (see N,N-di-*n*-butylacetamide). Evaporation of the dried ether extracts gave the crude nitramine in 98.5% yield, m.p. 21–22°. Distillation at 0.4 mm. gave a product melting at 23.5°, b.p. 138–140°, $n^{25}D$ 1.4598. Some decomposition at this distillation temperature was evidenced by the faint yellow color of the distillate.

Anal. Calcd. for $C_{14}H_{30}N_2O_2$: C, 65.07; H, 11.70; N, 10.84. Found: C, 65.3; H, 11.8; N, 10.20.

Nitrolysis of N,N-Di-*n*-butylbenzenesulfonamide.—The nitrolysis of this amide (prepared by the method of Wright[15]) was performed as described for N,N-di-*n*-butylacetamide. After extraction of the basic aqueous solution to remove the nitramine, the aqueous phase was concentrated to half volume and chilled to yield substantial amounts of what presumably was a mixture of nitrated potassium benzenesulfonates. Since fractional crystallization failed to yield pure compounds, further purification was not attempted.

Nitrolysis of Ethyl N,N-Diethylcarbamate.—To a mixture of 16.8 cc. (0.40 mole) of absolute nitric acid and 80 cc. (0.58 mole) of trifluoroacetic anhydride which had been prepared at 0°, was added dropwise 14.5 g. (0.10 mole) of the carbamate (prepared by the method of Braun[16]). Very efficient cooling was required to maintain the temperature at −5°, and a deep blue-green color developed, probably due to a nitrogen dioxide–nitrogen trioxide mixture. When addition was complete, the solution was distilled at 0° and reduced pressure to yield a deep blue oil which decomposed with gassing when the temperature was raised to 75° at 0.5 mm. This oil evolved gas copiously when poured onto 100 g. of ice. Extraction of the aqueous solution with 4 × 25 cc. of ether, followed by drying and distillation of the ethereal extracts gave 1.5 g. (12.8%) of ethyl N-ethylcarbamate, b.p. 170° (705 mm.), $n^{20}D$ 1.4215 (literature values[17] b.p. 174–175°, $n^{20}D$ 1.42192). The infrared spectrum of this compound was consistent with this structure since it showed amide I and II bands at 1709 and 1542 cm.$^{-1}$, which coincided with those of authentic ethyl N-*n*-butylcarbamate. No diethylnitramine was found. Distillation of the aqueous phase after ether extraction gave about 10 g. of yellow oil which could not be distilled or crystallized.

Nitrolysis of Ethyl N,N-Di-*n*-butylcarbamate.—This reaction was run similarly to that above except that upon pouring the blue reaction product onto ice the resulting suspension was made basic before ether extraction. Upon distillation of the ethereal extracts there was obtained 10.5 g. (72.5%) of ethyl N-*n*-butylcarbamate, b.p. 94.6° (10 mm.) (literature value[18] b.p. 100° (15 mm.)). Its infrared spectrum was identical with that of authentic monobutylcarbamate. Since di-*n*-butylnitrosamine was suspected as a possible impurity, comparison of the ultraviolet spectra of both authentic dibutylnitrosamine and this above product was made. By this means it was proven that the concentration of nitrosamine must be below 5% if present at all.

(15) J. W. Suggitt and G. F. Wright, THIS JOURNAL, **69**, 2073 (1947).
(16) V. Braun, *Ber.*, **36**, 2287 (1903).
(17) O. Schreiner, *J. prakt. Chem.*, [2] **21**, 125 (1880).
(18) V. Erp, *Rec. trav. chim.*, **14**, 18 (1895).

Nitrolysis of N,N-Diisopropylformamide.—To a mixture of 21.0 cc. (0.50 mole) of absolute nitric acid and 100 cc. (0.725 mole) of trifluoroacetic anhydride, prepared at 0°, was added rapidly 16.1 g. (0.125 mole) of N,N-diisopropylformamide (prepared as previously described[19]), at −5°. After standing two hours at 0° the solution was distilled at 0° and 20 mm. to approximately half-volume and poured onto 100 g. of ice. A 50% potassium hydroxide solution was added until the *p*H was between 1 and 2 (Aquatint paper) and the oil layer extracted with methylene chloride. After drying over magnesium sulfate, distillation of the ethereal solution gave 15.8 g. of oil, b.p. 98–101° (10.5 mm.). The infrared spectrum of this oil was identical with the spectrum of the oil shown above to be an adduct of N,N-diisopropylformamide and trifluoroacetic acid. Its neutral equivalent (364) indicated that it contained 67.5% of the starting amide. Since this oil gave no water-insoluble product when dissolved in dilute base, no diisopropylnitrosamine or nitramine was present.

Nitrolysis of N,N-Diisobutylacetamide.[18]—After nitrolysis in the usual manner (see N,N-di-*n*-butylacetamide) the crude reaction product was poured onto ice. This solution was partially neutralized with 50% potassium hydroxide and the acidic oil suspension, *p*H 1, extracted with methylene chloride; distillation of the organic extracts yielded the N,N-di-isobutylacetamide–trifluoroacetic acid complex described above. This was shown by titration with base to contain 81% of the starting amide. Upon dissolving the complex in 2 l. of water at *p*H 9 there was obtained by filtration 0.72 g. (4.1%) of di-isobutylnitramine, m.p. 81.5–82.5°. Recrystallization from 80% methanol did not raise this melting point. This compound has been reported previously by Chute, *et al.*,[14] as a liquid boiling at 104° (11 mm.). These authors carried out a nitration of diisobutylamine in acetic anhydride and described two of their products as "diisobutylacetamide," m.p. 73.4–74.5°, and "diisobutylnitramine," b.p. 104° (11 mm.). Our corresponding acetamide[19] and nitramine reversed these physical properties; *i.e.*, acetamide, b.p. 102.5–103° (9.8 mm.), and nitramine, m.p. 81.5–82.5°. Furthermore, Chute's literature reference in substantiation of the "diisobutylacetamide" structure actually referred to a different compound. Since our method of preparation of the acetamide is unequivocal, it is suggested that the identity of the two products was inadvertently reversed in the earlier work. An analysis was made of our product, postulated to be diisobutylnitramine.

Anal. Calcd. for $C_8H_{18}N_2O_2$: C, 55.2; H, 10.34; N, 16.1. Found: C, 55.0; H, 10.5; N, 16.2.

In a second experiment the nitrolysis reaction, after addition of the amide at −5°, was held at 20° for four hours, the volatile components removed by distillation at −5° and 20 mm., the resulting oil diluted with 100 g. of ice and then made basic with 50% potassium hydroxide. Filtration gave an oily solid which upon recrystallization from 80% methanol yielded 2.5 g. (14.5%) of the nitramine, m.p. 81.5–82.5°.

Nitrolysis of N,N-Di-*n*-butylurea.—This nitrolysis was performed on a 0.1-mole scale as described for N,N-di-*n*-butylacetamide. After pouring the reaction mixture onto ice and making basic, it was extracted with ether (4 × 50 cc.), the ethereal extracts dried over magnesium sulfate and concentrated to a crystalline slurry. Trituration of this mixture with 30 cc. of hexane allowed the filtration of a crystalline fraction which upon recrystallization from a 10:1 mixture of hexane–methyl isobutyl ketone gave 10.9 g. (45%) of di-*n*-butylammonium trifluoroacetate, m.p. 138–139°. The identity of this product was shown by the fact that its melting point was not depressed upon admixture with di-*n*-butylammonium trifluoroacetate prepared in the following manner: distilled di-*n*-butylamine in hexane was neutralized carefully with one equivalent of trifluoroacetic acid and the resulting precipitate recrystallized from a hexane–methyl isobutyl ketone mixture, m.p. 139–140°.

Distillation of the hexane extract yielded 1.2 g. (5.4%) of N,N-di-*n*-butyltrifluoroacetamide[19] and 3.2 g. (18.0%) of di-*n*-butylnitramine. Comparison of the infrared spectra of the latter two products with spectra of authentic samples proved their identity but showed them to be quite impure.

Attempted Nitration of Piperidine. A.—To a mixture of 18.3 cc. (0.44 mole) of absolute nitric acid in 67 cc. (0.49 mole) of trifluoroacetic anhydride prepared at 0° was added

(19) J. H. Robson and J. Reinhart, THIS JOURNAL, **77**, 498 (1955).

rapidly 14.8 g. (0.10 mole) of piperidinium nitrate, made by the method of Chute.[4] The resulting solution was maintained two hours at 25°, concentrated to approximately half-volume by distillation at reduced pressure, poured onto 100 g. of ice and then made basic (*p*H 9) with 10 *N* sodium hydroxide. This solution contained no water-insoluble N-nitropiperidine. Its continuous ether extraction (5 hours), followed by drying the ethereal solution over magnesium sulfate and saturating with dry hydrogen chloride, gave 7.31 g. (60.5%) of piperidinium hydrochloride, m.p. 238–240° (literature value[20] m.p. 237°).

B. With Chloride Catalysis.—The following reagents were mixed in the manner described in A above and allowed to react for one hour at 20° and one hour at 35° (reflux): 0.068 mole of piperidinium nitrate, 0.196 mole of trifluoroacetic anhydride, 0.034 mole of absolute nitric acid and 0.0034 mole of anhydrous zinc chloride. No water-insoluble N-nitropiperidine was formed; unreacted piperidine was not isolated in this experiment.

C. With Preliminary Formylation.—To 69 cc. (0.50 mole) of trifluoroacetic anhydride at 0° was added 5.66 cc. (0.15 mole) of 98% formic acid and then, at −50°, 8.4 g. (0.10 mole) of freshly distiled piperidine. The latter addition was very exothermic. When completed (20 minutes), the solution was warmed to −20° and 6.3 cc. (0.15 mole) of absolute nitric acid was added dropwise, causing a vigorous evolution of colorless gas. After one hour at −20°, the reaction mixture was concentrated to approximately half volume by distillation at −10° and 20 mm., then poured onto 100 g. of ice. After making basic (*p*H 9), no water-insoluble product was found, indicating N-nitropiperidine to be absent.

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(20) A. Ladenburg, *Ber.*, **18**, 2959 (1885).

[CONTRIBUTION FROM THE SCHOOL OF SCIENCE, BRANDEIS UNIVERSITY]

Azo-bis-diphenylmethane and the Decomposition of Aliphatic Azo Compounds. The Diphenylmethyl Radical[1]

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Azo-bis-diphenylmethane, $(C_6H_5)_2CH—N=N—CH(C_6H_5)_2$ (I), has been prepared and compared with the isomeric benzophenone benzhydrylhydrazone. The reduction of benzophenone hydrazone to benzhydrylhydrazine by lithium aluminum hydride is described. The azo compound I decomposed in toluene with first-order kinetics, E_A = 26.6 kcal. mole^{-1}, $\Delta S^{\pm}$ = 2.2 cal. mole^{-1} degree^{-1}. Comparison of azomethane, azo-bis-2-propane, 1-azo-bis-1-phenylethane and I indicates that symmetrical substitution of a pair of methyls for hydrogen lowers E_A 5 kcal., substitution of a pair of phenyls for hydrogen lowers E_A 12 kcal. The results are discussed in terms of resonance stabilization of the radicals. The decomposition of I leads to diphenylmethyl radicals which dimerize, forming 1,1,2,2-tetraphenylethane, quantitatively in the absence of solvent and in somewhat lower yield in several hydrocarbon solvents. The diphenylmethyl radical initiates the polymerization of styrene. Comparison with benzoyl peroxide indicates that the initiation step is slow and that the diphenylmethyl radical also terminates chains.

As part of our study of the decomposition of azo compounds and of the reactions of the free radicals which may thereby be produced, it was of interest to us to prepare and decompose azo-bis-diphenylmethane, $(C_6H_5)_2CH—N=N—CH(C_6H_5)_2$ (I), and to examine the chemistry of the diphenylmethyl radical. The preparation of this azo compound, the kinetics of its decomposition, the yield of 1,1,2,2-tetraphenylethane formed by its decomposition in several hydrocarbon solvents and its effectiveness as an initiator of the polymerization of styrene are described in this paper. The kinetics of decomposition and the initiation of polymerization are compared with those of some other relevant sources of free radicals.

Preparation of Azo-bis-diphenylmethane.—The azo compound I was prepared from benzophenone and hydrazine by the following series of reactions which are similar in general and differ in some details from the reactions used to convert other ketones to the respective secondary azo-bis-alkanes.[2,3]

$$(C_6H_5)_2C{=}O + H_2NNH_2 \longrightarrow$$

$$(C_6H_5)_2C{=}NNH_2 \xrightarrow{H^+ \text{ or } OH^-}$$

$$(C_6H_5)_2C{=}NN{=}C(C_6H_5)_2 \xrightarrow{2H_2,Pt}$$

$$(C_6H_5)_2CHNHNHCH(C_6H_5)_2 \xrightarrow{H_2O_2 \text{ or } HgO} (C_6H_5)_2CH—N=N—CH(C_6H_5)_2$$

The conversion of benzophenone to the azine *via* the hydrazone is convenient and makes unnecessary the use of a sealed tube.[4] The reduction of benzophenone azine to N,N′-bis-benzhydrylhydrazine and benzhydrylamine by sodium amalgam in ethanol had been described previously.[5] When our first attempts to carry out this hydrogenation catalytically failed, the reduction by lithium aluminum hydride was examined. Reaction in ether led to an unstable white compound which decomposed on standing to a yellow viscous mixture from which the original azine was recovered. Treatment of the azine with this reagent at 90–100° led to rupture of the molecule and isolation of 1,1,2,2-tetraphenylethane, and apparently, diphenylmethane. Conditions for satisfactory hydrogenation over platinum oxide at slightly elevated temperature to form N,N′-bis-benzhydrylhydrazine were then worked out. The oxidation of this hydrazine with mercuric oxide had been reported[5] to lead not to the azo compound I, but to the decomposition products 1,1,2,2-tetraphenylethane and nitrogen. The oxidation had been carried out at too high a temperature. Despite occasional difficulties in this preparation, oxidation of the hydrazine with either hydrogen peroxide or

(1) Presented at the Meeting of the American Chemical Society, New York, September 13, 1954.

(2) H. L. Lochte, W. A. Noyes and J. R. Bailey, THIS JOURNAL, **44**, 2556 (1922).

(3) See S. G. Cohen, S. J. Groszos and D. B. Sparrow, *ibid.*, **72**, 3947 (1950), for other references.

(4) E. R. Blout, V. Eager and R. M. Gofstein, *ibid.*, **68**, 1983 (1946).

(5) A. Darapsky, *J. prakt. Chem.*, **67**, 112, 164 (1903).