

monium chloride; (b) hydrogenation of this material gave dieneopentylamine; (c) the infrared spectrum of the material showed a very narrow, pronounced absorption at 6.01μ characteristic of the C=N group and a wider, less pronounced absorption at 3.00μ indicating the presence of NH.

EXPERIMENTAL^{6,7}

t-Butylmagnesium chloride and trimethylacetonitrile. To a titrated ether solution of 0.172 mole of *t*-butylmagnesium chloride in a stainless steel autoclave was added 11.6 g. (0.135 mole) of trimethylacetonitrile (b.p. $104-105^\circ$). The autoclave was quickly sealed under a blanket of nitrogen and heated for 12 hr. at 150° . After the autoclave was cooled, the contents were hydrolyzed in an aqueous solution of ammonium chloride at 0° , and the ether layer and ether extracts of the aqueous layer were dried over anhydrous sodium sulfate. The ether was removed by fractionation through a sixteen-plate column and the residue was fractionated further from a column of small holdup to give the following cuts: 1-3 ether; cuts 4-5, b.p. $68-71^\circ$, n_D^{25} 1.3803-1.3829, 1.10 g., impure trimethylacetaldehyde; cut 6, b.p. $71-92^\circ$, n_D^{25} 1.3900, 0.45 g.; cuts 7-8, b.p. $92-118^\circ$, n_D^{25} 1.3860-1.3898, 0.81 g., impure trimethylacetonitrile and hexamethylethane; cut 9, b.p. $118-141^\circ$, n_D^{25} 1.4029, 0.36 g.; cuts 10-15, b.p. $141-145^\circ$, n_D^{25} 1.4080-1.4099, 3.42 g., 2,2-dimethylpropylidene-2',2'-dimethylpropylamine; cuts 16-19, b.p. $110-115^\circ$ (15 mm.), n_D^{25} 1.4334-1.4376, 3.58 g., high boiling mixture of unknown structure; residue 0.59 g. The material from cuts 4-5 gave a 2,4-dinitrophenylhydrazone, m.p. $205-206^\circ$; melting point when mixed with an authentic sample of 2,4-dinitrophenylhydrazone of trimethylacetaldehyde. $206-207^\circ$.

Cuts 10-15 were further purified by means of gas-liquid partition chromatography. The infrared spectrum of the aldimine (I) was identical to the aldimine prepared from trimethylacetaldehyde and neopentylamine.⁵ Infrared spectrum included bands at $3.40(s)$, $3.56(s)$, $5.98(s)$, $6.77(s)$, $6.95(m)$, $7.18(m)$, $7.33(s)$, $8.00(w)$, $8.26(m)$, $9.38(m)$, $9.89(w)$, $10.52(w)$, $11.13(m)$, and $13.42(w) \mu$.

Infrared analysis of the gas collected when the autoclave was vented showed that it consisted of a mixture of isobutylene and ether.

A second experiment in which 2.6 molar equivalents of Grignard reagent were used was carried out as indicated above starting with 10 g. (0.120 mole) of trimethylacetonitrile and 0.316 mole of *t*-butylmagnesium chloride. After fractionation there was obtained trimethylacetaldehyde 1.72 g. (17%), 2,2-dimethylpropylidene-2',2'-dimethylpropylamine 2.39 g. (26%) and 4.42 g. b.p. $86-90^\circ$ (9 mm.) of the high-boiling material of unknown structure.

Hydrogenation of the high-boiling material. The material from cuts 16-19, 548 mg., methanol, 15 ml., and Raney nickel catalyst, approximately 150 mg., were stirred under one atmosphere of hydrogen in a microhydrogenation apparatus for 34 hr. A total uptake of 100.9 ml. of hydrogen at 18° was recorded. This corresponds to an equivalent weight of 128 ± 5 . The basic product from this reduction was separated by extraction with acid and was regenerated with base. The phenylthiourethane melted at $138-140^\circ$; melting point when mixed with a known sample of the phenylthiourethane of dieneopentylamine,⁵ $138-140^\circ$.

Hydrolysis of the high-boiling material. To 20 ml. of 6*N* hydrochloric acid was added 500 mg. of high boiling material. The reaction mixture was heated for 30 min. at 100°

(6) All melting points and boiling points are uncorrected; microanalysis was done by Microchemical Specialties Company, Berkeley, Calif.

(7) Infrared spectra were taken with a Perkin-Elmer Model 21 Recording Infrared Spectrophotometer.

because the material appeared to be quite unreactive in the acid solution. The ether extract gave a 2,4-dinitrophenylhydrazone, m.p. $205-206^\circ$; melting point when mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of trimethylacetaldehyde, $205-206^\circ$. Ammonium chloride was isolated from the aqueous acid layer by evaporation. After standing one month white crystals had separated in the vial containing the high boiling material. These crystals were separated, washed with petroleum ether and sublimed; m.p. $153.5-154.5^\circ$; melting point when mixed with an authentic sample of trimethylacetamide $154-155^\circ$.

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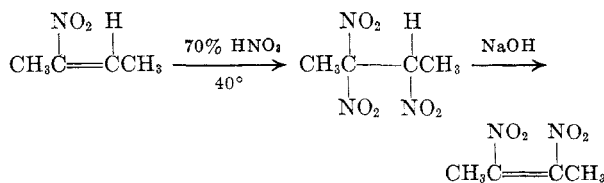
Nitration of Nitroolefins with Nitric Acid

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The addition of dinitrogen tetroxide to simple olefins has been studied extensively by Levy and Scaife¹ who isolated and characterized three types of reaction products—dinitroalkanes, nitroalcohols, and nitroalkylnitrates. This reaction has also been applied to nitroolefins. The addition of dinitrogen tetroxide to 2-nitro-2-butene and 2,3-dinitro-2-butene has given 2,2,3-trinitrobutane² and 2,2,3,3-tetranitrobutane,³ respectively. The nitration of olefins with nitric acid has been studied by various workers,⁴ but to our knowledge the reaction of nitroolefins and nitric acid has not been reported.

We have studied the reaction of 2-nitro-1-propene, 2-nitro-1-butene, and 2-nitro-2-butene with 70% nitric acid under various conditions. Mixtures were obtained from these reactions and only in the case of 2-nitro-2-butene, where a solid product was obtained, was it possible to purify and identify the major product. When the nitric acid was warmed to 40° and 2-nitro-2-butene was added dropwise at this temperature, there was isolated a 25.3% yield of a white solid, m.p. $46-48^\circ$. The analysis of this product corresponded to an empirical formula of $C_4H_7N_3O_6$, a trinitrobutane. The structure of the trinitrobutane was established as 2,2,3-trinitrobutane by degradation with base to the known 2,3-dinitro-2-butene:



(1) N. Levy and C. W. Scaife, *J. Chem. Soc.*, 1093, 1096, 1100 (1946).

(2) OSRD Rept. 2016, Nov. 15, 1943.

(3) C. E. Gabriel, D. E. Bisgrove, and L. B. Clapp, *J. Am. Chem. Soc.*, **77**, 1293 (1955).

(4) H. Wieland and E. Sakellarios, *Ber.*, **53**, 201 (1920); A. D. Petrov and M. A. Bulygina, *Doklady Akad. Nauk, S.S.S.R.*, **77**, 1031 (1951).

EXPERIMENTAL^{5,6}

Nitration of 2-nitro-2-butene. Nitric acid, 150 ml. of 70%, was warmed to 40° and 25 g. (0.25 mole) of 2-nitro-2-butene⁷ was added dropwise in 90 min. The temperature was maintained at 39 to 41° by intermittent cooling during the addition and for 1 hr. after the addition was completed.⁸ At the end of this time, the temperature began to drop, indicating that the reaction was completed. The mixture was cooled to 5°, causing a white solid to separate, and poured onto ice. The white solid was collected, washed thoroughly with water, and dried *in vacuo* over potassium hydroxide. The yield of 2,2,3-trinitrobutane was 12.1 g. (25.3%), m.p. 42–45°. Recrystallization from isopropyl ether raised the melting point to 46–48°. A Liebermann test for the nitro group was negative.

Anal. Calcd. for C₄H₇N₃O₆: C, 24.88; H, 3.65; N, 21.76; mol. wt., 193. Found: C, 24.85; H, 3.75; N, 22.00; mol. wt., 211.

Proof of structure of 2,2,3-trinitrobutane. A solution of 19.3 g. (0.10 mole) of 2,2,3-trinitrobutane in 150 ml. of ether was cooled to 18–20° and a solution of 4.0 g. (0.10 mole) of sodium hydroxide in 50 ml. of water was added dropwise with stirring. The yellow ether layer was separated and the orange aqueous layer was extracted with ether. The combined ether extracts were dried and concentrated leaving 13.3 g. (91.2%) of yellow liquid. A sample was distilled from a Claisen flask, b.p. 102–103° (2.5 mm.), *n*_D²⁵ 1.4830, m.p. 26°.⁹

Anal. Calcd. for C₄H₆N₂O₄: C, 32.86; H, 4.12; N, 19.17. Found: C, 32.69; H, 4.19; N, 18.79.

When treated with ammonia it produced 2-amino-3-nitro-2-butene, m.p. 159–160°, identical to the product previously obtained from the reaction of 2,3-dinitro-2-butene with ammonia.¹⁰

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(5) All melting points are uncorrected.

(6) Microanalyses by Elek Microanalytical Laboratories, Los Angeles, Calif.

(7) H. B. Hass, *J. Org. Chem.*, **15**, 8–14 (1950).

(8) When 2-nitro-2-butene and 70% nitric acid were mixed at 5–10° and then allowed to warm up, a fume off occurred.

(9) E. M. Nygaard and T. T. Noland, U. S. Patent 2,396,282, March 12, 1946, reported 2,3-dinitro-2-butene to have a boiling point of 97–100° (1–2 mm.) and a melting point of 25.9°.

(10) L. B. Clapp, J. F. Brown, Jr., and L. ZefTel, *J. Org. Chem.*, **15**, 1043 (1950).

Amount of β -Isomer Formed in the Bromination of Naphthalene¹

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In connection with a recent study of the kinetics of bromination of naphthalene in 50% aqueous

(1) Taken from the senior honors thesis of F. J. Ochs, 1957.

acetic acid,² it seemed important to determine the amount of β -bromonaphthalene formed under these conditions. The extent of β -bromination has not previously been determined in solution, but its presence could be inferred from other data. Wibaut and co-workers have determined the amount of α - and β -bromonaphthalene in uncatalyzed *liquid phase* bromination in the temperature range 85–215°, and in the gas phase.³ In the gas phase above 300° the reaction follows a free-radical course, but in the liquid phase a polar reaction occurs, and the amount of β -isomer varies with temperature from 3% to 6.8%. Small amounts of β -isomer are formed in nitration,⁴ and apparently also in chlorination⁵ and iodination.⁶ More significant amounts are obtained in the Friedel-Crafts acylation⁷ and alkylation,⁸ and in sulfonation,⁹ although, at least in the last two cases, the proportions of isomers are determined by their equilibrium concentrations, rather than their rates of formation.¹⁰

The amount of β -bromination of naphthalene at 25° in 50% aqueous acetic acid was determined by the isotopic dilution method, using molecular bromine containing the isotope Br⁸² as the substituting agent and adding an excess of inactive β -bromonaphthalene to the completed reaction mixture. From the amount and the activity of the recovered pure β -bromonaphthalene, the extent of β -bromination could be calculated. The percentages of β -isomer in three different runs, each 0.01M in naphthalene, 0.1M in potassium bromide, and approximately 0.005M in bromine, were 1.07 \pm 0.056, 0.981 \pm 0.024, and 0.992 \pm 0.032. The weighted average¹¹ is 1.00 \pm 0.02, and this represents the percent β -bromonaphthalene in the total bromination products.

(2) E. Berliner and M. C. Beckett, *J. Am. Chem. Soc.*, **79**, 1425 (1957).

(3) (a) J. F. Suyver and J. P. Wibaut, *Rec. trav. chim.*, **64**, 65 (1945); (b) G. M. Badger, *The Structure and Reactions of the Aromatic Compounds*, Cambridge University Press, Cambridge, 1954, pp. 259–262.

(4) See M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 1441 (1956) for the most recent determination and for previous references.

(5) Quoted by R. W. Beattie and F. C. Whitmore, *J. Chem. Soc.*, 50 (1934); for iodine-catalyzed vapor phase chlorination, see J. P. Wibaut and G. P. Bloem, *Rec. trav. chim.*, **69**, 586 (1950).

(6) A. Edinger and P. Goldberg, *Ber.*, **33**, 2875 (1900).

(7) Ref. 3b, Chapter 7: L. F. Fieser and M. Fieser, *Organic Chemistry*, Third Edition, D. C. Heath and Co., Boston, Mass., 1956, Chapter 31. G. Baddeley, *J. Chem. Soc.*, S99 (1949).

(8) C. C. Price in *Org. Reactions*, Vol. III, pp. 1–82 (1946).

(9) C. M. Suter and A. W. Weston in *Org. Reactions*, Vol. III, pp. 141–197 (1946).

(10) For the view that acylation of naphthalene is also a reversible reaction see P. H. Gore, *Chem. Revs.*, **55**, 229 (1955).

(11) A. G. Worthing and J. Geffner, *Treatment of Experimental Data*, John Wiley and Sons, Inc., New York, N. Y., Sixth Printing, 1950, Chapter VIII.