

with aqueous sodium bicarbonate and water. Recrystallization from ethanol gave 0.9 g. (50%) of yellow plates. Part was decolorized with Norite, giving lighter yellow, long needles, m.p. 149–150°.

α -Chloro-N-(*p*-methoxyphenyl)-succinimide. A.—To a suspension of 2.0 g. (0.009 mole) of the maleamic acid in 18 ml. of dry acetone, 5.5 g. (0.07 mole) of acetyl chloride was added. The mixture was refluxed gently on a steam-bath for 30 minutes to effect complete solution, after which the condenser was removed and heating continued while a stream of air was directed into the flask. The tan-yellow residue was washed with a few ml. of cold ethanol, and the off-white residue recrystallized from ethanol twice, giving 0.5 g. (30%) of fine, colorless needles, m.p. 144–145.5° (lit. 145–146°,⁸ 142–143°¹⁰).

*Anal.*¹⁵ Calcd. for C₁₁H₁₀O₂NCl: C, 55.12; H, 4.21; Cl, 14.80. Found: C, 55.26; H, 4.04; Cl, 14.62.

B.—A solution of 53 mg. of N-(*p*-methoxyphenyl)-maleimide in 2 ml. of glacial acetic acid was cooled in an ice-

(15) For the α -chlorosuccinimides, Piutti reported molecular weights larger than calculated for maleimides. Moreover, because low values of 56% C were obtained in several analyses of the α -chloro-N-(*p*-ethoxyphenyl)-succinimide (*i.e.*, low assuming a maleimide structure), he hydrogenated it to the succinimide (apparently the α -chlorine is easily hydrogenolyzed) for which a correct analysis was obtained.

bath while moist hydrogen chloride, obtained by heating concentrated hydrochloric acid, was bubbled in for about 15 minutes. The solution then was warmed slowly to 80° in a water-bath. On pouring into water, a white precipitate formed and was filtered off, washed with aqueous sodium bicarbonate and with water. Recrystallization from ethanol gave 25 mg. (40%) of colorless needles, m.p. 145–147°, not depressed on mixing with the compound prepared with acetyl chloride in A.

Other Maleimides and Chlorosuccinimides.—The experimental procedures were similar to those described for the N-(*p*-methoxyphenyl) derivatives.

Compound	Yield, %	Color	M.p., °C. Obsd.	Lit.
N-(<i>p</i> -Ethoxyphenyl)-maleimide	75	Yellow	133.5–134.5	134–135 ^{9,14}
N-Phenylmaleimide	46	Yellow	89.5–90	90–91 ¹¹
N-(<i>p</i> -Nitrophenyl)-maleimide	58	Off-white	162–165	167–168 ¹¹
α -Chloro-N-(<i>p</i> -ethoxyphenyl)-succinimide	..	Colorless	125–127	127, ⁸ 125 ¹⁰

(16) Searle (reference 11) has reported a m.p. of 75° which could not be reproduced.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Reaction of Dinitrogen Tetroxide with Acetylenes¹

BY JEREMIAH P. FREEMAN AND WILLIAM D. EMMONS

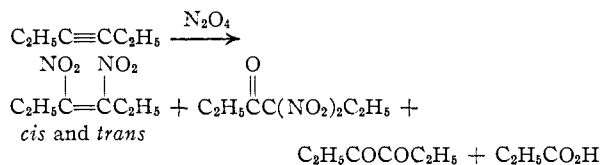
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The addition of dinitrogen tetroxide to dialkylacetylenes has been effected; the products isolated were the corresponding *cis*- and *trans*-dinitroolefins, an α -diketone and an α,α -dinitroketone. The stereochemistry of the dinitroolefins and possible mechanisms for these reactions are discussed.

Although much is known about the reaction of dinitrogen tetroxide with olefinic compounds,² relatively little study has been made of its reaction with acetylenes. Most of the work on acetylenes has been done with tolane^{3–5} where the products have been identified as the *cis*- and *trans*-dinitrostilbenes and 5-nitro-2-phenylisatogen. Wieland also has reported addition to phenylacetylene and phenylpropionic acid, but the structures of these rather unstable products were not proven rigorously.⁴ Very recently the reaction of dinitrogen tetroxide with 2-butyne was reported.⁶ Only one compound was isolated and it was assigned the *trans*-2,3-dinitro-2-butene structure on rather tenuous grounds. As this work has a direct bearing on that reported herein, it will be considered later.

In general it was found that the product mixtures from these reactions were rather unstable and frequently decomposed during the fractional distillations required to purify them. As the 3-hexyne reaction mixture proved to be relatively more stable than that from other acetylenes, most of the work was carried out with this compound. It was found that the reaction is much more com-

plex than a simple addition to produce dinitroolefins, and the instability of the mixtures is apparently due to the formation of minor reactive products. In all, five components of the mixture obtained from dinitrogen tetroxide and 3-hexyne were identified; these included propionic acid (6%), dipropionyl (16%), *cis*- and *trans*-3,4-dinitro-3-hexene (4.5 and 31%, respectively) and 4,4-dinitro-3-hexanone (I) (8%). The structure of the dinitroketone, one of a rare group of compounds,⁷ was established by degradation evidence



and infrared analysis. Upon treatment with methanolic potassium hydroxide, the ketone was cleaved to produce potassium 1-nitro-2-propylnitronate and presumably potassium propionate. When the ketone was heated with aniline, it was cleaved to N-phenylpropionamide and the aniline salt of dinitropropane (not isolated). The infrared spectrum of the dinitroketone had a strong band at

(7) Dinitroketones of this type have previously been reported by M. Filati and G. Ponzio [*J. prakt. Chem.*, **55**, 186 (1897)]. They obtained two of these compounds by the action of nitric acid on ethyl isopropyl and ethyl isobutyl ketones. Hydrolysis provided dinitroethane establishing the position of the nitro groups on the methylene group of the ethyl radical. We are indebted to the referee for pointing out this reference.

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

(2) (a) N. Levy and J. D. Rose, *Quart. Revs.*, **1**, 358 (1948); (b) H. Schechter and F. Conrad, *THIS JOURNAL*, **75**, 5610 (1953).

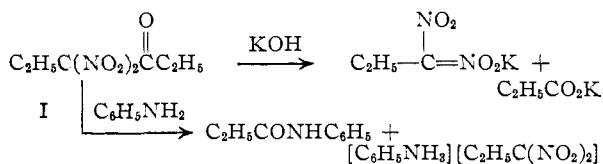
(3) J. Schmidt, *Ber.*, **34**, 619 (1901).

(4) H. Wieland and E. Blumlich, *Ann.*, **424**, 100 (1921).

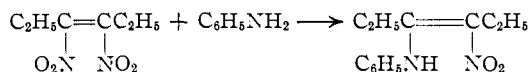
(5) K. N. Campbell, J. Shavel, Jr., and B. K. Campbell, *THIS JOURNAL*, **75**, 2400 (1953).

(6) H. H. Schlubach and W. Rott, *Ann.*, **594**, 59 (1955).

1741 cm^{-1} attributable to a negatively substituted carbonyl group and a strong band at 1575 cm^{-1} attributable to the unsymmetrical stretching frequency of a *gem*-dinitro group.⁸



The less predominant dinitroölefin was identical to the 3,4-dinitro-3-hexene of unknown stereochemistry obtained by the action of alkali on 1-chloronitropropane.⁹ Both of the dinitroölefins reacted with aniline¹⁰ to produce the same amino-



nitroölefin.¹¹ This reaction and the comparative similarity of their infrared and ultraviolet spectra established these two compounds as *cis* and *trans* isomers.

2-Hexyne was also examined in this reaction. A mixture of dinitroölefins was obtained and they were characterized by elementary analysis and infrared spectrum. No efforts were made to separate the two isomers.

The 2-butyne-dinitrogen tetroxide reaction mixture was much less amenable to purification and only became tractable after an alkaline wash. As this undoubtedly destroyed the dinitroketone and washed out much of the biacetyl, the results of this reaction are much less definitive. After treatment of 2-butyne with excess dinitrogen tetroxide in ether at 0°, two isomeric dinitrobutenes were obtained in a ratio of 5:1, total yield 41%, together with smaller amounts of biacetyl and acetic acid. The higher boiling, less predominant isomer was identical to the 2,3-dinitro-2-butene of unknown stereochemistry produced by the action of alkali on 1-chloro-1-nitroethane.⁹ Both of the dinitroölefins reacted with aniline¹⁰ to produce the same aminonitroölefin, establishing the structure of the lower boiling product as the isomeric 2,3-dinitro-2-butene.¹²

The infrared spectrum of the crude reaction product before treatment with base had a carbonyl band at *ca.* 1750 cm^{-1} and a band attributable to a *gem*-dinitro group at 1578 cm^{-1} . These bands were not present in the spectrum of the product after the alkaline wash, and it is presumed that they

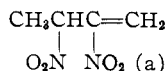
(8) J. F. Brown, Jr., *THIS JOURNAL*, **77**, 6341 (1955).

(9) (a) E. M. Nygaard and T. T. Noland, U. S. Patent 2,396,282; (b) D. E. Bisgrove, J. F. Brown, Jr., and L. B. Clapp, *Org. Syntheses*, in press. We are indebted to Dr. Clapp for a preprint of this preparation.

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

(11) For a discussion of these interesting compounds, see J. P. Freeman and W. D. Emmons, *THIS JOURNAL*, **78**, 3405 (1956).

(12) Because of the vast difference in boiling points between the two isomers, the possibility that the lower boiling material was the isomer (a) was considered. However, the infrared spectrum of such a compound should exhibit bands due to two distinct nitro groups (~ 1550 , 1520 cm^{-1}) and to the terminal methylene wagging vibrations (~ 940 cm^{-1}).⁸ As is clear from Fig. 1 no such bands are present, and this possibility was ruled out.



were due to the presence of 3,3-dinitro-2-butanone. Apparently this compound was quite unstable and caused purification of the product mixture to be difficult and dangerous.

The stereochemistry of the dinitroölefins is rather difficult to establish chemically. The most reasonable method would appear to be conversion to the corresponding diamines, but in view of the recent report on the racemization accompanying the reduction of optically active nitro compounds,¹³ it did not appear safe to employ reduction in this series. However, assuming that reduction might provide some indication of the stereochemistry, it appeared that the higher boiling dinitrobutene (the chloronitroethane-alkali product) was the *cis* isomer as it gave *meso*-2,3-butanediamine upon catalytic reduction.¹⁴ Thus, the lower boiling isomer would have the *trans* configuration.

The infrared spectra of the four dinitroölefins were examined in an attempt to establish the configurations. In this connection the spectra of the definitely established *cis* and *trans*-dinitrostilbenes were used as models (Fig. 1). Two significant fea-

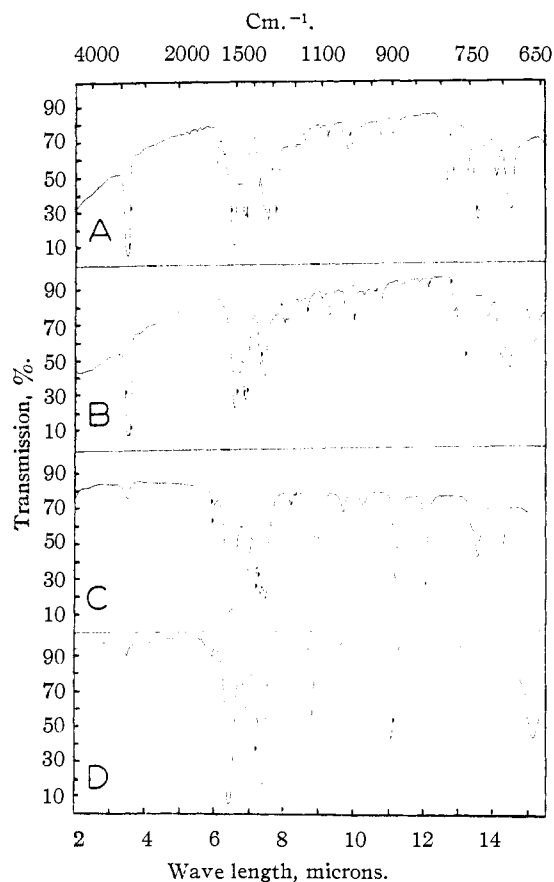


Fig. 1.—Infrared spectra of: A, *cis*-1,2-dinitrostilbene (Nujol); B, *trans*-1,2-dinitrostilbene (Nujol); C, *cis*-2,3-dinitro-2-butene (cap. layer); D, *trans*-2,3-dinitro-2-butene (cap. layer).

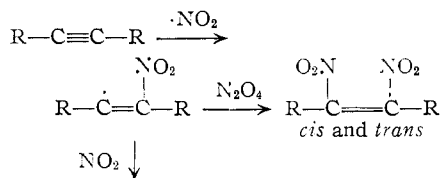
tures stand out. *cis*-Dinitrostilbene exhibits a band at 1642 cm^{-1} absent in the *trans* isomer,

(13) N. Kornblum and L. Fishbein, *THIS JOURNAL*, **77**, 6266 (1955).

(14) For the reasoning behind this assignment, see ref. 10, footnote 16a.

which may be attributed to the olefinic double bond.¹⁵ Secondly, the "fingerprint region" of the *cis* isomer is considerably more complex than that of the *trans* compound as is to be expected because of its less symmetrical nature. The other pairs of dinitroolefins were assigned configuration on the basis of the comparative complexity of their spectra and the presence or absence of a band attributable to an olefinic linkage. For comparison the spectra of the two dinitrobutenes may be seen in Fig. 1. It is apparent that the lower boiling isomer possesses the less complex spectrum with no indication of an olefinic linkage,¹⁶ while the higher boiling product does show a band attributable to a double bond at 1676 cm.⁻¹. Therefore the lower boiling isomer was assigned the *trans*-2,3-dinitro-2-butene structure while the higher boiling isomer (and therefore the chloronitroethane-alkali product)^{9,17,18} must have the *cis* configuration.¹⁹ The dinitrohexenes were assigned their structures similarly. The higher boiling isomer exhibits its olefinic absorption at 1667 cm.⁻¹ while the lower boiling compound has no band in this region. The difference in spectral complexity of this pair of isomers was much less apparent, due presumably to the lengthening of the carbon chain.

The most reasonable mechanistic proposal to explain the origin of these products involves free radical intermediates. Although the reactions of dinitrogen tetroxide with unsaturated compounds were explained originally by an ionic mechanism,²⁰ more recently it has been demonstrated that a radical mechanism is more consistent with the facts.^{2b,5,21} For the acetylene reaction the following reaction path is envisioned



(15) *cis*-Stilbene does not exhibit a band above 1605 cm.⁻¹ in the infrared attributable to an olefinic bond, but it does show this band at 1630 cm.⁻¹ in its Raman spectrum [A. Dadiou, A. Pongratz and K. W. F. Kohlrausch, *Monatsh.*, **60**, 231 (1932)]. It is interesting that the introduction of the two nitro groups appears to enhance the double bond character of this linkage as indicated by its appearance at a higher frequency.

(16) The weak band at 1680 cm.⁻¹ appears to be due to an impurity which we have not been able to eliminate completely. Its intensity diminished markedly during the purification process. The spectrum of this material as reproduced by Schlubach and Rott⁶ is free of this band.

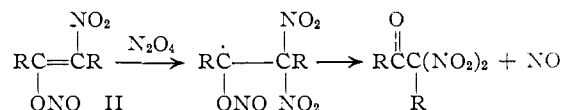
(17) The mechanism recently proposed for the formation of the dinitrobutene in this reaction [M. F. Hawthorne, *THIS JOURNAL*, **78**, 4980 (1956)] does not permit an assignment of configuration.

(18) In a private communication, Dr. J. F. Brown, Jr., of the General Electric Research Laboratory informed us that he has obtained both isomers from this reaction. The infrared spectrum and other physical properties of the lower boiling material were identical to those reported herein.

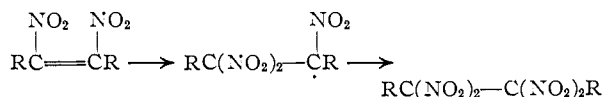
(19) The German study⁶ of the 2-butyne-dinitrogen tetroxide reaction reported only one dinitroolefin, b.p. 90° (1 mm.), m.p. 28°, and assigned it the *trans* structure. The physical properties correspond to the higher boiling isomer isolated in this study and also to the chloronitroethane-alkali product. However, the spectrum recorded in the paper corresponds to that of the lower boiling isomer. It is not possible to reconcile these differences at this time.

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

(21) I. C. D. Brand and I. D. R. Stevens, *Chemistry of Industry*, 169 (1956)

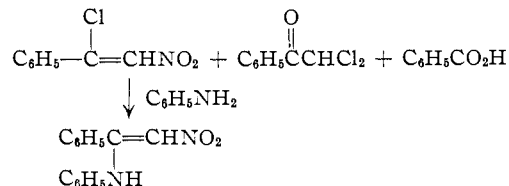
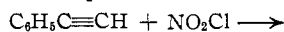


This scheme represents simply a rationalization of the experimental results and says nothing about the possible intervention of other species such as nitric oxide in the reaction. The reaction of a second molecule of dinitrogen tetroxide with the nitronitrite II can be viewed as a concerted process with the loss of nitric oxide accompanying the addition of nitrogen dioxide. No product corresponding to a second addition to the dinitroolefin was observed, presumably because the intermediate radical is a relatively high energy species. The addition of dinitrogen tetroxide to dinitroolefins has been effected under forcing conditions to produce tetranitroparaffins.²² At this time no completely satisfac-



tory explanation for the production of the diketones is apparent. Whether unsaturated dinitrites or dinitrodinitrites are the precursors of these materials is unknown. They are possibly intermediates in the oxidation processes that produce the acid fragments.

Efforts to extend these reactions to terminal acetylenes met with no success. In most cases very unstable reaction mixtures were obtained. In the case of pentyne-1, distillation of the mixture was possible but no identifiable products were obtained. As a corollary to this work the reaction of nitril chloride with acetylenes was briefly examined. This reagent did not appear to offer any advantages over dinitrogen tetroxide so that only its reaction with phenylacetylene was examined in any detail. A difficultly separable mixture of products was obtained whose main constituent was a solid nitrochlorostyrene which is assigned the structure of α -chloro- β -nitrostyrene²³ on the basis of its melting point, elementary analysis, ultraviolet spectrum (λ_{max} 285 m μ ϵ_{max} 3800) and its reaction with aniline which produced α -anilino- β -nitrostyrene.²³



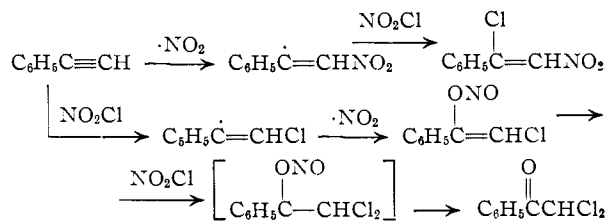
A mixture of liquid nitrochlorostyrenes also was obtained along with some α,α -dichloroacetophenone and benzoic acid. All the nitrostyrenes were shown to have the β -nitro structure by their reaction with aniline to give α -anilino- β -nitrostyrene. No α -nitro- β -chlorostyrene, a reported product of this reaction,²⁴ was found. The mechanistic pro-

(22) C. E. Grabel, D. E. Bisgrove and L. B. Clapp, *THIS JOURNAL*, **77**, 1293 (1955).

(23) This material appears to be identical to that obtained by the reaction of nitrosyl chloride with phenylacetylene [R. Perrot and R. Berger, *Compt. rend.*, **235**, 185 (1952)].

(24) W. Steinkopf and M. Kuhnert, *Ber.*, **75B**, 1323 (1942).

posals for the dinitrogen tetroxide reaction appear to be applicable to this reaction. It is interesting that, as in the case of the nitryl chloride-acrylate reaction,²⁵ nitro compounds were formed only where initiation involved formation of a carbon-nitrogen bond. If initiation was by carbon-chlorine bond formation, no C-nitro compounds were formed.



Experimental

Reaction of 2-Butyne with Dinitrogen Tetroxide.—A solution of 33.8 g. (0.36 mole) of dinitrogen tetroxide in 250 ml. of dry ether was prepared by distilling the dry, previously weighed oxide into the ether at 0–10°. At the same temperature 27 g. (0.2 mole) of 2-butyne²⁶ was added dropwise. The resulting mixture was packed in ice and allowed to come to room temperature overnight. It was then washed with water and 10% sodium bicarbonate solution and dried. The solvent was evaporated to leave 26 g. of a crude brown oil. This material was distilled in a falling film still to yield two fractions. The residue proved to be very unstable and was discarded.

The first fraction upon redistillation gave a pale yellow liquid, b.p. 70–72° (8 mm.), n_D^{20} 1.4678, d_4^{25} 1.2654, yield 9.9 g. (34%).

Anal. Calcd. for $\text{C}_4\text{H}_8\text{N}_2\text{O}_4$: C, 32.86; H, 4.13; N, 19.19. Found: C, 33.40; H, 4.35; N, 18.90.

When treated with aniline it produced 2-nitro-3-anilino-2-butene, m.p. 103–104°, identical to the product previously obtained from the reaction of 2,3-dinitro-3-butene with aniline.¹⁰ On the basis of its elementary analysis and infrared spectrum (Fig. 1), this dinitroolefin was designated as *trans*-2,3-dinitro-2-butene.

The second fraction upon redistillation gave a yellow oil, b.p. 96–100° (1.5 mm.), n_D^{20} 1.4776, d_4^{25} 1.2748, which crystallized from ethanol when cooled in a Dry Ice-acetone-bath, m.p. 25–27° yield 2.1 g. (7%). This material was identical to the dinitrobutene obtained from the reaction⁸ of chloronitroethane with alkali and on the basis of its infrared spectrum was assigned the *cis*-2,3-dinitro-2-butene structure.

Since it was apparent that the water and bicarbonate wash removed large amounts of material, a run was conducted in which the crude reaction product was flash-distilled without treatment. Acetic acid and biacetyl (dioxime, m.p. 232–234°) were found in the trap. The distillate consisted in the mixture of dinitrobutenes. The pot residue was very unstable and tended to fume off near the end of the distillation. It is believed that this instability was due to the presence of 3,3-dinitro-2-butanone. This material was destroyed by the alkaline wash, rendering the mixture more tractable.

Reaction of 3-Hexyne with Dinitrogen Tetroxide.—The same procedure was employed. The crude product from the reaction of 41 g. (0.5 mole) of 3-hexyne²⁶ with 68 g. (0.73 mole) of dinitrogen tetroxide in 300 ml. of dry ether was washed thoroughly with water, dried and concentrated to leave 61.2 g. of a yellow orange oil. This oil was distilled through a spinning band column to produce four main fractions. In the vacuum pump trap was found 2.2 g. (6%) of propionic acid.

The first fraction, b.p. 48–54° (50 mm.), upon redistillation gave a bright yellow oil, b.p. 63–64° (64 mm.), 123–125° (atm.), n_D^{20} 1.4100, d_4^{20} 0.9392, yield 9 g. (16%). This material was identified as bipropionyl by conversion to the

known quinoxaline, m.p. 50–52° (lit.²⁷ m.p. 49–50°). It also formed a dioxime, m.p. 196–197.5°.

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2$: C, 50.00; H, 8.33; N, 19.44. Found: C, 50.58; H, 8.76; N, 19.67.

This dioxime which formed a yellow precipitate when treated with nickel(II) acetate was not identical to that previously reported (lit.²⁸ m.p. 185°). Apparently it is a geometric isomer. Bipropionyl also formed a bis-2,4-dinitrophenylhydrazone, m.p. 292° dec. (from nitrobenzene).

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_6\text{O}_6$: C, 45.57; H, 3.80; N, 23.63. Found: C, 45.91; H, 4.72; N, 23.45.

The second fraction, b.p. 28–40° (0.4 mm.), was redistilled to give 26.7 g. (31%) of *trans*-3,4-dinitro-3-hexane, b.p. 53–55° (1 mm.), n_D^{20} 1.4640, n_D^{25} 1.4582. Infrared bands, cm^{-1} (cap. layer): 2940(s), 2850(s), 1540(vs), 1460(vs), 1439(m), 1350(vs), 1274(m), 1124(m), 1055(m), 942(m), 907(m), 807(vs).

Anal. Calcd. for $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_4$: C, 41.37; H, 5.78; N, 16.08. Found: C, 41.79; H, 5.99; N, 15.48.

The third fraction, b.p. 36–42° (0.2 mm.), was redistilled to give 7.9 g. (8%) of 4,4-dinitro-3-hexanone, b.p. 69–71° (1 mm.), n_D^{20} 1.4548. Repeated efforts to purify this compound for analysis by distillation were unsuccessful. Upon treatment with methanolic potassium hydroxide, it cleaved to produce the potassium salt of 1,1-dinitropropane, as proven by comparison of its infrared spectrum with that of an authentic sample.^{9b} When heated with aniline, it produced N-phenylpropionamide, m.p. 100–102° (lit.²⁹ m.p. 103°).

The last fraction, b.p. 44–52° (0.1 mm.), crystallized from ethanol when cooled in a Dry Ice-acetone-bath, m.p. 29–31°, n_D^{20} 1.4692. Its infrared spectrum was identical to that of the dinitrohexene, m.p. 31–32°, produced by the action of alkali on 1-chloronitropropane.^{9b} It was assigned the structure of *cis*-3,4-dinitro-3-hexene. Infrared bands, cm^{-1} (cap. melt): 2940(s), 2840(s), 1667(m), 1539(vs), 1455(vs), 1424(s), 1350(vs), 1270(m), 1200(w), 1122(m), 1063(s), 968(w), 904(m), 822(vs), 810(vs), 741(m), 733(m), 675(m).

Reaction of 2-Hexyne with Dinitrogen Tetroxide.—Using the same procedure, there was obtained from 34 g. (0.37 mole) of dinitrogen tetroxide and 28.7 g. (0.35 mole) of 2-hexyne, 27.2 g. of crude product after washing with water and 10% sodium hydroxide solution. Upon flash distillation there was obtained 14 g. (23%) of a yellow oil whose infrared spectrum indicated that it consisted of a mixture of dinitroolefins. Redistillation through a Holzman column yielded a yellow oil, b.p. 50–58° (0.6 mm.), n_D^{20} 1.4587–1.4598.

Anal. Calcd. for $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_4$: C, 41.38; H, 5.79; N, 16.09. Found: C, 41.69; H, 6.00; N, 15.40.

Reaction of Nitryl Chloride with Phenylacetylene.—To a solution of 84 g. (1.0 mole) of nitryl chloride²⁸ in 500 ml. of ether was added 75 g. (0.75 mole) of phenylacetylene. The resulting mixture was packed in ice and allowed to come to room temperature overnight. It then was concentrated *in vacuo* to yield 94.5 g. of a yellow oil. This product was distilled through an 18" spinning band column to produce the following fractions: (a) b.p. 45–64° (0.3 mm.). Base extraction of this material followed by acidification produced 3 g. of benzoic acid. The organic material was redistilled to yield 11.8 g. (9%) of α,α -dichloroacetophenone, as shown by the identity of its infrared spectrum with that of an authentic sample.³⁰ It formed a bis-2,4-dinitrophenylhydrazone,³¹ m.p. 292–294°.

(b) B.p. 60–71° (0.1 mm.). This fraction contained a mixture of nitrochlorostyrenes. By crystallization from petroleum ether (30–60°) at Dry Ice temperature the solid isomer was removed. Repeated recrystallizations from pe-

(27) E. Urien, *Ann. chim.*, **1**, 54 (1934).

(28) E. Urien, *Compt. rend.*, **191**, 263 (1930).

(29) R. L. Shriner and R. C. Fuson, "The Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 222.

(30) E. C. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 538.

(31) J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., *THIS JOURNAL*, **75**, 4765 (1953).

(25) H. Shechter, F. Conrad, A. L. Daulton and R. B. Kaplan, *THIS JOURNAL*, **74**, 3052 (1952).

(26) Obtained from March Research Laboratories, Cleveland, Ohio.

trolcum ether produced bright yellow needles of α -chloro- β -nitrostyrene, m.p. 54–55°, yield 34%.

Anal. Calcd. for $C_8H_6ClNO_2$: C, 52.33; H, 3.29; N, 7.63. Found: C, 52.80; H, 3.52; N, 7.45.

Upon treatment with aniline in ethanol, α -anilino- β -nitrostyrene, m.p. 125–127°, was obtained. The oily isomer was not further characterized except that it formed this amino-nitroolefin also.

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Crystallizable Polystyrene. I. Polymerization of Styrene with Alfin Catalysts¹

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Alfin catalysts polymerize styrene to give an amorphous polymer which can be heated in a suitable crystallizing medium to produce crystalline polystyrene. Suitable polymerization media are pentane, hexane, cyclohexane, benzene and triethylamine. Efficient crystallization media are hydrocarbon solvents boiling above 90° and diethyl ether. Detailed procedures for the preparation and characterization of Alfin catalysts are given. Methods for the preparation of highly crystalline polystyrene are described.

The preparation of crystallizable polystyrene using Alfin catalysts was reported briefly in a previous communication.² Further information and experimental details are given in the present paper.

Polymerization of Styrene with Alfin Catalysts.—Morton³ has shown that the intrinsic viscosity of Alfin-catalyzed polystyrene increases with higher ratios of sodium isopropoxide to allylsodium. Our work has confirmed this, but we have found that the ultimate degree of crystallinity is independent of the catalyst ratio. Typical examples are listed in Table I.

TABLE I

POLYMERIZATION OF STYRENE BY VARIOUS ALFIN CATALYSTS^a

Catalyst ratio i-PrONa/allyl Na	Basicity, meq./ml.	Polystyrene viscosity [η]	Max. cryst.
90/10	1.10	2.27	Medium
80/20	0.86	1.58	Medium
73/27	.94	1.29	Medium
50/50	.90	1.05	Medium
20/80	.50	0.79	Medium

^a Charge: 30 ml. of styrene, 200 ml. of hexane and 30 ml. of catalyst in a 380-ml. pressure bottle. Polymerizations were run at room temperature.

With each catalyst, a certain minimum amount was required to produce high yields of polymer. Above this minimum, larger amounts of styrene could be added to the catalyst without decreasing the percentage yield of polymer based on styrene. This effect is shown in Table II for a catalyst having a sodium isopropoxide to allylsodium ratio of 73 to 27 and a basicity of 0.85 meq. per milliliter.

As expected, the rate of polymerization, using Alfin catalysts, was dependent upon the temperature. With 30 ml. of styrene and 30 ml. of catalyst (sodium isopropoxide/allylsodium = 73/27; basicity 0.94 meq./ml.) in 200 ml. of hexane, the results shown in Table III were obtained at 0 and at 60°.

(1) Communication No. 1844 from the Kodak Research Laboratories.

(2) J. L. R. Williams, J. VanDenBerghe, W. J. Dulmage and K. R. Dunham, *THIS JOURNAL*, **78**, 1260 (1956).

(3) A. A. Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950).

X-Ray comparison of the polymers indicated that a larger percentage of the polymer made at the lower temperature was crystallizable.

Although polymerizations were generally run in hexane, interesting results were obtained with other media, as shown in Table IV.

TABLE II

EFFECT OF CATALYST CONCENTRATION

Catalyst, ml.	Hexane, ml.	Styrene, ml.	Time, min.	Temp., °C. ^a	Yield, %	Crystallinity
10	200	30	160	24	0
15	200	30	180	25	16	Medium
20	200	30	120	29.1	80	Medium
25	200	30	85	30.6	83	Medium
30	200	30	60	32.4	87	Medium
30	200	50 ^b	52	41.9	91	Medium
30	200	50	40	38.2	95	Medium

^a The temperature was recorded by means of a metal-stem dial thermometer taped to the side of the polymerization bottle. The bottles were shaken in air at room temperature and the polymerization was stopped immediately after the temperature had passed a maximum. ^b The styrene was added in 20-ml. increments during the course of the polymerization.

TABLE III

EFFECT OF TEMPERATURE ON THE RATE OF POLYMERIZATION

Polymerization Time, min.	Temp., °C.	Yield, %	Crystallinity
60	0	2.6	High
120	0	5.9	High
480	0	40	High
1140	0	77	High
2	60	37	Medium
5	60	72	Medium
10	60	92	Medium

Natta⁴ suggested that a heterogeneous catalyst was necessary to produce isotactic polymers. This theory holds true, for on long standing the solid phase of an Alfin catalyst settles out to some extent, leaving a small upper layer of clear solvent. A 30-ml. portion of the clear hexane layer from an Alfin catalyst failed to initiate the polymerization

(4) G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mezzanti and C. Moraglio, *THIS JOURNAL*, **77**, 1708 (1955).