[Contribution from the Research Laboratories of the Aerojet-General Corporation]

THE PREPARATION OF SUBSTITUTED NITROÖLEFINS[1]

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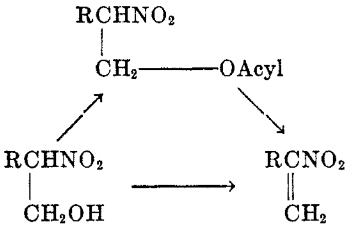
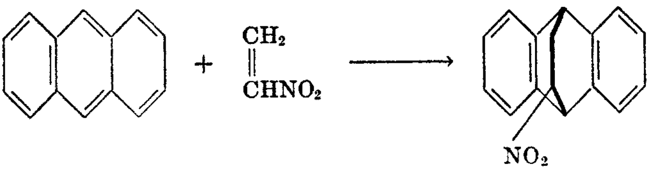
Nitroolefins are generally prepared by dehydration of nitroalcohols (1, 2) or by decomposition of esters of nitroalcohols following several procedures (3–5):



$R = H, CH_3, C_2H_5, C_6H_{11}$, etc.

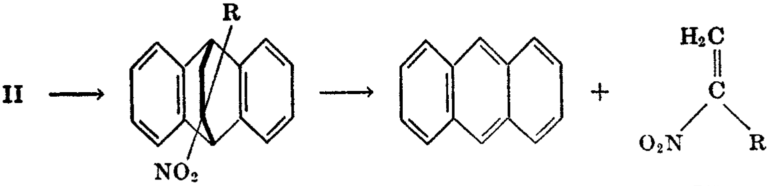
These procedures generally give good yields, but are only applied to compounds in which R does not contain functional groups. Direct substitution of nitroölefins, *e.g.* nitroethylene, in order to prepare substituted nitroölefins has not yet been recorded.

This paper deals with a simple method of preparation of substituted nitroölefins by applying substitution reactions and thermal dissociation of the compounds obtained from the Diels Alder reaction products of nitroölefins. The nitroölefins contain a dienophilic double bond capable of forming Diels Alder products with dienes (6–11). Anthracene (I) which has not been previously used in Diels Alder reactions with nitroölefins, reacts with nitroethylene to give *endo*-nitroethyleneanthracene (II) according to the equation:



I II

While nitroethylene does not contain a reactive hydrogen, the *endo*-nitroethyleneanthracene contains a reactive hydrogen atom in the ethylene bridge capable of undergoing replacement reactions (III).



III I IV

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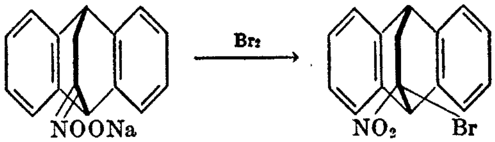
[1] This work was performed under a contract with the Office of Naval Research.

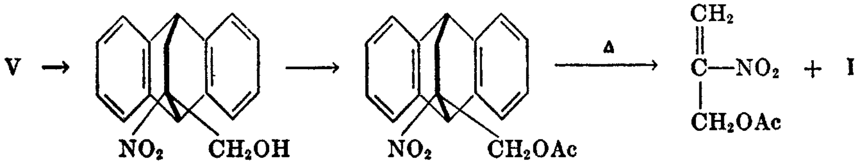
Alder and Rickert (12–14) found that cyclohexadienes containing an *endo* ethylene bridge are thermally unstable and decompose with the formation of an aromatic ring liberating the *endo* bridge as an olefin. Similarly, the substituted *endo*-nitroethyleneanthracene (III) as a cyclic hexadiene follows the rule of Alder and Rickert (12) and can be split into the starting anthracene and the substituted nitroölefin (IV). Thus, the Diels Alder reaction serves to protect the double bond of the nitroölefins, thereby permitting further reaction. In the thermal dissociation, the double bond is regenerated, yielding the substituted nitroölefin. The double bond of acrylonitrile has been similarly protected in the preparation of allylamine (17).

Using this series of reactions, a number of substituted nitroölefins have been prepared. Treatment of the starting *endo*-nitroethyleneanthracene (II) with sodium methoxide in refluxing methanol gave the aci-sodium salt (V). This, upon bromination, gave the *endo*-1-bromonitroethyleneanthracene, a crystalline compound, m.p. 129° (VI).



V VI

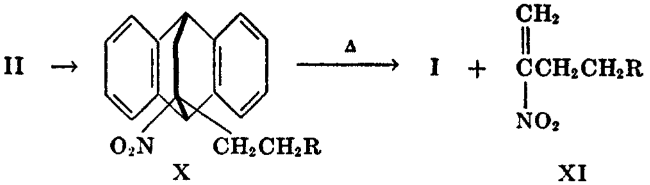
The aci-sodium salt underwent the Henry reaction (15) with formaldehyde yielding the *endo*-1-nitroethyleneanthracene (VII). Thermal decomposition of the acetate (VIII) of this compound in a vacuum at 20–30 mm. and 200° gave 2-nitro-3-acetoxypropene (IX) according to the equation:



VII VIII IX

It is of interest to note that the free alcohol did not yield 2-nitro-3-propen-1-ol, but depending on the conditions gave *endo*-nitroethyleneanthracene (II) and formaldehyde or anthracene, formaldehyde, and nitroethylene polymer.

The Michael (16) reaction of the aci-sodium salt of *endo*-nitroethyleneanthracene with methyl acrylate or acrylonitrile led to crystalline addition products (Xa) and (Xb) respectively. These compounds were cleaved in a vacuum-distillation at 20–30 mm. and 200–240° into anthracene and methyl 4-nitro-4-pentenoate (XIa) and 4-nitro-4-pentenonitrile (XIb) respectivelv:



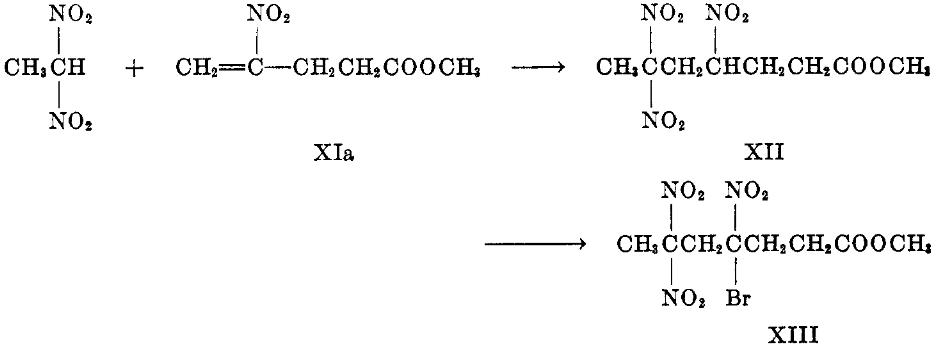
X XI

(a) R = COOCH₃
(b) R = CN

The generality of this procedure makes it possible to prepare a wide variety of substituted nitroölefins, provided that the olefin is capable of withstanding the vigorous treatment during the pyrolytic cleavage.

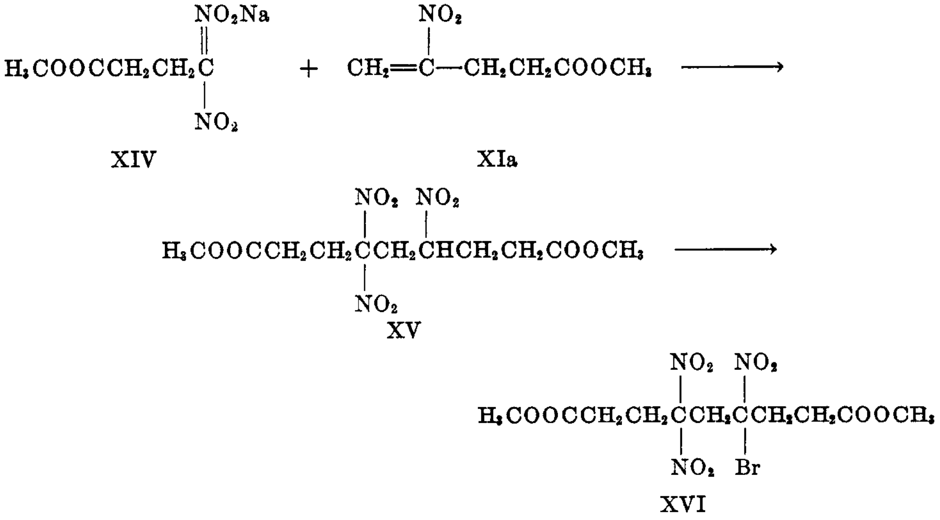
Diels and Thiele (18) found that the affinity of maleic anhydride for anthracene is greater than that of other dienophilic compounds. Thus, they found it possible to replace the *endo* bridge of substituted *endo*-ethyleneanthracene derivatives by reacting those compounds with an excess of maleic anhydride, to form *endo*-succinic anhydride anthracene and the *endo* bridge olefin. It has been found that nitro group-containing *endo*-ethyleneanthracene derivatives do not follow the principle found by Diels and Thiele. Apparently the Diels Alder products with nitroethylene have the same or a greater affinity for anthracene than maleic anhydride.

One of the greatest handicaps in the synthesis of aliphatic polynitro compounds containing functional groups was the inavailability of suitable intermediates. Methyl 4-nitro-4-pentenoate (XIa) appears to be an excellent intermediate for condensation reactions with polynitro compounds in Michael type reactions—*e.g.* when 1,1-dinitroethane was reacted with methyl 4-nitro-4-pentenoate (XIa) methyl 4,6,6-trinitroheptanoate (XII) was formed according to the equation:



$$CH_3\underset{NO_2}{\overset{NO_2}{C}}H + \underset{\text{XIa}}{CH_2{=}\overset{NO_2}{C}{-}CH_2CH_2COOCH_3} \longrightarrow \underset{\text{XII}}{CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{C}HCH_2CH_2COOCH_3}$$

$$\longrightarrow \underset{\text{XIII}}{CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\underset{Br}{\overset{NO_2}{C}}CH_2CH_2COOCH_3}$$



$$\underset{\text{XIV}}{H_3COOCCH_2CH_2\underset{NO_2}{\overset{NO_2Na}{\overset{\|}{C}}}} + \underset{\text{XIa}}{CH_2{=}\overset{NO_2}{C}{-}CH_2CH_2COOCH_3} \longrightarrow$$

$$\underset{\text{XV}}{H_3COOCCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{C}HCH_2CH_2COOCH_3} \longrightarrow$$

$$\underset{\text{XVI}}{H_3COOCCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2\underset{Br}{\overset{NO_2}{C}}CH_2CH_2COOCH_3}$$

The structure of the latter compound was confirmed by a crystalline bromo derivative (XIII).

When methyl sodium-4,4-dinitrobutyrate (XIV) was condensed with methyl 4-nitro-4-pentenoate (XIa) the dimethyl 4,4,6-trinitro-1,9-nonanedioate (XV) was formed which was characterized by conversion into the crystalline dimethyl 4-bromo-4,6,6-trinitro-1,9-nonanedioate (XVI).

EXPERIMENTAL[2]

endo-Nitroethyleneanthracene (II). A 100-ml. flask provided with a reflux condenser and a thermometer was charged with 1.80 g. of anthracene, 5 ml. of *o*-dichlorobenzene, and 2 ml. of nitroethylene (200% excess). The mixture was heated to 145–150° for 45 minutes. At this temperature refluxing of the solution started. After cooling, the solvent was evaporated and the residual yellow honey-like mass was treated with ether until it was all crystallized. After filtering, the melting point of the crude material was 92–95°. Two recrystallizations gave 1.8 g. of colorless crystals, m.p. 113–114°.

Anal. Calc'd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57.

Found: C, 76.42; H, 5.27; N, 5.59.

endo-(1-Bromo-1-nitroethylene)anthracene (VI). A solution 1.25 g. of *endo*-(nitroethylene)-anthracene in 25 ml. of methanol was refluxed for 30 minutes with a solution of 0.28 g. of sodium methoxide in 10 ml. of methanol. After evaporation to dryness a white solid was obtained. The melting point of the crude material was 156° with decomposition. This solid was dissolved without purification in 25 ml. of water and cooled to 0°. Bromine was added until the bromine color was no longer bleached, then the mixture was extracted with ether, and the ether solution was washed with water and dried over sodium sulfate. After evaporation of the ether 1.22 g. of a crystalline solid was obtained, which was recrystallized from boiling hexane. After a second recrystallization, 1.05 g. of colorless needles were obtained having m.p. 128–129°.

Anal. Calc'd for $C_{16}H_{12}BrNO_2$: C, 58.23; H, 3.67; Br, 24.22.

Found: C, 57.87; H, 3.38, Br, 24.83.

endo-(1-Nitro-1-methylolethylene)anthracene (VII). A mixture of 15 gm. of *endo*-nitroethyleneanthracene, 3.5 g. of sodium methoxide, and 75 ml. of methanol was refluxed for 60 minutes and the methanol was evaporated. The sodium salt obtained was dissolved in 50 ml. of water and 5.4 g. of formaldehyde (37% by weight) was added at once. The mixture was allowed to stand for 4 hours, then was filtered and washed with water. After drying over potassium hydroxide in a desiccator, 11 g. of crude material was obtained. This was refluxed with an excess of isopropyl ether, filtered, and concentrated until crystals precipitated. These were collected yielding 7.0 g. of *endo*-(1-nitro-1-methylolethylene) anthracene. The melting point after several recrystallizations was 157–158°.

Anal. Calc'd for $C_{17}H_{13}NO_3$: C, 72.58; H, 5.38; N, 4.98.

Found: C, 72.50; H, 5.45; N, 4.99.

endo-(1-Nitro-1-(2′-carbomethoxyethyl)ethylene)anthracene (Xa). The aci-sodium salt, prepared from 5 g. of *endo*-nitroethyleneanthracene, 1.14 g. of sodium methoxide, and 40 ml. of methanol, was dissolved in 25 ml. of water and treated with 5.16 g. of methyl acrylate (200% excess). The temperature increased to 30° and a color change from brown to green was observed. The mixture was stirred for 6 hours to complete the reaction, filtered, and washed with water. The yield was 7.1 g. of crude material. After dissolving in 150 ml. of methanol and treating with charcoal, the solution was concentrated to about 25 ml. The product (3.4 g.) was recrystallized from isopropyl ether, m.p. 154–155°. The slightly blue crystals were dissolved in hot acetic acid and the resulting solution was diluted with methanol. Colorless crystals were obtained, m.p. 155°.

[2] The analyses have been conducted at Dr. Adalbert Elek's Microanalytical Laboratory, Los Angeles, California.

Anal. Calc'd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15; OCH_3, 9.20.
Found: C, 71.77; H, 5.96; N, 3.88; OCH_3, 9.14.

endo-(1-Nitro-1-(2'-cyanoethyl)ethylene) anthracene (Xb). A round-bottomed flask with an attached reflux condenser, was charged with 5 g. of *endo*-nitroethyleneanthracene, 1.14 g. of sodium methoxide, and 35 ml. of methanol. The mixture was refluxed for 60 minutes and evaporated. The residue was dissolved in 35 ml. of water and 7.5 ml. of acrylonitrile was added. The temperature increased to 60° and the mixture was stirred for 6 hours. A yellow oil settled and the water layer was decanted; the remaining oil was washed with water and dissolved in 10 ml. of methanol. After two days crystals were formed. These were filtered and washed with methanol to yield 2.9 g., m.p. 114–115°. Upon recrystallization from acetic acid and methanol, prisms were obtained, m.p. 121–122°.

Anal. Calc'd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.21.
Found: C, 75.82; H, 5.40; N, 9.43.

Methyl 4-nitro-4-pentenoate (XIa). A bulb tube was charged with 1 g. of *endo*-(1-nitro-1-(2'-carbomethoxyethyl)ethyleneanthracene and was heated at 21 mm. to 195–200°. At this temperature, decomposition was noted and a light yellow liquid distilled (0.28 g.). The residue later was distilled at 230–240° and a crystalline fraction was obtained (0.62 g.). These crystals were dissolved in tetrahydrofuran; the excess tetrahydrofuran was evaporated and the concentrate was diluted with methanol from which crystals immediately precipitated. After filtration, 0.37 g. of white leaves was obtained, m.p. 214–215°. The liquid fraction (0.28 g.) was purified by distillation at 1 mm. and 85–90° air-bath temperature.

Anal. Calc'd for $C_6H_9NO_4$: C, 45.28; H, 5.70; N, 8.80.
Found: C, 45.24; H, 5.74; N, 8.87.

4-Nitro-4-pentenonitrile (XIb). A bulb tube was filled with 0.8 g. of *endo*-(1-nitro-1-(2-cyanoethyl)ethyleneanthracene and heated to 195–200° at 28 mm. A yellow liquid and crystals distilled. The distillate was dissolved in ether and was filtered from the insoluble anthracene. The extract was evaporated and distilled at 120° (airbath temperature) and 5 mm. producing a greenish-yellow liquid with a refractive index, n_D^{22} 1.4735.

Anal. Calc'd for $C_5H_6N_2O_2$: C, 47.61; H, 4.80; N, 22.22.
Found: C, 47.97; H, 4.94; N, 22.62.

endo-(1-Nitro-1-acetoxymethylethylene)anthracene (VIII). The mixture of 4.5 g. of *endo*-(1-nitro-1-methylolethylene)anthracene and 15 ml. of acetic anhydride was refluxed for 60 minutes. The excess of acetic anhydride was removed by vacuum-distillation. The residue was dissolved in ether and hexane was added dropwise. This precipitated 4.2 g. of white crystals of the *endo*-(1-acetoxymethyl-1-nitroethylene)anthracene which, after recrystallization from isopropyl ether or methanol, had m.p. 103–105°.

2-Nitro-3-acetoxypropene (IX). A bulb tube charged with 1 g. of *endo*-(1-nitro-1-acetoxymethylethylene)anthracene was heated to 200–220° at 28 mm. in an airbath. Decomposition was observed and a greenish-yellow liquid was distilled, accompanied by crystals. After redistillation at 90–120° (airbath temperature) and 5 mm. the light-yellow liquid (0.1 g.) gave the following analysis:

Anal. Calc'd for $C_5H_7NO_4$: C, 41.38; H, 4.86; N, 9.65.
Found: C, 41.53; H, 5.45; N, 8.83.

The anthracene fraction was purified by crystallization from tetrahydrofuran and methanol. The melting point and mixture melting point with pure anthracene were 214–216°.

Methyl 4,6,6-trinitroheptanoate (XII). A 3-necked flask provided with a stirrer, thermometer, and dropping-funnel was charged with a solution of 0.56 g. of sodium methoxide in 5 ml. of water, and 1.20 g. of dinitroethane was added. When all of the nitroparaffin was converted into the salt, the mixture was cooled to 18°. Then a solution of 1.59 g. of methyl 4-nitro-4-pentenoate in 5 ml. of methanol was added dropwise over a period of 15 minutes and the temperature was increased to 29–30°. The mixture was heated at 40–45° for two hours and the oily compound which separated was extracted with ether; the ether solution was washed 3 times with water, and then dried over sodium sulfate. The ether was evaporated and the oil obtained was converted to a crystalline compound by cooling. After recrystallization from absolute ether, 1.7 g. of colorless needles were obtained, m.p. 56°.

Anal. Calc'd for $C_8H_{13}N_3O_8$: C, 34.41; H, 4.69; N, 15.05.
Found: C, 34.79; H, 4.62; N, 16.07.

Methyl 4-bromo-4,6,6-trinitroheptanoate (XIII). A solution of 0.3 g. of sodium methoxide in 10 ml. of methanol was added to 1.0 g. of methyl 4,6,6-trinitroheptanoate and the mixture was refluxed for 10 minutes. The yellow solution obtained was evaporated and the residue was dissolved in 25 ml. of water. Bromine was added to the solution at 0° until the bromine color was no longer bleached. An oil separated which was extracted with ether, and the ether solution was dried over sodium sulfate and concentrated. The remaining yellow oil was diluted with absolute ether and cooled to −70°. The crystals formed were filtered and recrystallized, m.p. 78–79°. The yield was 1.0 g.

Anal. Calc'd for $C_8H_{12}BrN_3O_8$: N, 11.73; Br, 22.31.
Found: N, 12.67; Br, 22.48.

Dimethyl 4-bromo-4,6,6-trinitro-1,9-nonanedioate (XVI). A water solution of 2.14 g. of the sodium salt of methyl 4,4-dinitrobutyrate in 5 ml. of water was mixed with a solution of 1.59 g. of methyl 4-nitro-4-pentenoate in 5 ml. of methanol. The temperature increased to 40–45°. After 2 hours stirring at room temperature, the brown mixture was twice extracted with ether. The ether solution was washed with water and dried over sodium sulfate. After the ether was evaporated, the brown oil which did not crystallize and which decomposed when distilled in a high vacuum, was dissolved in 5 ml. of methanol. A solution of 0.6 g. of sodium methoxide in 5 ml. of methanol was added and a dark-brown mixture was obtained. After refluxing on a steam-bath for 15 minutes, the methanol was evaporated in a vacuum. The residue obtained was dissolved in 25 ml. of water and was cooled to −5–0°. Bromine was added dropwise with good agitation to the cloudy solution. When bromine was no longer decolorized, the water was decanted and the insoluble portion was dissolved in ether, dried over sodium sulfate, and the ether was evaporated. The residue crystallized from absolute ether upon cooling. After two recrystallizations from methanol the melting point was 105°.

Anal. Calc'd for $C_{11}H_{16}BrN_3O_{10}$: C, 30.71; H, 3.75; N, 9.77.
Found: C, 30.72; H, 3.86; N, 9.43.

SUMMARY

1. Substituted nitroölefins can be prepared by a reversed Diels Alder cleavage of *endo*-nitroethyleneanthracene and its derivatives.

2. 2-Nitro-3-acetoxypropene, methyl 4-nitro-4-pentenoate, and 4-nitro-4-pentenonitrile were prepared.

3. Methyl 4-nitro-4-pentenoate was reacted with terminal dinitro compounds to yield polynitro compounds in Michael type reactions.

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REFERENCES

(1) WIELAND AND SAKELLARIOS, *Ber.*, **52,** 898 (1919).
(2) BUCKLEY AND SCAIFE, *J. Chem. Soc.*, 1471 (1947).
(3) SCHMIDT AND RUTZ, *Ber.*, **61,** 2142 (1928).
(4) SCHWARZ AND NELLES, U. S. Patent 2,257,980.
(5) GOLD, *J. Am. Chem. Soc.*, **68,** 2544 (1946).
(6) ALDER AND RICKERT, *Ann.*, **543,** 11 (1940).
(7) ALLEN, BELL, AND GATES, *J. Org. Chem.*, **8,** 373 (1943).
(8) ALDER, STEIN, ROLLAND, AND SCHULZE, *Ann.*, **514,** 211 (1934).
(9) ALDER, RICKERT, AND WINDEMUTH, *Ber.*, **71,** 2451 (1938).

(10) KENYON AND YOUNG, *J. Chem. Soc.*, 263 (1941).
(11) JONES AND WALLIS, *J. Am. Chem. Soc.*, **48,** 169 (1926).
(12) ALDER AND RICKERT, *Ann.*, **524,** 180 (1936).
(13) ALDER AND RICKERT, *Ber.*, **70,** 1364 (1937).
(14) DIELS AND ALDER, *Ber.*, **62,** 2337 (1929).
(15) HENRY, *Compt. rend.*, **120,** 1265 (1895).
(16) MICHAEL, *J. prakt. Chem.*, [2] **45,** 62, (1892).
(17) Allylamine, *Neuere Methoden der preparativen Organischen Chemie*, p. 340, Verlag Chemie, 1943.
(18) DIELS AND THIELE, *Ber.*, **71,** 1173 (1938).