*Anal.* Calcd. for $C_{14}H_{28}N_6O_8$: C, 41.17; H, 6.91; N, 20.58. Found: C, 40.94; H, 6.83; N, 20.29.

*5-Methyl-5-nitro-2-hexanone.* To a solution of 8.16 g. (0.2 mole) of 98% assay sodium hydroxide in 60 ml. of methanol and 40 ml. of water were added 17.8 g. (0.2 mole) of 2-nitropropane and 16.4 g. (0.2 mole) of anhydrous sodium acetate at 0–5°. After salt formation was complete, 26.0 g. (0.2 mole) of 3-ketobutyl acetate was added dropwise over a 15-min. period. The temperature was raised to 40–45° and maintained there for 20 hr. The methanol was then removed *in vacuo* and the residual material extracted with small portions of ether. Removing the solvent *in vacuo* and distilling gave 29.4 g. (92% yield) of *5-methyl-5-nitro-2-hexanone*, b.p. 88–91° at 2 mm., $n_D^{20.0}$ 1.4450, lit. value,[14] $n_D^{20.6}$ 1.4444.

*The 2,4-dinitrophenylhydrazone derivative* melted at 130.5–131.5°, lit. value,[14] m.p. 130.5–131.5°.

*5-Nitro-2-heptanone.* To a stirred solution of 12.24 g. (0.3 mole) of 98% assay sodium hydroxide in 60 ml. methanol and 30 ml. of water which was cooled to 0–5°, were added 26.7 g. (0.3 mole) of 1-nitropropane and 24.6 g. (0.3 mole) of anhydrous sodium acetate. After salt formation was complete, the temperature was raised to 35° and 39.0 g. (0.3 mole) of 3-ketobutyl acetate dissolved in 60 ml. of methanol was added dropwise over a 45-min. period. The temperature was then increased to 40–45° and maintained there for approximately 17 hr. Removing the solvent *in vacuo*, extracting with ether, evaporating the solvent and distilling the remaining oil, gave 34.4 g. (72% yield) of product, b.p. 100–105° at 5 mm. Redistillation afforded 5-nitro-2-heptanone, b.p. 102° at 4.8 mm., $n_D^{20}$ 1.4410.

*Anal.* Calcd. for $C_7H_{13}NO_3$: C, 52.83; H, 8.17; N, 8.80. Found: C, 52.86; H, 8.35; N, 8.82.

*Acknowledgment.* We are indebted to the Office of Naval Research for the financial support of this work. We also wish to express gratitude to Dr. A. T. Nielsen and Mrs. Carol Anderson for carrying out some of the experiments.

LAFAYETTE, IND.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

# Diels-Alder Reactions with Nitro Olefins Generated *In Situ*[1]

HENRY FEUER, ROBERT MILLER, AND CORNELIUS B. LAWYER

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Nitro olefins generated *in situ* from the corresponding 2-nitroalkyl acetates with sodium acetate react readily in the Diels-Alder reaction with cyclopentadiene in hydroxylic and nonhydroxylic solvents, and with anthracene in nonhydroxylic solvents.

The Diels-Alder reaction of nitro olefins with suitable dienes has been employed for many years, without any substantial improvement in the original procedure of Alder and co-workers.[2] Thus, the addition of nitro olefins to dienes has been effected generally either at elevated temperatures and pressures[3,4] with or without solvents or in high boiling solvents at atmospheric pressure.[5,6] Several workers have carried out these reactions at approximately room temperature,[7–9] but even here, as in the former cases, the nitro olefins had to be prepared and purified separately. The nitro olefins are usually prepared from the corresponding alcohols by dehydration or by dehydroacetylating the corresponding nitroalkyl acetates.[10] In both procedures the olefin is removed from the reaction medium by distillation, and purified by rectification. Generally, the high temperatures employed in the preparation and purification leads to some decomposition of the nitro olefin.

It was postulated that this difficulty could be overcome to a large extent if the olefins were generated *in situ*. Since it had been found that 2-nitroalkyl acetates could be converted readily to nitro olefins under mild conditions,[10] it was decided to employ these esters directly as the source of nitro olefins in the Diels-Alder reaction. The results of these experiments are listed in Table I.

Recently,[11] 2,2-dinitroethanol was employed directly in a Diels-Alder reaction. Dehydration *in situ* to 1,1-dinitroethene was achieved on adding 2,2-dinitroethanol to a refluxing solution of cyclopentadiene in chlorobenzene. Also, Kaplan and Shechter[12] have prepared 4-nitrocyclohexene from 1,3-butadiene and nitroethylene which was generated *in situ* from 2-nitroethyl acetate and catalytic amounts of sodium acetate at 95–105° or

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(1) (a) From the Ph.D. Thesis of Robert Miller, Purdue University, September 1958. (b) Much of the work described in this paper was presented at the fall, 1959, ACS meeting in Atlantic City, N. J.

(2) K. Alder, H. F. Rickert, and E. Windemuth, *Ber.*, **71**, 2451 (1938).

(3) D. V. Nightingale, M. Maienthal, and J. A. Gallagher, *J. Am. Chem. Soc.*, **75**, 4852 (1953).

(4) S. Sugasawa and K. Kodama, *Ber.*, **72**, 675 (1939).

(5) K. Klager, *J. Org. Chem.*, **20**, 650 (1955).

(6) W. E. Noland, H. I. Freeman, and M. S. Baker, *J. Am. Chem. Soc.*, **78**, 188 (1956).

(7) W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952).

(8) J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Am. Chem. Soc.*, **76**, 450 (1954).

(9) A. E. Tienne, A. Spire, and E. Toromanoff, *Bull. Soc. Chim. France*, 750 (1952).

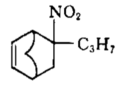
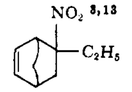
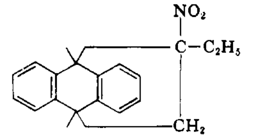
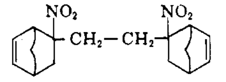
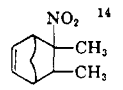
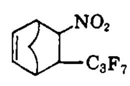
(10) For an extensive compilation of the literature, reference is made to H. Feuer and R. Miller, *J. Org. Chem.*, **26**, 1348 (1961).

(11) M. H. Gold, E. E. Hamel, and K. Klager, *J. Org. Chem.*, **22**, 1665 (1957).

(12) Private communication from H. Shechter, Ohio State University.

TABLE I

DIELS-ALDER REACTION WITH NITRO OLEFINS PREPARED *In Situ*

| Dienophile | Product[a] | Yield, % |
|---|---|---|
| 2-Nitropentyl acetate |  | 73,[b,g] 80[c,h] |
| 2-Nitrobutyl acetate |  [8,13] | 44,[e,h] 73[c,h] |
| 2-Nitrobutyl acetate[j] |  | 40[f,i] |
| 1,6-Diacetoxy-2,5-dinitrohexane |  | 87,[c,g] 93,[c,h] 76[e,h] |
| 3-Nitro-2-butyl acetate |  [14] | 38[d,h] |
| 2-Perfluoropropyl-2-acetoxy-1-nitroethane |  | 79[b,g] |

[a] The diene was cyclopentadiene unless otherwise specified. [b] Solvent was absolute ethanol. [c] Solvent was 95% ethanol. [d] Solvent was aqueous *t*-butyl alcohol. [e] Solvent was anhydrous benzene. [f] Solvent was anhydrous xylene. [g] Slight excess of cyclopentadiene employed. [h] Large excess of cyclopentadiene employed. [i] Large excess of 2-nitroalkyl acetate was employed. [j] The diene was anthracene.

from nitroethanol and phthalic anhydride at 100–150°.

In the case of the reactions with cyclopentadiene, we found that best results were obtained when the diene was used in excess and the 2-nitroalkyl acetate and sodium acetate were used in equivalent amounts. With 2-nitro-1-alkenes and 1-nitro-1-alkenes, a reaction temperature of 40–55° and a reaction time of eighteen to twenty-five hours was usually sufficient in such solvents as ethanol or *t*-butyl alcohol. With 2-nitro-2-alkenes, however, a longer reaction time was required. In nonhydroxylic solvents such as benzene, the reactions were usually slower and it was therefore necessary to employ a higher reaction temperature as well as a longer reaction time in order to obtain optimum yields.

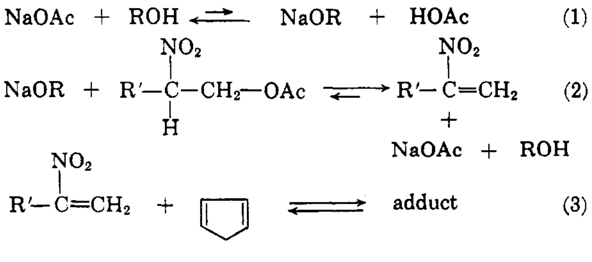
The reactions carried out in alcoholic solvents were usually found to contain a small amount of the nitro ether which resulted from a Michael type addition of the alcohol (alkoxide ion) to the nitro olefin. Ether formation, however, could be minimized by employing a 100% excess of cyclopentadiene. If the Diels-Alder reaction was slower than the ether formation as in the reaction with 3-nitro-2-butyl acetate in ethanol, only a very small amount of the expected 5,6-dimethyl-5-nitro-2-norbornene was obtained. The infrared spectrum of the reaction mixture indicated that the majority of the nitro olefin was converted to its ethyl ether. It was found that by employing an alcohol with relatively large steric requirements, such as *t*-butyl alcohol, ether formation was minimized, and the amount of the expected bicyclic compound was increased. It should be noted though, that even here the yield of the Diels-Alder adduct was relatively low, and a large amount of unchanged 2-nitro-2-butene was recovered.

1,6-Diacetoxy-2,5-dinitrohexane reacted with cyclopentadiene in the presence of sodium acetate in hydroxylic and nonhydroxylic solvents, affording good yields of the expected bisbicyclo compound. It should be noted that reactions employing 1,6-diacetoxy-2,5-dinitrohexane in hydroxylic solvents were susceptible to polymerization. This difficulty could be minimized by conducting the reaction, first at room temperature (25°) for approximately one hour and then raising the temperature slowly to 43–45° and maintaining it there for a specified length of time.

The Diels-Alder reaction with nitro olefins prepared *in situ* was also successful with anthracene. Due to the lower reactivity of this diene, it was necessary to carry out the reaction in nonhydroxylic solvents to avoid ether formation. Best results were obtained by allowing the anthracene to react with an excess of the 2-nitroalkyl acetate in the presence of sodium acetate in refluxing xylene.

## DISCUSSION

The observations and results of the reactions carried out in hydroxylic solvents suggest the following reaction path:



$$\mathrm{NaOAc} + \mathrm{ROH} \rightleftarrows \mathrm{NaOR} + \mathrm{HOAc} \quad (1)$$

$$\mathrm{NaOR} + \mathrm{R'}\!-\!\overset{\overset{\large NO_2}{|}}{\underset{\underset{\large H}{|}}{C}}\!-\!CH_2\!-\!OAc \rightleftarrows \mathrm{R'}\!-\!\overset{\overset{\large NO_2}{|}}{C}\!=\!CH_2 + \mathrm{NaOAc} + \mathrm{ROH} \quad (2)$$

Step (1) of the mechanism involves the alcoholysis of sodium acetate. Although this step lies far to the left, the utilization of the alkoxide ion in producing the nitro olefin in step (2) shifts the equilibrium of step (1) to the right. In step (3) the nitro olefin reacts with the diene to afford the Diels-Alder adduct.

Although the presence of alkoxide ion is indicated by ether formation, further proof that the

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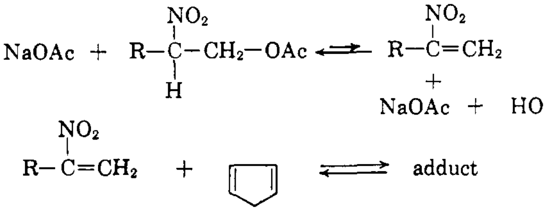
(13) We are grateful to Mrs. C. J. Anderson for carrying out these experiments.

(14) W. E. Noland and R. E. Bambury, *J. Am. Chem. Soc.*, 77, 6386 (1955).

nitro olefin is formed by the reaction of the 2-nitroalkyl acetate with alkoxide ion rather than acetate ion lies in the fact that when the Diels-Alder reaction did not proceed well, a large portion of the nitroolefin could be isolated from the reaction mixture. Thus, as was previously stated, the reaction of 3-nitro-2-butyl acetate in *t*-butyl alcohol afforded a sizable amount of unchanged nitroolefin. If the acetate ion had reacted directly with the 2-nitroalkyl acetate to produce the olefin, the mechanism would be the same as that proposed in nonhydroxylic solvents, in which the olefin is formed in step (1) by a direct attack of the sodium acetate on the 2-nitroalkyl acetate. However, this step lies far to the left as indicated by the fact that when the Diels-Alder reaction did not proceed most of the unchanged 2-nitroalkyl acetate was reclaimed. Thus, in nonhydroxylic solvents it is necessary for the Diels-Alder reaction to proceed in step (2), in order to shift the equilibrium of step (1) to the right.



$$\text{NaOAc} + \text{R}-\overset{\overset{\text{NO}_2}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}-\text{CH}_2-\text{OAc} \rightleftharpoons \text{R}-\overset{\overset{\text{NO}_2}{|}}{\text{C}}=\text{CH}_2 + \text{NaOAc} + \text{HOAc} \qquad (1)$$

$$\text{R}-\overset{\overset{\text{NO}_2}{|}}{\text{C}}=\text{CH}_2 + \quad \rightleftharpoons \text{adduct} \qquad (2)$$

## EXPERIMENTAL

*Reagents.* Cyclopentadiene was prepared by the cleavage of dicyclopentadiene.[15]

Commercial grade anthracene was purified by several recrystallizations from a mixture consisting of 4:1 ratio of benzene to xylene, and decolorizing carbon.

*5-Nitro-5-propyl-2-norbornene.* To a stirred mixture containing 8.2 g. (0.1 mole) of sodium acetate, 13.2 g. (0.2 mole) of cyclopentadiene, and 100 ml. of 95% ethanol was added 17.5 g. (0.1 mole) of 2-nitropentyl acetate.[12] Heating at 48–50° for 17 hr. and removing ethanol, acetic acid, and dicyclopentadiene *in vacuo* left an oily solid which was kept at 0–5° while a solution of 3 g. of sodium hydroxide in 20 ml. of water cooled to 0–5° was added. The mixture was dissolved in methanol at 0–5°, allowed to warm up to room temperature and kept there for 12 hr. Removing the methanol *in vacuo*, extracting the oil with ether, and distilling afforded 14.5 g. (80% yield) of crude product, b.p. 93–97° at 4.5 mm.; $n_D^{20}$ 1.4826. Redistillation gave *5-nitro-5-propyl-2-norbornene*, b.p. 98° at 4.9 mm., $n_D^{20}$ 1.4832.

*Anal.* Calcd. for $C_{10}H_{15}NO_2$: C, 66.30; H, 8.29; N, 7.73. Found: C, 66.54; H, 8.55; N, 8.02.

*5-Ethyl-5-nitro-2-norbornene.*[13] (a) *Employing 95% ethanol.* A mixture of 12.3 g. (0.15 mole) of sodium acetate, 24.15 g. (0.15 mole) of 2-nitrobutyl acetate, 19.8 g. (0.3 mole) of cyclopentadiene, and 160 ml. of 95% ethanol was heated at 48–50° for 17 hr. The reaction mixture was worked up as in the preceding experiment. Distillation of the residual oil afforded 18.23 g. (73% yield) of *5-ethyl-5-nitro-2-norbornene*, b.p. 95–100° at 10 mm. Subsequent distillations afforded the analytical sample, b.p. 94° at 10 mm., $n_D^{20}$ 1.4860, lit.[3] $n_D^{20}$ 1.4888.

*Anal.* Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.40; H, 7.87; N, 8.37.

(b) *Employing anhydrous benzene.* A mixture of 32.2 g. (0.2 mole) of 2-nitrobutyl acetate, 16.4 g. (0.2 mole) of anhydrous sodium acetate, 13.2 g. (0.2 mole) of cyclopentadiene, and 200 ml. of anhydrous benzene was heated at reflux for 22 hr. At this time, 13.2 g. (0.2 mole) of cyclopentadiene was added to the mixture and refluxing was continued for 21 more hr. The reaction mixture was filtered through a sintered glass funnel and the benzene, acetic acid, and dicyclopentadiene were removed from the filtrate *in vacuo*. The residual oil was distilled and the fraction, b.p. 74–85° at 5 mm. was collected. This material was dissolved in a small amount of ether and shaken with 100 ml. of 1*N* sodium hydroxide solution for approximately 10 min. The aqueous layer was then extracted with several portions of ether, the ether extracts were combined with the original ethereal solution and the solvent was removed *in vacuo*. Distillation of the residual oil afforded 14.8 g. (44% yield) of *5-ethyl-5-nitro-2-norbornene*, $n_D^{20}$ 1.4864.

*5,6-Dimethyl-5-nitro-2-norbornene.* (a) *Employing t-butyl alcohol.* A mixture of 16.1 g. (0.1 mole) of 3-nitro-2-butyl acetate, 8.2 g. (0.1 mole) of sodium acetate, and 130 ml. of anhydrous *t*-butyl alcohol was heated to 60° for 1 hr. and then 4.0 g. of cyclopentadiene was added all at once. The temperature of the reaction was maintained, and after 4 hr., 4.0 g. more of cyclopentadiene was added. Further additions of 4.0-g. and 3.0-g. portions of cyclopentadiene were made after a reaction time of 24 and 29 hr., respectively. The reaction was allowed to continue for 16 more hr. and the solvent was then removed *in vacuo*. The residual liquid was taken up in ether and filtered through a sintered glass funnel to remove the sodium acetate. The ether was removed *in vacuo*, and the residual oil was distilled through a steam heated condenser. A fraction consisting of a mixture of solid and liquid was collected at 64–65° at 1.3 mm., representing 6.3 g. (38% yield) of product. The liquid portion of this product decomposed slowly at room temperature as indicated by a darkening of its color. The solid was separated from the liquid by first cooling the mixture to 0–5°, and then transferring the solid mass to a clay plate at room temperature. A solid remained which was dissolved in hexane and filtered. Evaporation of the hexane yielded *5,6-dimethyl-5-nitro-2-norbornene*, m.p. 76–77°, lit.[14] m.p. 84.5–86.5°.

*Anal.* Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.68; H, 7.80; N, 8.08.

The infrared spectra of both the liquid and solid portions were found to be very similar indicating that they were probably diastereoisomers.

(b) *Employing 95% ethanol.* A mixture of 32.2 g. (0.20 mole) of 3-nitro-2-butyl acetate, 16.4 g. (0.20 mole) of sodium acetate, 15.8 g. (0.24 mole) of cyclopentadiene and 200 ml. of 95% ethanol was heated at 49–51° for 21 hr. The solvent was then removed *in vacuo* and the residual oily solid was transferred to a separatory funnel with the aid of a small amount of water and ether. Extraction of the aqueous portion with several portions of ether, and evaporation of the solvent yielded an oil. Distillation of the oil afforded a large forerun, b.p. 47–58° at 1.5 mm. The infrared spectrum of this material showed an absorption peak in the 9 μ region, indicating an ether linkage, and probably consisted mainly of 2-ethoxy-3-nitrobutane. The desired product distilled at 66–68° at approximately 1.5 mm. and amounted to 4.0 g. or a 12% yield. The infrared spectrum of this material was identical with the analytical sample obtained from procedure (a).

*6-Perfluoropropyl-5-nitro-2-norbornene.* A mixture of 15.05 g. (0.05 mole) of 2-perfluoropropyl-2-acetoxy-1-nitroethane, 4.96 g. (0.75 mole) of cyclopentadiene, 4.10 g. (0.05 mole) of sodium acetate and 140 ml. of absolute ethanol was heated at 48–50° for 18 hr. The ethanol was then removed *in vacuo* and 20 ml. of ether was added to the residual

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(15) R. B. Moffet, *Org. Syntheses*, **32**, 41 (1952).

material. The reaction mixture was then filtered through a sintered glass funnel, the sodium acetate washed with several portions of ether, the ether removed *in vacuo* and the residual oil distilled. Distillation yielded 12.1 g. (79% yield) of product, b.p. 70–71° at 3 mm. Redistillation gave *6-perfluoropropyl-5-nitro-2-norbornene*, b.p. 67° at 2.5 mm., $n_D^{20}$ 1.4021.

*Anal.* Calcd. for $C_{10}H_8F_7NO_2$: C, 39.08; H, 2.61; N, 4.56. Found: C, 38.96; H, 2.61; N, 4.69.

*1,2-Bis(2-nitro-5-norbornen-2-yl)ethane.* (a) *Employing a small excess of cyclopentadiene.* A mixture of 2.46 g. (0.03 mole) of sodium acetate and 4.38 g. (0.015 mole) of 1,6-diacetoxy-2,5-dinitrohexane was suspended in 50 ml. of 95% ethanol and 2.5 g. (0.037 mole) of cyclopentadiene was added immediately. The reaction temperature was maintained at 25° for 1 hr. and then raised slowly over a 1-hr. period to 41–43° and maintained there for 22 hr. The reaction mixture was then evaporated to dryness *in vacuo* and the adduct was removed from the sodium acetate by triturating the solid residue with a warm solution consisting of equal amounts of ethyl ether and acetone, and filtering the supernatant liquid through a sintered glass funnel. The solvents were removed *in vacuo* and the residual oily solid was shaken with 10 ml. of 70% aqueous ethanol and the ethanol was decanted after cooling to −78°. The brown solid that remained was dried on a clay plate and weighed 4.0 g. representing an 87% yield of crude product, m.p. 130–150° dec. One isomer was separated from the crude material by recrystallizing it from heptane and decolorizing carbon, m.p. 205–207° dec. Recrystallization of this material from 95% ethanol raised the melting point to 209.5–211° dec.

*Anal.* Calcd. for $C_{16}H_{20}N_2O_4$: C, 63.15; H, 6.57; N, 9.21. Found: C, 62.94; H, 6.69; N, 9.41.

The infrared spectra of the crude material and the analytical sample were similar, indicating that practically all of the material obtained from the reaction consisted of a mixture of diastereoisomers.

(b) *Employing a large excess of cyclopentadiene.* The amounts of materials utilized in this experiment were the same as in experiment (a), except that 3.96 g. (0.06 mole) of cyclopentadiene was employed. The reaction temperature was maintained at 25° for 1 hr. and then raised slowly over a 1-hr. period to 43–45° and kept there for 18 hr. The reaction mixture was worked up as in part (a) and yielded 4.3 g. of product (93% yield), m.p. 135–150° dec. The infrared spectrum of this material was identical with the analytical sample obtained in procedure (a).

(c) *Using dry benzene.* A mixture of 1.64 g. (0.02 mole) of anhydrous sodium acetate, 2.92 g. (0.01 mole) of 1,6-diacetoxy-2,5-dinitrohexane, 1.32 g. (0.02 mole) of cyclopentadiene and 75 ml. of anhydrous benzene was refluxed for 22 hr. At this time, 1.32 g. (0.02 mole) more of cyclopentadiene was added to replace the part which was converted to dicyclopentadiene. The reaction mixture was refluxed for 19 more hr. and then filtered while hot through a sintered glass funnel. The sodium acetate on the funnel was washed with several portions of hot benzene. The washings were combined with the filtrate and the benzene was removed *in vacuo*, leaving a dark brown solid. This solid was washed with 10 ml. of 95% ethanol, that had been cooled to approximately −50°, and filtered immediately. The precipitate thus obtained, weighed 2.28 g. (75% yield) and had a melting range of 160–170° dec. One of the isomers was separated by crystallizing the brown solid from hot heptane and decolorizing carbon. Subsequent cooling of the heptane yielded a white crystalline solid, m.p. 204–206° dec. A mixed melting point determination with this material and an authentic sample of 1,2-bis(2-nitro-5-norbornen-2-yl)-ethane showed no depression.

*9,10-(11-Ethyl-11-nitroethano)-9,10-dihydroanthracene.* A mixture of 4.1 g. (0.5 mole) of anhydrous sodium acetate, 8.9 g. (0.05 mole) of anthracene, 16.1 g. (0.1 mole) of 2-nitrobutyl acetate, and 90 ml. of xylene was refluxed for 12.5 hr. (a small evolution of oxides of nitrogen was noticed after 9 hr.). The reaction mixture was filtered while hot through a sintered glass funnel and the filtrate was cooled to 0–5° and after several hours, the unchanged anthracene was filtered off. Additional amounts of anthracene were removed by reducing the filtrate to one half of its volume, cooling to 0–5° and filtering. The filtrate was taken to dryness *in vacuo* and the solid residue was then taken up in a minimum amount of hot isopropyl ether, cooled to −78° and filtered, yielding 4.1 g. of crude *9,10-(11-ethyl-11-nitroethano)-9,10-dihydroanthracene*, m.p. 107–109°. Concentrating and cooling the filtrate afforded 1.5 g. more of product, or a 40% yield of crude product. The material was recrystallized first from isopropyl ether and then from isopropyl alcohol and decolorizing carbon. To ensure the removal of the last traces of anthracene, the product was placed under high vacuum for 2 days, m.p. 108–111°.

*Anal.* Calcd. for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.56; H, 6.12; N, 4.78.

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LAFAYETTE, IND.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

# The Syntheses of Some Highly Hindered Potential Dienophiles

N. J. HUDAK[1] AND J. MEINWALD

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The syntheses of four olefins, 5-cyano-3,3-dimethyl-1-nitro-1-pentene, 6-methoxy-3,3-dimethyl-1-nitro-1-hexene, ethyl 7-methoxy-4,4-dimethyl-2-heptenoate, and 7-methoxy-4,4-dimethyl-2-heptenoic acid, to act as potential dienophiles in condensations with cyclopentadiene, are described.

The sesquiterpene longifolene has been assigned structure I principally on the basis of x-ray diffraction studies.[2] Longifolene can be considered as a derivative of norbornane in which the carbon atoms at the 2 and 7 positions are joined by a four carbon chain to form a seven-membered ring. An attractive synthetic route to this unusual structure appeared, therefore, to lie through a series of appropriate 2,7-disubstituted norbornanes.

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[1] Monsanto Chemical Company Fellow, 1957–1958.

[2] R. H. Moffett and D. Rogers, *Chem. and Ind.*, 916 (1953).