## Chloronitrostyrenes in the Diels-Alder Reaction[1]

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The Diels-Alder reaction of nitroalkenes with conjugated dienes has been reported by Alder, Windemuth, and Rickert,[5] and similar reactions of β-nitrostyrenes have been reported by Allen, Bell, and Gates.[6,7] However, there is little information in the literature concerning the use of chlorine-substituted β-nitrostyrenes in the Diels-Alder reaction.

TABLE I

New β-Nitrostyrene Derivatives

| Substituted β-Nitro-styrene | M.P.[a] | Yield, % | Calcd., % C | Calcd., % H | Calcd., % N | Found, % C | Found, % H | Found, % N | Preparation Method |
|---|---|---|---|---|---|---|---|---|---|
| 2,4-Dichloro- | 112–113 | 62 | 44.07 | 2.31 | 6.43 | 44.37 | 2.35 | 6.29 | Thiele |
| 3,4-Dichloro- | 89–90 | 68 | 44.07 | 2.31 | 6.43 | 44.40 | 2.33 | 5.63 | Thiele |
| 2,4-Dichloro-β-methyl- | 80–81 | 38 | 46.58 | 3.04 | 6.04 | 46.76 | 3.05 | 5.80 | Knoevenagel and Walter |
| 3,4-Dichloro-β-methyl- | 77–78 | 59 | 46.58 | 3.04 | 6.04 | 46.78 | 2.88 | 5.81 | Knoevenagel and Walter |
| *p*-Chloro-β-methyl- | 85 | 60 | 54.69 | 4.08 | 7.09 | 55.16 | 4.10 | 6.91 | Knoevenagel and Walter |
| *o*-Chloro-β-methyl- | 38 | 50 | 54.69 | 4.08 | 7.09 | 54.84 | 4.04 | 6.40 | Knoevenagel and Walter |
| *o*-Chloro-β-ethyl | 36 | 50 | 56.74 | 4.76 | 6.62 | 57.00 | 4.60 | 5.75 | Knoevenagel and Walter |

[a] Melting points are uncorrected.

A variety of β-nitrostyrenes was prepared using previously published procedures. A slight modification of the method reported by Thiele[8] was employed for condensations of nitromethane. Sodium hydroxide was used in place of potassium hydroxide, and it was necessary to employ more alcohol than indicated by the literature. Otherwise, the mixture became extremely thick and difficult to stir. Thiele's method is not applicable to the reaction of nitroethane and 1-nitropropane. Therefore, Knoevenagel and Walter's method[9] was used, employing methylamine hydrochloride and sodium carbonate as the condensation catalyst. The β-nitrostyrene derivatives not previously reported are shown in Table I.

The reactions of these compounds, and several other previously reported β-nitrostyrenes, with butadiene and cyclopentadiene were studied. Seven Diels-Alder adducts not previously reported in the literature were obtained and are shown in Table II.

None of the β-alkyl-β-nitrostyrenes gave adducts, probably because of steric factors. This result was not surprising as only a few examples are known of compounds entering into the Diels-Alder reaction as a dienophile which have more than one radical other than hydrogen on each end of the double bond. The most puzzling result is that *p*-chloro-β-nitrostyrene could not be made to condense with cyclopentadiene, even though it condensed with butadiene, whereas *o*-chloro-, 2,4-dichloro-, and 3,4-dichloro-β-nitrostyrenes reacted readily with both cyclopentadiene and butadiene to form the expected products. This reaction was tried a number of times under a variety of conditions without success: (1) at room temperature in a variety of solvents; (2) at 90° and at 155° in sealed tubes; and (3) refluxed in toluene and in ether.

### EXPERIMENTAL

*2,4-Dichloro-β-nitrostyrene* (*Modification of Thiele's method*[8]). Thirty-five grams (0.2 mole) of 2,4-dichlorobenzaldehyde, 12.2 g. (0.2 mole of nitromethane, and 100 ml. of methanol were placed in a 2-l., three-neck flask equipped with a stirrer and immersed in an ice-salt bath. A sodium hydroxide solution (5 g. of sodium hydroxide in 20 ml. of water) was added dropwise with stirring at such a rate as to keep the temperature between 10–15°. A thick white paste

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(1) This paper is taken from theses submitted to the faculty of Ohio University in partial fulfillment of the requirements for the degree of Master of Science by Eugene W. Goldberg and Richard W. Fairchild, and was presented at the 122nd meeting of the American Chemical Society in September, 1952, Paper 129, Division of Organic Chemistry.

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(5) K. Alder, H. F. Rickert, and E. Windemuth, *Ber.*, **71**, 2451–2461 (1938).

(6) C. H. F. Allen and A. Bell, *J. Am. Chem. Soc.*, **61**, 521 (1939).

(7) C. H. F. Allen, A. Bell, and J. W. Gates, Jr., *J. Org. Chem.*, **8**, 373 (1943).

(8) J. Thiele, *Ber.*, **32**, 1294 (1899).

(9) E. Knoevenagel and L. Walter, *Ber.*, **37**, 4502 (1904).

TABLE II

DIELS-ALDER ADDUCTS FROM CHLORINE-CONTAINING β-NITROSTYRENES

| Name | M.P.[a] | Yield, % | Calcd., % (Found, %) C | H | N |
|---|---|---|---|---|---|
| 4-*p*-Chlorophenyl-5-nitrocyclohexene[b] | 87 | 50 | 60.64<br>(60.43 | 5.09<br>4.81 | 5.89<br>5.90) |
| 4-*o*-Chlorophenyl-5-nitrocyclohexene | 78 | 55 | 60.64<br>(60.96 | 5.09<br>5.04 | 5.89<br>5.74) |
| 4-(3,4-Dichlorophenyl)-5-nitrocyclohexene | 95 | 14 | 52.96<br>(53.00 | 4.08<br>3.91 | 5.15<br>5.01) |
| 4-(2,4-Dichlorophenyl)-5-nitrocyclohexene | 75 | 20 | 52.96<br>(53.22 | 4.08<br>3.99 | 5.15<br>4.51) |
| 5-*o*-Chlorophenyl-6-nitro-[2.2.1]bicyclo-2-heptene | 68 | 85 | 62.53<br>(62.82 | 4.84<br>4.85 | 5.61<br>5.53) |
| 5-(3,4-Dichlorophenyl)-6-nitro-[2.2.1]bicyclo-2-heptene | 119–120 | 42 | 54.94<br>(55.13 | 3.90<br>3.87 | 4.93<br>4.74) |
| 5-(2,4-Dichlorophenyl)-6-nitro-[2.2.1]bicyclo-2-heptene | 105–106 | 42 | 54.94<br>(55.28 | 3.90<br>3.89 | 4.93<br>4.87) |

[a] All melting points are uncorrected. [b] This adduct was reported by A. C. Huitric and W. D. Kumler, *J. Am. Chem. Soc.*, **78**, 614–622 (1956), after the paper on which this manuscript is based was presented.

was formed. The reaction mixture was allowed to stand for 15 min. after the addition of the sodium hydroxide. Enough ice water was added to dissolve the paste. The resulting solution was run into 200 ml. of a dilute hydrochloric acid solution (1 ml. of concd. hydrochloric acid to 1.5 ml. of water) with stirring, at such a rate that the stream just failed to break into drops. The resulting yellow precipitate was filtered by suction and washed with water. After recrystallization from ethanol, the yield was 27 g. (62%). 3,4-Dichloro-β-nitrostyrene was prepared by the same method.

*4-o-Chlorophenyl-5-nitrocyclohexene.* An iron reaction tube, made of 1/8-in.-wall pipe welded closed at one end and fitted with a threaded cap at the other end (internal dimensions: 1 × 26 in.), was charged with 37.6 g. (0.2 mole) of *o*-chloro-β-nitrostyrene and a solution of 32 g. (0.6 mole) of butadiene in 80 ml. of toluene. The tube was tightly capped and heated in a Carius tube furnace at 120° for 5 hr. The contents were removed when the tube had cooled to room temperature (12 hr.). The resulting dark brown solution was steam distilled to remove unchanged butadiene and the toluene solvent. The residue, a viscous brown liquid, solidified when cooled in an ice bath. The solid was dissolved in boiling ethanol, charcoal was added, and the hot solution was filtered. Gray-brown crystals separated upon cooling and were filtered with suction and pressed dry. The dry crystalline mass contained pieces of a black material, apparently polymeric, which were picked out and discarded. The remaining material was crystallized several times from ethanol before a white product was obtained and was finally vacuum distilled. The yield of white odorless crystals was 26 g. (55%). 4-*p*-Chlorophenyl-5-nitrocyclohexene, 4-(2,4-dichlorophenyl-5-nitrocyclohexene, and 4-(3,4-dichlorophenyl)-5-nitrocyclohexene were made by the same procedure.

*5-o-Chlorophenyl-6-nitro[2.2.1]bicyclo-2-heptene.* Eleven grams (0.05 mole) of 2,4-dichloro-β-nitrostyrene, 6.3 ml. (0.075 mole) of freshly distilled cyclopentadiene, and 20 ml. of toluene were mixed and placed in a tightly capped bottle. The reaction mixture was allowed to stand at room temperature for 2.5 days. After cooling, the crystals were removed by filtration and purified by several recrystallizations from ethanol with charcoal treatment to give white odorless crystals. The yield was 6 g. (42%). 5-(3,4-Dichlorophenyl-6-nitro[2.2.1]-bicyclo-2-heptene and 5-(3,4-dichlorophenyl)-6-nitro[2.2.1]bicyclo-2-heptene were made by the same procedure.

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## Some Properties of Aryl and Alkyl Thiatriazoles[1]

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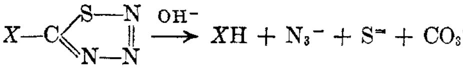
The thiatriazole ring system, first reported in 1896 by Freund, Schander, and Schwartz,[2] has received almost no attention until recently, when the studies of Lieber and co-workers[3] put the earlier structural assignments on a firmer basis. At the inception of the present work, all reported studies dealt only with 5-mercapto- or 5-aminothiatriazoles (I), whose characteristic behavior is alkaline hydrolysis to azide, sulfide, and carbonate, and thermal decomposition to cyano compounds, sulfur, and



$$\text{I} \longrightarrow X\text{—CN} + \text{S} + \text{N}_2$$

nitrogen. The reported conversion of chlorodifluorothioacetyl fluoride to chlorodifluoroacetonitrile by heating with sodium azide is also probably an example of the formation and decomposition of a thiatriazole.[4]

When most of the present work had been completed, Bacchetti and Alemagna[5a] described 5-

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