The Diels-Alder Reaction of Cyclopentadiene with Nitroölefins. With 1-Nitroheptene and 1-Nitroöctene

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Cyclopentadiene is known to undergo Diels-Alder reactions with several 1-nitroalkenes: β-nitrostyrene in 86[1] to 95%[2,3] yield, nitroethylene[4] in 61[5] to 66%[6] yield, 1-nitropropene in 55[4] to 59%[7] yield, and 1-nitropentene in 72% yield,[4] giving adducts containing secondary nitro groups. Furthermore, cyclopentadiene reacts with some nitro-olefins, giving adducts containing tertiary nitro groups, as in the reaction with 2-nitropropene,[8,9] 2-nitro-1-butene,[8] and 2-nitro-2-butene.[9] The report of Nightingale and Janes[10] that all efforts to condense 1-nitroheptene with cyclopentadiene were negative would appear, therefore, to be anomalous.

We have now obtained the corresponding adducts from reactions of 1-nitroheptene and 1-nitroöctene with excess refluxing cyclopentadiene. With this removal of the last remaining contrary evidence, the conclusion now appears justified that the Diels-Alder reaction of 1-nitroalkenes with cyclopentadiene is a general reaction.

EXPERIMENTAL

5-Nitro-6-pentylbicyclo-[2,2,1]-2-heptene. Matheson, Coleman and Bell technical grade *n*-hexaldehyde was distilled and purified through the bisulfite addition compound.[11] *n*-Hexaldehyde and nitromethane were condensed in the presence of an equivalent amount of sodium hydroxide to form 1-nitro-2-heptanol[10] in 83% yield by the method of Sprang with Degering[12] for 1-nitro-2-octanol, except that it was found desirable, after adding the sodium hydroxide over a period of 4 hours, to leave the reaction mixture at 10° for 2 more hours before diluting and neutralizing it with acetic acid. 1-Nitro-2-heptanol was acetylated by the method of Tindall[13] and dehydroacetylated in 78% yield to 1-nitroheptene[10] by refluxing in ether solution with potassium bicarbonate for 13 hours by the method of Schmidt and Rutz.[14]

1-Nitroheptene (13.0 g., 0.0907 mole, n_{D}^{25} 1.4551) and freshly cracked cyclopentadiene (34.0 g., 0.514 mole) were warmed on the steam-bath until refluxing of the cyclopentadiene ceased (3 hours) and for 2 more hours. The solution was vacuum-distilled, removing dicyclopentadiene and a considerable forerun and yielding a pale yellow liquid (12.5 g., 0.0598 mole, 66%), b.p. 122–123° (~5 mm.), n_{D}^{28} 1.4788. Redistillation gave 5-nitro-6-pentylbicyclo-[2,2,1]-2-heptene as an almost colorless liquid, b.p. 121° (~3–4 mm.), n_{D}^{25} 1.4800; $\nu_{\mathrm{NO_2}}$ (cm.$^{-1}$) 1544, 1375.

Anal. Calc'd for $C_{12}H_{19}NO_2$ (209.28): C, 68.86; H, 9.15; N, 6.69. Found: C, 68.64; H, 9.37; N, 6.66.

5-Nitro-6-hexylbicyclo-[2,2,1]-2-heptene. 1-Nitro-2-octanol[12] was acetylated and pyrolyzed to 1-nitroöctene[14 15] by the method of Cerf de Mauny.[15] Crude 1-nitroöctene (37.1 g., 0.236 mole, n_{D}^{25} 1.4501) and freshly cracked cyclopentadiene (72.0 g., 1.09 moles) were warmed on the steam-bath until refluxing of the cyclopentadiene ceased (2 hours) and for 2 more hours. The solution was vacuum-distilled, removing dicyclopentadiene and a considerable forerun and yielding several fractions of pale yellow liquid (17.2 g., 0.0771 mole, 33%), b.p. 112–131° (~1.5–2 mm.), n_{D}^{25} 1.4707. Redistillation gave 5-nitro-6-hexylbicyclo-[2,2,1]-2-heptene as a pale yellow liquid, b.p. 103° (~0.5 mm.), n_{D}^{25} 1.4792; $\nu_{\mathrm{NO_2}}$ (cm.$^{-1}$) 1543, 1373.

Anal. Calc'd for $C_{13}H_{21}NO_2$ (223.31): C, 69.92; H, 9.48; N, 6.27. Found: C, 70.09; H, 9.55; N, 6.22.

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The Base-Catalyzed Reaction of Benzyl Mercaptan with Styrene Oxide

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In connection with another problem, the reaction of benzyl mercaptan with styrene oxide in basic solution was investigated briefly. Styrene oxide normally reacts with basic reagents B to give the secondary alcohol $C_6H_5CHOHCH_2B$.[1] Alkali mer-

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