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THE REACTION BETWEEN NITROSOBENZENES AND ALKENES[1]

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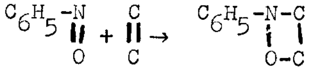
The smooth cycloaddition of nitrosobenzene to two substituted alkenes has been reported[2]:



$$\begin{array}{c}C_6H_5-N\\ \|\\ O\end{array} + \begin{array}{c}C\\ \|\\ C\end{array} \rightarrow \begin{array}{c}C_6H_5-N-C\\ \quad\quad\;\; |\quad\; |\\ \quad\quad\;\; O-C\end{array}$$

In a study to determine the electronic and steric factors facilitating cyclization in this reaction we found that changes in structure of either nitrosocompound or alkene seem to alter the course of the reaction in many instances . Nitrosobenzene for instance yields an oxazetisine[3] with 1,2-diphenylethylene , but we found that 3-bromonitrosobenzene under similar conditions does not . Cycloaddition of nitrosobenzene to triphenylethylene , cis- or trans-stilbene has also not been observed in this laboratory . With other substituted alkenes , such as tetrachloroethylene , no reaction seems to take place at all .

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[1] This investigation is supported by a grant of the Petroleum Research Fund .

[2] B.G. Gowenlock and W. Luettke , Quart.Rev. 12,321 (1958)

[3] C.K. Ingold and S.D. Weaver, J.Chem.Soc. 125,1146 (1924)

However , when a reaction does take place without cyclization , the major product of the reaction between nitrosobenzene or derivatives and alkenes was found to be the corresponding azoxycompound . Some representative alkenes found to yield azoxycompounds are the following : cyclopentene , cyclohexene , propylene , isobutylene , 1-butene , cis- and trans-2-butene triphenylethylene , cis- and trans-stilbene .

The formation of azoxycompounds by this reaction requires a few seconds to several days for completion , depending on nitrosocompound and alkene employed . It requires a few seconds only for p-nitronitrosobenzene to form the azoxycompound in nearly quantitative yield in the presence of either cyclopentene or cyclohexene. The green color of p-bromonitrosobenzene in alcohol solution disappears in about 15 minutes when treated at room temperature with cis- or trans-2-butene ; it takes several days for the green color to disappear when treated with allene under similar conditions , but the solution remains green indefinitely when treated with tetrachloroethylene .

An interesting aspect of the reaction is that in many instances we have found the reaction product to be the trans-azoxycompound , but in some instances what appears to be the cis-azoxycompound , and occasionnally a mixture of both .

Cis-2-butene and p-bromonitrosobenzene seem to yield exclusively trans-p,p'-dibromoazoxybenzene , m.p. 168-169.5°C (Lit.[4] 169-170.5°C) . Trans-2-butene and p-bromonitrosobenzene seem to yield exclusively a compound which we believe to be cis-p,p'-dibromoazoxybenzene , m.p. 119-120°C . (Found : C , 40.25 ; H , 2.38 ; N, 7.67 ; Br , 44.58 . Calcd. for $C_{12}H_8N_2Br_2$: C , 40.48 ; H , 2.26 ; N , 7.87 ; Br , 44.89) . The infrared spectra in KBr of the two products are similar but not identical . The infrared spectrum of the high melting product was identical with that reported for trans-p,p'-dibromoazoxybenzene[5] . Propylene and p-bromonitrosobenzene yielded a mixture of the high and low melting products .

Ethanol was employed as a solvent in these reactions , since p,p'-dibromoazoxybenzene is only sparingly soluble in this solvent. The reaction however proceeds equally well in chloroform , carbon tetrachloride, or in the alkene itself without a solvent . The presence of at least one equivalent of alkene is necessary for the conversion of nitrosocompound into azoxycompound . The nitrosocompounds were only partially transformed into the azoxycompound with smaller amounts of alkene present .

The oxygen lost by the formation of the azoxycompound from the nitrosocompound did not oxidize the starting material , since nitrocompounds were found to be absent in the reaction mixture after termination of the reaction , as were aniline derivatives .

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[4] A. Addamiano , J. Phys. Chem. **62** , 1018 (1958)

[5] W. Maier and G. Englert , Z. Elektrochem. **62** , 1020 (1958)

The solvent ethanol also was not oxidized , since acetic acid or acetaldehyde were shown to be absent after termination of the reaction by gas chromatographic analysis . Hydroxyethers were not found to be present either . In one instance have we been able to find a reaction product which has been tentatively identified as an epoxide .