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FORMATION OF DIAZOOLEFINS IN THE REACTION OF 4-DIAZOINDENO[2,3-c]1,2,5-THIADIAZOLES WITH ACETYLENECARBOXYLATES WITHOUT LIGHT

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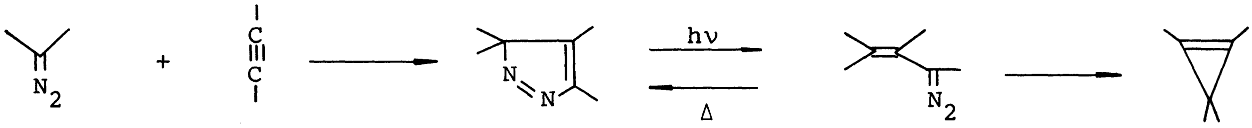
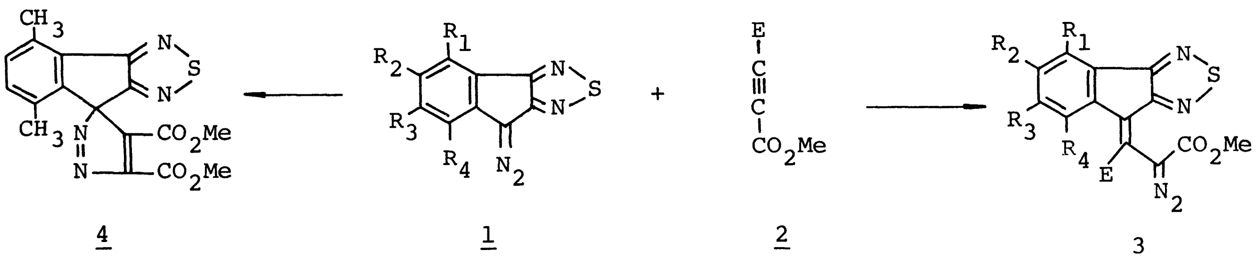
The reaction of 4-diazoindeno[2,3-c]1,2,5-thiadiazoles (1) with acetylenecarboxylates (2) afforded diazoalkenes (3) in high yields without light.

The reaction of diazoalkanes with acetylenes is well known$^{1)}$ to afford pyrazolenines which, on photolysis, give cyclopropenes with the loss of nitrogen via diazoolefins. Only when the photolysis is carried out at low temperature, the formation of diazoolefins is recognized because the diazoolefins are thermally labile and easily cyclize into pyrazolenines.



In this communication, we wish to report the first example of the direct formation of the diazoolefins by the reaction of diazoalkanes with acetylenes without the participation of light.

The reaction of 4-diazoindeno[2,3-c]1,2,5-thiadiazoles$^{2)}$ (1) with acetylenecarboxylates (2) was carried out under the following conditions; (i) in refluxing benzene or ethanol for 10 min, or (ii) at room temperature in benzene for 24 hr, and the corresponding diazoolefins (3) were isolated in fair yields, respectively (60-84%). All diazoolefins (3)$^{3)}$ show a characteristic band at 2090-2110 cm^{-1}.



4 1 2 3

1a; $R_1=R_2=R_3=R_4=H$

1b: $R_1=R_4=CH_3$, $R_2=R_3=H$

1c; $R_1=R_4=H$, $R_2=R_3=CH_3$

2a; $E=CO_2Me$

2b; $E=H$

3a; $R_1=R_2=R_3=R_4=H$, $E=CO_2Me$

3b; $R_1=R_4=H$, $R_2=R_3=Me$, $E=CO_2Me$

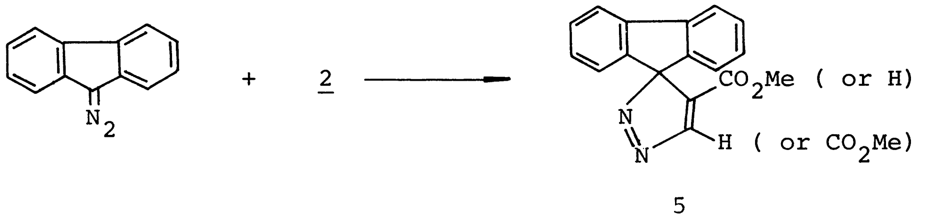
3c; $R_1=R_2=R_3=R_4=H$, $E=H$

3d; $R_1=R_4=CH_3$, $R_2=R_3=H$, $E=H$

In order to check the participation of light in these reactions, the reaction of 1a with 2a in refluxing benzene was carried out in the dark and the ir spectrum of the reaction mixture was found to be identical with that of the reaction mixture in day light. This implies that the formation of 3 was not caused by light and to our knowledge, these reactions are the first example of the ring-opening reaction of pyrazolenines into diazoolefins without light.

When the reaction of 1b and 2a was carried out under the conditions mentioned above, pyrazolenine 4 was obtained in 91% yield and the formation of the corresponding diazoalkene was not observed.

It was reported[4)] that the reaction of diazofluorenone, a benzo analog of 1, with acetylene carboxylates gave pyrazolenines (5).



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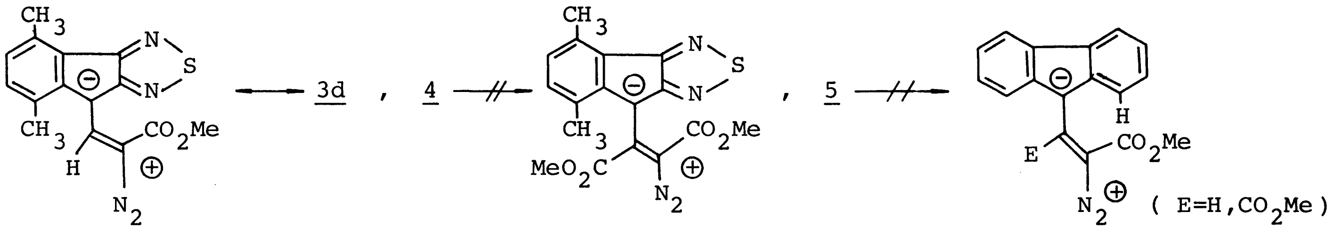
We presume now that the formation of 3 might be rationalized by the resonance stabilization (for example, 3d ⟶ 3d′) and that the ring-opening of 4 or 5 into the corresponding diazoalkenes would be unfavorable because such a stabilization may be prohibited by the steric hindrance between ester group and methyl group in 5 position of the indenothidiazole ring or between diazoester group and hydrogen atom in peri position of fluorenone nuclei.



3d′

The reaction with other acetylenes is under investigation.

References and Notes

1) G. L. Closs, W. A. Böll, H. Heyn and V. Dev, J. Am. Chem. Soc., 90, 173 (1968).

2) The compounds 1 were prepared by HgO-oxidation of the corresponding hydrazones and the parent ketones were prepared by the reaction of N_4S_4 with 2-oximino-1-indanones in refluxing toluene.

3) Compounds 3 and 4 gave satisfactory elemental analyses and spectral data.
3a; mp 133° (d.), 3b; mp 118° (d.), 3c; mp 120° (d.), NMR ($CDCl_3$); δ 3.91 (3H, s, $\underline{CH_3}$), 7.01 (1H, s, $>C=C<_{\underline{H}}$), 7.2-7.9 (4H, broad singlet, aromatics).
3d; mp 128° (d.), NMR ($CDCl_3$); δ 2.55, 2.65, 3.89 (each 3H, s, $\underline{CH_3}$), 7.01 (1H, s, $>C=C<_{\underline{H}}$), 6.90 (2H, broad singlet, aromatic).
4; mp 135-7° (d.).

4) H. Reimlinger, Chem. Ber., 100, 3097 (1967).

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