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Addition Reactions of Diazotropilidene with Monosubstituted Ethylenes Leading to 3-Substituted Indanones

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Reactions of tropone tosylhydrazone sodium salt with monosubstituted ethylenes afforded 3-substituted indanones via dipolar additions of diazotropilidene to the ethylenes followed by rearrangements involving norcaradiene forms.

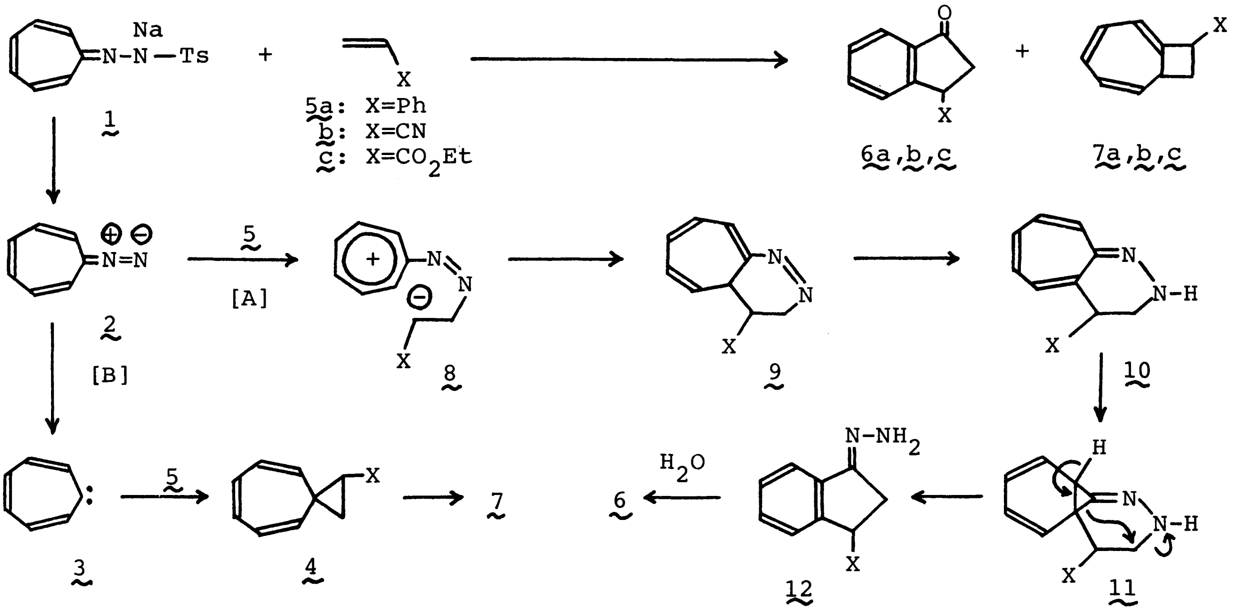
Tropone tosylhydrazone sodium salt (**1**) is known to generate cycloheptatrienylidene (**3**) via diazotropilidene (**2**).1) The reactions of **3** have been well investigated and were reported to give spiro[2.6]nonatrienes (**4**) via 1,2-additions to 1,2-disubstituted ethylenes.2) On the other hand, no document has been published on the reaction of **2** except the generation of **3** and the formation of benzodiazepines via dipolar additions with acetylenes.1) In order to investigate the reactivity of **2**, we studied the reaction of **1** with monosubstituted ethylenes and found a novel reaction of **2** giving 3-substituted indanones (**6**) in addition to bicyclo[5.2.0]nonatrienes (**7**). Here the results are discussed.

Tropone tosylhydrazone sodium salt (**1**) was treated with four molar equivalents of styrene (**5a**) in diglyme at 130 °C for 15 min. After evolution of nitrogen gas had ceased the reaction mixture was poured into water and extracted with ether. After evaporation of the solvent the residue was chromatographed to give 3-phenylindanone (**6a**) and bicyclo[5.2.0]nonatriene derivative (**7a**)3) in 13.8 and 20.4% yields, respectively. The similar reactions using acrylonitrile (**5b**) and ethyl acrylate (**5c**) gave **6b**, **7b**, and **6c**, **7c** in 12.9, 24.9, and 7.0, 21.6% yields, respectively.4) Treatments of **7** under the reaction conditions as above resulted in quantitative recoveries of the starting materials.

The structures of **6a** and **7a** were determined by coincidence of their spectral properties with those of the authentic samples.3,5) The structures of **6b**, **6c**, **7b**, and **7c** were deduced on the basis of their spectral properties and confirmed by their resemblance to those of the analogous compounds.3,5)

The reaction is considered to proceed as follows. The decomposition products **2** from **1** can react through two different reaction paths A and B. The 1,3-dipolar addition of **2** to ethylenes gives tetrahydropyridazines (**9**) (Path A). The regioselectivity of the reaction is attributable to the stabilization effect of substituents in the ionic intermediates **8**. Formation of **6** from **9** is considered to proceed analogously to the known rearrangements of **4** to indanes via **7**2,3,6) or **1** to 2H-indazoles.7) Thus, hydrogen migration in **9** forms azaheptafulvene (**10**). Subsequent valence isomerization to norcaradienes (**11**)8) followed by skeletal rearrangement finally affords hydrazone derivatives (**12**). The strain energy in the three-membered ring, the electronegativity of the nitrogen atom in **11**, and the stability of the benzene ring in **12** seem to be the driving forces of this step. 3-Substituted indanones (**6**) can be produced by hydrolysis of **12**. Diazotropilidene (**2**) can further decompose to generate **3** (Path B), which affords **7** via **4**.[2,3,6]

In the reaction of **1** with 1,2-disubstituted ethylenes,[2] path B would be more favorable than path A because the steric repulsion caused by the substituents on the ethylenes should prevent the attack of **2** to the ethylenes.



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4) The spectral properties of the new compounds are as follows:
6b: Found: m/z 157.0549. Calcd for $C_{10}H_7NO$: m/z 157.0527. Mass m/z (rel intensity): 157 (M^+, 100), 129 (89), 117 (33). IR (oil): 1723 cm^{-1}. NMR ($CDCl_3$) δ ppm: 2.96 (dd, 1H J=18 and 5 Hz), 3.19 (dd, 1H J=18 and 9 Hz), 4.52 (dd, 1H J=5 and 9 Hz), 7.5 (m, 4H).
6c: Found: m/z 204.0757. Calcd for $C_{12}H_{12}O_3$: m/z 204.0786. Mass m/z (rel intensity): 204 (M^+, 9), 190 (100), 161 (30). IR (oil): 1730 cm^{-1} (broad). NMR ($CDCl_3$) δ ppm: 1.29 (t, 3H), 2.86 (dd, 1H, J=19 and 10 Hz), 3.12 (dd, 1H, J=19 and 5 Hz), 4.25 (m, 3H), 7.6 (m, 4H).
7b: Found: m/z 143.0712. Calcd for $C_{10}H_9N$: m/z 143.0735. Mass m/z (rel intensity): 143 (M^+, 5), 129 (85), 118 (31). IR (oil): 2240 cm^{-1}. NMR ($CDCl_3$) δ ppm: 3.08 (m, 1H), 3.26 (m, 2H), 4.08 (m, 1H), 5.18 (m, 1H), 5.93 (m, 2H), 6.20 (m, 2H).
7c: Found: m/z 190.0984. Calcd for $C_{12}H_{14}O_2$: 190.0993. Mass m/z (rel intensity): 190 (M^+, 100), 178 (28), 161 (27). IR (oil): 1730 cm^{-1} (broad). NMR ($CDCl_3$) δ ppm: 1.26 (t, 3H), 3.08 (m, 1H), 3.22 (m, 2H), 4.20 (m, 3H), 5.17 (m, 1H), 5.84 (m, 2H), 6.12 (m, 2H).
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