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REACTIONS OF TROPONE TOSYLHYDRAZONE SODIUM SALT WITH ACETYLENE DERIVATIVES: A NOVEL SYNTHESIS OF 1H-1,2-BENZODIAZEPINE DERIVATIVES

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The reactions of tropone tosylhydrazone sodium salt (1) with acetylenes (3a-3c) afforded 1H-1,2-benzodiazepines (8a-8c), which are considered to be formed by additions of diazotropylidene (2) with the acetylenes via norcaradiene intermediates (6).

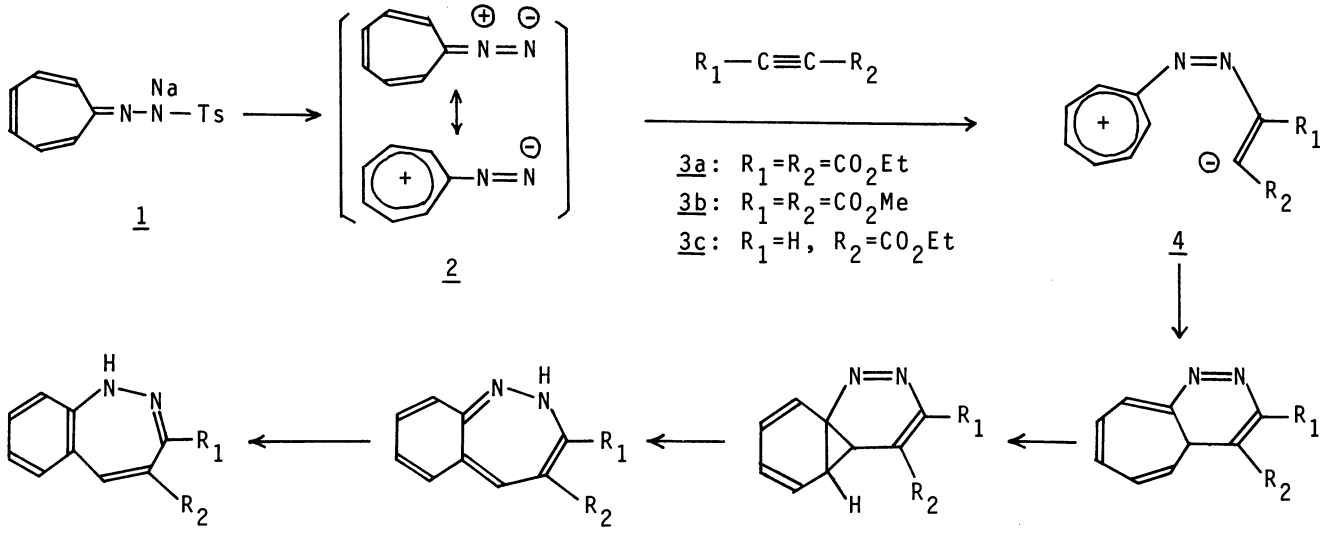
Tropone tosylhydrazone sodium salt (1) is known to generate cycloheptatrienylidene, which is considered to be a nucleophilic singlet carbene.[1] The author has been studying the application of 1 to the synthesis of heterocyclic compounds and has reported that 2-tosylindazole was formed by reaction of 1 with silver chromate.[2] Recently, 1H-1,2-benzodiazepine derivatives have attructed much attention and a number of reports have been published concerning their chemical behavior and synthesis.[3] These facts prompted the author to report the current results of the reactions of 1 with some acetylene derivatives leading to 1H-1,2-benzodiazepine derivatives.

Tropone tosylhydrazone sodium salt (1) was allowed to react with acetylene dicarboxylic acid diethyl ester (3a) in anhydrous diglyme at 120°C for 15 min to give red crystals of 1H-1,2-benzodiazepine derivative (8a)[3a, 3b] in a yield of 33%. Under the same conditions as above, 1 was reacted with acetylene dicarboxylic acid dimethyl ester (3b) and acetylene carboxylic acid ethyl ester (3c) to afford red crystals of 8b and 8c in yields of 35 and 52%, respectively. The structure of 8a was determined by comparison of its mp and spectral properties with those of the authentic sample.[3a, 3b] The structures of 8b and 8c were determined by resemblance of their spectral properties to those of the analogous 1H-1,2-benzodiazepines.[3a, 3b] The physical data of 8b and 8c are as follows.

8b; mp 154-155°C; UV_{max} (EtOH): 204 nm (log ε, 4.21), 257 (4.16), 285 (sh, 4.02); IR (KBr): 3350, 3020, 2950, 1730, 1640, 1600 cm^{-1}; NMR (CD_3COCD_3) δ: 3.70 (3H, s), 3.71 (3H, s), 6.8-7.4 (4H, m), 7.86 (1H, s), 8.10 (1H, broad s); MS m/e (rel intensity): 260 (M^+, 22), 175 (17), 143 (100), 115 (34).

8c; mp 93-94°C; UV_{max} (EtOH): 211 nm (log ε, 4.13), 258 (4.22), 303 (sh, 3.45); IR (KBr): 3320, 3020, 2950, 1710, 1630, 1595 cm^{-1}; NMR (CD_3COCD_3) δ: 1.30 (3H, t), 4.24 (2H, q), 6.7-7.2 (4H, m), 7.32 (1H, d, J=1.5 Hz), 7.68 (1H, broad s), 7.78 (1H, d, J=1.5 Hz); MS m/e (rel intensity): 216 (M^+, 63), 171 (14), 143 (100), 115 (21).

The formation mechanism of 8 is considered to be as follows. The negatively charged nitrogen atom of diazotropylidene (2) attacks the electron deficient olefinic carbons of 3 to yield the ionic intermediate (4). This mechanism is supported by



the fact that no adducts corresponding to 8 were obtained from the analogous reaction of 1 with phenylacetylene or diphenylacetylene, both of which have no electron withdrawing groups. It is well known that tropylidene skeletone in the intermediate (5) which is derived from 4, tautomerizes to the norcaradiene structure represented by 6.[4] The cleavage of the three-membered ring and the hydrogen migration of 6 give the diazepine derivative (7) containing an o-quinoid structure. The isomerization of 7 to the final product (8) has been proposed in the literature to explain the formation of the analogous 1H-1,2-benzodiazepine derivatives.[3c]

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