December, 1987] © *1987 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 60, 4447—4448 (1987)* 4447

Reactions of Tropone Tosylhydrazone Sodium Salt with 2-Pyrone Derivatives: Nucleophilic Addition of 1,2,4,6-Cycloheptatetraene to 2-Pyrone Derivatives

Katsuhiro SAITO* and Hiraku ISHIHARA
Department of Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

(Received June 1, 1987)

Synopsis. The reaction of tropone tosylhydrazone sodium salt with 3- or 5-methoxycarbonyl-2-pyrones afforded benzotropilidene derivatives. These products are considered to be formed via addition reactions of the 2-pyrone derivatives with 1,2,4,6-cycloheptatetraene derived from cycloheptatrienylidene, which is the initial product of the decomposition of tropone tosylhydrazone sodium salt.

It has been reported that upon heating or irradiation tropone tosylhydrazone sodium salt (**1**) generates cycloheptatrienylidene (**2**), which is considered to be a nucleophilic singlet carbene because of a contribution of a 6π-electrons type aromatic structure (**2a**).[1] The possibility of a rearrangement of the carbene (**2**) to an allene, 1,2,4,6-cycloheptatetraene (**3**) has been pointed out by Unch et al.[2] The present authors[3] have documented some experimental examples of the rearrangement and Alder et al.[4] have reported a theoretical investigation of the rearrangement.

Recently, Waali et al. documented that **2** is actually a planar transition state for the interconversion of chiral, nonplanar allenes (**3**), which could have nucleophilicity because the strained cyclic allene, 1,2-cyclohexadiene, had a nucleophilicity.[5] As one part of our research on the reactivities of **2** and **3**,[3] we invesitigated the reactions of **1** with 3- (**4a**) or 5-methoxycarbonyl-2-pyrone (**4b**). Here, the results of these reactions will be discussed.

A mixture of **1** and three molar equivalents of **4a** in anhydrous diglyme was heated at 120 °C for 15 min. The separation and purification of the reaction mixture by chromatography afforded 2-methoxycar-

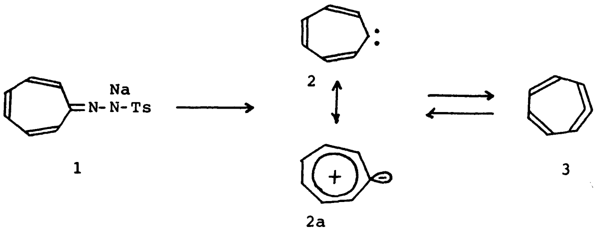

Fig. 1.

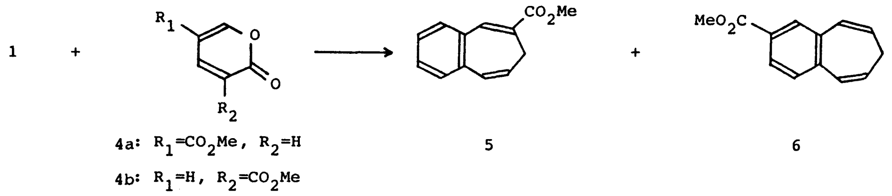

Fig. 2.

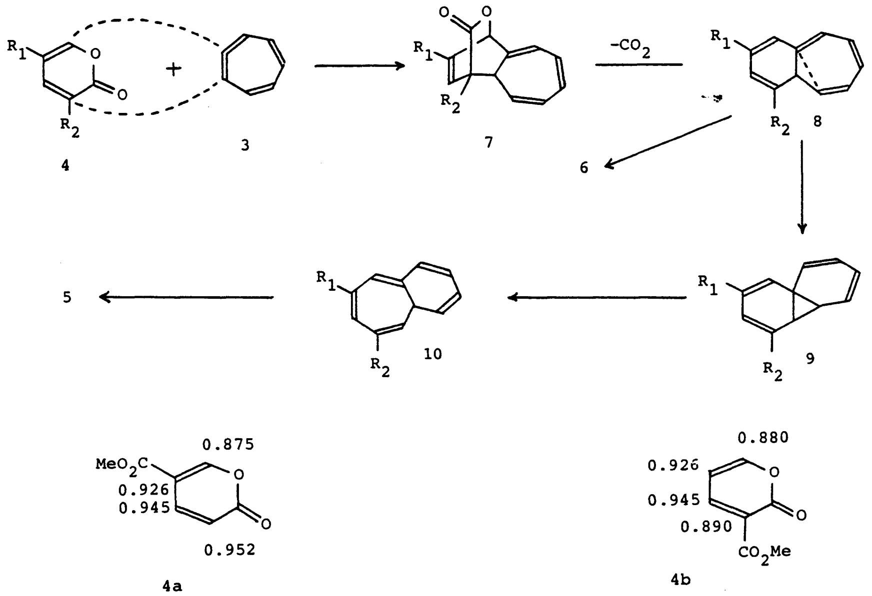

Fig. 3.

bonylbenzo[*f*]-1,4,5a-cycloheptatriene (**5**) and 8-methoxycarbonylbenzo[*f*]-1,4,5*a*-cycloheptatriene (**6**) in 8.1 and 15% yields, respectively. The same reaction, but using **4b**, gave **5** in 2.8% yield. The structures of **5** and **6** were deduced on the basis of their spectral properties, especially from their NMR spectral properties, and confirmed by comparisons of these spectral properties with those of analogous compounds.[3,6)]

The products are considered to be formed via a reaction mechanism resembling that of the reaction of **1** with cyclopentadienone derivatives.[1e,3c)] A $[4\pi+2\pi]$-type cycloaddition of **3** with **4** gives **7**, which generates **8** via an elimenation of carbon dioxide. A hydrogen migration in **8** gives **6**. On the other hand, a valence tautomerization of **8** yields a norcaradiene form **9**,[7)] which again undergoes a valence tautomerization to tropilidene form **10**. A hydrogen migration of **10** affords **5**. The reaction of **3** with **4b** proceeds via almost the same mechanism as above. The low product yield from the reaction of **4b** is due to a steric hindrance of the methoxycarbonyl group.

The electron densities on carbon atoms of **4a** and **4b** are known to be as shown in Fig. 3.[8)] The 2-position carbons bear the smallest electron densities in both **4a** and **4b**. Considering the above fact, the experimental result that the allenic carbon atom of **3** attacks the 2-position carbon atoms of both **4a** and **4b**, seems to prove the nucleophilicity of the allene **3**.

Experimental

NMR spectra were measured with Varian XL 200 or Hitachi R 20B spectrometers with tetramethylsilane as an internal standard. IR spectra were measured with a DS 701G spectrometer. Mass spectra were measured with Hitachi M-52 or JMS DX300 spectrometers. Diglyme was dried over Molecular Sieves 3A, 1/16. Wako gel C 200 and Wako gel B5F were used for column and thin-layer chromatography, respectively.

Reaction of 1 with 4a. A mixture of **1** (8.40 g, 28.4 mmol), and **4a** (13.20 g, 85.7 mmol) in diglyme (100 ml) was heated at 120 °C for 15 min. The reaction mixture was poured into water, extracted with ethyl acetate, washed with water and brine, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the oily residue was column chromatographed to give an oily mixture of **5** and **6** (1.10 g) by the use of pet. ether (bp 35—60 °C)-benzene 1:4 and crystals of tropone tosylhydrazone (2.63 g, 31%) by the use of benzene-ether 9:1. The NMR spectrum of the mixture of **5** and **6** showed that the mixture contained 35% of **5** (8.1% yield)[9)] and 65% of **6** (15.0% yield).[9)] Each compound was separated by thin-layer chromatgraphy using benzene-ether 3:1 as a developing solvent (**5**, R_f=0.60; **6**, R_f=0.55). 2-Methoxycarbonylbenzo[*f*]-1,4,5a-cycloheptatriene (**5**): Found: *m/z* 200.0819. Calcd for $C_{13}H_{12}O_2$: M, 200.0836. MS *m/z* (rel intensity): 200 (M^+, 29), 186 (25), 155 (57), 127,(100). IR (oil): 3030, 2950, 1720, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.80 (d, 2H, *J*=7 Hz), 3.90 (s, 3H), 5.6—6.8 (m, 3H), 7.1—8.0 (m, 4H).

8-Methoxycarbonylbenzo[*f*]-1,4,5a-cycloheptatriene (**6**): Found: *m/z* 200.0864. Calcd for $C_{13}H_{12}O_2$: M, 200.0836. MS *m/z* (rel intensity): 200 (M^+, 100), 169 (95), 139 (43), 127 (53). IR (oil): 3030, 2970, 1725, 1440 cm^{-1}. ^1HNMR ($CDCl_3$) δ=2.50 (t, 2H, *J*=7 Hz), 3.80 (s, 3H), 5.6—6.8 (m, 4H), 7.2—8.0 (m, 3H).

Reaction of 1 with 4b. A mixture of **1** (8.88 g, 30 mmol) and **4b** (13.86 g, 90 mmol) in diglyme (100 ml) was heated at 120 °C for 20 min. The same procedure as above using column chromatography gave an oil **5** (0.12 g, 2.8%,[9)] benzene-ether 17:3) and crystals of tropone tosylhydrazone (2.28 g, 27.8%, benzene-ether 9:1).

The authors are indebeted to Professor Toshio Mukai of Tohoku University for his fruitfull suggestions. The present work was supported by a Grant-in-Aid for Science Research No. 61540367 from the Ministry of Education, Science and Culture.

References

1) a) T. Mukai, T. Nakazawa, and K. Isobe, *Tetrahedron Lett.*, **1968**, 565; b) W. M. Jones and C. L. Ennis, *J. Am. Chem. Soc.*, **91**, 6391 (1969); c) W. M. Jones, B. N. Hamon, R. C. Joines, and C. L. Ennis, *Tetarhedron Lett.*, **1969**, 3909; d) W. M. Jones, *Angew. Chem., Int. Ed. Engl.*, **11**, 325 (1972); e) T. Mitsuhashi and W. M. Jones, *J. Chem. Soc., Chem. Commun.*, **1974**, 103.

2) K. Untch, G. J. Mattheus, and T. Hylton, Abstract of International Symposium on the Chemistry of Non-Benzenoid Aromatic Compounds, Sendai, Japan (1970), p. 79; C. Mayor and W. M. Jones, *Tetrahedron Lett.*, **1977**, 3855.

3) a) K. Saito, Y. Omura, and T. Mukai, *Chem. Lett.*, **1980**, 349; b) *idem, Bull. Chem. Soc. Jpn.*, **58**, 1663 (1985); c) K. Saito and H. Ishihara, *ibid.*, **58**, 2664 (1985); d) *idem, ibid.*, **59**, 1095 (1986).

4) M. Z. Kassaee, M. R. Nimlos, K. E. Downie, and E. E. Waali, *Tetrahedron*, **41**, 1579 (1985); R. W. Alder, J. C. Petts, and T. Clark, *Tetrahedron Lett.*, **26**, 1585 (1985).

5) S. Harnos, S. Tivakornpannarai, and E. E. Waali, *Tetrahedron Lett.*, **27**, 3701 (1986).

6) C. H. Jutz, I. Rommel, I. Lengyel, and J. Feeney, *Tetrahedron*, **22**, 1809 (1966); A. S. Kende, *Tetrahedron Lett.*, **1967**, 2661; T. Toda, K. Saito, and T. Mukai, *ibid.*, **1972**, 1981; M. Yasuda, K. Harano, and K. Kanematsu, *J. Am. Chem. Soc.*, **103** (1981).

7) E. Ciganek, *J. Am. Chem. Soc.*, **87**, 1149 (1965); T. Mukai, H. Kubota, and T. Toda, *Tetarhedron Lett.*, **1967**, 3581; R. Hoffmann, *ibid.*, **1970**, 2907; H. Gunther, *ibid.*, **1970**, 5173.

8) J. A. Reed, C. L. Shilling, Jr., R. F. Jarrin, T. A. Rettig, and J. K. Stille, *J. Org. Chem.*, **34**, 2188 (1969).

9) The yields were calculated based on the amount of really consumed **1**.