BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 339—340 (1973)

Reaction of Troponoid with Ylide. IV.[1] A Conversion of Tropone into Cyclooctatrienone

Yukio SUGIMURA, Nobuo SOMA, and Yukichi KISHIDA
Central Research Laboratories, Sankyo Co., Ltd., Hiromachi, Shinagawa-ku, Tokyo

(Received March 13, 1972)

We have studied the reaction of tropone with various ylides and found a convenient one-step synthesis of 2,3-homotropones by the reaction of tropone with stable sulfonium ylide.[2] It has been reported that benzylsulfonium ylide is stable in solution at −70°C under a nitrogen atmosphere, but when treated with sodium hydroxide at 60°C, in an aqueous medium *p*-nitrobenzyldimethylsulfonium tosylate, it is converted quantitatively into a mixture of *cis* and *trans*-4,4′-dinitrostilbene.[3]

We attempted the reaction of tropone with *p*-nitrobenzyldimethylsulfonium bromide pretreated with sodium hydride at −40°C for five minutes, and obtained the products 2,3-di-*p*-nitrophenylpropiophenone (**3**, 44%), 2-*p*-nitrophenylcycloocta-2,4,6-trien-1-one (**4**, 6%), and 4,4′-dinitrodibenzyl[4] (**5**, 34%). The structural assignments of **3** and **4** were given by spectroscopic data. **3**: mp 110°C, $C_{21}H_{16}O_5N_2$ (elemental analysis and high resolution mass spectrum); IR: $\nu_{C=O}$ (Nujol) 1680 cm^{-1}; NMR (in $CDCl_3$, δ ppm): 3.20 (1H, d of d, J=14.0 and 7.5 Hz), 3.70 (1H, d of d, J=14.0 and 7.5 Hz), 5.02 (1H, t, J=7.5 Hz), 7.2—7.6 (7H, m), 7.8—8.2 (6H, m). **4**: pale yellow oil, $C_{14}H_{11}O_3N$ (elemental analysis and mass spectrum); IR: $\nu_{C=O}$ (liquid) 1660 cm^{-1}; NMR and NMDR (in $CDCl_3$, δ ppm, Fig. 1): 3.20 (2H, d, J=8.3 Hz, H-8). 5.87 (t of d, J=8.3 and 10 Hz, H-7), 6.46 (d of d of d, J=10, 4.5 and 2.0 Hz, H-6), 6.48 (d of d of d, J=12.0, 7.5 and 2.0 Hz, H-4), 6.71 (d of d, J=12.0 and 4.5 Hz, H-5), 7.03 (d of d, J=7.5 and 1.0 Hz, H-3), 7.45 (2H, A_2B_2), 8.13 (2H, A_2B_2).

A plausible mechanistic path for the formation of **3** and **4** is shown in Fig. 2. From the reaction of tropone with stable sulfur ylide[2] whose carbanion attacked the 2-position of tropone to give homotropone, it is considered that the carbanion of the benzylsulfonium ylide attacked the 1-position of tropone. The ring enlargement of tropone to cyclooctatrienone in the reaction of tropone with diazoalkane has been reported by Franck-Neumann,[5] but the reaction proceeded *via* cycloaddition to the 2-, 3-positions of tropone (Δ^1-pyrazoline). For our present reaction, an intermediacy of carbene would be denied, because dinitrostilbene was not isolated and the isolation of the dibenzyl, **5**, suggests an intervention of radical mechanism.[6]

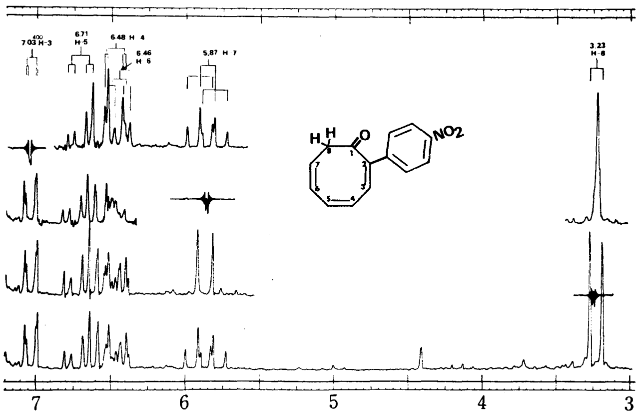
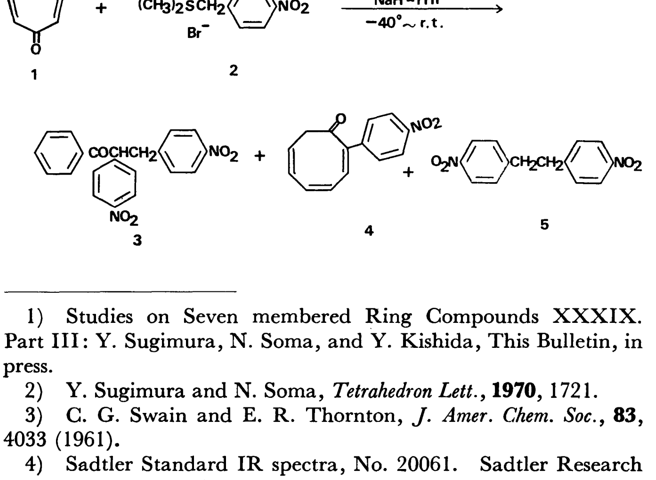


Fig. 1. NMR and NMDR of eight-membered ring protons of 2-*p*-Nitrophenylcycloocta-2,4,6-trien-1-one (**4**).



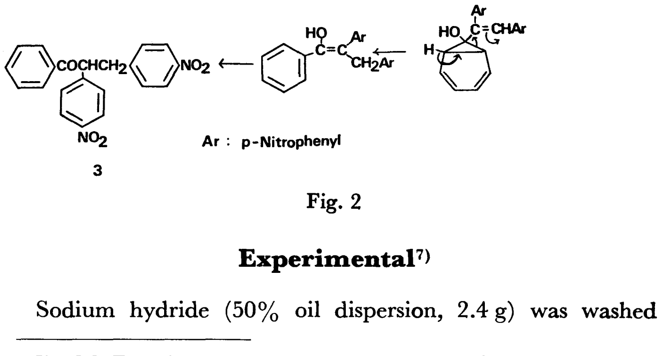


Fig. 2

Experimental[7]

Sodium hydride (50% oil dispersion, 2.4 g) was washed

---

[1] Studies on Seven membered Ring Compounds XXXIX. Part III: Y. Sugimura, N. Soma, and Y. Kishida, This Bulletin, in press.

[2] Y. Sugimura and N. Soma, *Tetrahedron Lett.*, **1970**, 1721.

[3] C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, **83**, 4033 (1961).

[4] Sadtler Standard IR spectra, No. 20061. Sadtler Research Laboratories, Inc. (Philadelphia).

[5] M. Franck-Neumann, *Tetrahedron Lett.*, **1970**, 2143.

[6] J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, **1970**, 576.

[7] All mp are uncorrected. NMR spectra were taken with a Varian HA-100.

three times, each time with 30 ml of dry *n*-hexane, suspended in dry tetrahydrofuran and cooled to −40°C in aceton–dry ice bath. To the suspension, 13 g of *p*-nitrobenzyldimethylsulfonium bromide was added at the same temperature. After being stirred for five minutes, 5 g of freshly distilled tropone was added and the reaction mixture was stirred at −40°C for two hours, then warmed gradually to room temperature with stirring. The reaction mixture was poured onto ice–water and extracted with chloroform. The extract was dried over magnesium sulfate, condensed to give oily residue, and then subjected to silica gel (500 g) column chromatography. The first benzene eluate: 2.15 g (34%) of 4,4′-dinitro-dibenzyl (**5**), mp 180°C, which was identified with an authentic sample.[4] The second benzene eluate: 2.8 g (44%) of 2,3-di-*p*-nitrophenylpropiophenone (**3**), mp 111°C. Found: C, 66.93; H, 4.32; N, 7.39%. Calcd for $C_{21}H_{16}O_5N_2$: C, 67.01; H, 4.29; N, 7.44%. High resolution mass spectrum, M^+ (*m/e*) Found: 376.109. Calcd: 376.106. Benzene–chloroform (1:1) eluate: 0.24 g (6%) of 2-*p*-nitrophenylcycloocta-2,4,6-trien-1-one (**4**). Found: C, 62.53; H, 5.92; N, 6.88%. Calcd for $C_{10}H_{11}O_3N$: C, 62.16; H, 5.74; N, 7.25%. Chloroform eluate: 3.16 g of the starting tropone.

We are grateful to Prof. T. Nozoe for his helpful discussion.