

TWO SYNTHESSES OF NAPHTHO[2,3-b]- AND NAPHTHO[2,3-d]TROPONES

VIA CYCLOADDITION REACTION OF TROPONE

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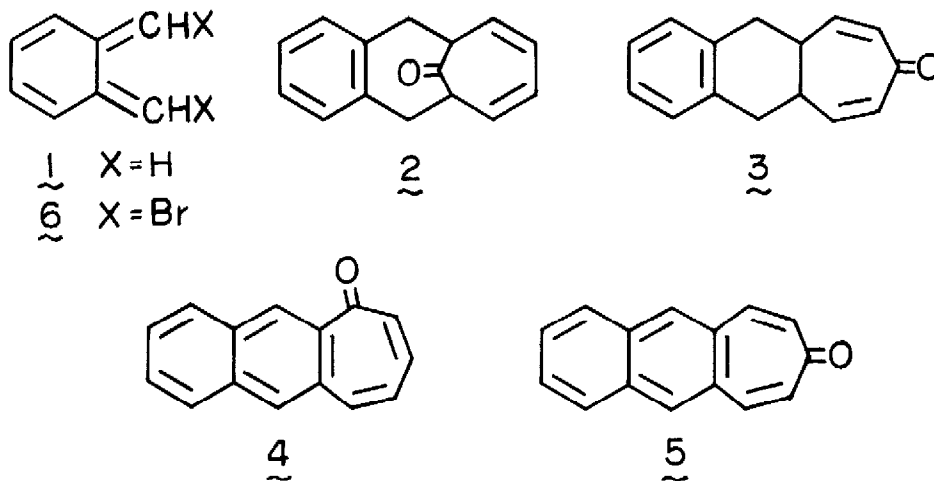
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Of eight possible naphthotropones, only three have been synthesized (1). We wish to report two simple syntheses of two isomers, known naphtho[2,3-d]tropone and unknown naphtho[2,3-b]tropone, utilizing the cycloaddition of tropone, the reaction shown to be useful for constructing nonbenzenoid aromatic compounds (2).

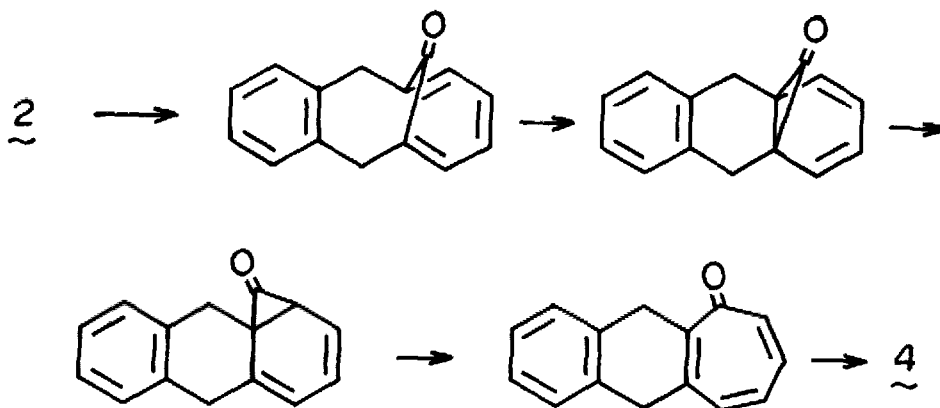
o-Xylylene 1 generated at room temperature in DMF (3) in the presence of excess tropone afforded, after silica gel chromatography, two major adducts 2, yellow oil, (29% yield) and 3, colorless prisms, m.p. 142-143° (14%). Both of the products were proved to be the 1:1 adduct from



their mass spectra [m/e 210 (M^+), 104 (base peak, $C_8H_8^+$)]. The structure 2 was deduced for the major product from its spectra [ν^{oil} 1703, 744 cm^{-1} ; λ_{max}^{MeOH} 238.5 (ϵ 2830), 247.5 (3290), 255.5 (3850), 265 (3410), 292 nm (380); δ^{CDCl_3} 2.97 (2H, dd, $J=14.2, 6.4$), 3.19 (2H, dd, $J=14.2, 9.5$), 3.66 (2H, m), 5.43-5.61 (4H, m), 7.05-7.15 (4H, complex)] which show the presence of a diene system and a β, γ -unsaturated carbonyl in addition to *o*-xylylene moiety. The structure 3 was suggested for the minor product also from its spectra [ν^{KBr} 1643, 1603, 747 cm^{-1} ; λ_{max}^{MeOH} 236.5 (ϵ 10180), 268.5 (3370), 275 nm (3190); δ^{CDCl_3} 3.04 (6H, m), 6.09 (2H, d, $J=11.5$), 6.46 (2H, dd, $J=11.5, 4.9$), 7.11 (4H, s)], which indicate the cross conjugate dienone moiety along with *o*-xylylene. Although tropone is known to behave as 6π , 4π and 2π cycloaddend (4), formation of 3 is the first clear example of tropone reacted entirely at its 4,5-position (5).

Dehydrogenation of 2 with triphenylcarbinol in trifluoroacetic acid (6) under reflux for 14 hours afforded as a sole product, naphtho[2,3-*b*]tropone 4, yellowish brown oil, in 39% yield. 4 was also obtained in lower yield by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) dehydrogenation. The structure of 4 was based on its spectroscopic properties: m/e 206 (M^+), 178 (M^+-CO , base peak); λ_{max}^{MeOH} 223.5 (sh. ϵ 18970), 228.5 (18180), 244 (21990), 252 (24290), 298 (8850), 306.5 (8610), 325.5 (sh. 3150), 360 (sh. 1950), 398 nm (sh. 1440); $\lambda_{max}^{70\% H_2SO_4}$ 221.5 (ϵ 13240), 247 (21540), 260 (23450), 275 (sh. 17700), 313 (23200), 340 (sh. 14810), 380 (5750), 399 (sh. 2210), 520 nm (2850); ν^{oil} 1641, 1605 (s), 1569 (s), 895 cm^{-1} ; δ^{CCl_4} 6.46 (1H, ddd, $J=11.8, 7.0, 2.0$), 6.73-6.95 (2H, m), 7.29 (1H, br. d, $J=11.8$), 7.45-8.10 (4H, m), 8.02 (1H, br. s), 8.90 (1H, br. s). NMR spectrum is similar with that of benzo[*b*]tropone (7). Signal due to one of the protons on the central ring appears at a very low field (δ^{CCl_4} 8.90) compared with the other (δ^{CCl_4} 8.02) revealed the location of the carbonyl group.

The transformation from 2 to 4 would involve dehydrogenation, disrotatory electrocyclic reaction and thermal [1,5]-sigmatropic rearrangement as shown in the following scheme (8). Dibenzotropone, which would form *via* dehydrogenation at the benzylic positions of 2 was not observed at all.



Dehydrogenation of the minor cycloaddition product **3** with triphenylcarbinol in trifluoroacetic acid under reflux for 8.5 hours gave naphtho[2,3-d]tropone **5**, brownish yellow plates, *m.p.* 214-216°, in 72% yield. Spectroscopic properties of **5** are in agreement with those reported by Heilbronner (1c). [$^5\text{CDCl}_3$ 6.70 (2H, AA'XX' type, $J_{\text{AX}}=13$), 7.54 (2H, AA'XX' type, $J_{\text{A'X'}}=13$), 7.57-8.00 (4H, AA'BB' type), 8.14 (2H, br.s)]. Dehydrogenation by DDQ (benzene, 120°, 40 hours) afforded **5** in lower yield (23%).

Still better one-step synthesis of these naphthotropones has further been developed. α,α' -Di-bromo-*o*-xylylene **6** generated *in situ* from α,α,α' -tetrabromo-*o*-xylene with Cu powder and tert-butylisocyanide at 80° for 10 hours (9) in the presence of tropone afforded, after SiO_2 chromatography, **4** and **5** in 5% and 63% yield, respectively. In this case, α,α' -dibromo-*o*-xylylene might have cycloadded directly with tropone at 4,5- and 2,3-double bond. No trace of either dibromo intermediates or the [6+4] cycloaddition products was indicated.

References and Footnotes

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- 4) Cf. S. Itô and Y. Fujise, in "Topics in Nonbenzenoid Aromatic Chemistry", Vol. 2, ed. T. Nozoe et al., Hirokawa Publ. Co., Inc., Tokyo, in press.
- 5) Although not isolated, the cycloadduct of this type was postulated as an intermediate in the reaction of tropone with nitrile oxide (C. De Micheli, R. Gaudolfi and P. Grunanger, Tetrahedron, 30, 3765 (1974). H. Takeshita, Y. Wada, A. Mori and T. Hatsui, Chemistry Letters, 335 (1973).
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- 8) Similar rearrangement always occurs when tetrahydro-1,6-methano[10]annulen-11-ones was subjected to dehydrogenation (H. Ohtani, M. Fujii and S. Itô, unpublished result. Cf. ref. 4). Also see T. Sasaki, K. Kanematsu and K. Hayakawa, Tetrahedron Letters, 343 (1974).
- 9) Cf. Y. Ito, K. Yonezawa and T. Saegusa, J. Org. Chem., 39, 2769 (1974).