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TROPONES INCORPORATED INTO 7-OXANORBORNADIENE SKELETON. SYNTHESIS AND ACID-CATALYZED REARRANGEMENT TO 1-HYDROXY-7H-BENZOCYCLOHEPTENES

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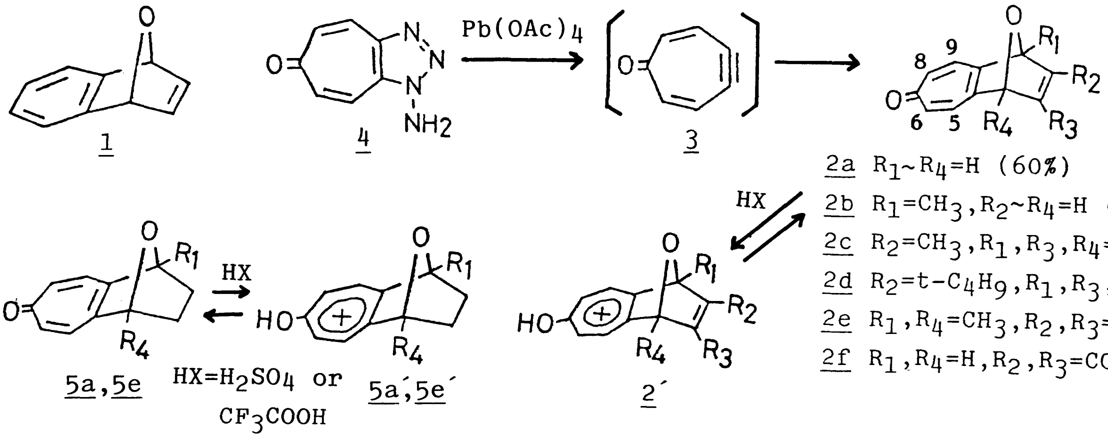
Tropones incorporated into 7-oxanorbornadiene skeleton, 1,4-dihydro-1,4-epoxy-7H-benzocyclohepten-7-ones have been synthesized by the cycloaddition reaction of 4,5-dehydrotropone with furans and their intramolecular π-π interactions and acid-catalyzed rearrangement to 1-hydroxy-7H-benzocyclohepten-7-ones have been studied.

7-Oxabenzonorbornadiene (1) has the marked dienophilicity and dipolarophilicitiy owing to its ring strain and orbital participation of the nonbonding electrons of oxygen atom.[1] The photochemical reactions of 1 are also of interest as the molecule has the divinylmethane system.[2] We have synthesized tropones, heptafulvenes, and tropylium ions incorporated into bicyclo[2.2.1]heptadiene or bicyclo[2.2.2]octadiene and demonstrated that the bridged tropylium ions exihibited unambiguous intramolecular π-π interactions.[3] In connection with these studies we wish to communicate the synthesis of tropones incorporated into 7-oxanorbornadiene skeleton, 1,4-dihydro-1,4-epoxy-7H-benzocyclohepten-7-ones (2) and their acid-catalyzed rearrangement to 1-hydroxy-7H-benzocyclohepten-7-ones (6).

In order to synthesize 2, we have applied a methodology to construct bridged tropones using cycloaddition reaction of a novel dehydroaromatic species, 4,5-dehydrotropone (3).[3a,b] In the presence of large excess of furan, a solution of 1-amino-6H-cycloheptatriazol-6-one (4) in anhydrous dichloromethane was treated with an equivalent of lead tetraacetate under nitrogen at 5 °C for 2-3 h. After filtration of lead oxides precipitated the resulting solution was concentrated



2a R_1~R_4=H (60%)
2b R_1=CH_3,R_2~R_4=H (80%)
2c R_2=CH_3,R_1,R_3,R_4=H (80%)
2d R_2=t-C_4H_9,R_1,R_3,R_4=H (75%)
2e R_1,R_4=CH_3,R_2,R_3=H (45%)
2f R_1,R_4=H,R_2,R_3=$COOCH_3$ (27%)

under reduced pressure at 0 °C,4) followed by chromatography on alumina in dichloromethane, giving a pale yellow solution of an adduct, 1,4-dihydro-1,4-epoxy-7H-benzocyclohepten-7-one (2a).5) The adducts 2b - 2f were also obtained under the same conditions. The structures of the adducts were elucidated by their spectral data.5) Considerable deshielding (ca. 1.2-1.5 ppm) of the chemical shifts of protons on tropone ring in CF_3COOH compared with those in $CDCl_3$ in ^1H NMR spectra is due to the formation of the hydroxytropylium ions. On diimide reduction (KO_2CNNCO_2K/CH_3COOH in CH_3OH), 2a and 2e gave 5a and 5e respectively.6)

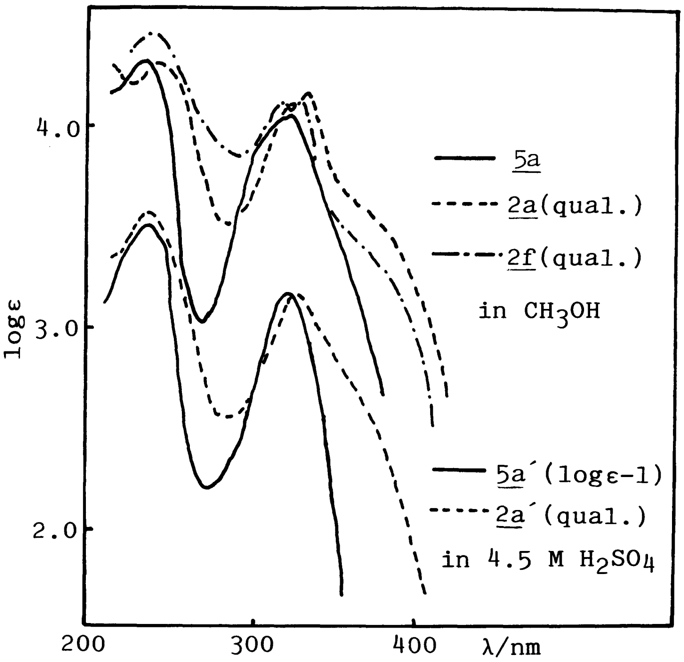
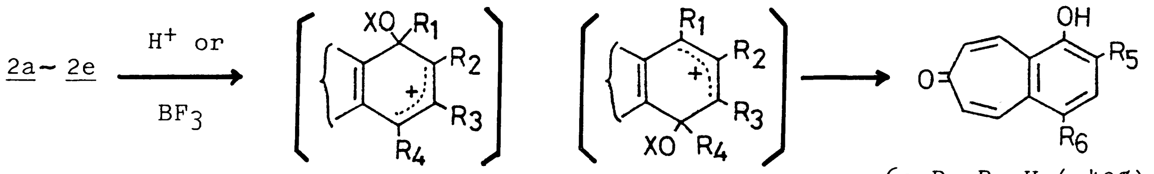


Fig.1. Electronic spectra of 2a, 2f, and 5a in methanol, and 2a´and 5a´in 4.5 M H_2SO_4.

The comparison of the electronic spectra of 2a and 2e with those of 5a and 5e in methanol shows that the introduction of a double bond into the ethano-bridged tropones 5 causes a slight bathochromic shift (8 nm, 5a → 2a ; 13 nm, 5e → 2e) of the absorption maxima(>320 nm) and an obvious increase of the intensity at wavelength longer than 360 nm, as illustrated in Fig.1 in the cases of 2a and 5a. The effect of a double bond was observed more clearly between the spectra of the hydroxytropylium ions 2a' and 5a' as shown in Fig.1.7) Taking into consideration the similar results obtained from our studies on bridged heptafulvenes,3b) these



7 or 8

X=H or $^{-}BF_3$

6a R_5,R_6=H (≈40%)
6b R_5=H,R_6=CH_3 (≈20%)
6c R_5=CH_3,R_6=H (≈20%)
6d R_5=t-C_4H_9,R_6=H (≈40%)
6e R_5,R_6=CH_3 (≈30%)

observations could be rationalized by the intramolecular charge-transfer transitions in the bicyclo[2.2.1]heptadiene skeleton condensed with seven-membered aromatics. As to the substituent effect, a slight hypsochromic shift was observed in the electronic spectrum of 2f, which has two electron-withdrawing groups on the etheno-bridge, as shown in Fig.1.

In relation to the facile acid-catalyzed rearrangement of 1 to α-naphthol (CH_3OH-concd HCl, 10 min, rt),[8] the reactions of adducts 2 with acids were studied. A solution of 2a in CH_3OH-concd HCl (20:1) or in CH_3OH-6 M H_2SO_4 (20:1) was gently refluxed for 10 h to afford a rearranged product, 1-hydroxy-7H-benzocyclohepten-7-one (6a).[9] Under the same conditions, 2b-2d gave 6b-6d.[9] The reaction sequence presumably involves the acid-catalyzed ring opening of 2 to a stabilized allyl cation 7 or 8, followed by deprotonation to benzocycloheptenes 6. The lower reactivity of 2 toward the acid than that of 1 would be due to the formation of the hydroxytropylium ion 2' in equilibrium with the tropone 2 under the reaction conditions, which prevents the smooth ring opening of the oxanorbornadiene. Regioselective formation of 6c and 6d from 2c and 2d, respectively, could reasonably be explained by the fact that the intermediate allyl cations 7 (R_1, R_3, R_4=H, R_2=CH_3 or t-C_4H_9) are more stable than the alternative cationic intermediates 8. Although 2e was recovered unchanged under the similar conditions, on treatment with a large excess of boron trifluoride etherate in moistured dichloromethane at room temperature for several days, it afforded 2,4-dimethyl-1-hydroxy-7H-benzocyclohepten-7-one (6e) via the migration of a methyl group in the intermediate 7 or 8 (R_1, R_4=CH_3, R_2, R_3=H).[9,10]

The studies on the dienophilicity and photochemistry of 2 are now in progress. This work was supported by a Grant-in-Aid for Scientific Research No.56470017 from the Ministry of Education, Science and Culture.

References

1) T. Sasaki, K. Kanematsu, and K. Hayakawa, J. Chem. Soc., Perkin Trans. 1 1972, 1951; T. Sasaki, K. Kanematsu, K. Hayakawa, and M. Uchide, ibid., 1972, 2750.

2) G. R. Ziegler, J. Am. Chem. Soc., 91, 446 (1969).

3) a) T. Nakazawa and I. Murata, Angew. Chem., Int. Ed. Engl., 14, 711 (1975); T. Nakazawa, K. Kubo, and I. Murata, ibid., 20, 189 (1981); H. Yamochi, K. Nakasuji, T. Nakazawa, and I. Murata, Chem. Lett., 1982, 459.
   b) T. Nakazawa, Y. Niimoto, and I. Murata, Tetrahedron Lett., 1978, 569.
   c) T. Nakazawa and I. Murata, J. Am. Chem. Soc., 99, 1996 (1977); T. Nakazawa, Y. Niimoto, K. Kubo, and I. Murata, Angew. Chem., Int. Ed. Engl., 19, 543 (1980); T. Nakazawa, K. Kubo, A. Okimoto, J. Segawa, and I. Murata, ibid., 20, 813 (1981).

4) All adducts dimerize easily in neat or in concentrated solution at room temperature. Attemts to separate and purify the dimers were without success.

5) 2a: UV (CH_3OH) λmax 244, 334 nm; ^1H NMR (CD_2Cl_2) δ 5.79(bs, H-1,4), 7.13(d, J=11 Hz, H-6,8), 7.27(bs, H-2,3), 7.54(d, J=11 Hz, H-5,9); (CF_3COOD) δ 6.23(m, H-1,4), 7.41(m, H-2,3), 8.25(bs, J=10.8 Hz, H-6,8), 8.61(bs, J=10.8 Hz, H-5,9); ^{13}C NMR (CD_2Cl_2) δ 85.7, 132.9, 142.2, 143.6, 159.2, 186.9.
   2b: UV (CH_3OH) λmax 244, 335 nm. 2c: UV (CH_3OH) λmax 244, 336 nm.
   2d: UV (CH_3OH) λmax $\approx$ 235, 337 nm. 2e: UV (CH_3OH) λmax 244, 337 nm; ^1H NMR ($CDCl_3$) δ 1.88(s, $2CH_3$), 6.82(s, H-2,3), 7.01(d, J=12 Hz, H-6,8), 7.19(d, J=12 Hz, H-5,9); (CF_3COOD) δ2.10(s, $2CH_3$), 7.05(s, H-2,3), 8.27(d, J=11 Hz, H-6,8), 8.41(d, J=11 Hz, H-5,9). 2f: UV (CH_3OH) λmax 241, 319, 332 nm; ^1H NMR (CCl_4) δ 3.75(s, $2CH_3$), 5.67(s, H-1,4), 6.78(d, J=11 Hz, H-6,8), 7.19(d, J=11 Hz, H-5,9); (CF_3COOH-CCl_4) δ 3.97(s, $2CH_3$), 6.33(s, H-1,4), 8.37(d, J=11 Hz, H-6,8), 8.71(d, J=11 Hz, H-5,9).

6) 5a: colorless needles, mp 96.5-98.0 °C; UV (CH_3OH) λmax(logε) 235(4.32), 324 nm(4.06). 5e: colorless needles, mp 76.5-77.5 °C; UV (CH_3OH) λmax(logε) 237(4.29), 324 nm(4.05).

7) Slow reactions of 2a with acids prevented the measurement of pKa value. A structural analog of 2a, 1,4-dihydro-1,4-methano-7H-benzocyclohepten-7-one and its 2,3-dihydro-derivative gave pKa of protonated form, $\approx$1.4 ± 0.1 and $\approx$1.8 ± 0.15 respectively, as roughly estimated value (20 - 25 °C).

8) G. Wittig and L. Pohmer, Chem. Ber., 89, 1334 (1956).

9) 6a: colorless prisms, mp 232-234 °C; UV (CH_3OH) λmax(logε) 222(4.26), 287 nm (4.42); (1 M NaOH) 223(4.34), 314(4.54), 412 nm(3.72); ^1H NMR (DMSO-d_6) δ 6.63 (d, J=12.7 Hz, H-6,8), 7.13-7.61(m, H-2,3,4) 7.59(d, J=12.7 Hz, H-5 or 9), 8.13(d, J=12.7 Hz, H-9 or 5). 6b: colorless needles, mp 237-239 °C. 6c: colorless plates, mp 178-180 °C. 6d: colorless microneedles, mp 228-230 °C. 6e: colorless needles, mp 224-227 °C; UV (CH_3OH) λmax(logε) 226(4.36), 296nm (4.56); (1 M NaOH) 228(4.34), 327(4.60), 425 nm(3.71).

10) The structure of 6e was unambiguously determined by its electronic spectra in methanol and in 1 M NaOH aqueous solution, which are similar to those of 6a but not those of 2-hydroxy-7H-benzocyclohepten-7-one.[11)]

11) T. Nakazawa, M. Ashizawa, F. Nishikawa, M. Jinguji, H. Yamochi, and I. Murata, unpublished results.

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