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SYNTHESES OF 1,6-METHANO[10]ANNULEN-11-ONES FROM TROPONE

Shô Itô, Hiroyuki Ohtani, Sen-ichi Narita and Hinako Honma

Department of Chemistry, Tohoku University

Sendai 980, Japan

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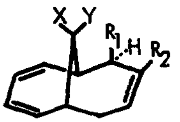
Although 1,6-methano[10]annulene is well known to be aromatic (1), those with trigonal C_{11} provides additional interesting problem with respect to the interaction of the P_z orbital of bridge and peripheral 10π-electron system. Thus, 11-methylene-1,6-methano[10]annulene synthesized by Vogel (2) disclosed practically no interaction between two π-electron systems. However, attempted syntheses of another compound of this type, 1,6-methano[10]annulen-11-one, by oxidation of the corresponding alcohol yielded only naphthalene and α-naphthaldehyde (2). In the course of our study on cycloaddition of tropone with dienes, we have obtained a bicyclo[4.4.1]undecan-11-one system and derived the longed ketone therefrom.

When tropone was heated at 130° in xylene for 10 hrs with either butadiene or sulfolene, two types of the 1:1 adduct were obtained: The [6+4] adduct I (75% yield) [liquid, M^+ 160, ν 1702 cm^{-1}, λ_{max} 247.5 (ε 4600), 255 (4800), 264 (3500), 290 nm (740), δ 2.53 (4H, m, $C\underline{H}_2$), 3.51 (2H, br.q, J=6.2, 6.2, 5.8, $C\underline{H}$), 5.5-6.4 (6H, m, -$C\underline{H}$=). Semicarbazone, m.p. 198-201° (decomp.)]and a mixture of the [4+2] adducts II (8% yield) [liquid, ν 1665 cm^{-1}; λ_{max} 233.5 nm (ε 6650), δ 1.1-2.6 (2H, m), 2.6-3.7 (3H, m), 4.8-5.3 (2H, m), 5.4-6.8 (4H, m), 6.8-7.4 (1H, m) (3,4)].

$NaBH_4$ reduction of I afforded the alcohol III, m.p. 96-98°, in 60% yield [λ_{max} 238 (ε 3970 sh), 248 (5800), 255 (6500), 265 nm (6220), ν 3400 cm^{-1}, δ 2.21 (1H, d, J=10.5, $O\underline{H}$), 2.33 (4H, m, $C\underline{H}_2$), 3.00 (2H, m), 3.97 (1H, m), 5.62 (2H, quintet, J=6, 3, 3, -CH=CH-), 5.70 (2H, br.m, -$C\underline{H}$=CH-CH=$C\underline{H}$-), 5.83 (2H, dt, J=13, 3.5, 3.5, -CH=$C\underline{H}$-$C\underline{H}$=CH-)], and the alcohol IV, unstable crystals,in 11% yield [δ 1.50 (1H, s), 1.72-2.32 (2H, m), 2.5-3.0 (3H, m), 3.12 (1H, m), 4.47 (1H, m), 5.43-5.8 (6H, m)]. The orientation of the hydroxyl group in III was determined by NMR using $Eu(DPM)_3$. Signals due to diene



I X,Y=O, $R_1=R_2=H$

III X=OH, $Y=R_1=R_2=H$

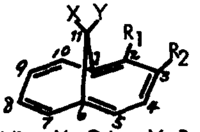
IV $X=R_1=R_2=H$, Y=OH

V X=OAc, $Y=R_1=R_2=H$

VIII X,Y=O, $R_1=Me$, $R_2=H$

X X,Y=O, $R_1=H$, $R_2=Me$

II

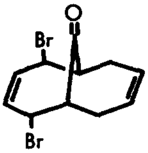


VI X=OAc, $Y=R_1=R_2=H$

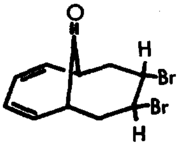
VII X,Y=O, $R_1=R_2=H$

IX X,Y=O, $R_1=Me$, $R_2=H$

XI X,Y=O, $R_1=H$, $R_2=Me$



XII



XIII

system shifted down-field nearly twice as much as the quintet due to the other olefinic hydrogens. Acetylation of III yielded the acetate V, m.p. 93° [λmax 237 (ε 4450 sh), 246 (6500), 254 (7300), 263 nm (4700), ν 1726, 1240, 1023 cm^{-1}, δ^{CCl_4} 1.93 (3H, s, CH_3CO), 2.33 (4H, m, CH_2), 2.93 (2H, m, $-\underset{|}{C}H-$), 5.17 (1H, t, J=4), 5.45-5.90 (6H, m, -CH=)]. Heating of V with NBS in the presence of azobisisobutyronitrile yielded, after SiO_2 chromatography, 11-acetoxy-2,6-methano[10]-annulene (VI), m.p. 93-93.5° (9.1% yield) with the same physical properties with those reported by Vogel (2). VI was also obtained in lower yield by heating V with dichlorodicyanobenzoquinone (DDQ) at 100° for 10 hrs in benzene; the reagent used by Nelson and Untch (5).

Taking advantage of the direct formation of the 1,6-methano[10]annulene system from its tetrahydro derivative, I was heated with DDQ at 120° in benzene for 24 hrs. After SiO_2 chromatography of the reaction mixture, 1,6-methano[10]annulen-11-one (VII), easily sublimable, colorless prisms (from cyclohexane), m.p. 183-185° (sealed tube), was obtained in 8.5% yield together with a trace of naphthalene. However, I was recovered quantitatively from the reaction with NBS.

The structure of VII was based on its spectroscopic properties. UV spectrum with maxima at 250.5 (ε 77500), 296 (7000), 352 (95), 362 (124), 371 (169), 379 (228), 391 (275) and 402 nm (326), is practically superimposable with those of 1,6-methano[10]annulene (1) and 11-methylene-1,6-methano[10]annulene (2). IR spectrum exhibits a strong carbonyl band at 1743 cm^{-1} besides those due to CH and C=C at 3024, 1520, 1390, 805, 783 and 710 cm^{-1}. Its NMR spectrum consists of eleven olefinic proton signals (AA'BB') centered at 7.46 ppm. Analysis of the pattern disclosed the following parameters: $\delta_{2,5}$=7.55,

$\delta_{3,4}$=7.36, $J_{2,3}$=9.22, $J_{3,4}$=9.21, $J_{2,4}$=0.04, $J_{2,5}$=0.70. Mass spectrum of VII displays very weak M^+ peak (m/e 156) and a strong M-CO peak (m/e 128, base peak), the rest of the spectrum being very similar with that of naphthalene (6).

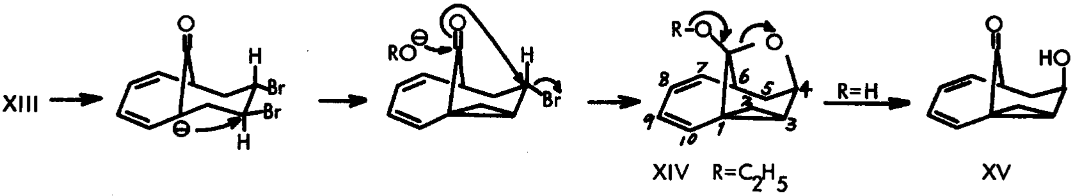
These physicochemical data disclosed not only the structure of VII but also the similarity of the geometry of peripheral chromophors between VII and other 1,6-methano[10]annulenes, and the absence of appreciable interaction between the 10π-electron system and the bridged carbonyl group.

The reaction sequence has general applicability. Thus, heating tropone with trans-piperylene under the same condition yielded the [6+4] adduct VIII, colorless liquid, in 60% yield [λ_{max} 237 (ε 3200 sh), 247 (3900 sh), 253 (4100), 263 (3200 sh), 288 nm (500), ν 1705, 730, 675 cm^{-1}, δ^{CCl_4} 1.11 (CH_3, d, J=6.5), 2.45 ($H_5H_{5'}$, m), 2.87 (H_2, m), 3.04 (H_1, ddd, J=8.0, 7.0, 1.4), 3.35 (H_6, br.q, J=7.5, 6.5, 5.0, 1.4), 5.32-6.10 (6H, olefinic, m)]. Dehydrogenation of VIII using DDQ under the same condition afforded 2-methyl-1,6-methano[10]annule-11-one (IX), pale yellow prisms, m.p. 159-162°, in 5% yield [λ_{max} 254.5 (ε 63700), 306 (6800), 399.5 (320), 408 nm (320), ν 1745, 813, 760, 680 cm^{-1}, δ 2.68 (CH_3), 7.20-7.83 (7H), MS m/e 170 (M^+, 3.7%), 142 (100%), 141 (93.5%), 115 (38.1%), 89 (1.8%)].

Likewise tropone and isoprene yielded the adduct X, colorless liquid, in 86% yield which can be dehydrogenated to the annulenone XI, colorless prisms, m.p. 132-134°, in 2% yield [λ_{max} 255 (ε 69200), 297 (7360), 387 (220 sh), 395 (240), 405.5 nm (220), ν_{max} 1748, 818, 705 cm^{-1}, δ 2.65 (CH_3), 7.12-7.65 (7H), MS m/e 170 (M^+, 2%), 142 (100%), 141 (88.3%), 115 (34%), 89 (2.2%)].

Application to I of the another general method (bromination-dehydrobromination (1)) used for the syntheses of 1,6-methanoannulenes did not lead the desired ketone VII. Bromination of I yielded the dibromo compound with isolated olefines XII, m.p. 117-118°, in 4% yield [ν 1702 cm^{-1}, δ 2.46 (4H, m, $-CH_2-$), 3.30 (2H, dd, J=12.5, 5.0, -CH-), 5.03 (2H, dd, J=7.5, 3.5, C<u>H</u>Br), 5.95 (4H, m, -CH=)] and the one with conjugated diene XIII, m.p. 81-82°, in 33% yield [λ_{max} 246 (ε 4500), 252 (4800), 262 nm (3400 sh), ν 1700 cm^{-1}]. NMR spectrum of XIII is complex but NMTR irradiating at δ 2.2 and δ 2.9 ($C\underline{H}_2$) simplify C<u>H</u>Br to a clear AB pattern (J=5.2) at 4.67 and 4.74 ppm. The coupling constant of this AB pattern suggests, when dipole-dipole interaction of the bromine atoms is taken into consideration, the trans configuration of bromine atoms. Dehydrobromination of XIII with KOH in EtOH led the ketal

XIV, m.p. 55.5-56.5°, in 50% yield [ν 1197, 1066 cm^{-1} (no C=O), λ_{max} 262.5 (ε 6200), 268 (6260), 280 nm (3630 sh)]. Structure of XIV was based on the following NMR parameters deduced by a detailed NMDR analysis in pyridine: $\delta_{2\alpha}$=0.58, $\delta_{2\beta}$=1.29, δ_3=1.34, δ_4=4.02, $\delta_{5\alpha}$=1.28, $\delta_{5\beta}$=2.56, δ_6=3.01, δ_{7-10}=5.4-6.1, $J_{2\alpha,2\beta}$=5.6, $J_{2\alpha,3}$=8.6, $J_{2\beta,3}$=3.6, $J_{3,4}$=$J_{4,5\alpha}$=~0, $J_{4,5\beta}$=5.3, $J_{5\alpha,5\beta}$=11.3, $J_{5\alpha,6}$=6.3, $J_{5\beta,6}$=11.2, δ 1.10 (3H, t, J=7.0, $C\underline{H}_3$), δ 3.70, 3.73 (2H, $\underline{AB}X_3$, J_{AB}=9.5, J_{AX_3}= J_{BX_3}=7.0, $-C\underline{H}_2-O$). Similar dehydrobromination using KOH in aqueous dioxane yielded the hydroxy-ketone XV, m.p. 110-111.5° [λ_{max} 261 (ε 6600), 270 (5610 sh), 302 nm (560), ν^{CCl_4} 3615 (free OH), 3597 (intramol. hydrogen-bonded OH (7)), NMR $\delta_{2\alpha}$=1.11, $\delta_{2\beta}$=1.34, δ_3=1.43, δ_4=4.22, $\delta_{5\alpha}$=2.40, $\delta_{5\beta}$=2.08, δ_6=3.11, δ_{7-10}=5.5-6.2, $J_{2\alpha,2\beta}$=5.0, $J_{2\alpha,3}$=8.3, $J_{2\beta,3}$=5.4, $J_{3,4}$=4.4, $J_{4,5\alpha}$=5.5, $J_{4,5\beta}$=4.8, $J_{5\alpha,5\beta}$=13.7, $J_{5\alpha,6}$=6.8, $J_{5\beta,6}$=5.8. The formation of the cyclopropyl ketones XIV and XV can be explained by the following scheme. Incooporation of two deuteriums at C_1 and C_6 of I by heating I with KOD in dioxane-D_2O supported occurrence of the 1st step.



Study on the structural detail and the chemical reactions of VII is in progress and will be reported elsewhere.

References and Footnotes

1) E. Vogel, Chem. Soc. Spec. Publ., No. 21, 113 (1967).

2) E. Vogel, F. Weyres, H. Lepper and V. Rauteustranch, Angew. chem. internat. Edit., 5, 732 (1966).

3) Spectral data refer to the following conditions unless otherwise stated: UV; MeOH solution, IR; KBr disk for solid and $CHCl_3$ solution for liquid, NMR; $CDCl_3$ solution.

4) This is probably a mixture of regional isomers and stereoisomers.

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