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TROPONE AND 8,8-DICYANOHEPTAFULVENE INCORPORATED IN BICYCLO[2.2.1]HEPTANE AND BICYCLO[2.2.2]OCTANE RING SYSTEMS

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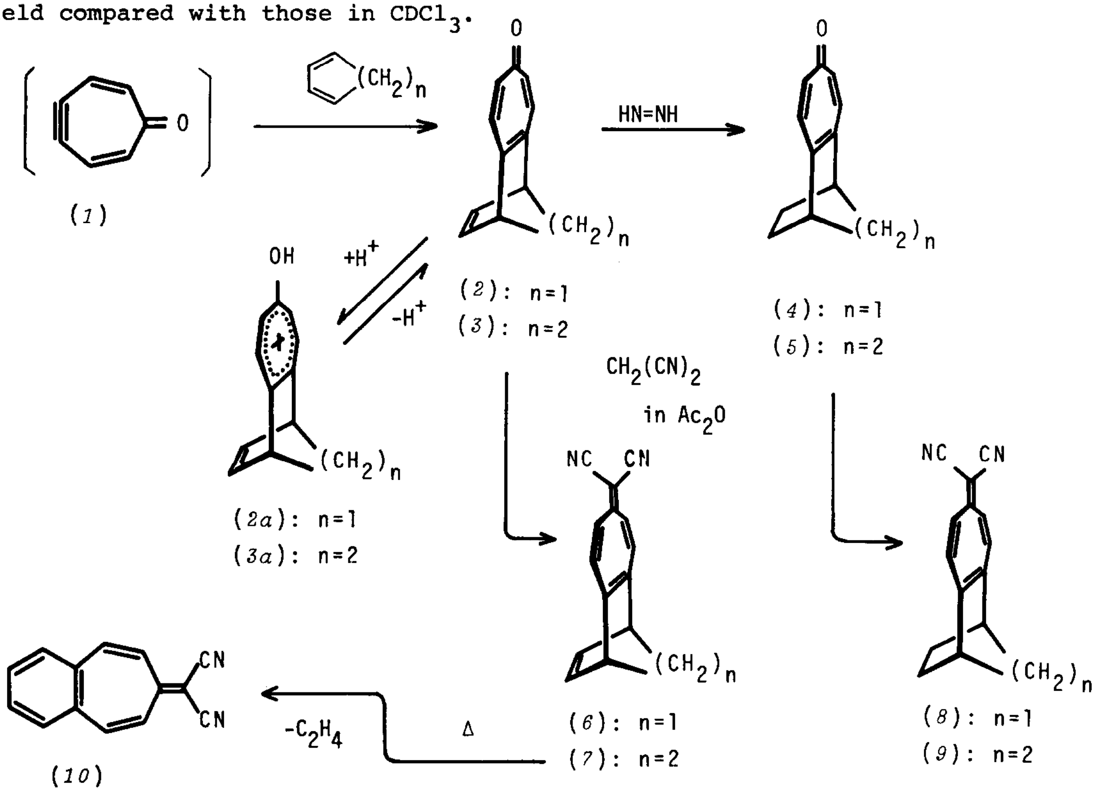
Recently we have reported the formation and the trapping of 4,5-dehydrotropone (*1*)1) as a novel reactive species. Taking into account the wide applicability of dehydroarenes (arynes) in organic synthesis,2) the dehydrotropone will be possibly of a potential and useful intermediate for the synthesis of new bridged troponoids which could hardly be derived by other known methods. From this point of view, it is of interest to examine the reactivity and the synthetic utility of *1*. As a part of this program, we wish to communicate the reaction of *1* with typical 1,3-dienes, cyclopentadiene and cyclohexa-1,3-diene, and some of the spectroscopic properties of the tropone and 8,8-dicyanoheptafulvene incorporated in bicyclo[2.2.1]heptane and bicyclo[2.2.2]octane ring systems being derived by the above reaction.

In the presence of a large excess of cyclopentadiene or cyclohexa-1,3-diene, a mixture of 1-amino-1*H*- and 2-amino-2*H*-cycloheptatriazol-6-one (3∼1:1)1) was reacted with lead tetraacetate in dry methylene chloride at room temperature under nitrogen. After usual work-up, the products were isolated using basic alumina chromatography (CH_2Cl_2) to give the desired 1,4-adducts, 1,4-dihydro-1,4-methano-7*H*-benzocyclohepten-7-one (*2*) as pale yellow oil3) (∼50%) or 1,4-dihydro-1,4-ethano-7*H*-benzocyclohepten-7-one (*3*) as colorless needles of mp 82-84°C (45%), respectively. The structural assignments follow elemental analyses4) and the spectral data shown in Table 1.

Tropones, *2*, *3*, exist in trifluoroacetic acid as hydroxytropylium ion form, *2a* and *3a*, in ^{1}H-NMR spectra of which were shifted the signals of tropone ring protons by 1.1-1.4 ppm and those of the others by less than 0.7 ppm to downfield compared with those in $CDCl_3$.



Diimide reduction of *2* and *3* gave *4* as colorless needles of mp 58.5-60°C (60%) and *5* as colorless needles of mp 119.5-120.5°C (60%), respectively.

Compounds, *2*, *3*, *4*, and *5* could be converted to corresponding dicyanoheptafulvene derivatives, *6* as reddish brown needles of mp 190.5-191.5°C, *7* as reddish orange needles of mp 181-182°C (d), *8* as reddish orange needles of mp 151.5-153°C (d), and *9* as reddish orange needles of mp 215-216°C (d), respectively, by treatment with malononitrile in refluxing acetic anhydride.$^{5)}$

Thermolysis of *7* at its melting point gave the benzoheptafulvene *10* as yellow prisms of mp 178 -180°C quantitatively.

In view of the fact that tropone and heptafulvene were obvious examples of molecules which might potentially exhibit significant contributions from dipolar resonance structures,$^{6)}$ the question has been raised on the intramolecular charge-transfer interactions between the etheno-π-system and the tropone or the hepta-

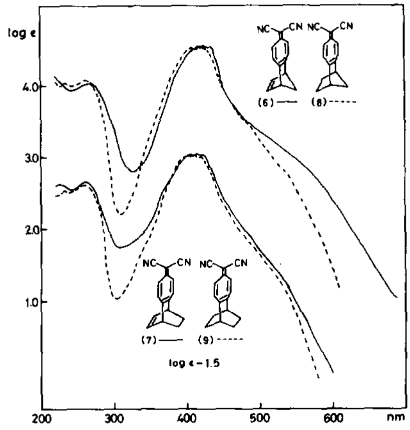


Fig. 1. Comparison of Electronic Spectra of *6*, *8* and *7*, *9*.

fulvene in *2*, *3*, or *6*, and *7*.[7] However, as Table-1 indicates, ^{1}H- and ^{13}C-chemical shifts of the etheno-bridge were virtually invariant when those values were compared with those of benzonorbornadiene (δ_H=6.75,[8] 6.77,[9] δ_C=142.8[10]) and benzobicyclo[2.2.2]octadiene (δ_H=6.40,[11] δ_C= 134.9[11]), suggesting no appreciable π-π interaction between remote π-systems in the molecules. Furthermore, introduction of a double bond to the bicyclo[2.2.1]heptane system [(*4*)→(*2*)] and the bicyclo[2.2.2]octane system [(*5*)→(*3*), (*9*)→(*7*)] give rise to slight bathochromic shift of 2-4 nm and 4-6 nm, respectively, on the longer wavelength maxima. On the other hand, as can be seen from Figure 1, well-defined difference was observed between the spectra of *8* and *6*, in which an significant increase in the intensity due to the introduction of a double bond, not observed by comparison of the spectra of *9* and *7*. This finding could tentatively be explained by the intramolecular π-π interaction in *6*.[12]

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2) Cf. R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, 1967.

3) Although this compound is very labile as liquid state, it could be stored at 0°C as a methylene chloride solution.

4) All new compounds described gave acceptable analytical data except for *2*.

5) M. Oda, M. Funamizu, and Y. Kitahara, Bull. Chem. Soc. Jpn., 42, 2386 (1969).

6) Cf. D. M. G. Lloyd, "Carbocyclic Non-benzenoid Aromatic Compounds", Elsevier Publ. Co., 1966; P. J. Garratt, "Aromaticity", McGraw-Hill Book Co., (1971).

7) We have recently reported the synthesis of the 9,10-dihydro-9,10-(1,2-tropylio)anthracene tetrafluoroborate, in which strong intramolecular CT interaction was observed despite the minimized overlap of the orbital systems of both donor and acceptor. T. Nakazawa and I. Murata, J. Am. Chem. Soc., 99, 1996 (1977).

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11) K. Kitahonoki, K. Sakurawi, K. Tori, and M. Ueyama, Tetrahedron Lett., 263 (1976).

12) For electron spin resonance studies on radical anions of three polycyclic tropones, *3*, *5*, and 5,11-dihydro-5,11[1',2']benzeno-8*H*-cyclohepta[*b*]naphthalen-8-one : see P. Fürderer, F. Gerson, I. Murata, and T. Nakazawa, J. Phys. Chem., in press.

Table 1. Spectral Data of Compounds *2*, *3*, *4*, *5*, *6*, *7*, *8*, and *9*.

2 : MS m/e 170 (M^+, 51%), 142 (77), 141(100), 116(42), 115(72); UV $_{max}$(in hexane) 240, 317, 330 nm, (in CH_3OH) 240, 330 nm; IR ν(neat) 1610, 1546, 1511 cm^{-1}; PMR δ($CDCl_3$) 3.85(m, H-1,4, $J_{1,10s}=J_{1,10a}$=1.5 Hz), 6.87(m, H-2,3), 7.29(d, H-5,9, $J_{5,6}=J_{8,9}$=11.5 Hz), 6.93(d, H-6,8), 2.35(dt, H-10s, $J_{10s,10a}$=7.0 Hz), 2.25(dt, H-10a); δ(CF_3COOH) 4.34(m, H-1,4, $J_{1,10s}=J_{1,10a}$= 1.5 Hz), 7.13(m, H-2,3), 8.48(d, H-5,9, $J_{5,6}=J_{8,9}$=11.0 Hz), 8.08(d, H-6,8), 2.72(t, H-10s, 10a); CMR δ($CDCl_3$) 142.75(C-2,3).

3 : MS m/e 184(M^+, 14%), 156(7), 128(100); UV λ_{max}(in n-hexane) 234 nm(log ε 4.29), 308(3.92), 320(3.89), (in CH_3OH) 237(4.34), 323(4.09); IR ν(KBr) 1623, 1603, 1547, 1510 cm^{-1}; PMR δ($CDCl_3$) 3.96(m, H-1,4), 6.48(m, H-2,3), 7.17(d, H-5,9, $J_{5,6}=J_{8,9}$=11.5 Hz), 6.94(d, H-6,8), 1.51(m, H-10,11), δ(CF_3COOH) 4.61(m, H-1,4), 6.70(m, H-2,3), 8.57(d, H-5,9, $J_{5,6}=J_{8,9}$=11.3 Hz), 8.22(d, H-6,8), 1.51-2.07(m, H-10,11); CMR δ($CDCl_3$) 133.4(C-2,3).

4 : UV λ_{max}(in n-hexane) 235 nm(log ε 4.26), 312(3.97), 324(3.96), 400(sh. 2.37), (in CH_3OH) 240(4.36), 327(4.17); IR ν(KBr) 1620, 1608, 1554, 1512 cm^{-1}; PMR δ($CDCl_3$) 3.28(m, H-1,4) 1.10-2.10(m, H-2,3,10), 7.18(d, H-5,9, $J_{5,6}=J_{8,9}$=11 Hz), 6.96(d, H-6,8).

5 : UV λ_{max}(in n-hexane) 233 nm(log ε 4.31), 236(4.31), 306(3.98), 318(3.96), (in CH_3OH) 234 (4.42), 237(4.42), 319(4.16); IR ν(KBr) 1615, 1560, 1510 cm^{-1}; PMR δ($CDCl_3$) 2.96(m, H-1,4), 1.26-2.06(m, H-2,3,10,11), 7.10(d, H-5,9, $J_{5,6}=J_{8,9}$=12.0 Hz), 7.00(d, H-6,8).

6 : MS m/e 218(M^+, 100%), 192(24), 190(35); UV λ_{max}(in n-hexane) 214 nm(log ε 4.14), 222(sh, 4.14), 266(3.93), 393(sh, 4.34), 399(4.40), 407(4.45), 415(4.46), 426(4.38), 436(4.34), (in CH_3OH) 266(4.04), 410(sh, 4.49), 415(4.53), 426(4.54), 434(4.54); IR ν(KBr) 2210 cm^{-1}; PMR δ($CDCl_3$) 3.86(m, H-1,4, $J_{1,10s}=J_{1,10a}$=1.5 Hz), 6.90(m, H-2,3), 7.30(d, H-5,9, $J_{5,6}=J_{8,9}$= 11.5 Hz), 7.20(d, H-6,8), 2.38(dt, H-10s, $J_{10s,10a}$=7.5 Hz), 2.32(dt, H-10a); CMR δ($CDCl_3$) 142.2(C-2,3).

7 : MS m/e 232(M^+, 12%), 204(24), 203(100); UV λ_{max}(in n-hexane) 260 nm(log ε 4.14), 392(sh, 4.45), 398(4.48), 405(4.48), 417(4.39), 425(4.35), (in CH_3OH) 228(4.10), 262(4.15), 406 (4.53), 416(4.53), 423(sh, 4.52); IR ν(KBr) 2210 cm^{-1}; PMR δ($CDCl_3$) 3.94(m, H-1,4), 6.46(m, H-2,3), 7.28(d, $H_{5,6}=J_{8,9}$=11.0 Hz), 7.05(d, H-6,8), 1.38-1.61(m, H-10,11); CMR δ($CDCl_3$) 133.2 (C-2,3).

8 : UV λ_{max}(in n-hexane) 257 nm(log ε 4.00), 396(sh, 4.41), 403(4.45), 410(4.45), 420(4.36), 430 (4.32), (in CH_3OH) 261(4.09), 411(4.52), 420(4.53), 427(sh, 4.52); IR ν(KBr) 2210 cm^{-1}; PMR δ($CDCl_3$) 3.27(m, H-1,4), 1.10-2.10(m, H-2,3,10), 7.30(d, H-5,9, $J_{5,6}=J_{8,9}$=11.0 Hz), 7.09 (d, H-6,8).

9 : UV λ_{max}(in n-hexane) 259 nm(log ε 4.05), 389(sh, 4.41), 396(4.44), 403(4.45), 412(sh, 4.35), 422(4.30), (in CH_3OH) 235(4.05), 261(4.14), 404(4.51), 414(4.51), 420(sh, 4.50); IR ν(KBr) 2210 cm^{-1}; PMR δ($CDCl_3$) 2.95(m, H-1,4), 1.25-1.90(m, H-2,3,10,11), 7.37(d, H-5,9, $J_{5,6}=J_{8,9}$= 11.0 Hz), 7.01(d, H-6,8).