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The Dissociation of 7-Triphenylmethyl-1,3,5-cycloheptatriene in *m*-Xylene*1

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The enthalpy of the dissociation of bitropyl (bis-2,4,6-cycloheptatrien-1-yl) into the tropyl (cycloheptatrienyl) radicals has recently been evaluated to be 35±1 kcal/mol using ESR spectroscopy,1) whereas that of "hexaphenylethane," whose structure has been proved to be 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene (I),2) into the trityl (triphenylmethyl) radicals is known to be only about 11.5 kcal/mol.3) When these two values are available, it should be of considerable interest to know the value of the dissociation energy of 7-trityltropilidene (7-triphenylmethyl-1,3,5-cycloheptatriene), a coupling product of the trityl and the tropyl radicals.

Incidentally, we have synthesized this compound4) by the coupling of the two unlike radicals in connection with our studies of the one-electron reduction of the tropylium ion;5) we undertook the measurement of the degree of the dissociation by means of ESR spectroscopy in order to evaluate the enthalpy of the dissociation of this compound.

A degassed solution (0.1M) of 7-trityltropilidene in *m*-xylene gave the ESR signals of the trityl radical at 60—100°C; the signal gradually increased in intensity and became constant after 1—5 hr at 85—90°C or after 10—20 hr at 65°C. The concentrations of the trityl radical were estimated to be 3×10^{-6}—6×10^{-5}M at 60—95°C by a comparison of the integral spectrum constructed from the first derivative spectrum, recorded under overmodulated conditions (modulation width, 5.0 G), with that of a standard diphenylpicrylhydrazyl solution. The signal intensity of the trityl radical in a sample preheated at 100°C decreased when the sample was kept at lower temperatures, thus reaching the same value as that of another sample not preheated. After each measurement, no discoloration of the solution was observed, and the TLC analysis of an aliquot gave a sole spot with the same R_f value as that of the authentic 7-trityltropilidene.6)

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*1 Presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969. Abstracts of Papers, III, p. 1712; Studies of the Dissociation of a Carbon-Carbon Bond. Part I.

1) G. Vincow, H. J. Dauben, Jr., F. R. Hunter and W. V. Volland, *J. Amer. Chem. Soc.*, **91**, 2823 (1969); we are grateful to Professor Vincow for informing us of this result before publication and for his valued correspondence.

2) a) H. Lankamp, W. Th. Nauta and C. MacLean, *Tetrahedron Lett.*, **1968**, 249; we have followed their NMR experiments and confirmed the reported structure; b) R. D. Guthrie and G. R. Weisman, *Chem. Commun.*, **1969**, 1316.

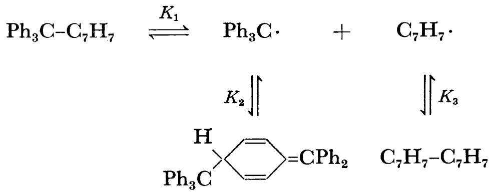
3) a) K. Ziegler and L. Ewald, *Ann.*, **473**, 163 (1929); b) E. Müller and I. Müller-Rodloff, *ibid.*, **521**, 89 (1936); c) F.S. D'yachkovskii, N.N. Bubnov and A.E. Shilov, *Doklady. Akad. Nauk S.S.S.R.*, **122**, 629 (1958).

4) 7-Trityltropilidene was first synthesized from triphenylmethylsodium and tropylium fluoroborate by M. R. Rifi and H. J. Dauben, Jr. (M. R. Rifi, Ph. D. Thesis, p. 105, the University of Washington, 1963); we are indebted to Professor K. M. Harmon of the University of Washigton for informing us of the details of Dr. Rifi's thesis.

5) K. Okamoto, K. Komatsu and H. Shingu, This Bulletin, **42**, 3249 (1969).

6) It has been found that 7-trityltropilidene gave a small amount of an oily product when heated in refluxing benzene for 4.5 days (F. R. Hunter, Ph. D. Thesis, p. 155, the University of Washington, 1966); we are grateful to Professor K. M. Harmon for informing us of the details of Dr. Hunter's thesis.

The ESR signal for the tropyl radical was not observed under the conditions here employed. This is most probably the result of the lowering of the concentration of the tropyl radical due to its dimerization to bitropyl. Since the trityl radical is also in equilibrium with the cyclohexadiene I ("hexaphenylethane"), we may assume the following equilibration scheme:



(I)

If the above scheme holds under the conditions employed, the equilibrium consant, K_1, for 7-trityltropilidene can be calculated from Eq. (1):

$$K_1 = (b/a)\{-1+\sqrt{1+(16b^2/K_2K_3)+(8b/K_3)}\}(K_3/4) \tag{1}$$

where a and b are, respectively, the concentrations of 7-trityltropilidene and the trityl radical.[7] The results are summarized in Table 1, along with the thermodynamic parameters.

Thus, in the temperature range from 60 to 95°C, the values of the equilibrium constant are in the sequence: the cyclohexadiene I>$Ph_3C–C_7H_7$> $C_7H_7–C_7H_7$, whereas the values of ΔH and of ΔS are in the sequence: $Ph_3C–C_7H_7$>$C_7H_7–C_7H_7$>the cyclohexadiene I. It seems to be difficult to explain the abnormally high values of ΔH and of ΔS for 7-trityltropilidene on the basis of the steric and the electronic factors which were considered in the cases of genuine hexaphenylethane[8] and bitropyl.[1] These quenstions remain to be elucidated in the future.[9]

TABLE 1. EQUILIBRIUM CONSTANTS, ENTHALPY AND ENTROPY FOR THE DISSOCIATION OF 7-TRIPHENYLMETHYL-1,3,5-CYCLOHEPTATRIENE IN m-XYLENE

Temp. °C	Concn. of Ph_3C a) M × 10^6	Equlibrium constant $Ph_3C–C_7H_7$ $K_1\times10^{16}$ c)	I b) $K_2\times10^3$ d)	$C_7H_7–C_7H_7$ $K_3\times10^{17}$ d)
60.0	2.71	1.50	1.41	2.24
65.0	4.16	3.96	1.82	4.68
70.0	8.07	18.4	2.29	10.0
75.0	7.17	19.6	2.95	20.4
80.0	17.4	53.4	3.63	39.8
83.0	24.1	213	4.17	63.2
85.0	15.8	127	4.52	81.3
88.0	41.1	691	5.18	126
90.0	25.1	360	5.69	162
93.0	50.8	1250	6.36	235
95.0	55.0	1617	6.92	309
ΔH	(kcal/mol)	50±2	11 d)	35 d)
ΔS(60°C)(e.u.)		78.4	20.0	27.3

a) The initial concentration of 7-trityltropilidene was 0.1M.

b) I=1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene.

c) Calculated from Eq. (1) (see text).

d) The values for K's were extrapolated from data at the other temperatures: see Refs. 1 and 7.

Experimental

7-Trityltropilidene. This was synthesized by the coupling of the trityl radical with the tropyl radical in benzene-acetonitrile. To a stirred benzene solution (18 ml) of the cyclohexadiene I (1.13 mmol) containing zinc dust (2.94 g), an acetonitrile solution (18 ml) of tropylium fluoroborate (4.50 mmol) was added, drop by drop, under a nitrogen atmosphere over a 15-min period at room temperature. The reaction mixture was then filtered; the filtrate was washed with water, dried, and concentrated to give an oily solid (0.849 g), which was then chromatographed over slica gel (70 g). Bitropyl (0.185 g, 45.3%) and 7-trityltropilidene (0.459 g, 61.0% yield based on the cyclohexadiene I; 30.5% yield based on the tropylium ion) were eluted with 95 : 5 and 90 : 10 n-hexane - benzene respectively. 7-Trityltropilidene melts at 167—170°C (dec.) (lit, mp 156°C[4]). Found: C, 93.52; H, 6.62. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63%. NMR spectrum: τ 2.80 (15H, singlet, aromatic), 3.25 (2H, triplet, 3- and 4-C), 3.81 (2H, multiplet, 2- and 5-C), 4.72 (2H, doublet of doublet, 1- and 6-C) and 7.06 (1H, triplet, 7-C); UV: $\lambda_{max}^{CH_3OH}$ 260 mμ (log ε=3.66) and two shoulders at 265.5 and 272 mμ (lit,[4] $\lambda_{max}^{95\%\ EtOH}$ 259 mμ ($\varepsilon=4.7\times10^3$) and 272 m$\mu$ (shoulder, $\varepsilon=3.20\times10^3$)).

ESR Measurements. The ESR spectra were taken on a Japan Electron Optics X-band spectrometer, model JES-3BS-X, equipped with a 100 kc/s field modulation unit. The evacuated sample tube to be heated was placed in a JEO Associates JES-UCT-2X quartz Dewar sleeve set in a TE_{011} JEO cavity.

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[7] The values of K_2 and ΔH for the dissociation of the cyclohexadiene I were taken to be, respectively, 2×10^{-4} (25°C) and 11 kcal/mol in benzene.[3b] The values of K_3 and ΔH for the dissociation of bitropyl were evaluated by means of ESR spectroscopy following the method of Vincow and his collaborators;[1] K_3 for a 2.9M solution of bitropyl in m-xylene, 1.2×10^{-13} (126°C); ΔH (the average value for three runs), 34.5 kcal/mol (124.5—152.0°C) (lit, ΔH for a neat sample, 35±1 kcal/mol[1])).

[8] a) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, New York (1955), Section 7·6; b) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[9] The sequence of ΔH $Ph_3C–C_7H_7$>$C_7H_7–C_7H_7$ may suggest that the ΔH for the genuine $Ph_3C–CPh_3$, which has not yet been prepared,[2a] might be greater than that of $Ph_3C–C_7H_7$.