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AUTOMERIZATION IN [4.2.2]PROPELLA-2,4,7,9-TETRAENE SYSTEM

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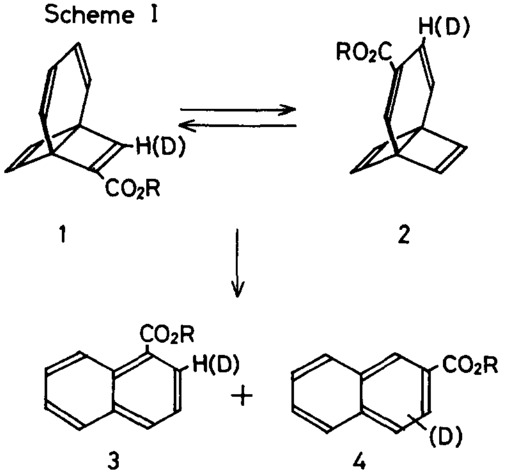
Summary: 7-[4.2.2]Propella-2,4,7,9-tetraenecarboxylates, 1, when heated at 200°, undergo reversible automerization giving 2 in preference to the aromatization to naphthalene derivatives which is promoted by free radicals.

In a recent communication,[1] we have reported the synthesis of methyl 7-[4.2.2]propella-2,4,7,9-tetraenecarboxylate, 1a. During the subsequent investigation on the chemical behavior of 1a, we observed that 1a underwent a novel automerization when heated at 200° in solution. Valence isomerization of unsaturated polycyclic compounds has been a subject of much attention and studied intensively.[2] The automerization of 1a, in which the aromatization of the Dewar benzene moiety is inhibited by a 1,3-butadiene bridge, is of considerable interest. We report here the results of investigation on the thermal reaction of 1.

Degassed dilute solutions of 1a (~0.01 M) in glass ampoules were heated at 200°. The thermolysates were analyzed by GLC after appropriate reaction times, which showed the formation of three major products, namely methyl 3-[4.2.2]-propella-2,4,7,9-tetraenecarboxylate, 2a, and, 1- and 2-naphthalenecarboxylic acid esters, 3a and 4a. The assignment of the structure for 2a was made on the basis of its spectroscopic properties: Mass(24 eV), m/e(rel. intensity) 186(M^+, 5), 155(100), 128(23), 127(53); ^{1}H-NMR($CDCl_3$), δ 6.99(br s, 1H), 6.45(AB q, J=2.0 Hz, 4H), 6.18(d of d, J=1.0 and 9.8 Hz, 1H), 5.97(d of d, J=2.0 and 9.8 Hz, 1H), 3.76(s, 3H). The observation of an AB quartet having a small coupling constant (2.0 Hz), characteristic to coupling between olefinic protons in cyclobutene, with the absorption intensity of four protons is in good agreement with the assigned unsymmetrically 1,4-disubstituted Dewar benzene structure. The examination of coupling constants among the three residual olefinic protons ruled out a possibility that the product has the 2-methoxycarbonyl structure. Study of the NMR spectrum with the aid of Eu(fod)$_3$ also supported the above assignment. The formation of 3a and 4a was

Scheme I



a, R=CH_3 : b, R=$CH_2C(CH_3)_3$

Table 1. Thermolysis of Propellatetraenes, **1** and **2**, in Solution at 200°

Sub-strate	Solvent[a]	Reaction time(h)	Yield[b] (%)	Product Composition(%)[b] **1**	**2**	**3**	**4**	[**1**]/[**2**] ratio
1a	DME	20	89.3	79.3	9.4	9.8	1.4	89:11
	DME-Et_3N(1%)	20	87.0	81.2	10.0	7.9	0.7	89:11
	DME-^{t}BuOH(1:10)	20	73.3	83.6	10.6	4.4	1.5	89:11
	benzene	20	85.0	87.1	11.1	1.3	0.5	89:11
		40	70.0	79.8	16.6	2.7	0.9	83:17
		60	59.6	75.2	18.7	4.4	1.7	80:20
1b	DME	20	94.0	76.6	8.4	13.9	1.1	90:10
		60	84.1	60.2	14.0	22.5	3.3	81:19
	benzene	20	95.5	87.1	10.8	1.4	0.7	89:11
		60	83.6	74.9	18.2	3.9	3.0	80:20
2a	benzene	20	86.7	36.7	60.3	0.3	2.7	38:62
		40	82.9	57.7	39.3	0.5	2.5	59:41
		60	78.7	65.4	29.9	1.0	3.8	69:31

a) Dimethoxyethane(DME) and benzene were distilled from LAH or benzophenone ketyl and, t-BuOH from t-BuOK/t-BuOH under argon just before use. The solutions were degassed by freeze-thaw cycles under 10^{-3} mmHg. b) Average of at least three runs. Determined by GLC by peak area comparison with that of the corresponding compound of similar concentration.

confirmed by the comparison of their spectra with those of the authentic samples. The results are summarized in Table 1. When the rearranged product, **2a**, was heated at 200° in degassed benzene, **1a** was regenerated, thus proving the reversibility of the rearrangement. Neither variation of solvent polarity[3] nor 5-fold difference in the initial concentration of **1** measurably affected the rate of formation of **2**. The addition of triethylamine (1% to DME) also did not bring about noticeable alteration in the reaction. Therefore, the reaction is probably unimolecular and catalysis by acid or base may be absent. The yields of the naphthalene derivatives were markedly dependent on the solvent employed, which is discussed in a later section. The rate of formation of **2** was unaltered upon substitution of the methyl group with more bulky neopentyl group. The material balance, however, was improved appreciably. Probably, bulky alkyl group would partially suppress the susceptibility of cyclobutenecarboxylic ester moiety towards bimolecular side reaction. The variation in the composition of the

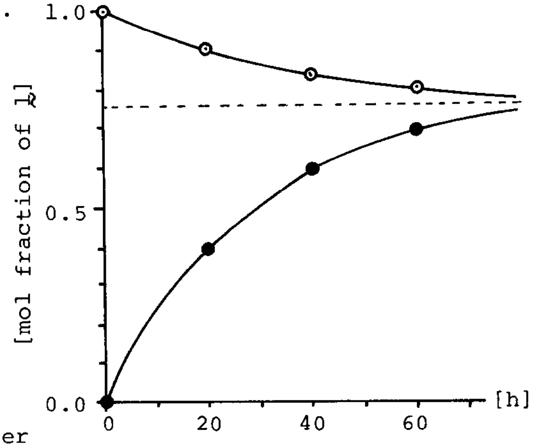
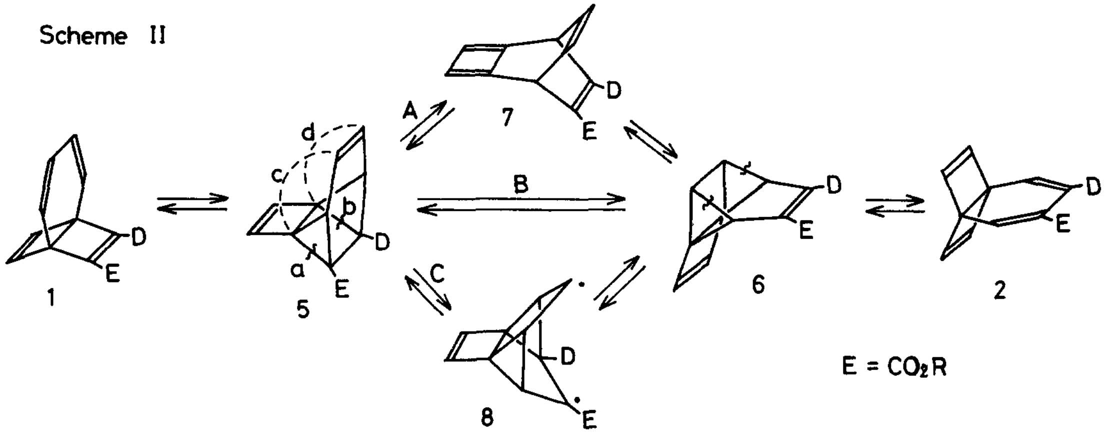


Figure 1. Variation of composition, [**1**]/[**2**], vs. reaction time at 200° starting from **1a**(○) and **2a**(●)

equilibrating mixture with the elapse of reaction time starting from 1a and 2a, respectively, is shown in Figure 1, which indicates the molar ratio, [1]/[2], will eventually converge upon ca. 3, though the equilibrium is not yet attained even after 60 h at 200°. In order to obtain further mechanistic information, 8-deutero-1a was prepared and subjected to thermolysis in degassed DME at 200°. In the recovered starting material, the deuterium was retained at C-8 and, in the rearranged products, it was found almost exclusively at C-4 in 2a and at C-2 in 3a.

On the basis of the above observations, we will propose a mechanism outlined in Scheme II. An intramolecular [2+4] cycloaddition between the cyclobutene and cyclohexadiene moieties[4] produces highly strained 5. Cleavage at the bonds, a and b, and concomitant bond formation at c and d affords 6. The transformation of 5 into 6 itself is an automerization. Subsequent retro-Diels-Alder reaction of 6 gives 2 in an excellent agreement with the labeling study. The unimportance of solvent polarity effect on the reaction is also in accord with the above mechanism. For the rearrangement between 5 and 6, there may be at least two mechanistic alternatives. A [π2+σ2+σ2] cycloreversion-[π2+π4] cycloaddition by way of a cyclobutadiene intermediate, 7, is one of the possibilities and a radical pathway by way of a biradical, 8, is another.[5] At present, however, we can not conclude which mechanism operates.

Scheme II



All the reactions summarized in Table 1 were carried out under degassed conditions. When a nondegassed DME solution of 1a, but prepared otherwise in the same way as before was heated at 200°, 92% of the starting material was consumed in only 0.5 h and the naphthalene derivatives were formed in a good yield (70%, 3a/4a=97/3). The rearranged product, 2a, was not detected. It is well known that DME is liable to form hydroperoxide on exposure to air.[7] We inferred that radical species derived from the hydroperoxide might promote the isomerization of 1 to 3 and 4. To prove the presumption, a DME solution of 1a containing 0.06 mol equivalent of $(t\text{-BuO})_2$ was degassed and heated for 1 h at the temperature lower than that in the standard conditions, but high enough to induce the decomposition of the peroxide (170°).[8] As expected, 55% of 1a had been consumed and, 3a and 4a were obtained in 62 and 2% yields, respectively.[9] There are some precedents for such radical-induced aromatization of unsaturated polycyclic compounds including the isomerizations of homofulvenes to substituted benzenes[10] and of azulenes to naphthalenes.[11] The major fraction, if not all, of the naphthalene derivatives formed in degassed DME might also be produced under catalytic action of impuritie which had somehow remained in the reaction mixture even under very carefully controlled reaction conditions. The yields of **3** and **4** were indeed remarkably reduced in degassed benzene, in which peroxide formation was less likely.[12]

Thus, the propellatetraene, **1**, undergoes the reversible thermal automerization to **2** in preference to the isomerization to the naphthalene derivatives, **3** and **4**, in spite of enormous difference in their thermodynamic stabilities.[12] The latter products are presumably produced via free radical processes, which is promoted by a trace amount of impurities present in the system.

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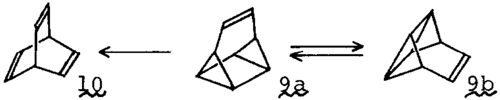
2) For an overview of recent studies, see: A. W. Murray, "Organic Reaction Mechanism·1979", Ed by A. C. Knipe and W. E. Watts, John Wiley & Sons, Ltd., New York (1981).

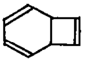
3) Z-value: benzene, 54; DME, 62.1; t-BuOH, 71.3: E. M. Kosower, "An Introduction Physical Organic Chemistry", John Wiley & Sons, Inc., New York (1968).

4) Analogous intramolecular [2+4] reactions, see: L. A. Paquette, R. E. Wingard, Jr., and J. M. Photis, J. Amer. Chem. Soc., 96, 5801 (1974).

5) Valence isomerization of **9** has been examined theoretically and it has been shown that the rearrangement to **10** and the automerization which correspond to the reaction pathways, A and B, in the present system, respectively, are energetically more demanding than the retro-Diels-Alder cleavage to **11**.[6] The analogous reaction of **5**, however, regenerates **1**, otherwise leads to a sterically strained cyclobutadiene, **12**. Inhibition of the rearrangement to **12** would enable the present automerization to proceed.



10 **9a** **9b**



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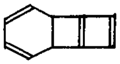

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6) H. Iwamura and H. Kihara, Bull. Chem. Soc. Jpn., 48, 512 (1975).

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9) It appears that oxygen itself does not induce the aromatization of **1**. Thermolysis of **1** in benzene in the presence of air afforded neither **2** nor **3**/**4** in an appreciable yield, though **1** was consumed fairly rapidly.

10) R. Criegee, D. Schoenleber, R. Huber, C. Schweickhardt, R. Wolf, and R. Ramirez, Chem. Ber., 106, 857 (1973).

11) R. W. Alder and G. Whittaker, J. Chem. Soc, Perkin Trans. 2, 714 (1975).

12) Besides peroxide(s), a trace amount of impurities in the starting material and the solvent, and glass wall might also promote the aromatization of **1** and **2**. It is not certain how much fraction, if any, of the naphthalenes obtained in the present reactions was produced unimolecularly.

13) The heat of formation of [4.2.2]propella-2,4,7,9-tetraene is estimated by group equivalent techniques to be 134 kcal/mol. The heat of formation of naphthalene is 36.1 kcal/mol: E. Kováts, H. H. Günthard, and P. A. Plattner, Helv. Chim. Acta, 38, 1917 (1955); 40, 2008 (1957).

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