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THERMAL REACTIONS OF ALKOXYCYCLOHEPTATRIENES AT 300-800°C[1)]

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The thermal reactions of methoxy- and ethoxycycloheptatrienes at several temperatures from 300 to 800°C were studied. 7-Alkoxycycloheptatriene (1) isomerized to the 1-isomer (3) at 450°C in quantitative yield, and rearranged to aromatic compounds (5 - 8) at temperatures higher than 450°C. These findings were not consistent with the observation of Harrison et al. that the dissociation of the $O-CH_3$ bond in 1a occurred at 400°C to give the hydroxytropylium radical (11).

The shift of a group[3-11)] (for example, the hydrogen 1,5-shift), the skeletal rearrangement,[12-14)] and the Berson-Willcott rearrangement[15)] have been well documented for the thermal behaviours of 7-substituted cycloheptatrienes. However, Harrison et al. have reported in a mass spectroscopic study that 7-methoxycycloheptatriene (1a) dissociated to hydroxytropylium (11) and methyl radicals by the cleavage of the $O-CH_3$ bond at 400°C.[16)] Interested in their report, we have studied the thermal reactions of alkoxycycloheptatrienes over a wide range of temperatures (300-800°C) by means of the conventional flow method, and found that 7-alkoxycycloheptatriene (1) isomerized to the 1-isomer (3) in quantitative yield at 450°C, and rearranged to aromatic compounds (5 - 8) above 450°C. No evidence for the formation of 11 from 1 was obtained in our studies. In order to clarify the discrepancy between the results obtained by us and previous authors,[16)] the mass spectrum of 1 and 3 was compared. This report concerns our studies on this point as well as on the mechanism of the thermal rearrangements of 1 to 3 - 8.

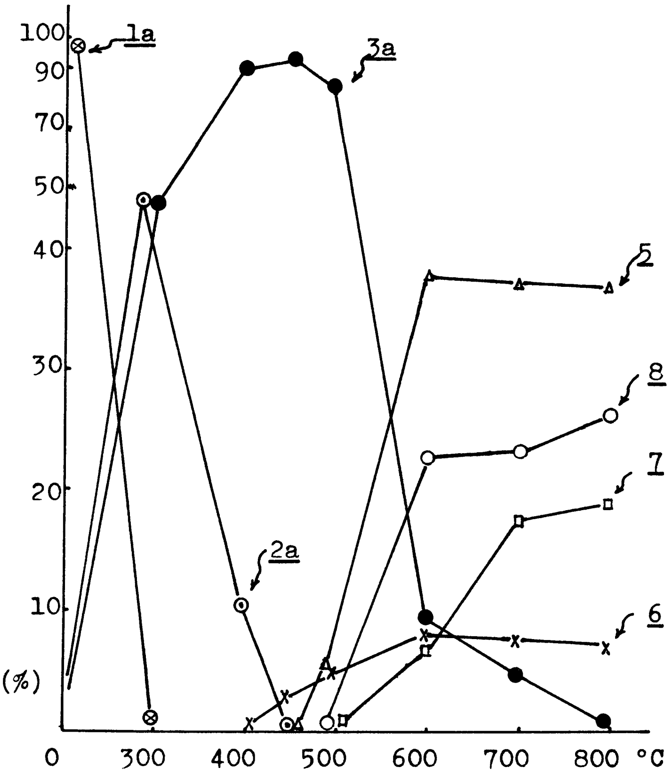


Fig. 1 Product yields in pyrolysis of 1a at 300 - 800°C.

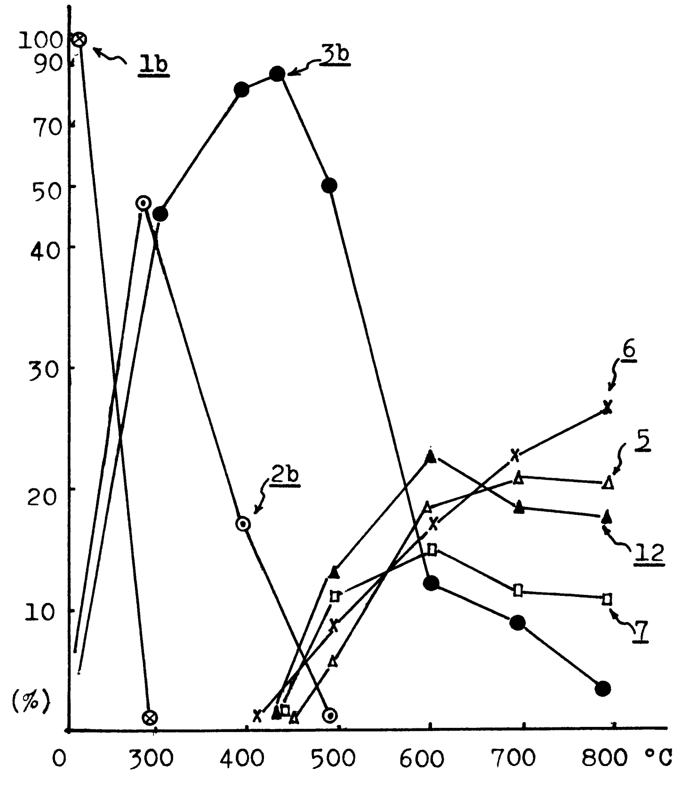


Fig.2 Product yields in pyrolysis of 1b at 300 - 800°C.

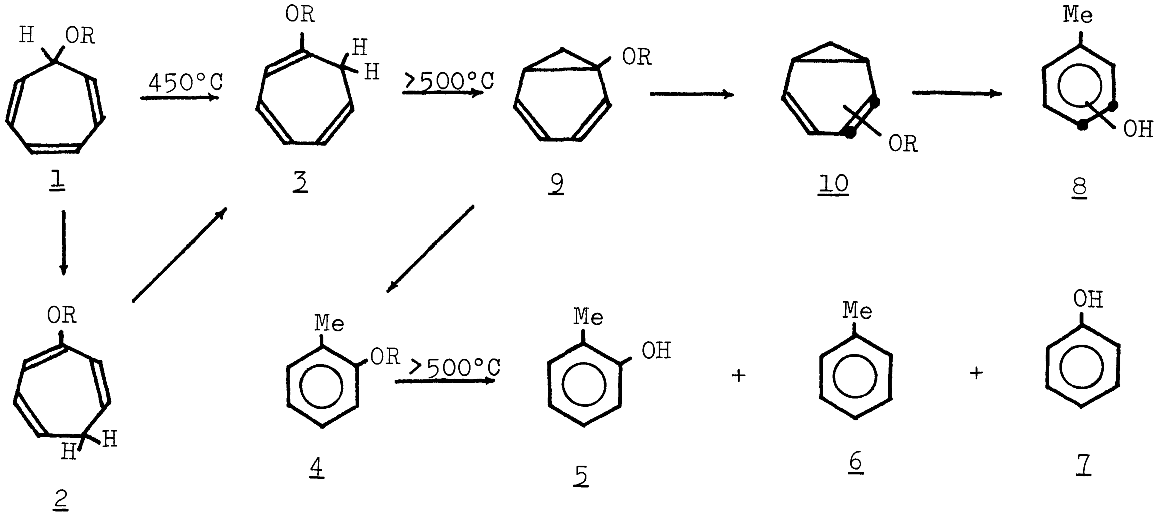
7-Methoxycycloheptatriene (1a)(neat) was pyrolyzed by passing through a quartz column containing quartz tips at several temperatures from 300-800°C,17) by which isomeric methoxycycloheptatrienes (2a and 3a) and aromatic compounds (5 - 8) were formed in the yields presented in Fig. 1, along with a small amount (∿10% for the pyrolyses above 500°C) of unidentified products. The identification and estimation of the relative yields of these compounds were based on the nmr (for 2a and 3a),5,18) GPC (for 5 - 8), and the formation of derivatives, 4-(p-tolylazo)-2-methylphenol (for 5) and phenyl p-nitrobenzoate (for 7).

3- and 1-Methoxycycloheptatrienes (2a and 3a) were formed in a complete consumption of 1a at 300-400°C; the 1-isomer (3a) became the sole cycloheptatriene derivative (94%; isolated yield)19) at 450°C. The quantitative formation of 3a from 1a at 450°C is to be noted, since it may be of value for the rapid preparation of 3a. According to the literature, it takes 48 hours at 150°C to obtain 3a from 1a.5) The formation of 3a at 450°C is a consequence of the double hydrogen 1,5-shift9) via 2a, since the pyrolysis of 2a at 450°C gave 3a in good yield.

The aromatic compounds (5 - 8) formed above 500°C may arise from 3a, since the pyrolysis of 3a at 600°C, for example, afforded 5 - 8 in 26, 4, 19, and 18% yields, respectively. A precursor of 5, 6, and 7 must be o-cresol methyl ether (4a) which was formed from 3a via 9a, since the pyrolysis of 4a at 700°C gave 5 - 7 in 52, 20, and 6% yields, respectively. The isomeric cresol (8) may arise from 1a via 10a by the Berson-Willcott15) and subsequent norcaradiene-benzenoid rearrangements.12-14) On the basis of these facts, the mechanistic pathway for the formation of 2a, 3a 5, 6, 7, and 8 is visualized as shown in Scheme 1.

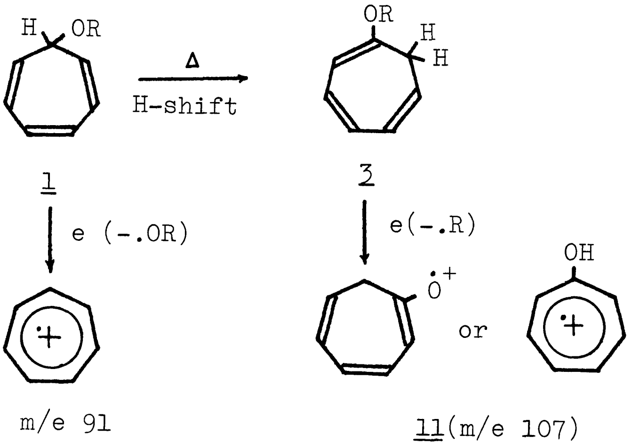
The above finding, i.e. the quantivative formation of 3a from 1a at 450°C, was not consistent with the observation by the previous authors that 1a dissociated at 400°C to the methyl and hydroxytropylium (11) radicals, which was identified by the appearance of the m/e 107 ion in the mass spectrum.16) We examined whether such products as tropone and benzaldehyde which are expected to arise from 11, are present in the reaction mixture at 450 and 500°C. However, we could not obtain any indication for the presence of such compounds. Therefore, we suspect that the hydroxytropylium radical (11) identified mass spectrometrically by the previous authors arises through a sequence of reactions: 1a isomerizes in the mass chamber at 400°C to give 3a, from which 11 is formed by the cleavage of the O-CH_3 bond by electron impact, as shown in Scheme 2.

Scheme 1



a: R= Methyl ; b: R= Ethyl

Scheme 2



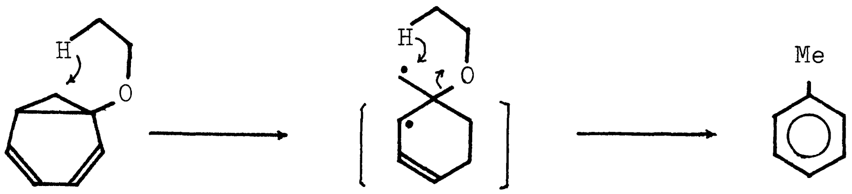
a: R= Methyl ; b: R= Ethyl

In fact, this assumption was confirmed by comparing the mass spectrum of 1a [m/e (% at 70 eV at 80°C) 122 (38), 121 (63), 107 (15), 92 (30), 91 (100), and 77 (57)] and 3a [m/e 122 (100), 121 (49), 107 (54), 91 (65), and 77 (70)]. The m/e 107 (11) arose as an intense ion peak in the mass spectrum of 3a, whereas it appeared only as a low intensity peak in that of 1a.

The pyrolysis of 7-ethoxycycloheptatriene (1b) under the same conditions gave almost similar results. The 1-isomer (3b) was formed in good yield at 450°C; the aromatic compounds (5, 6, and 7), and the ketone (12)[20)] having ν_{co} 1700 cm^{-1} were formed at temperatures higher than 450°C (Fig. 2). The aromatic compounds arose from 3b, since the pyrolysis of 3b at 600°C gave 5 - 7 in 12, 10, and 16% yields, respectively. The formation of these compounds may be interpreted in a manner similar to that of 1a (Scheme 1). In addition, the mass spectrum of 1b [m/e (%) 136 (8), 135 (13), 108 (15), 107 (41), 92 (73), 91 (100), and 77 (52)] and 3b [136 (49), 108 (91), 107 (100), 91 (30), 90 (22), 79 (50), and 77 (62)], showed a similarity with those of 1a and 3a, respectively.

However, it is to be noted that there are two remarkable differences in the products from 1a and 1b; the yield of toluene (6) from 1b was considerably higher compared to that from 1a, and the ketone compound (12)[20] was formed in ca. 10-20% yield at 500-800°C in the case of 1b. The higher yield of toluene in the case of 1b may be interpreted as a consequence of the participation of the ethyl group in the reaction. An examination of the Dreiding model indicated that a β-hydrogen of the ethyl group in 9b, norcaradiene isomer of 3b, is located so close to the top of the cyclopropane ring that it may participate in the formation reaction of toluene as shown in Scheme 3. This may be regarded as a modified retro-ene type reaction.[21,22]

Scheme 3



9b

6

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17) When a benzene solution of 1a or 1b was pyrolyzed, almost the same results were obtained with the exception that the amount of toluene in this case was a little lower than in the case of the pyrolysis of the neat sample. This may be due to the work-up procedure.

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19) In this case, toluene was formed in 4% yield.

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