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THE FLASH THERMOLYSIS OF 3-ISOPROPYLIDENETRICYCLO[3.2.1.0^{2,4}]OCT-6-ENE: A NEW REARRANGEMENT TO THE CYCLOOCTATETRAENE SYSTEM

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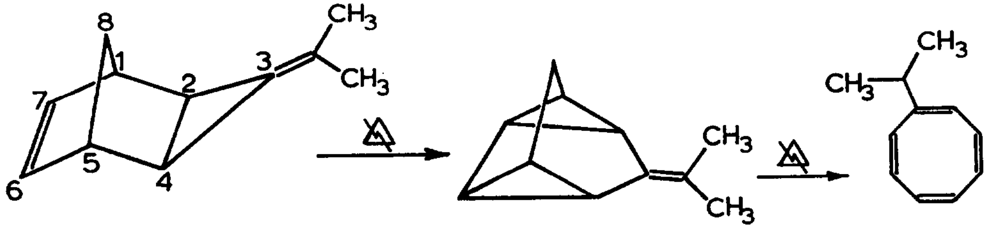
Much attention has been drawn to the photochemical and thermal rearrangement of C_8H_8 compounds.[2] In the present paper, we wish to report the (flash) thermal rearrangement of 3-isopropylidenetricyclo[3.2.1.0^{2,4}]oct-6-ene (I) to give isopropylcyclooctatetraene (III) *via* 3-isopropylidenetetracyclo[3.3.0.0^{4,6}.0^{2,8}]octane (II).



(I) (II) (III)

Scheme 1

The addition of isopropylidene carbene, prepared *in situ* from 1-chloro-2-methyl-propene and potassium *t*-butoxide[3] or from 1,1-dibromo-2-methylpropene[4] and methyllithium[5], to norbornadiene afforded the starting compound I in 12% or 24% yield, respectively, b.p. 85°/40 mm. Nuclear magnetic resonance, infrared, and mass spectra, and elemental analysis of this compound were in good agreement with the structure I. $\delta_{TMS}^{CCl_4}$[6]: 0.85 and 0.95 ppm (AB system, 2H, $J_{AB} = 8$ Hz, H_8), 1.39 (broad singlet, 2H, H_2 and H_4), 1.74 (triplet, 6H, $J_{Me, H_2 \text{ and } H_4} = 1.5$ Hz, methyl hydrogen), 2.86 (broad singlet, 2H, H_1 and H_5), and 6.24 (triplet, 2H, $J = 2$ Hz, H_6 and H_7). The *exo*-configuration of I was assigned from spin decoupling experiments.[7]

Flash thermolysis of hydrocarbon I was carried out at various temperatures in a previously described apparatus.[8] At 400°, compound I rearranges to compound II in almost quantitative yield.[9] The elemental analysis and mass spectral data showed that II is an isomer of the starting compound I. The nmr spectrum has a singlet at $\delta = 1.70$ ppm (allylic methyl) and multiplets between 2.13 and 1.33 ppm, but no absorption in the olefinic proton region; nevertheless an olefinic bond was detected by a positive bromine test. The structure was confirmed by ozonolysis to the corresponding ketone, characterised as the 2,4-dinitrophenylhydrazone.[10]

The thermal rearrangement of I to II, being the formal result of a $\sigma 2s + \pi 2s$ cycloaddition, a concerted process, is consequently orbital-symmetry forbidden.[11] Rather, an homolytic rupture of the C_2-C_4 bond of the cyclopropane occurs, giving rise to a substituted trimethylenemethane. Such rearrangements have been recently reported to occur in analogous systems not involving the exo double bond, where the 1,3-diradical formed was stabilised by phenyl or trifluoromethyl substituents.[12] In the present case, the trimethylenemethane (stabilised by allylic resonance) allows a facile C_2-C_4 bond rupture in the first step, and consequently provides the driving force of the rearrangement. This cycloaddition I → II appears to be the first reported intramolecular trapping of a trimethylenemethane by a double bond.[13]

When the temperature of thermolysis was increased to 600°, the main product was III (29%) together with compound II (19%). Mass and infrared spectral data were consistent with structure III. Three signals were observed in the nmr spectrum at 20°, i.e. $\delta = 1.02$ ppm (doublet, 6H, $J = 6.6$ Hz, methyl hydrogens), 2.25 (heptet, 1H, $J = 6.5$, isopropyl methine attached to a double bond), and 5.69 (singlet) with very broad singlet at $\delta = 5.45$ (7H, olefinic hydrogens). The temperature dependence of the olefinic hydrogen peaks was observed in this system and is consistent with the data described in the literature for the cyclooctatetraene system.[14] Chemical evidence for the structure was obtained by comparison with an authentic sample synthesised by reaction of bromocyclooctatetraene[15] with lithium diisopropylcopper.[16]

At a higher temperature, e.g. 900°, no C_{11} compound was detected, but several aromatic substances were observed (by vpc), along with some polymer. The main products identified were benzene (13%), cumene (6%) and α-methylstyrene (14%); they were characterised by comparison of ir spectra, nmr spectra, and vpc retention times with those of the authentic samples.

This temperature dependence of the products in the flash thermolysis of compound I is clearly illustrated in the Figure. These curves suggest strongly that tricyclooctene I rearranges first to II, which then subsequently rearranges further to cyclooctatetraene III. The aromatic derivatives produced at a high temperature could be formed from compound III.[17] Indeed, in confirmation, the flash thermolysis of compound II at 600° gave 40%[18] of isopropylcyclooctatetraene (III) and 34%[18] of unreacted II. At 800° isopropylcyclooctatetraene itself gave benzene (30%)[18], cumene (18%)[18] and α-methylstyrene (7%)[18].

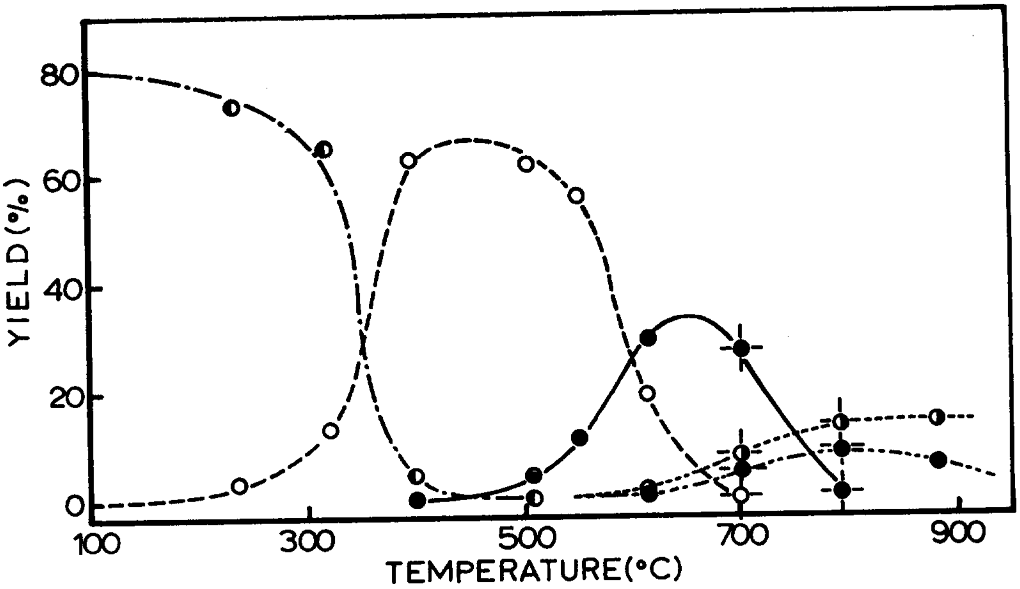
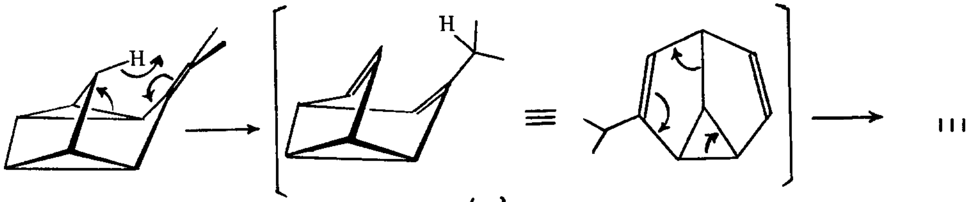


Figure. Temperature dependence of the yield in the flash thermolysis of 3-isopropylidenetricyclo[3.2.1.0^{2,4}]oct-6-ene (I)

◐ 3-isopropylidenetricyclo[3.2.1.0^{2,4}]oct-6-ene (I); ○ 3-isopropylidenetetracyclo[3.3.0.0^{4,6}.0^{2,8}]octane (II); ● isopropylcyclooctatetraene (III); ● cumene; ◑ α-methylstyrene.

Points with additional lines ⌖ are calibrated from relative yields.

A plausible mechanism for the rearrangement II → III is depicted in Scheme 2. One of the



(II) (IV)

Scheme 2

bridge methylene hydrogens is sterically available for transfer to the double bond hence the first step II → IV which could be analogous to the well documented thermal bond reorganisation of the cis-1-methyl-2-vinylcyclopropanes.[19] Then the rearrangements of the semibullvalene IV to the cyclooctatetraene III, a formal $[_{\pi}4_a + _{\pi}2_a]$ cycloreversion, is quite feasible on the basis of microscopic reversibility, since the reverse reaction has been recently observed with substituted cyclooctatetraenes.[2c, 20]

References and Notes

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