Tetrahedron Letters No.40, pp. 4257-4260, 1968. Pergamon Press. Printed in Great Britain.

THERMAL REARRANGEMENT OF CROSS CONJUGATED METHYLENECYCLOHEXADIENES

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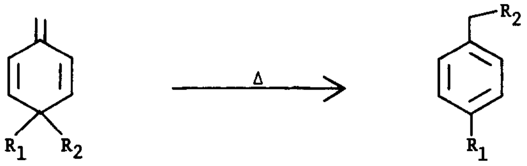
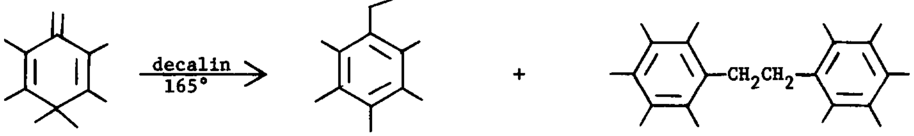
(Received in USA 22 May 1968; received in UK for publication 5 July 1968)

3-Methylene-1,4-cyclohexadienes rearrange thermally to aromatic compounds. The reaction[1] was discovered at the turn of the century by Auwers[2] in connection with studies on the Reimer-Tiemann and related reactions. Accordingly, the common migrating groups (R_2) have been $CHCl_2$ and CCl_3.[3] Bird and Cookson[4] presented kinetic data which suggested a free radical chain mechanism when R_2 = $CHCl_2$.



We wish to report the first example of simple alkyl (methyl) migration in this reaction, and to present conclusive evidence for the free radical and intermolecular nature of the reaction.[5] Hexamethyl-3-methylene-1,4-cyclohexadiene 1 was found to rearrange thermally to ethylpentamethylbenzene 2; the reaction has been studied in solution and in the vapor phase.

Heating a 0.21M decalin solution of 1 at 165° gave a 90% yield of 2, together with a trace of decamethylbibenzyl 3. The half-time at 165° is 49 min. The yield of 3 increased to 48% when the reaction was performed in the vapor phase (420°, 6 sec. contact time). Hoping to trap the suspected pentamethylbenzyl and/or methyl radicals by hydrogen abstraction, we carried out the rearrangement in cumene at 150°. As seen, the yield of 2 was highest with high



1 2 (90%) 3 (trace)

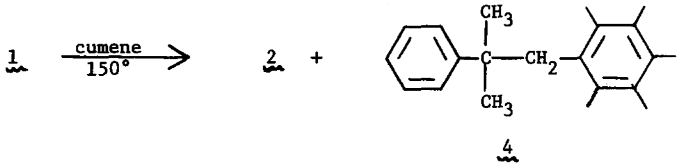


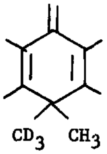
TABLE I

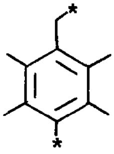
Yields as a function of Initial Triene Concentration

Molarity of 1	Isolated Yield, % 2	4
1.0	87	6
0.45	78	10
0.09	54	32

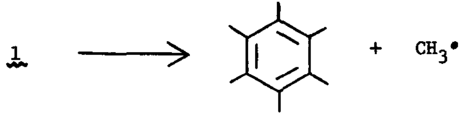
initial concentrations of 1, suggesting that 2 is formed in a bimolecular step. The rearrangement in cumene was completely interrupted by thiophenol, the only products derived from 1 being hexamethylbenzene and phenyl pentamethylbenzyl sulfide.[6]

The best evidence for intermolecular methyl transfer came from studies with labeled 1. The nmr spectrum of 2 derived from 1 labeled as shown[7] indicated a 50:50 distribution of the label between the asterisked positions, as expected for either intra- or intermolecular methyl transfer. The mass spectrum, however, showed (see Figures) essentially statistical distribution between product with 0, 1 and 2 labeled methyl groups (i.e., the sum of the relative intensities at m/e 176 (d_0) and 182 (d_6) was equal to the relative intensity at m/e 179 (d_3)). This was true for reaction in cumene or decalin under several sets of conditions.





One scheme which can rationalize these data is shown:



(1)

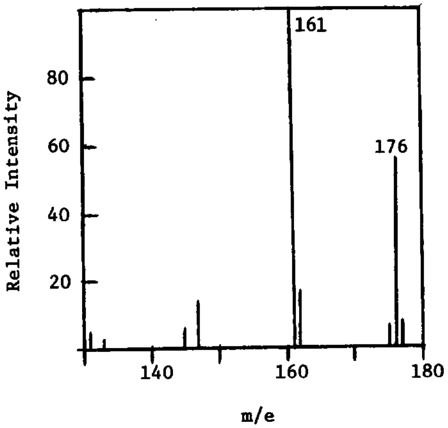


Fig. 1 Partial Mass Spectrum of Unlabelled Ethylpentamethylbenzene

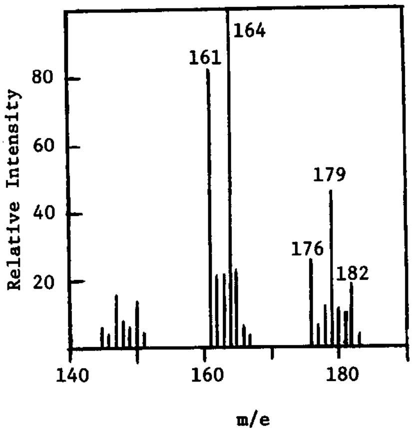
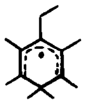


Fig. 2 Partial Mass Spectrum of Ethylpentamethylbenzene from Pyrolysis of 0.1M 6-CD_3-1 in Cumene, 145°

$$CH_3^{\bullet} + 1 \longrightarrow$$



5 (2)

$$5 \longrightarrow 2 + CH_3^{\bullet} \qquad (3)$$

$$\text{or} \quad 5 + 1 \longrightarrow 2 + 5 \qquad (4)$$

At low concentrations of 1 in cumene, hydrogen abstraction competes with addition (step 2) leading to less 2 and more 4 (Table I). Thiophenol traps both radicals produced in step 1. At 420°, the large difference in reactivity of methyl and pentamethylbenzyl radicals is diminished; both radicals add to 1, resulting in nearly equal yields of 2 and 3.

Other alkyl groups are expected to migrate by the same mechanism suggested here, though allyl groups may rearrange via a Cope mechanism.[8]

Acknowledgement. We are indebted to the National Science Foundation and to the Minnesota Mining and Manufacturing Company for generous support.

REFERENCES

1. Sometimes referred to as the 'semibenzene' rearrangement.
2. K. Auwers and G. Keil, *Chem. Ber.*, **36**, 1861 (1903); K. Auwers, *Ann.*, **352**, 219 (1907); K. Auwers, *Chem. Ber.*, **55**, 2167 (1922).
3. For examples and references, see R. C. Fuson and T. G. Miller, *J. Org. Chem.*, **17**, 316 (1952); R. L. Tse and M. S. Newman, *ibid.*, **21**, 638 (1956); D. J. Patel and D. I. Schuster, *J. Am. Chem. Soc.*, **89**, 184 (1967).
4. C. W. Bird and R. C. Cookson, *J. Org. Chem.*, **24**, 441 (1959).
5. The statement in the abstract, American Chemical Society 155th National meeting, San Francisco, 1968, paper P-27 that the shift in solution is intramolecular is incorrect.
6. The mole ratio of thiophenol/**1** varied from 1:1 to 8:1; at the lower ratio, a trace (<3%) of **2** was produced.
7. Prepared from compound **16** in H. Hart and D. W. Swatton, *J. Am. Chem. Soc.*, **89**, 1874 (1967), by back-exchange with sodium methoxide in unlabeled methanol.
8. All new compounds reported here (**2**, **4**, phenyl pentamethylbenzyl sulfide) gave satisfactory elemental analyses, and nmr spectra consistent with the assigned structures.