**Tetrahedron Letters No.39, pp. 4655-4658, 1966. Pergamon Press Ltd.
Printed in Great Britain.**

THERMAL REARRANGEMENTS OF 7-SUBSTITUTED NORBORNADIENES TO CYCLOHEPTATRIENES

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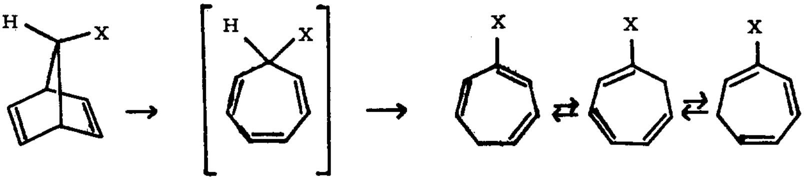
(Received 25 June 1966)

We have found that introduction into norbornadiene of 7-alkoxy or 7-phenyl substituents causes a striking difference in the course and rate of thermal isomerization. Compounds Ia-Id rearrange in good yields at 170° to corresponding mixtures of III, IV, and V.[3,4] Aromatic isomers are not observed.



I II III IV V

a) X = $OC(CH_3)_3$
b) X = OCH_3
c) X = $OCH_2CH_2OCH_2CH_3$
d) X = C_6H_5

First-order rate constants for the rearrangements are listed in the table. The absence of a large solvent effect in the isomerization of

TABLE

Isomerization of 7-Substituted Norbornadienes at 170°

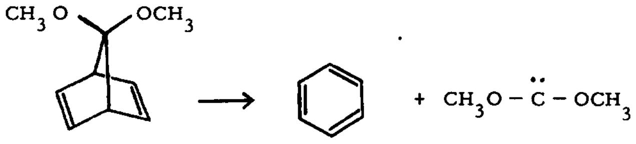
Compound	Solvent	$k \times 10^5$ (sec^{-1})
Ia	gas phase (~60 mm)	(~3)
"	*n*-decane	14.3
"	diethyleneglycol dimethyl ether	21.7
"	2-ethoxyethanol	22.8
"	neat	(~16)
Ib	*n*-decane	1.83
Ic	2-ethoxyethanol	2.37
Id	*n*-decane	2.63

Ia mitigates against the possibility that ionic intermediates are involved. The activation parameters for the isomerization of Ia in *n*-decane are $\Delta H^{\ddagger} = 34.5$ kcal and $\Delta S^{\ddagger} = +1$ eu.

Observation that the product isomers (IIId, IVd, and Vd) are formed sequentially from Id suggests that II is an intermediate in the reactions. Both IIb and IId are known to undergo thermal 1,5-hydrogen migrations to give corresponding mixtures of isomers which are formed in the sequenc III $\rightleftarrows$ IV $\rightleftarrows$ V.[5] The rearrangements of IIb and IId are sufficiently rapid at 170° that these compounds would not easily be detectable in the reaction mixtures formed from Ib and Id. Formation of IIIc, IVc, and Vc when a solution of Ia in 2-ethoxyethanol is rearranged also is consistent with the presence of II as an intermediate in these rearrangements. Ether Ia and cycloheptatrienes IIIa, IVa, and Va are stable to attack by 2-ethoxyethanol under the reaction conditions, but IIa is converted rapidly to a mixture of IIIa, IVa, and Va.

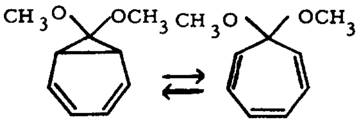
The thermal isomerization of norbornadiene to cycloheptatriene requires much higher temperatures and is accompanied by formation of toluene, cyclopentadiene, and acetylene.[6] In contrast, pyrolyses of norbornadienone ketals and thioketals occur at temperatures comparable to that used in this work but, instead of cycloheptatrienes, furnish as products benzene and compounds derived from the ketal or thioketal function.[7] Pyrolyses of halogen substituted norbornadienone ketals occur at lower temperatures and lead also to aromatic compounds, though products that involve retention of the ketal carbon as a substituent on the aromatic ring are formed as well as products that have lost the ketal function.[8]

It is interesting to speculate that norcaradienes may be involved as intermediates in at least some of these reactions.[9] For example, the formation from VI of benzene and products thought to arise from

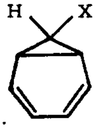


VI

dimethoxycarbene may result from fragmentation of VII. Either VII or



VII VIII



IX

VIII, which should be in thermal equilibrium with each other, might be formed initially from VI. Norcaradiene IX should be in equilibrium with

II, but its fragmentation would result in a less stable carbene and might be slower relative to the competing 1, 5-hydrogen transfer.

Acknowledgements. We are grateful for support of this research by the National Science Foundation and by funds made available by the Alfred P. Sloan Foundation. We are pleased to acknowledge the assistance of the National Science Foundation in providing funds to aid in the purchase of the Varian A-60 nmr spectrometer used in this research.

REFERENCES

1. Supported (1964-66) by a Fellowship (5-F1-GM-23, 263-02) from the National Institute of General Medical Sciences.
2. Alfred P. Sloan Foundation Research Fellow.
3. Rearrangement of Ia is accompanied by a secondary reaction in which the cycloheptatrienes decompose to dihydrotropones and *i*-butene. *t*-Butyl alcohol also is formed in small amounts.
4. In a reaction which may be related to those reported here, 7-norbornadienol forms benzaldehyde and cycloheptatriene at 170°.
5. A. P. ter Borg, E. Razenberg, and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 1230 (1965), and references therein.
6. W. C. Herndon and L. L. Lowry, *J. Am. Chem. Soc.*, **86**, 1922 (1964), and references therein. See also S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 585 (1966).
7. D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965).
8. D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966), and references therein.
9. This possibility has been considered for thermal reactions of halogenated norbornadienone ketals.[8]