Tetrahedron Letters No.39, pp. 3423-3426, 1970. Pergamon Press. Printed in Great Britain.

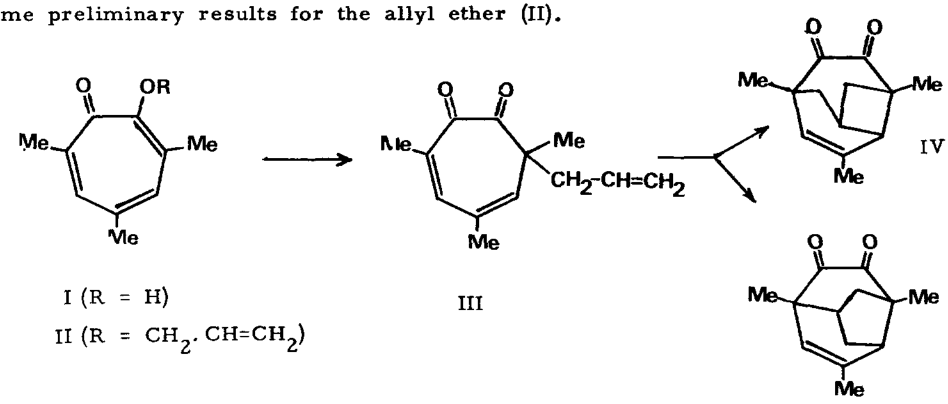
CLAISEN REARRANGEMENT OF 2-ALLYLOXY-3,5,7-TRIMETHYLTROPONE

M. M. Al Holly and J. D. Hobson

Department of Chemistry, The University, P. O. Box 363, Birmingham.

(Received in UK 13 July 1970; accepted for publication 22 July 1970)

Few examples of the Claisen rearrangement of tropolone allyl ethers have been previously recorded,[1] and detail is lacking concerning the peculiarities of the reaction in these systems, especially in 'ortho-' substituted compounds. The rearrangement of ethers of 3,5,7-trimethyltropolone (I) appeared to offer interesting comparisons with the well studied mesityl ethers,[2] and we disclose here some preliminary results for the allyl ether (II).



I (R = H)

II (R = $CH_2.CH{=}CH_2$)

III

IV

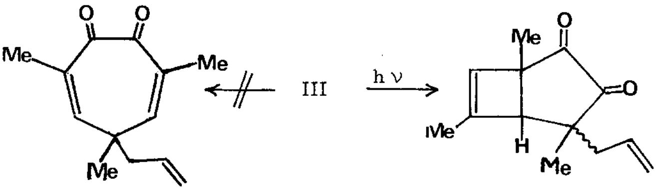
V

Rearrangement of (II)[3] proceeded rapidly at 160° (no solvent) giving a three component mixture, readily separable by g.l.c. The major (75%) product (III) was a yellow oil showing IR bands at 1715 (C:O) and 1655cm^{-1} (unsat. C:O), typical[4] homoannular dienone UV absorption at $\lambda_{max.}$ 222 and 309 nm (ϵ 6200 and 4100) together with weak α-diketone bands[5] at $\lambda_{max.}$ 401 and 445 nm (ϵ 90). Structure (III) was further substantiated by the presence in its NMR spectrum of singlets at τ 3.36 and 4.30 (ring protons), a pair of doublets at 7.98 and 8.07 (*J* 1.5 and 2 Hz respectively; allylic Me groups), and a singlet at 8.70 (sat. C-Me), in addition to signals (τ 4.4 - 5.2) due to the C-allyl group.

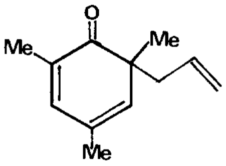
Of the two minor products, both of which were isomeric with (III), being formed from it by further heating at the rearrangement temperature, the more abundant (15%) was obtained as yellow crystals, m.p. 65°, $\lambda_{max.}$ 250 and 387 nm (ε 730 and 50), while the other was an oil, $\lambda_{max.}$ 254, 263, 363, 382 and 409 nm (ε 1200, 1200, 95, 120, and 145). Vinyl peaks in the 900 - 1000 cm^{-1} region were absent from the IR spectra of both compounds, which showed carbonyl absorption as a broad band at 1710 for the solid isomer, and twin peaks at 1745 and 1725 cm^{-1} in the case of the oil. Both NMR spectra showed a single olefinic proton weakly coupled (J 1.5 Hz) to one of the methyl groups, while the signals due to the other two methyls appeared as a single broad peak at higher field. The absence of spectroscopic features characteristic of vinyl and conjugated ketone functions in these compounds, together with their mode of formation, clearly indicate structures (IV) and (V), arising from intramolecular 1,4-cycloaddition. A tentative distinction can be made on spectroscopic grounds since an examination of molecular models suggests that the dihedral angle between the carbonyl groups is rather greater in (IV) than in (V): the former is therefore[5] assigned to the diketone, m.p. 65°, which shows the characteristic α-diketone UV absorption near 400 nm at rather shorter wave-lengths than its congener.

No evidence was obtained for the formation of the 3,6-diendione (VI), either thermally or photochemically; prolonged heating at 140° (neat liquid, or in decalin) of the initially pure 3,5-diendione (III) accompanied by frequent t.l.c. and g.l.c. examination showed only slow conversion to (IV) and (V), together with a small amount of reversion to the allyl ether (II). Irradiation (tungsten lamp) of a cyclohexane solution cleanly isomerised (III) to an approximately equimolar mixture of two compounds, evidently stereoisomers of the ring-collapsed valence tautomer (VII). In addition to IR and UV spectra in accordance with expectation, the NMR spectrum showed co-incident signals arising from the ring proton and allylic methyl group of each isomer at τ 3.15 and 8.16 (doublet, J 1.5 Hz) respectively; the saturated C-methyl groups appeared as separate singlets of approximately equal intensity at 8.54, 8.57, 8.71, and 8.88 (coupled and uncoupled signals identified by measurement at 60 and 100 MHz and by double resonance).

Kinetic data for the rearrangement of (II) at 140° in decalin, obtained by monitoring absorbance at 325 nm, showed initial first order behaviour with subsequent deviation due to further isomerisation of (III). The derived rate constant, $k_1^{140^\circ} = 1.8 \times 10^{-4}$ sec^{-1}, points to a notably smaller activation energy for this reaction relative to the Claisen rearrangement of mesityl allyl ether,[2] where



VI VII



VIII

thermal equilibration greatly favours the aromatic ether over the derived cyclohexa-2,4 (VIII) and -2,5-dienones.

It is noteworthy that the symmetry-forbidden ortho-ortho rearrangement[2,6] (an apparent [3,5]-sigmatropic shift) observed in the case of the cyclohexa-2,4-dienone (VIII) has been suggested to proceed via a transient, and so far unisolated, 1,4-cycloadduct, for which (IV) provides a close analogy. The recently reported thermal isomerisation of 7-allyloxycycloheptatriene to tricyclodecane derivatives are also closely related.[7] The possible occurrence of the counterpart of the ortho-ortho rearrangement, and also the interesting potentialities for [3,7] versus [3,3]-sigmatropic shifts in tropolone allyl ethers, are under investigation.

Acknowledgments

The authors are indebted to the Calouste Gulbenkian Foundation for financial support, and to the Ministry of Education of the Government of Iraq for the award of a research studentship.

References

[1] E. Sebe and S. Matsumoto, Proc. Japan. Acad., **29**, 207 (1953);
Y. Kitahara and M. Funamizu, Bull Chem. Soc. Jap., **31**, 782 (1958).

[2] P. Fahrni and H. Schmid, Helv. Chim. Acta, **42**, 1102 (1959);
H. J. Hansen and H. Schmid, Chem. Brit., **5**, 111 (1969).

[3] 3,5,7-Trimethyltropolone (T. Nozoe, T. Mukai, and K. Takase, Sci. Reps. Tohoku Univ., **36**, 40 (1952)) was converted into its sodium salt and reacted with allyl bromide in dimethyl sulphoxide.

[4] A. J. Waring in "Advances in Alicyclic Chemistry" ed. H. Hart and G. J. Karabatsos, Acad. Press, New York, **1**, 129 (1966).

[5] N. J. Leonard and P. M. Mader, J. Amer. Chem. Soc., **72**, 5388 (1950).

[6] A. Jefferson and F. Scheinmann, Quart. Revs., **22**, 391 (1968).

[7] C. A. Cupas, W. Schumann, and W. E. Heyd, J. Amer. Chem. Soc., **92**, 3237 (1970).