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^{1}H-NMR SPECTRAL EVIDENCES FOR THE DOUBLE-CHAIR CONFORMATION OF THE 9-AZABICYCLO[3.3.1]NONANE-3,7-DIONE SYSTEM

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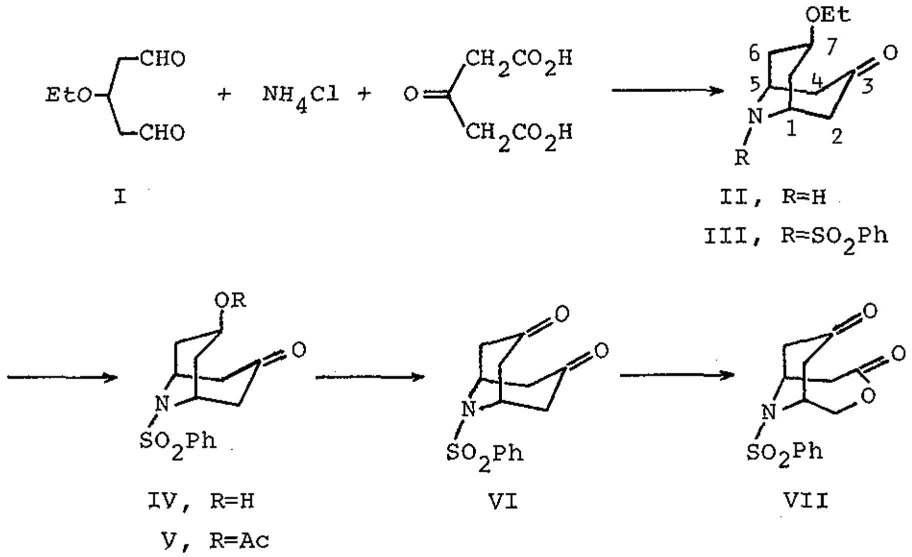
N-Benzenesulfonyl-9-azabicyclo[3.3.1]nonane-3,7-dione was synthesized, and its conformation was shown to be of a double-chair form by ^{1}H-nmr spectrum evidences.

Of the conformation of bicyclo[3.3.1]nonanes, a chair-boat as well as twin-chair form are known today. In general, the 9-azabicyclo[3.3.1]nonan-3-one system is known[1] to exist in the double-chair conformation, but the carbocyclic bicyclo[3.3.1]nonan-3-one has been shown to undergo 'chair'-'boat' isomerization in the cyclohexanone ring as evidenced by the nuclear magnetic resonance (nmr)[2] and electron spin resonance study.[3] The bicyclo[3.3.1]-nonane-3,7-dione system has been reported to be in the double-chair conformation from the nmr spectrum evidence by Dreiding et al.[4] and from the ir spectrum evidence by Eglinton et al.,[5] but 9,10-benzobicyclo[3.3.2]dec-9-ene-3,7-dione was reported[6] to be in equilibrium between a double-chair and double-boat form.[7]

As for 9-azabicyclo[3.3.1]nonane-3,7-dione, there have been no reports describing its conformation. In the present paper, we describe the ^{1}H-nmr evidence for the double-chair conformation of 9-azabicyclo[3.3.1]nonane-3,7-dione.

N-Benzenesulfonyl-9-azabicyclo[3.3.1]nonane-3,7-dione (VI), which was needed for some of our works concerning the structure-reactivity relationships of the bicyclo[3.3.1]nonane-3,7-dione system,[8] was synthesized as follows.



I

II, R=H

III, R=SO_2Ph

IV, R=H

V, R=Ac

VI

VII

The Robinson-Schöpf condensation of β-ethoxyglutaraldehyde (I) with ammonium chloride and acetonedicarboxylic acid gave an amino ketone (II),[9] which was converted to a sulfonamide (III), m.p. 131-133°; IR (KCl): 1715, 1350, 1165 cm^{-1}. The ketol (IV), m.p. 181-183°; IR (KCl): 3400 cm^{-1}, was obtained in 78% yield upon treatment of III with boron tribromide. Its acetate (V), m.p. 136-137°; IR (KCl): 1750, 1710 cm^{-1}, displays an ^{1}H-nmr signal[10] due to the C_7-H as a nine-line multiplet ($W_{\frac{1}{2}}$=22Hz) at δ 4.91ppm, the feature of which suggests an equatorial orientation for the C_7-substituent in II-V. Oxidation of IV with chromium trioxide-pyridine gave the diketone (VI), m.p. 161-162°; IR ($CHCl_3$): 1730 cm^{-1}; MS: m/e 293(M^+, 6%), in 80% yield. In the ^1H-nmr spectrum of VI (Fig. 1), the signal for the axial hydrogens at C_2, C_4, C_6, C_8 appears as a double-doublet (J=16Hz, 6Hz) at δ 2.71ppm, and that for the equatorial counterparts as a doublet (J=16Hz) at δ 2.38ppm. In addition, the bridgehead hydrogens at C_1 and C_5 positions appear as a pseudo-triplet centered at δ 4.93ppm with half-width of 10Hz and base-width of 22Hz.[11] These results indicate that VI exists in the double-chair conformation despite the dipolar repulsion resulting from the two facing ketone carbonyls.

Peracid oxidation of VI with m-chloroperbenzoic acid in boiling methylene chloride gave a keto lactone (VII) [m.p. 165-167°; IR (KCl): 1750, 1720 cm^{-1}; 68% yield] possibly via the through-space participation[8] of the facing carbonyls.

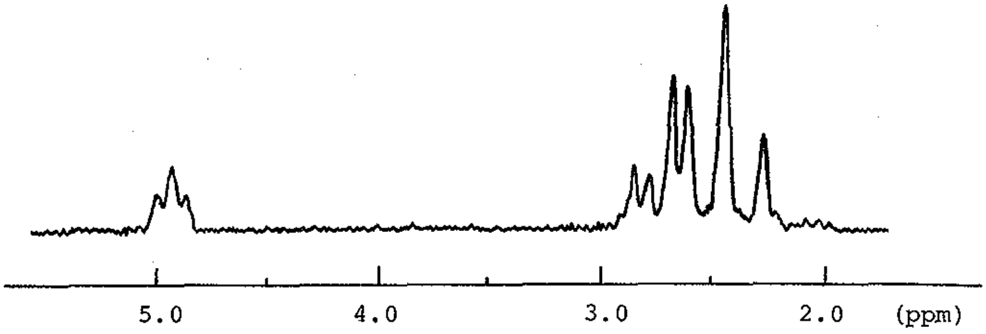


Fig. 1 The nmr spectrum of compound VI

NOTES AND REFERENCES

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2. M. R. Vegar and R. J. Wells, *ibid.*, 1971, 2847.
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5. Eglinton and co-workers have ascribed its carbonyl absorption (1729 cm^{-1}) in the anomalously high frequency region to the dipolar interaction between two facing carbonyls in the double-chair conformation; G. Eglinton, J. Martin, and W. Parker, *J. Chem. Soc.*, 1965, 1243.
6. B. Föhlisch, V. Dukek, I. Graessle, B. Novotny, E. Schupp, G. Schwaiger, and E. Widmann, *Liebigs Ann. Chem.*, 1973, 1839.
7. Dreiding et al., in contrast to the result of Föhlisch et al.,[6] have shown that 9,10-benzobicyclo[3.3.2]dec-9-ene-3,7-dione is in the double-chair conformation; C. B. Chapleo and A. S. Dreiding, *Helv. Chim. Acta*, 1974, **57**, 2420.
8. See, for example, T. Momose, S. Atarashi, and O. Muraoka, *Tetrahedron Letters*, 1974, 3697.
9. The N-methyl derivative of II was prepared by Stetter et al.; H. Stetter and R. Mehren, *Liebigs Ann. Chem.*, 1967, **709**, 170.
10. ^{1}H-nmr spectra were measured for the CDCl$_3$ solution with TMS as an internal standard on a Hitachi R-22 spectrometer operating at 90MHz.
11. In the tropane system in which the piperidine ring is in a chair form, the half-width and the base-width of the two bridgehead protons are reported to be 9.5-10.2Hz and 17.5-21Hz, respectively: see C.-Y. Chen and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1965, 3473.

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