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BICYCLO(3,3,1) NONANE-2,9-DIONES

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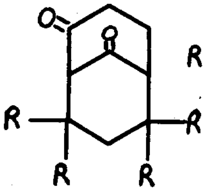
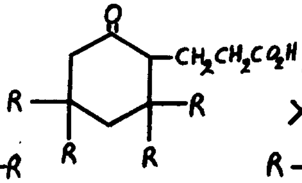
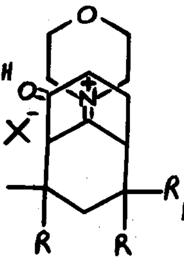
Reaction of acryloyl chloride with 4-cyclohex-1'-enylmorpholine in benzene has previously been shown[1] to give a benzene insoluble adduct which on mild hydrolysis yielded a compound tentatively assigned the bicyclo (3,3,1)nonane-2,9-dione structure (I, R = H), based on the well defined double peak in the carbonyl absorption region, characteristic of β - diketones[2]. This structure has now been confirmed as follows. The carbonyl stretching absorption showed similar solvent dependence (Table I) to that previously reported[3] for 1,5-dimethylbicyclo(3,3,1)nonane-2,9-dione and Jones oxidation[3] of the recently reported[4] 2-hydroxybicyclo(3,3,1) nonane-9-one gave a dione identical with ours in every respect.



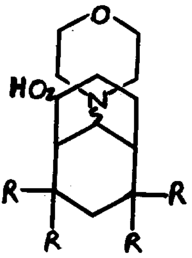
[I]



[II]



[III]



[IV]

Bicyclo(3,3,1)nonane-2,9-dione had previously been reported[5] to be formed by cyclisation of methyl β-2-oxocyclohexylpropionate, but the properties described, namely m.p. 141°, solubility in dilute sodium hydroxide solution and λ_{max} (MeOH) 254 mμ (logε 3.72), did not correspond to those of ours [m.p. 115-117°, decomposed by alkali to give β-2-oxocyclohexylpropionic acid (II, R = H), no $FeCl_3$ colouration, and λ_{max} (MeOH) 281 mμ (logε 1.84)] . The latter properties are also more in keeping with those expected from application of Bredt's rule to a bridged bicyclic diketone of this type.

TABLE I

Solvent dependence of carbonyl stretching absorptions

Solvent	Bicyclo(3,3,1)nonane -2,9-dione	1,5-Dimethylbicyclo (3,3,1)nonane-2,9-dione[a]
Acetonitrile	1725, 1701 cm^{-1}	1728, 1702 cm^{-1}
Chloroform	1728, 1702	1729, 1701
Carbon tetrachloride	1735, 1710	1737, 1707
n-Hexane	1740, 1712	1741, 1712

[a] Ref.3.

Evidence for the nature of the initially formed adduct (III, R = H, X = Cl) has also been obtained from the reaction of acryloyl chloride and the morpholine enamine of 3,3,5,5-tetramethylcyclohexanone. In this case the adduct (III, R = CH_3, X = Cl) was sufficiently stable to be isolated and recrystallised, as the less soluble iodide, from aqueous alcohol. (Found: C, 50.25; H, 7.0; N, 3.5; I, 31.3. $C_{17}H_{28}NO_2I$ requires: C, 50.4; H, 6.9;

N, 3.45; I, 31.3%). Analysis and spectroscopic data agreed with the proposed bicyclic structure III ($R = CH_3$, $X = I$), and sodium borohydride reduction gave IV, m.p. 124 - 126° (Found: C, 72.4; H. 11.0; N, 5.0. $C_{17}H_{31}NO_2$ requires: C, 72.6; H, 11.0, N, 5.0%). Hydrolysis of the adduct gave a mixture of 4,4,6,6-tetramethyl-β-2-oxocyclohexylpropionic acid (II, $R = CH_3$), m.p. 112 - 114°, and 6,6,8,8-tetramethylbicyclo(3,3,1)-nonane-2,9-dione (I, $R = CH_3$), m.p. 78° [Found: C, 74.8; H, 9.7. $C_{13}H_{20}O_2$ requires: C, 75.0; H, 9.6%; ν_{max} 1727, 1705 cm^{-1} in CCl_4, λ_{max} (MeOH) 285 mμ (log ε 2.04)], separated by chromatography on alumina.

Since there is a tendency for some substituted cyclohexanones, and 1,4-cyclohexadiones in particular, to exist in a nonchair conformation[6], it was of interest to see whether one of the chair-boat conformations of 6,6,8,8-tetramethylbicyclo(3,3,1)nonane-2,9-dione, in which the 3,7-transannular hydrogen interactions have been minimised without the creation of 3,9- or 7,9- "bowsprit" interactions, was favoured over the generally accepted twin-chair conformation. The n.m.r. spectrum of 6,6,8,8-tetramethylbicyclo(3,3,1)nonane-2,9-dione showed the methyl groups as three singlets in carbon tetrachloride, deuterochloroform and pyridine, and as four singlets in benzene. The solvent dependence is recorded in Table II.

TABLE II

Solvent dependence of the methyl resonances in 6,6,8,8-tetramethylbicyclo(3,3,1)nonane-2,9-dione

Solvent	Chemical Shift (in c/s from T.M.S.)[a]			
Carbon tetrachloride	115	113*	93	
Pyridine	104*	95	88	
Deuterochloroform	117	115*	96	
Benzene	89	88	73	60

a Measured at 100 Mc. * Corresponds on integration to two methyl groups.

Recent work[7] has illustrated the value of such solvent shifts in structure elucidation. Specific assignments of the methyl resonances have not been made, but there is no doubt that the resonances of all four methyl groups are shifted to lower field in changing from benzene to deuterochloroform solvent. This indicates that all four methyl groups lie behind the carbonyl groups and rules out the possibility of a boat conformation for the dione ring (Dreiding Models). Consideration of the chemical shifts in pyridine relative to carbon tetrachloride indicates that there is a strong possibility (3:1) that one methyl resonance has been shifted to higher field in carbon tetrachloride, indicating that at least one methyl group lies in front of one of the planes, through the α-carbon atoms, perpendicular to the plane of the carbonyl group. The twin-chair conformation must therefore be preferred to the other boat-chair conformation (in which the cyclohexanone ring has a boat conformation), since all the methyl groups lie well behind both these planes in the latter

(Dreiding Models) and would therefore be expected to be shifted to lower field. In confirmation it may be noted that high frequencv bands at 2995 cm^{-1} and 1476 cm^{-1} were observed in the infrared spectrum of this compound, characteristic of compounds which exist in a distorted twin-chair conformation[3].

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