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THE VALENCE ISOMERISATION OF HOMOCUBANE DERIVATIVES

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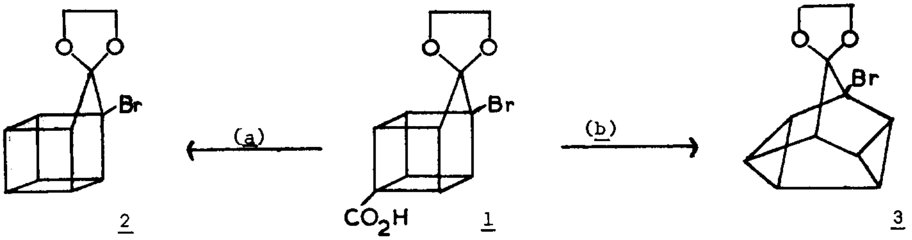
In several recent reports catalysis by transition-metal compounds of symmetry-forbidden isomerisations is described.[1] The isomerisation of cubane derivatives to syn-tricyclo-octadienes has been achieved by using rhodium(I) compounds and Cassar, Eaton, and Halpern[1c] have provided evidence that the isomerisations of cubane which they report, and possibly other symmetry-forbidden isomerisations,[1d] may proceed by a non-concerted mechanism. By using silver(I) compounds as catalysts a totally different type of isomerisation has been achieved for cubane derivatives,[1c] for homocubane,[1b] and for 1,1'-bishomocubane derivatives,[1a,1b] but Dauben et al.[1a] report that a 1,1'-bishomocubane derivative failed to isomerise with mineral acid, mercuric, cuprous, zinc, iron or rhodium compounds as catalysts, and no catalyst apart from silver compounds has been found.

We now report that the serendipitious reaction involving copper-bronze which we have discovered for a homocubane derivative is an example of an analogous rearrangement to those recently reported[1a,1b] for silver(I) compounds.

We were devising alternative methods of preparing homocubane and cubane derivatives[2,3] in order to study the chemical and physical properties of caged polycyclic systems. Eaton and Cole[4] had described the preparation of 1-bromopentacyclo(4.3.0.0^{2,5}.0^{3,8}.0^{4,7})nonan-9-one ethylene ketal, 2, from the ethylene ketal of 1-bromopentacyclo(4.3.0.0^{2,5}.0^{3,8}.0^{4,7})nonan-9-one-4-carboxylic acid, 1, by the formation of the t-butyl perester of 1 and its subsequent decomposition in boiling cumene — a reaction sequence which we have followed successfully. However, we tried the more direct preparation of 2 by decarboxylation of 1 with copper-bronze in refluxing quinoline for 2 h. The product from this reaction is 1-bromopentacyclo(4.3.0.0^{2,4}.0^{3,8}.0^{5,7})nonan-9-one ethylene ketal, 3, m.p. 108-109° (pentane); yield 79%; ir (KCl) 3068, 2994, 2912, 2880, no absorption 2800-1480 cm^{-1}; nmr ($CDCl_3$) τ 5.58-6.15 (sym.m., 4H), 7.51-8.17



($\underline{a}$) ... (i) $SOCl_2$, (ii) $(CH_3)_3COOH$, pyridine, (iii) cumene, 152°.

($\underline{b}$) ... Copper-bronze, refluxing quinoline

(complex, 7H); M^+ 254; satisfactory analysis for $C_{11}H_{11}BrO_2$.

The structure of the compound obtained by the thermal decomposition of the t-butyl perester of $\underline{1}$ is confirmed as $\underline{2}$ by its nmr spectrum [($CDCl_3$) τ 5.67-6.11 (sym.m., 4H), 6.44-6.87 (complex, 6H), 7.10-7.27 (m., 1H)] which shows the characteristic resonance of one cage-proton at higher field than those for the main group,[3,4] and the AA'BB' symmetry of the ethylene ketal absorptions (plane of symmetry through $C_1C_4C_5C_8C_9$). The nmr spectrum of the product from the copper-bronze-quinoline decarboxylation of $\underline{1}$ does not show the typical absorptions for homocubane compounds but still has the AA'BB' symmetry of the absorptions for the ethylene ketal protons. This is consistent with structure $\underline{3}$ (plane of symmetry through $C_1C_8C_9$; see the nmr spectra for the parent hydrocarbon and derivatives[5]). The ir spectrum (3068 cm^{-1}) confirms the presence of cyclopropane hydrogen atoms.[5]

We have also studied the isomerisation of 1-bromo-4-(methoxymethyl)pentacyclo(4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$)nonan-9-one ethylene ketal, $\underline{4}$,[6] under conditions similar to those used in copper-bronze-quinoline decarboxylations. Compound $\underline{4}$ is thermally stable and was unchanged on being heated in quinoline at 260° for 2.5 h. With copper-bronze-quinoline or with p-toluic acid-quinoline under these conditions a negligible amount of product is formed, but with copper-bronze-p-toluic acid-quinoline, compound $\underline{4}$ is completely converted into 1-bromo-4-(methoxymethyl)pentacyclo(4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$)nonan-9-one ethylene ketal, $\underline{5}$; m.p. 44-46° (light petroleum, b.p. 60-80°); yield 90%; ir (KCl) 3055, 2985, 2924, 2892, no absorption 2800-1480 cm^{-1}; nmr ($CDCl_3$) τ 5.60-6.15 (sym.* m., 4H), 6.31 and 6.54 (two AB doublets, 2H, J_{AB} = 10.8 Hz), 6.63 (s., 3H), 7.48-8.10 (complex, 6H);

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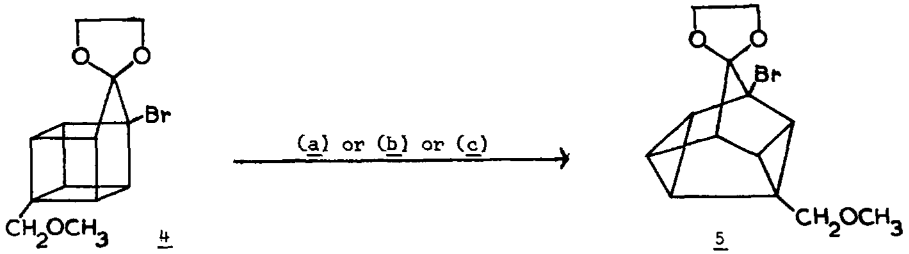
[*] Although the molecule does not contain a plane of symmetry, the methoxymethyl group is so remote from the ethylene ketal protons that they behave effectively as an AA'BB' system.



4

5

(a) ... Copper-bronze, p-toluic acid, quinoline.

(b) ... Copper-bronze, p-toluic acid, trigol.

(c) ... Silver nitrate, aqueous methanol.

satisfactory analysis for $C_{13}H_{15}O_3Br$. The nmr spectrum[6] of 4 shows a singlet absorption for the methylene protons of the methoxymethyl group because the two protons are enantiotopic (plane of symmetry through $C_1C_4C_5C_8C_9$). In compound 5 the methylene protons of the methoxymethyl group are now diastereotopic and so give rise to an AB quartet.

We have also prepared compound 5 by heating 4 in aqueous methanol with silver nitrate at 70° for 9 days,[1a] and by heating 4 in trigol with copper-bronze and p-toluic acid for 16 h at 120°.

Thus we have found that the type of isomerisation achieved previously by using silver(I) compounds can be brought about by systems containing copper and that even when homocubane carries substituents with lone pairs of electrons (ether, ketal, bromo groups) it is still capable of interacting with a metal derivative (silver, copper) to produce the observed catalytic behaviour.

This study of metal and metal-ion catalysis of reactions of strained polycyclic compounds is continuing.

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6. Preparation to be reported later.