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SMALL RING COMPOUNDS—XVII

THE METHANOLYSIS OF *TRANS*-α,α,α′,α′-TETRAMETHYL-1,2-CYCLOPROPANEDIMETHANOL

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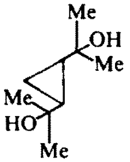
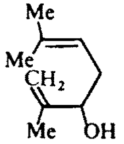
Abstract—The methanolyses of *trans*-α,α,α′,α′-tetramethyl-1,2-cyclopropanedimethanol and *trans*-2-isopropenyl-α,α-dimethylcyclopropanemethanol, using *p*-toluenesulphonic acid as catalyst, yielded methyl ethers and a ring-opened unsaturated ether. The reaction routes are discussed on the basis of the structures of the products and the results of VPC analysis.

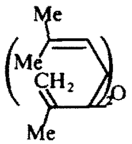
IN THE previous paper,[1] we reported that the dehydration of *trans*-α,α,α′,α′-tetramethyl-1,2-cyclopropanedimethanol (I) catalysed by potassium bisulphate gave the unexpected products, II, III and IV.



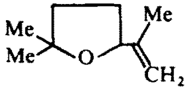
I



II

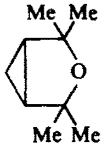


III

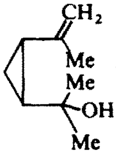


IV

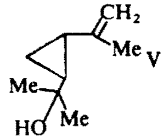
Furthermore, the dehydration of I in dioxan using *p*-toluenesulphonic acid as catalyst has shown that six products II, IV, V, VI, VII and VIII are formed according to the reaction routes shown below.[2] (Scheme 1.)



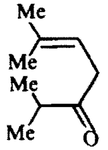
V



VI

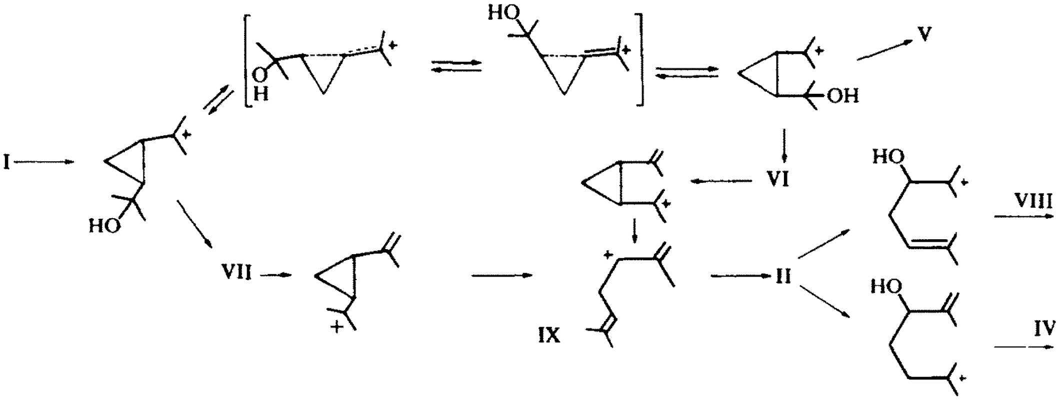


VII

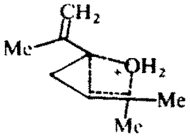


VIII

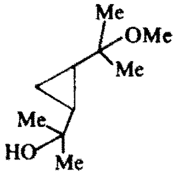
SCHEME 1



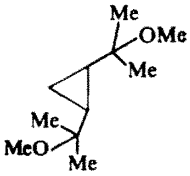
Scheme 1 indicates the formation of a carbonium ion stabilized by a cyclopropylcarbinyl-type delocalization of the positive charge. Thus, the possible formation of the cyclopropylcarbinyl cation in a proton donating solvent such as methanol was considered. Furthermore, the intramolecular migration of the OH group (X) is another possible route to form II from VII in dioxan* and this route may be examined by carrying out the solvolysis of VII in methanol. If the reaction is not intramolecular, XI may be produced instead of II.



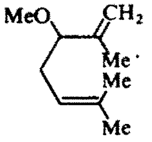
Thus, in the present study, the methanolysis of I was investigated to learn the detailed reaction routes in a proton donating solvent. The reaction was carried out at room temperature using 10 mole % of *p*-toluenesulphonic acid as catalyst and was followed by VPC analysis which indicated three peaks. The compound corresponding to each peak was isolated and identified on the basis of elemental and spectroscopic analyses. (XI, XII and XIII). The observed NMR data of XI (τ 8·84, 6H, two Me; 8·35, 3H, Me; 7·78, multiple triplet, 2H, —CH_2—; 6·92, 3H, OMe; 6·65, triplet, 1H, $-\mathrm{O}\overset{|}{\mathrm{C}}\mathrm{H}-$; 5·22, doublet, 2H, =$CH_2$; 5·03, triplet, 1H, —CH=) would be consistent with the proposed structure.



XII



XIII

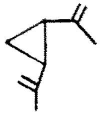


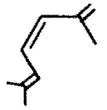
XI

The relative intensity of each vapour phase chromatographic peak was varied with the reaction time as shown in Fig. 1.

* The hypothesis of the intramolecular migration of OH group (X) is based on the following evidences.

1. The complete absence of (A) and (B) in the products.
2. The exclusive formation of II from VII in relatively high conversion under the reaction condition where the concentration of water is very low.


(A)


(B)

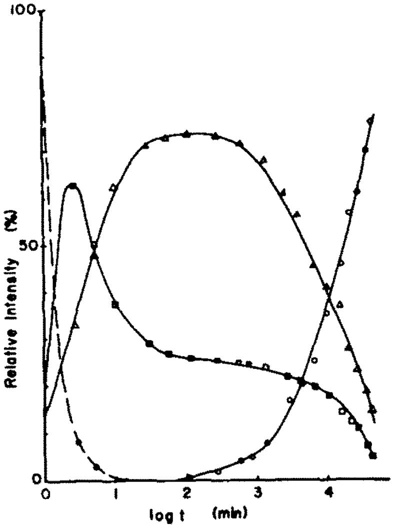


FIG. 1 Plot of relative intensity of each product vs. reaction time. (Starting from compound I.)

Compound I --●--●--
Compound XI ——○——○——
Compound XII ——□——□——
Compound XIII ----△——△——

Fig. 1 suggests that XII is the first product and the precursor of XI is not XII but XIII. Furthermore, similar reactions using XII or XIII as the starting compound were carried out to confirm the reaction routes. The results are shown in Figs. 2 and 3. The structure of XIV was confirmed by independent synthesis.

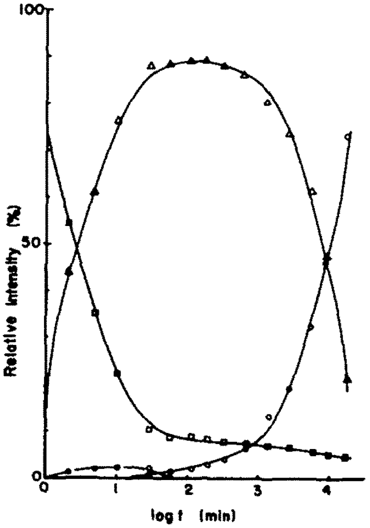


FIG. 2 Plot of relative intensity of each product vs. reaction time. (Starting from compound XII.)

Compound XI ——○——○——
Compound XII ——□——□——
Compound XIII ——△——△——
Compound XIV------○---○------

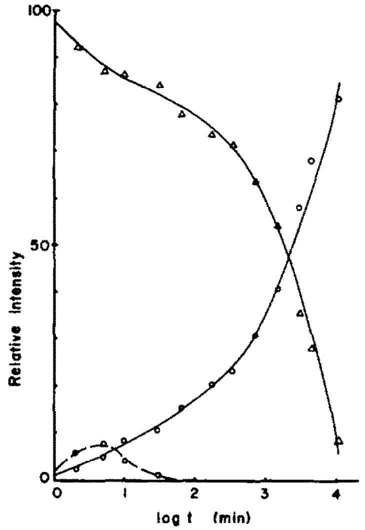
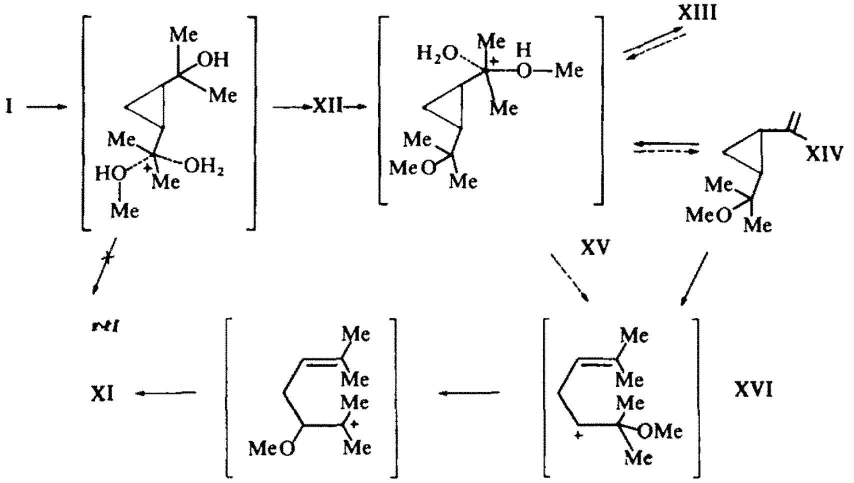


FIG. 3 Plot of relative intensity of each product vs. reaction time. (Starting from compound XIII.)

Compound XI —○—○— Compound XIII —△—△—
Compound XIV ------○---○------

The structures of the products and the facts shown in Figs. 1, 2 and 3 suggest the following reaction routes. (Scheme 2.) (The dotted arrow indicates slow reaction.)

SCHEME 2



When the *cis* isomer of I was treated in a similar way, only V was formed. This could be explained by supposing that the carbonium ion arising from the *cis* isomer of I interacts immediately with the intramolecular OH group at the time the ion is formed. The interaction between methanol and the carbonium ion formed from I may be similar to the above mentioned intramolecular interaction. The absence of VII, the first product of the dehydration of I in dioxan, and the exclusive formation of XIII from XII support this assumption. Thus, the formation of XII and XIII would be an SN_2-like reaction. Figs. 2 and 3 clearly indicate that XI comes from XIII. Hence, we could imagine an equilibrium between XIII and XV, and the rate of formation of XVI from XV may be much slower than that of XIII from XV. A cationic cleavage of an alkyl ether under such a mild condition would be somewhat unusual and this may indicate an olefinic character of the cyclopropane.

Next, the methanolysis of VII was studied to learn the possibility of the above-mentioned intramolecular migration of the OH group. The products isolated were XI, XII, XIII and XIV. The reaction was followed by VPC analysis and the result is shown in Fig. 4.

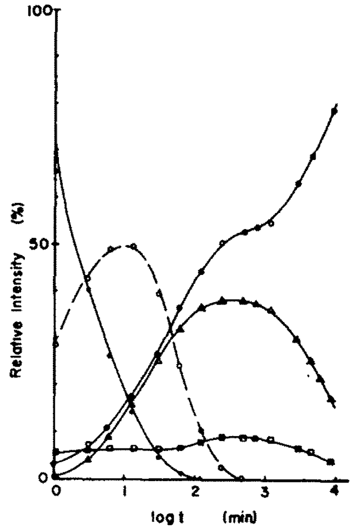
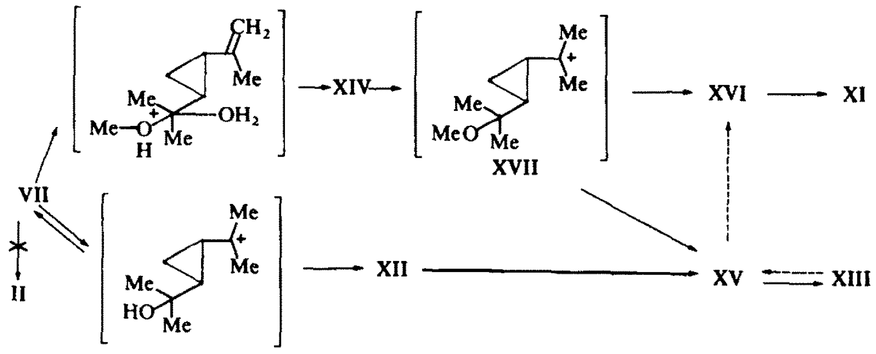


FIG. 4 Plot of relative intensity of each product vs. reaction time. (Starting from compound VII.)

Compound VII ——●——●——
Compound XII ——□——□——
Compound XIV ------○---○-----
Compound XI ——○——○——
Compound XIII ——△——△——

Fig. 4 and the reaction products would suggest the following reaction routes. (Scheme 3.)

The formation of XI and the absence of II suggests that the formation of II in dioxan is not intramolecular. It is, however, clearly shown in Fig. 4 that XI does not



derive from IX, the precursor of II, as the intensity of VII decreases rapidly while that of XI is slowly increasing. Thus, the absence of II in the products does not preclude the intramolecular migration of the OH group. The competitive formation of XI and XIII from XIV as shown in Fig. 4, implies that the carbonium ion XVII, formed from the olefin XIV by protonation, is a free ion in contrast with XV.

Consequently, it may be concluded that the reaction of I or VII in methanol differs considerably from the same reaction in dioxan.

EXPERIMENTAL

trans-*α,α,α′,α′-Tetramethyl*-1,2-*cyclopropanedimethanol* (I). To an ethereal soln of the Grignard reagent prepared from 426 g (3·0 mole) MeI and 28 g (3·0 mole) Mg, 79 g (0·5 mole) dimethyl *trans*-1,2-cyclopropanedicarboxylate was added dropwise to maintain a gentle boiling of the ether. After addition was complete, the reaction mixture was refluxed for an additional hr and then allowed to stand at room temp overnight. The mixture was worked up by usual method and I, m.p. 67·5–70° (recrystallized from ligroin–ether), was obtained as crystal after evaporation of the ether, the yield being 60 g, 76·8%. (Found: C, 68·33; H, 11·28. $C_9H_{18}O_2$ requires: C, 68·31; H, 11·47%.)

trans-2-*Isopropenyl-α,α-dimethylcyclopropylcarbinyl methyl ether* (XIV). During stirring, a soln of 3·5 g (0·025 mole) *trans*-2-isopropenyl-α,α-dimethylcyclopropanemethanol[1] in 10 ml 1,2-dimethoxyethane was added dropwise (40 min) to a suspension of 1·36 g (0·03 mole) NaH, washed with 1,2-dimethoxyethane prior to use, in 50 ml dry 1,2-dimethoxyethane. A soln of 4·3 g (0·03 mole) MeI in 10 ml 1,2-dimethoxyethane was added to the reaction mixture after it had been stirred for 3 hr at room temp. The resulting suspension was heated at 47° for 1 week in a pressure bottle and then filtered off. The filtrate was concentrated and distilled to give XIV, yield being 1·7 g (46·8%), b.p. 59°/10 mm; NMR data: 8·9–9·6 (multiplet, ring protons), 8·95 (doublet, $\mathrm{Me{-}\underset{OR}{\overset{|}{C}}{-}Me}$), 8·4 (doublet, $\mathrm{{=}\underset{|}{C}{-}Me}$), 6·9 (singlet, OMe), 5·45 (doublet, $=CH_2$). (Found: C, 78·16; H, 11·83. $C_{10}H_{18}O$ requires: C, 77·86; H, 11·76%.)

Isolation and identification of XI, XII *and* XIII. To a soln of 5·27 g (0·033 mole) of I in 12 ml MeOH, 0·573 g (0·003 mole) *p*-toluenesulphonic acid was added. After the soln had been stirred for 5 min, it was neutralized with $NaHCO_3$ aq. The resulting soln was extracted several times with ether. The ethereal soln was dried, evaporated and distilled to give a mixture of XII and XIII. Compounds XII and XIII were isolated by preparative VPC (column, PEG 6000) and redistilled. XII: b.p. 99°/21 mm, NMR data: τ 8·9–9·8 (multiplet, ring protons), 8·98 (doublet, $\mathrm{Me{-}\overset{OR}{\overset{|}{C}}{-}Me}$), 8·87 (singlet, $\mathrm{Me{-}\overset{OH}{\overset{|}{C}}{-}Me}$), 7·63 (singlet, OH), 6·9 (singlet, OMe). (Found: C, 70·01; H, 11·64. $C_{10}H_{20}O_2$ requires: C, 69·72; H, 11·70%.) XIII: b.p. 86°/23 mm, NMR data: τ 8·9–9·8 (multiplet, ring protons), 8·98 (doublet, $\mathrm{Me{-}\underset{|}{\overset{OR}{\overset{|}{C}}}{-}Me}$), 6·9 (singlet, OMe). (Found: C, 71·20; H, 11·93. $C_{11}H_{22}O_2$ requires: C, 70·92; H, 11·90%.)

A reaction mixture similar to that described above was neutralized after it had been allowed to stand for 9 days at room temp. The compound XI was obtained in a 16% yield by distilling the neutralized mixture; b.p. 81°/51 mm. (Found: C, 77·86; H, 11·88. $C_{10}H_{18}O$ requires: C, 78·19; H, 11·70%.)

Methanolysis of I *or* VII. The methanolysis of I or VII was carried out using *p*-toluenesulphonic acid as catalyst. The molar ratio of the catalyst to I or VII was 0·1. The reaction was followed by VPC analysis on a 2 m Polyethyleneglycol 6000 and Apiezon L columns at 140°. The results are shown in Figs. 1, 2, 3 and 4.

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[1] T. Shono, T. Yoshimura and R. Oda, *J. Chem. Soc. Japan* **87**, 1346 (1966).
[2] T. Shono, T. Yoshimura and R. Oda, *J. Org. Chem.* **32**, 1088 (1967).