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SMALL RING COMPOUND XIV
FORMOLYSIS OF (1,2-EPOXY-1-CYCLOPROPYLETHYL)-BENZENE

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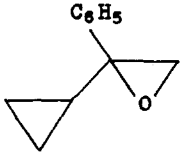
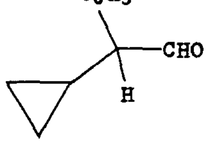
The unusual stability of the cyclopropylcarbonium ion has been studied in many recent works.(1) The acid catalyzed ring opening of unsymmetrically substituted epoxides in ionizing media has been thought to have an SN-1-like transition state,(2) thus the formolysis of (1,2-epoxy-1-cyclopropylethyl)-benzene(I), synthesized from cyclopropyl phenyl ketone using the Franzen method(3) (yield 78%, bp 70° at 2mm), was studied with the expectation that the transition state would involve a cyclopropylcarbonium ion.

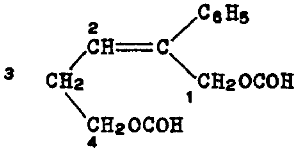
The solvolysis (60°, 3hr.) gave the following four major products, II (bp 61° at 4mm, 2,4-dinitrophenylhydrazone, mp 137°. Calcd. for $C_{17}H_{16}N_4O_4$: C,59.99; H,4.76; N,16.46%. Found: C,59.83; H,4.84; N,16.34%), III$_a$ (bp 141° at 3mm. Calcd. for $C_{13}H_{14}O_4$: C,66.65; H,6.02%. Found: C,66.37; H,6.15%. Infrared spectrum, $-CH{=}\overset{|}{C}-$, 1645, 860; formate 1710, 1170 cm^{-1}), III$_b$ (bp 138° at 3mm. Calcd. for $C_{13}H_{14}O_4$: C,66.65; H,6.02%. Found: C,66.78; H,6.27%. Infrared spectrum, $-CH{=}\overset{|}{C}-$ 1645, 850; formate 1720, 1160 cm^{-1}) and IV (mp 165°. Calcd. for $C_{11}H_{14}O$: C,82.46; H,7.55%. Found: C,82.72; H,7.66%).



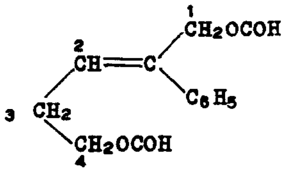
I



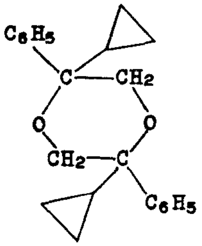
II



III$_a$



III$_b$



IV

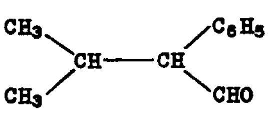
These products were stable under the reaction condition employed and their structures were supported by their nmr spectra: II (ring protons τ 8.63-9.73 multiplet, benzylic 7.4 quartet, phenyl 2.95 singlet, formyl 0.63 doublet); III$_a$$^{(4)}$ (C_1 protons 5.13 s., C_2 4.25 triplet, C_3 7.5 m., C_4 5.95 t., phenyl 2.95 m., formyl 2.3 s.); III$_b$ (C_1 5.35 s., C_2 4.4 t., C_3 7.75 m., C_4 6.05 t., phenyl 2.95 m., formyl 2.3 s.); IV (ring protons 9.4-9.9 m., phenyl 2.5-2.9 m., methylene 5.75-6.6 m.).

The distribution of these products was analyzed by vapour phase chromatograph (Column, Silicon DC 550) and depended heavily on the nature of the solvent. (TABLE 1)

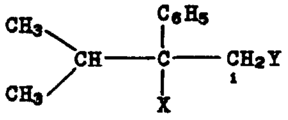
TABLE 1

Solvents	Product Distribution(%)				Total Yields (%)
	II	III$_a$	III$_b$	IV	
HCO_2H	10.3	44.0	38.5	7.2	64.0
HCO_2H + HCO_2Na(10:1.5)	36.0	35.0	28.2	0.8	71.6
HCO_2H + C_5H_5N(10:1)	51.5	26.3	21.5	0.7	80.0

The formolysis of (1,2-epoxy-1-isopropylethyl)-benzene(V), prepared by the same method as I (yield 86%, bp 111° at 25mm), was also studied for the purpose of learning the difference between the cyclopropyl and the isopropyl groups. VI (bp 58° at 3mm, 2,4-dinitrophenylhydrazone, mp 142°. Calcd. for $C_{17}H_{18}N_4O_4$: C,59.64; H,5.30; N,16.37%. Found: C,59.35; H,5.53; N,16.12%) and VII (bp 93° at 3mm, Calcd. for $C_{12}H_{16}O_2$: C,69.21; H,7.74%. Found: C,69.72; H, 8.02%) were the solvolysis products obtained, and they were stable under the reaction condition used. The observed chemical shift of C_1 methylene protons, τ 5.55 is consistent with the structure VII_b(5).



VI



VII_a: X=OCOH Y=OH

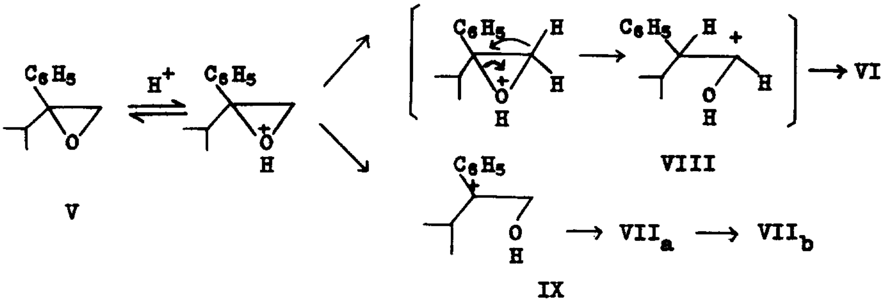
VII_b: X=OH Y=OCOH

TABLE 2

Solvents	Product Distribution(%)		Total Yields (%)
	VI	VII_b	
HCO_2H	99.4	0.6	94.8
HCO_2H + HCO_2Na(10:1.5)	63.3	36.7	70.1
HCO_2H + C_5H_5N(10:1)	47.2	52.8	65.2

The product distribution indicated in TABLE 2 implies that VII_b was formed through an SN-1-like transition state as shown in SCHEME 1.

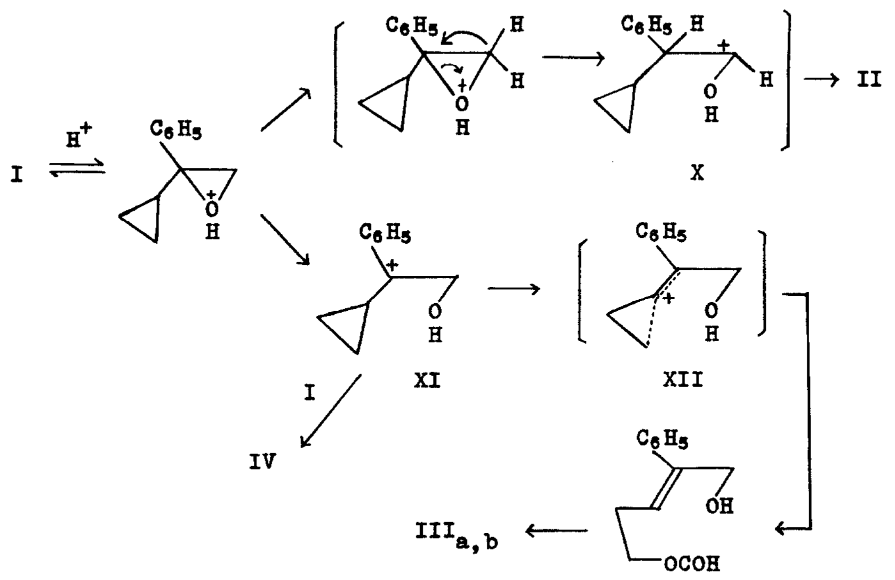
SCHEME 1



The rearrangement of VII_a to VII_b is generally supposed to be possible under such reaction conditions.(6)

The results given in TABLE 1 might suggest that an SN-2-like reaction route permits rationalization of the solvent effect on the formation of III. However, it is most unlikely that the formolysis of I possesses an SN-2-like transition state, in view of the SN-1-like character of solvolysis of V. This change in product distribution with ionizing power of solvent can be explained by assuming that the order of relative stability of the carbonium ion is $IX < VIII \cong X < XI$. Consequently, the increase in solvent polarity may be favorable to the formation of II or VII.

SCHEME 2



The remarkable stability of XI may be attributable to its homoallylic type of delocalization (XII). This reaction is the first example of a 1,6-addition reaction of (1,2-epoxyethyl)cyclopropanes. A more comprehensive study concerning the reaction mechanism is now proceeding and it will be reported shortly.

REFERENCES

1. For a summary of leading references see P.R.Schleyer and G.W.VanDine, J. Am. Chem. Soc., 88, 2321 (1966).
2. E.L.Eliel, in ''Steric Effect in Organic Chemistry'', M.S.Newman, ed., John Wiley and Sons, New York, N.Y., 1965, p.113.
3. V.Franzen and H.E.Driesen, Chem. Ber., 96, 1881 (1963).
4. The chemical shifts for C_1, C_2, C_3 and C_4 protons of III_a would be lower than those for the corresponding protons of III_b.
   M.S.Newman and G.Kaugers, J. Org. Chem., 31, 1379 (1966).
5. The chemical shift of C_1 methylene protons of VII_c(X=Y=OH) was τ 6.45.
6. T.Cohen, M.Dughi, V.A.Nontaro and G.Pinkus, J. Org. Chem., 27, 814 (1962).