

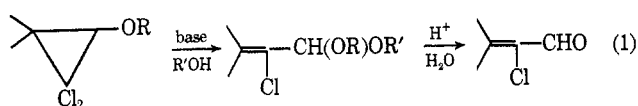
Chemistry of *gem*-Dihalocyclopropanes.
VII.¹ Ring Opening of
7,7-Dichloro-2-oxabicyclo[4.1.0]heptane.
The Synthesis of
2H-3,4-Dihydropyran-5-carboxaldehyde

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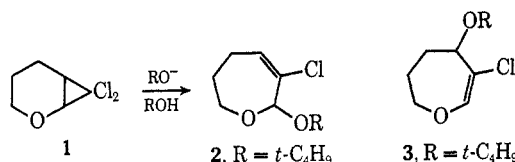
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The thermally induced ring opening of dihalocyclopropanes has been studied by several groups, but most extensively by Parham and coworkers.³ 1,1-Dihalocyclopropyl ethers are particularly prone to undergo ring opening; in the presence of alcohols, acetals are formed which can subsequently be hydrolyzed to aldehydes in high yields (eq 1).^{4,5} The main purpose of the



present note is to report reactions of 7,7-dichloro-2-oxabicyclo[4.1.0]heptane (1) under the above conditions.

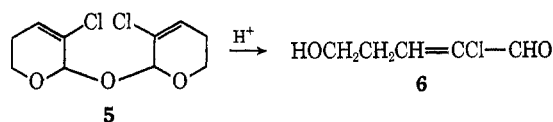
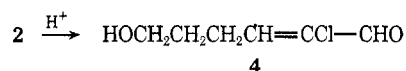
When 1 was heated under reflux with potassium *t*-butoxide in *t*-butyl alcohol a liquid product was obtained in 79% yield; the most reasonable structure would be 3-chloro-2-*t*-butoxy-2,5,6,7-tetrahydrooxepin (2), although the isomeric structure 3 could not *a priori*



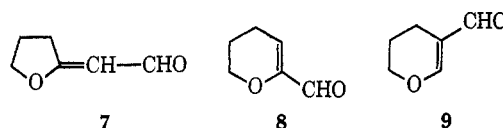
be excluded. The ir spectrum could not unequivocally distinguish between the two, but the nmr spectrum was quite conclusive. A singlet at δ 5.06 due to the tertiary proton could only be identified with structure 2 since, in the case of 3, it would be coupled with the neighboring methylene protons. Moreover, a weakly split triplet ($J < 1$ Hz) at δ 5.99 is only compatible with structure 2; the weak coupling is probably the result of an unfavorable dihedral angle between the olefinic and the methylene protons.⁶

Compound 2 formed a 2,4-dinitrophenylhydrazone derivative, mp 198° dec, which by elemental analysis and spectroscopic evidence was shown to derive from aldehyde 4. The latter would indeed be the expected hydrolysis product from 2 having close analogy in the literature; by acid hydrolysis of compound 5, Reese

and coworkers⁷ obtained the aldehyde 6, characterized as the 2,4-dinitrophenylhydrazone.



If, however, the acetal 2 was treated at room temperature with dilute aqueous acid a liquid product, C₈H₈O₂, was formed, the 2,4-DNP of which melted at 239° dec. The ir spectrum of the liquid showed strong bands at 1665 and 1625 cm⁻¹ and a medium intensity band at 2715 cm⁻¹, characteristic of an α,β -unsaturated aldehyde. This was confirmed by the uv absorption; in *n*-heptane a maximum appeared at 241.5 nm while in methanol it was shifted to 250 nm.⁸ Strong bands at 1245 and 1180 cm⁻¹ could be the C-O stretching vibrations of a vinyl ether.⁹ On the basis of this evidence three structures, 7, 8, and 9, appeared most likely. The



nmr spectrum showed a complex multiplet centered at δ 2.02 and a triplet at δ 4.20 due to the six ring protons, the latter representing the methylene group adjacent to oxygen. This is compatible with all of the above structures. The remaining protons appeared as singlets, the olefinic at δ 7.35 and the formyl at δ 9.18. The lack of coupling between these clearly rules out 7 as a possible structure. It proved more difficult, however, to distinguish between the dihydropyran structures 8 and 9, isomers of acrolein dimer. One would expect the olefinic proton in 8 to be coupled with the neighboring methylene protons, but because the magnitude is strongly dependent on the dihedral angle,⁶ it might only be very weak; in 2H-3,4-dihydropyran, however, the coupling is about 3 Hz. It is not expected that the formyl group of 8 should change the ring conformation significantly from that of dihydropyran and therefore the absence of coupling disfavors structure 8. Furthermore, the chemical shift of the olefinic resonance also is not compatible with this assignment, which becomes evident from the data of Table I. The deshielding effect of the formyl group on the β proton would be almost compensated by the shielding of the same proton by the ether oxygen; accordingly, the

TABLE I

Compd ^a	Chemical shift of olefinic hydrogen (δ ppm)	
	H α	H β
2H-3,4-Dihydropyran	6.37	4.65
Crotonaldehyde	6.13	6.87
9	7.35	
Cyclohexene	5.57	
<i>cis</i> -2-Butene	5.47	

^a Measured in CCl₄ as solvent.

(7) J. C. Anderson, D. G. Lindsay, and C. B. Reese, *Tetrahedron*, **20**, 2091 (1964).

(8) The large bathochromic shift caused by methanol is additional evidence for an α,β -unsaturated carbonyl structure: R. B. Woodward, *J. Amer. Chem. Soc.*, **68**, 1123 (1942); L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

(9) G. D. Meakins, *ibid.*, 4170 (1953).

(1) Part VI: L. Skattebøl, *Tetrahedron*, **23**, 1107 (1967).

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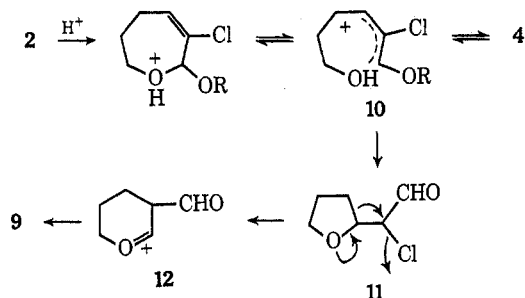
(3) For reviews, see W. E. Parham and E. E. Schweizer, *Org. React.*, **13**, 55 (1963); W. E. Parham, *Rec. Chem. Progr.*, **29**, 3 (1968). See also, S. R. Sandler, *J. Org. Chem.*, **32**, 3876 (1967), and references therein.

(4) L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1966).

(5) F. Nerdel, J. Buddrus, W. Brodowski, P. Hentschel, D. Klamann, and P. Weyerstahl, *Justus Liebig's Ann. Chem.*, **710**, 36 (1967).

(6) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

chemical shift of the olefinic proton in **8** should be shifted only slightly downfield as compared with cyclohexene; on the other hand a large (1.5–2.0 ppm) downfield shift would be expected for structure **9**, in agreement with observation. The following mechanistic scheme provides an explanation for the formation of **9**.



The protonation of **2** will result in the formation of the ring-opened allylic ion **10** which can either give the hydroxy aldehyde **4** or the tetrahydrofuran derivative **11**. The solvolysis of α -chloro aldehydes by an S_N1 mechanism would be expected to be quite slow; it is more reasonable to depict the reaction as an anchimerically assisted displacement of chloride ion on the aldehyde itself or on its hydrate. This would lead to the stabilized carbonium ion **12** and the observed product **9**. Cope and Graham¹⁰ and more recently Pasto¹¹ and coworkers have presented evidence for similar transformations in the solvolysis of α -halo ketones. One can think of other explanations for the formation of **9**, but it seems futile to elaborate further on this without more experimental results.

The reaction sequence represents a convenient route to the aldehyde **9**, particularly since the isolation of the intermediate oxepin derivative is not necessary.

Experimental Section¹²

3-Chloro-2-*t*-butoxy-2,5,6,7-tetrahydrooxepin (2).—To a solution of potassium *t*-butoxide from 8.6 g (0.22 g-atom) of potassium in 220 ml of *t*-butyl alcohol was added all at once 33.4 g (0.2 mol) of 7,7-dichloro-2-oxabicyclo[4.1.0]heptane.¹³ The mixture was heated under reflux for 24 hr; excess of *t*-butyl alcohol was distilled on a rotatory evaporator. The residue was added to water and the product extracted with ether. The extract was washed with water (containing some Na_2CO_3) and dried (Na_2CO_3 anhydrous). The ether was evaporated and the residue fractionated giving 32.2 g (79%) of **2**, bp 54–55° (0.5 mm), n_D^{20} 1.4670.

Anal. Calcd for $\text{C}_{10}\text{H}_{17}\text{ClO}_2$: C, 58.68; H, 8.37. Found: C, 58.62; H, 8.44.

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate, mp 198° dec. When heated further, the compound solidified and remelted at 222° dec, uv λ_{max} (ethanol) 372 nm (ϵ 18,800), 247 (10,000), 283 inf (5700).

Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{ClN}_4\text{O}_5$: C, 43.84; H, 3.99; N, 17.05. Found: C, 43.91; H, 4.03; N, 17.03.

2H-3,4-Dihydropyran-5-carboxaldehyde (9).—A mixture of the acetal **2** (51.1 g, 0.25 mol), 20 ml of dioxane, and 100 ml of 2 *N* HCl was shaken mechanically at room temperature overnight (~12 hr). A homogeneous yellow-colored solution was obtained from which the product was isolated by continuous extraction with ether. The dried (MgSO_4) extract was evaporated and the liquid residue distilled to give 25.9 g (92%) of the aldehyde **9**:

(10) A. C. Cope and E. S. Graham, *J. Amer. Chem. Soc.*, **73**, 4702 (1951).

(11) D. J. Pasto and M. P. Serve, *ibid.*, **87**, 1515 (1965); D. J. Pasto, K. Garves, and M. P. Serve, *J. Org. Chem.*, **32**, 774 (1967).

(12) Melting points and boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR 5 instrument. The nmr spectra were measured with a Varian A-60 instrument, using carbon tetrachloride as solvent and tetramethylsilane as internal standard.

(13) W. E. Parham, E. E. Schweizer, and S. A. Mierzwa, *Org. Syn.*, **41**, 76 (1961).

bp 68° (3 mm); n_D^{20} 1.5140; ν_{max} (liq) 2715, 1665 (–CHO), 1625 cm^{-1} (C=C); λ_{max} (heptane) 241.5 nm (ϵ 17,600), (methanol) 250 nm (ϵ 19,900).

Anal. Calcd for $\text{C}_6\text{H}_9\text{O}_2$: C, 64.27; H, 7.19. Found: C, 64.32; H, 7.40.

The 2,4-dinitrophenylhydrazone was recrystallized from chloroform, mp 239° dec, λ_{max} (ethanol) 391 nm (ϵ 17,100), 290 (6100), 258 (10,300).

Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_5$: C, 49.31; H, 4.14; N, 19.17. Found: C, 49.63; H, 4.17; N, 18.85.

Registry No.—**1**, 7556-13-0; **2**, 25090-31-7; **4** (2,4-dinitrophenylhydrazone), 15299-59-9; **9**, 25090-33-9; **9** (2,4-dinitrophenylhydrazone), 25111-11-9.

Pyrolysis of Heptafluorobutyric Anhydride

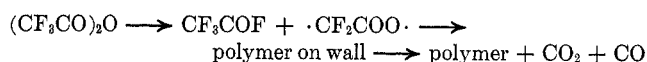
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Pyrolytic reactions of fluorocarbons containing functional groups have not been studied sufficiently that the mode of decomposition of a relatively simple compound such as heptafluorobutyric anhydride could be predicted. There is good precedent for radical decomposition followed by coupling. The pyrolyses of perfluoroacyl bromides¹ and perfluoroacyl hypobromites² give bromoperfluoroalkanes, the pyrolysis of trifluoroacetyl nitrite gives trifluoronitrosomethane,^{3,4} and the pyrolysis of pentafluoropropionic anhydride^{5a} and heptafluorobutyric anhydride^{5b} were reported to give perfluorobutane and perfluorohexane, respectively.

In contrast with these rather straightforward radical formation and coupling reactions, however, is the report that trifluoroacetic anhydride decomposes thermally to give trifluoroacetyl fluoride, carbon dioxide, and carbon monoxide.⁶ Mechanistically this was thought to involve first a dissociation to trifluoroacetyl fluoride and a difluoroacetoxy diradical.



At higher temperatures some tetrafluoroethylene was observed, probably from coupling of difluorocarbene arising from the diradical.

Related to this is the thermal decomposition of hexafluoroacetone⁷ which, at over 500°, produces trifluoroacetyl fluoride and difluorocarbene. At lower temperatures hexafluoroethane is formed, but mechanistic studies indicated that this reaction involved a first-order rearrangement rather than dissociation and coupling of radicals.

It has now been found that heptafluorobutyric anhydride decomposes by two pathways. The most prominent involves a fluoride transfer leading to hepta-

(1) J. D. Lazerte, W. H. Pearson, and E. A. Kauk, U. S. Patent 2,704,776 (May 22, 1955).

(2) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," Macmillan, New York, N. Y., 1962, pp 182–185.

(3) J. Banus, *J. Chem. Soc.*, 3755 (1953).

(4) R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. Creath, *ibid.*, 1350 (1966).

(5) (a) R. N. Haszeldine and K. Leedham, *ibid.*, 1548 (1953); (b) A. D. Kirshenbaum, A. G. Streng, and M. Hauptschein, *J. Amer. Chem. Soc.*, **75**, 3141 (1953).

(6) J. P. Corbett and E. Whittle, *J. Chem. Soc.*, 3247 (1963).

(7) W. Batey and A. B. Trentwith, *ibid.*, 1388 (1961).