

CYCLOPROPANONE DERIVATIVES FROM ALKOXYVINYL ESTERS.

THE PREPARATION OF 1-SUBSTITUTED CYCLOPROPANOLS.

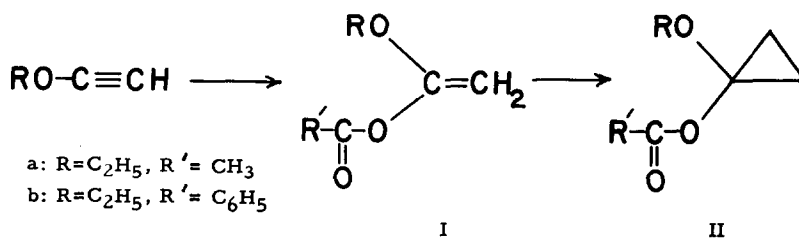
H. H. Wasserman and D. C. Clagett¹

Department of Chemistry, Yale University

New Haven, Connecticut

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In an earlier paper² we have described the preparation and some of the properties of 1-alkoxyvinyl esters (I) derivable from alkoxyacetylenes. We now report the conversion of esters of this type to the corresponding cyclopropanes (II), and some synthetically useful reactions of this system. In II, the carbonyl group provides a reactive site for nucleophilic attack not found in analogous cyclopropanone ketals.³ Such reactions

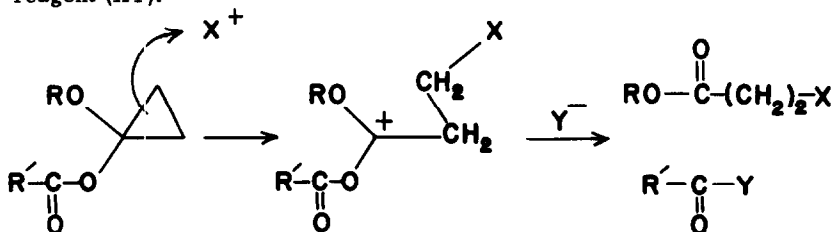


involving metal hydride or Grignard reagents show promise for the synthesis of cyclopropanols, as outlined below.

1-Ethoxycyclopropyl acetate (IIa) was prepared (35%) by the addition of 1-ethoxyvinyl acetate (Ia) and methylene iodide to zinc-copper couple in the presence of glyme.^{4,5} (Anal. Calcd. for C₇H₁₂O₃ :

C, 58.31; H, 8.39; mol. wt., 144. Found: C, 58.51; H, 8.42; mol. wt. (mass-spec.), 144. n_D^{23} 1.4160. $\nu_{\text{max}}^{\text{CCl}_4}$ 3101, 3016, 1758 cm^{-1} . The N. M. R. spectrum shows absorption at $\tau = 6.33$ (quartet, 2 protons), 8.04 (singlet, 3 protons), 8.86 (triplet, 3 protons), and 9.03 (multiplet, 4 protons).

IIa is a relatively stable liquid, b. p. 46-56°/4mm., which when pure may be stored at room temperature without decomposition. With acidic reagents, IIa undergoes ready ring opening yielding propionic acid with dilute aqueous HCl, and ethyl β -bromopropionate with aqueous bromine. These reactions, like those of the related 1,1-diethoxycyclopropane,³ appear to involve electrophilic attack on the cyclopropyl ring by the acidic reagent (XY):



Utilizing 1-ethoxyvinyl benzoate (Ib), reaction with methylene iodide under similar conditions yielded 1-ethoxycyclopropyl benzoate (IIb) (19%). (Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.88; H, 6.84. Found: C, 70.01; H, 7.05. n_D^{24} 1.5052. $\nu_{\text{max}}^{\text{CCl}_4}$ 1740 cm^{-1} . The N. M. R. spectrum has peaks at $\tau = 2.81$ (multiplet, 5 protons), 6.24 (quartet, 2 protons), 8.86 (triplet, 3 protons), 8.92 (singlet, 4 protons). IIb undergoes the same ring-opening reactions as IIa with aqueous HCl and aqueous bromine. Likewise, both IIa and IIb react with dilute alkali to form

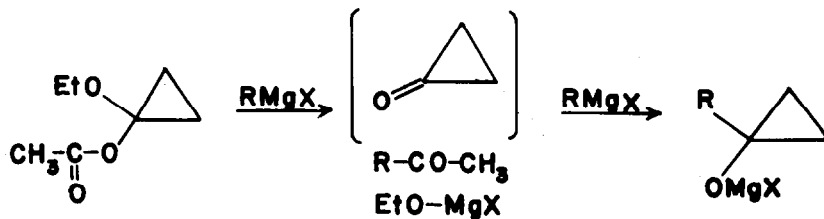
propionic acid and acetic or benzoic acid.

Treatment of IIa with excess lithium aluminum hydride in ethyl ether solution yielded cyclopropanol⁶ (48%). (Anal. Calcd. for C₃H₆O: C, 62.04; H, 10.41; mol. wt., 58. Found: C, 62.23; H, 10.29. mol. wt. (mass-spec.), 58. The N. M. R. spectrum shows absorption at $\tau = 6.30$ (singlet, 1 proton), 6.62 (sym. multiplet, 1 proton), 9.52 (multiplet, 4 protons).

With excess methylmagnesium iodide, IIa was converted to 1-methylcyclopropanol (46%). (Anal. Calcd. for C₄H₈O: C, 66.63; H, 11.18 mol. wt., 72. Found: C, 66.42; H, 11.06. mol. wt. (mass-spec.), 72. The N. M. R. spectrum shows absorption at $\tau = 5.37$ (singlet, 1 proton), 8.63 (singlet, 3 protons), 9.50 (A₂B₂ multiplet 4 protons).

Reaction of IIa and phenylmagnesium bromide produced 1-phenylcyclopropanol (64%), a clear hygroscopic oil. (Anal. Calcd. for C₉H₁₀O: C, 80.56; H, 7.51; mol. wt., 134. Found: C, 80.68; H, 7.37; mol. wt. (mass-spec.), 134. $n_D^{22.5}$ 1.5591. The N. M. R. spectrum has peaks at $\tau = 2.88$ (singlet, 5 protons), 6.23 (singlet, 1 proton), 9.04 (A₂B₂ multiplet, 4 protons).

We are investigating the possibility that formation of the above cyclopropanols⁷ takes place by the route shown below in which cyclopropanone is produced as a transient reaction intermediate.



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4. H. E. Simmons and R. D. Smith, J. Amer. Chem. Soc. 81, 4256 (1959). Glyme in amount equimolar to the methylene iodide was added to precipitate zinc iodide formed in the reaction (personal communication from Dr. Simmons).
5. We wish to acknowledge preliminary investigations on the synthesis of II by Drs. P. Forgione and D. Cohen.
6. We thank Prof. C. DePuy for comparison infrared and nuclear magnetic resonance spectra of cyclopropanol.
7. For recent reports on the synthesis and reactions of cyclopropanol and derivatives see: C. H. DePuy, G. M. Dappen, and J. W. Hausser, J. Amer. Chem. Soc. 83, 3156 (1961); C. H. DePuy, L. R. Mahoney, and K. L. Eilers, J. Org. Chem. 26, 3616 (1961); C. H. DePuy, R. A. Klein, and G. M. Dappen, J. Org. Chem. 27, 3742 (1962); C. H. DePuy and F. W. Breithel, J. Amer. Chem. Soc. 85, 2176 (1963).