Other vinyl ethers and aqueous iodine. Dihydropyran (0.0063 mole) was added to sodium acetate–acetic acid buffered water solution, excess standard iodine added and the excess back titrated; iodine consumed, 0.0039 mole for an ether/iodine ratio of 0.62. The ratio was raised to 0.73 in a similar experiment by the addition of 3 drops of pyridine as a polymerization inhibitor. It was raised still further to 0.91 by employing 80 ml. of methanol as the solvent. Divinyl ether (0.0109 mole), when titrated without buffer, required 0.0091 mole of iodine for a ratio of 0.83. On standing, the iodine color was regenerated. In a similar experiment buffered to *p*H 7 with phosphate, iodine was not regenerated. Vinyl ethyl ether, vinyl butyl ether, and dioxadiene gave iodine/ether ratios of 0.478, 0.381, and 1.58, respectively. In the latter case, even though enough methanol to ensure solution was used, an ether-insoluble solid was formed, direct evidence of extensive polymerization.

Peroxide test. A laboratory sample of ordinary dioxane from a bottle that had been in use several weeks gave a distinct yellow color when a few drops were added to an acidified aqueous solution of potassium iodide. Few samples of dioxane that have been exposed to the air and have not been specifically purified fail to give this test. When 3 drops of vinyl butyl ether was added to 1 ml. of the same dioxane, no test for peroxides could be obtained with water solutions if the volume of the water were equal to that of the dioxane. However, if only a few drops of aqueous potassium iodide and a drop of hydrochloric acid were added to a similar mixture of vinyl ether and the same dioxane, a strong test was obtained. Using mixtures of vinyl ethers and an ether known to contain peroxides, a positive test was always obtained in a 3:1 dioxane-water solution. The dioxane used as solvent was, of course, peroxide-free.[12] A negative test was always obtained when the same ether-peroxide–vinyl ether mixtures were subjected to the usual aqueous iodide test where water was present in large proportion.

An alternative test for the presence of peroxides in ether,[2b] the appearance of a pink or red coloration in the ether on shaking with ferrous thiocyanate solution, did not work in the presence of vinyl ethers, even though the samples under examination were known to contain large amounts of peroxides. In another experiment, a bright pink color was obtained by using a sample of typical sideshelf ethyl ether. When *n*-butyl vinyl ether was added to this test solution, the color gradually faded. The formation of black mercurous oxide on[13] shaking with a globule of metallic mercury was prevented by the presence of small percentages of vinyl ether in samples of ether that would otherwise give the test.

Acknowledgment. We wish to thank the E. I. du Pont Co. and the Research Corp. for research assistantships held by D.K.A.H.

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[12] K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938); R. N. Feinstein, *J. Org. Chem.*, **24**, 1172 (1959).

[13] C. R. Noller, *Chemistry of Organic Compounds*, W. B. Saunders Co., Philadelphia, 1951, page 139.

Attempted Thermal Rearrangement of Cyclopropylcarbinyl Phenyl Ether

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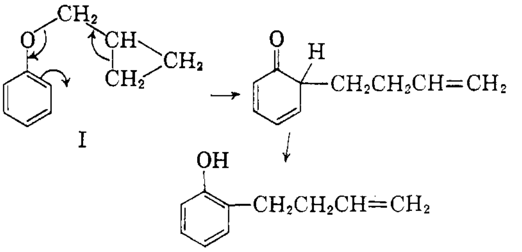
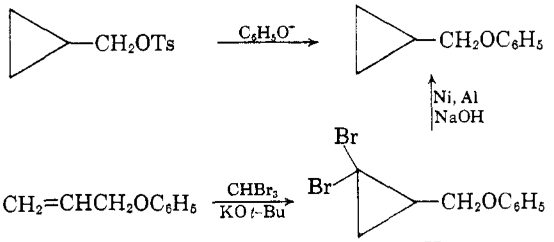
The cyclic nature of the transition state and the intermediacy of dienones in the Claisen rearrangement has been thoroughly established.[1] The cyclopropyl group sometimes displays chemistry similar to that of a carbon-carbon double bond.[2] It seemed possible, therefore, that the cyclopropylcarbinyl group might replace the allyl group in the Claisen rearrangement. A plausible mechanism can be envisioned and is depicted (1) for the thermal rearrangement of cyclopropylcarbinyl phenyl ether (I)



(1)

Compound I was synthesized by two independent methods: displacement by phenoxide ion on cyclopropylcarbinyl tosylate, and reduction of



II

2,2-dibromocyclopropylcarbinyl phenyl ether (II), the latter being prepared by the carbene reaction[3] on allyl phenyl ether.

When Compound I was refluxed (214°) for eighteen hours, or heated in a sealed tube at 300° for ten hours, it was recovered unchanged (identical infrared spectrum, negative ferric chloride test).[4] It is apparent, then, that the cyclopropylcarbinyl group does not behave like an allyl group in the Claisen rearrangement, at the ordinary tempera-

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[1] For a review, see D. J. Cram in M. S. Newman, *Steric Effects in Organic Chemistry*, John Wiley & Sons, Inc., New York, N. Y., 1956, pp. 295–303. For subsequent work, see especially D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, **79**, 3156 (1957); F. Kalberer and H. Schmid, *Helv. Chim. Acta*, **40**, 13, 779 (1957); W. Haegele and H. Schmid, *Helv. Chim. Acta*, **41**, 657 (1958); P. Fahrni and H. Schmid, *Helv. Chim. Acta*, **42**, 1102 (1959); H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958); W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

[2] For reviews, see R. A. Raphael in E. H. Rodd *The Chemistry of Carbon Compounds*, Elsevier Publishing Co., Amsterdam, 1953, Vol. IIA, pp. 25–28; E. Vogel, *Fortschr. Chem. Forsch.*, **3**, 430 (1955); E. Vogel, *Angew. Chem.*, **72**, 4 (1960).

[3] W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[4] Compound I was readily attacked both by acid and by potassium metal; the products have not yet been identified.

tures at which the rearrangement is generally executed.[5]

EXPERIMENTAL[6]

2,2-Dibromocyclopropylcarbinyl phenyl ether (II). To a stirred suspension of anhydrous potassium *t*-butoxide (0.5 mole) in a solution of 165 g. (1.2 moles) of allyl phenyl ether and 100 ml. of pentane there was added, during 1 hr., 126.5 g. (0.5 mole) of bromoform. After 5 hr. at room temperature (200 ml. of pentane was added to facilitate stirring), hydrolysis, extraction with pentane, drying over magnesium sulfate and distillation gave 133 g. of recovered allyl phenyl ether and 41.2 g. of material, b.p. 119–126° at 1 mm. which solidified at room temperature. After several recrystallizations from ethanol, the product (31.5 g., 21%) melted at 53–54°.

Anal. Calcd. for $C_{10}H_{10}Br_2O$: C, 39.23; H, 3.27; Br, 52.32. Found: C, 39.21; H, 3.31; Br, 52.43.

Cyclopropylcarbinyl phenyl ether (I). *A. Reduction of* II. To a mixture of 100 ml. of 95% ethanol, 60 g. of Raney nickel-aluminum alloy, and 10 g. (0.033 mole) of II was added in 1 hr. 600 ml. of 10% sodium hydroxide.[7] After two additional hours of reflux the mixture was filtered and the nickel was washed successively with 100 ml. of 10% sodium hydroxide and with 400 ml. of pentane. The aqueous layers were poured into 400 ml. of concd. hydrochloric acid, then extracted with pentane. The combined pentane extracts gave 3.0 g. (62%) of cyclopropylcarbinyl phenyl ether (I), b.p. 51–53° at 2 mm., n_D^{25} 1.5199.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.17. Found: C, 81.11; H, 8.29.

B. Displacement on cyclopropylcarbinyl tosylate by phenoxide ion. Cyclopropylcarbinyl tosylate was prepared by a procedure analogous to that used by Bergstrom and Siegel[8] for the benzenesulfonate. *p*-Toluenesulfonyl chloride (19.0 g., 0.1 mole) and 50 ml. of methylene chloride was added, at −3 to +3° during 45 min. to a mixture of 26.4 ml. of 2,4,6-collidine and 7.2 g. (0.1 mole) of cyclopropylcarbinol. Additional methylene chloride (25 ml.) was added, the mixture was stirred at 0° for 2 hr., and the collidine then neutralized with 25 ml. of 10N sulfuric acid, the temperature being kept below 15°. Layers were separated, the aqueous layer was extracted with methylene chloride, and the combined organic layers extracted with three 20-ml. portions of ice cold 2.5N sulfuric acid, then dried over potassium carbonate. The solvent was removed under reduced pressure with no external heat.

The red oil which remained was dissolved in 50 ml. of anhydrous ether and added at 0° over 30 min. to a suspension of sodium phenoxide (from 250 g. of phenol and 34.5 g. of sodium) in 200 ml. of ether. The solution was stirred at room temperature for 1.5 days, refluxed for 4 days, filtered, and washed successively with 10% alkali and with water. After drying and removal of the solvent there was obtained 3.5 g. (23%) of crude product which on fractionation gave 1.0 g. of pure cyclopropylcarbinyl phenyl ether, n_D^{25} 1.5199, whose infrared spectrum was identical with that prepared above.

Attempted thermal rearrangement of I. One milliliter of I was refluxed (214°) at atmospheric pressure for 6 hr. The infrared spectrum was unchanged, and 12 hr. of additional reflux also resulted in no change. One milliliter of I, sealed in an 11-ml. tube, was heated at 300 ± 4° for 10 hr., and recovered unchanged (infrared spectrum, negative ferric chloride test).

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(5) Pyrolysis of certain cyclopropylcarbinyl derivatives at 500–520°, however, does lead to rearrangements; see C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007 (1960).

(6) Analyses by Spang Microanalytical Laboratory, P. O. Box 1111, Ann Arbor, Mich.

(7) D. Papa, E. Schwenk, and B. Whitman, *J. Org. Chem.*, **7**, 587 (1942).

(8) C. G. Bergstrom and S. Siegel, *J. Am. Chem. Soc.*, **74**, 145 (1952).

Synthesis of β-Lactones from β-Hydroxyacids

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As a part of a study on compounds active on the central nervous system[1] we recently described a new general method of synthesis of β-lactones, (diazotization of α,α-disubstituted β-aminoacids in acetic acid at low temperature).[2] The β-lactones are useful intermediates for pharmacologically active compounds (α-alkyltropic acids and derivatives,[3a,b] dihydro 1,3-oxazine-2,4-diones,[4] α-methylatropine[5]).

Many β-lactones are recorded in literature, which were obtained by different methods.[6] However, recently two processes for the preparation of β-lactones by dehydration of the corresponding β-hydroxyacids have been published: Diassi and Dylion[7] cyclized yohimbic acid to the corresponding β-lactone by means of pyridine and ethyl chloroformate; Sheehan, *et al.*[8] cyclized *N*-trityl-L-serine by means of *N*,*N'*-diisopropylcarbodiimide. Their work prompted us to communicate our experiences in this field.

EXPERIMENTAL

When a benzene solution of α,α-diethyl-β-hydroxypropionic acid[2,5,9] was treated at 10° to 15° with 1 mole of thionyl chloride and 1 mole of pyridine, and water added after 30 min. and the mixture extracted with benzene a crystalline compound separated from the aqueous layer.

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(1) Paper XV of this series see E. Testa, L. Fontanella, G. F. Cristiani, and L. Mariani, *Helv. Chim. Acta*, **42**, 2370 (1959).

(2) E. Testa, L. Fontanella, G. F. Criastiani, and L. Mariani, *Ann.*, in press.

(3) (a) R. Fusco and E. Testa, *Farmaco* [*Ed. sci.*], **12**, 828 (1957); (b) E. Testa, *Farmaco* [*Ed. sci.*], **12**, 837 (1957).

(4) E. Testa, L. Fontanella, G. F. Cristiani, and G. G. Gallo, *J. Org. Chem.*, **24**, 1928 (1959).

(5) G. Melone, A. Vecchi, G. Pagani, and E. Testa, *J. Org. Chem.*, in press.

(6) H. E. Zaugg, *Org. Reactions*, 307 (1954).

(7) P. A. Diassi and C. M. Dylion, *J. Am. Chem. Soc.*, **80**, 3746 (1958).

(8) J. C. Sheehan, K. Hasspacher, and Y. Lieh Yeh, *J. Am. Chem. Soc.*, **81**, 6086 (1959).

(9) B. J. Ludwig, *J. Am. Chem. Soc.*, **72**, 5329 (1950).