ture. Distillation afforded 7.5 g (35%) of 1,1,1,3,3-pentachloropropene, 1.7 g (13%) of trichloroethylene, and 1.8 g (11%) of perchloroallene dimer which crystallized from the residue of the distillation, mp 90–91° (lit.[9] 90–91°). The ir spectrum was identical with that reported in the literature.[9]

Pyrolysis of 5 g of 1,1,1,3,3-pentachloropropene under identical conditions at 25-mm pressure produced products in the Dry Ice–acetone trap which gave a band in the ir at 1962 cm^{-1} at low temperature.

Decarboxylation of XIII.—A 20-g (0.09 mol) portion of XIII was pyrolyzed in a ketene generator under reduced pressure as described above. A 13-g (80%) portion of 1,1,1,3-tetrachloropropene was isolated from the Dry Ice trap. This olefin was approximately an equal amount of cis and trans isomers as evidenced by the nmr coupling constants for the vinyl protons.[14]

(14) R. Fields, R. N. Haszeldine, and D. Peter, *J. Chem. Soc. C*, 165 (1969).

Registry No.—I, 4288-03-3; *cis*-II, 35589-64-1; *trans*-II, 35621-77-3; III, 34624-15-2; IV, 34499-08-6; V, 34499-11-1; VI, 35621-81-9; *cis*-VII, 35621-82-0; *trans*-VII, 35621-83-1; *cis*-VIII, 35621-84-2; *trans*-VIII, 35621-85-3; *cis*-X, 35621-86-4; *trans*-X, 35621-87-5; *cis*-XI, 35621-88-6; *trans*-XI, 35621-89-7; *trans*-XIII, 28186-54-1; *cis*-β-bromo-β-chlorostyrene, 35621-91-1; *trans*-β-bromo-β-chlorostyrene, 35621-92-2; trichloromethylallene, 34819-62-0; 1,1,1-trichloro-2,3-pentadiene, 34819-63-1; 1,1,1-trichloro-2,3-hexadiene, 34819-64-2.

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A Novel Variant of the Favorskii Reaction[1]

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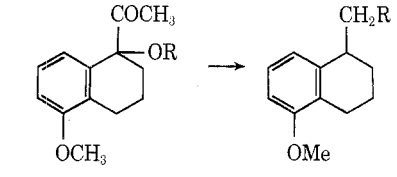
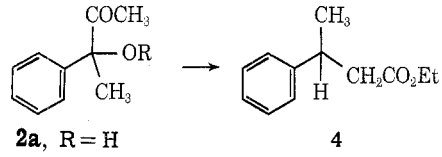
The first examples of α-hydroxy ketones undergoing the Favorskii reaction are presented. The alcohols 1-acetyl-1-hydroxy-5-methoxy-1,2,3,4-tetrahydronaphthalene (**1a**) and 3-phenyl-3-hydroxy-2-butanone (**2a**) undergo the rearrangement with NaH in diethyl carbonate to give the esters ethyl 5-methoxy-1,2,3,4-tetrahydronaphthalene-1-acetate (**3a**) and ethyl 3-phenylbutyrate (**4**), respectively. Possible mechanisms are discussed, and a cyclopropanone intermediate has been verified by the use of the ^{18}O-labeled ketone (**2a**).

Apart from α-halo ketones,[2] there is only one reported instance[3] of an effective α leaving group (2,3-epoxy ketones) generating the necessary intermediate, under the right experimental conditions, to yield the "Favorskii" type of products. We now wish to report a demonstration that the α-hydroxy ketones **1a** and **2a** can undergo the Favorskii rearrangement under suitable conditions.



1a, R = H
b, R = Ac

3a, R = COOEt
b, R = COOH
c, R = CH_2OH



2a, R = H
b, R = CH_3

4

The α-hydroxy ketone **1a** was prepared by the mercury-catalyzed hydration of 1-ethynyl-1-hydroxy-5-methoxy-1,2,3,4-tetrahydronaphthalene, which in turn was obtained from 5-methoxy-1-tetralone and acetylenemonomagnesium bromide.[4] Treatment of **1a** with NaH in diethyl carbonate at 100° under N_2 gave (instead of the desired Claisen condensation) the ester **3a** in nearly quantitative yield. The structure **3a** was confirmed by hydrolysis to the corresponding acid **3b**, and also by its reduction to the alcohol **3c** (3,5-dinitrobenzoate). Under the same conditions, the analogous open-chain alcohol **2a** was converted to **4** and identified by comparison (tlc and ir) with an authentic sample.

It is generally believed that the Favorskii reaction of an α-halo ketone with an α′ hydrogen atom occurs *via* a symmetrical (cyclopropanone)[5] intermediate, whereas α-halo ketones devoid of an α′ hydrogen follow a semibenzilic mechanism.[6]

The cyclopropanone mechanism is feasible in the present instance and could operate if the tertiary alcohol **2a** were converted into a carbonate leaving group. This could occur (Scheme I) by base-catalyzed transesterification with diethyl carbonate to form a mixed carbonate ester, with loss of ethoxide ion. Proton abstraction from the α-methyl group and internal attack with displacement of carbonate ion would then give the cyclopropanone **5**. Attack by ethoxide ion and collapse of the intermediate **6** by cleavage of bond a to afford the rearranged ester **4** correlates well with the expected[7] greater stability of the benzylic carbanion **8** over the primary carbanion **9** formed by fission of bond b. No trace of the isomeric ester **7** was found.

The semibenzilic mechanism, proceeding *via* an intermediate dianion, which was originally proposed[6] only for α-halo ketones without an α′ hydrogen, has in fact been shown[8] to occur also in α-halo ketones with an

(1) Acknowledgment is made to the U. S. Public Health Service (Grant No. MH-04582) for financial support.

(2) A. S. Kende, *Org. React.*, **11**, 261 (1960).

(3) H. O. House and W. F. Gilmore, *J. Amer. Chem. Soc.*, **83**, 3972 (1961).

(4) L. Skattebøl, *Tetrahedron*, **21**, 1357 (1965).

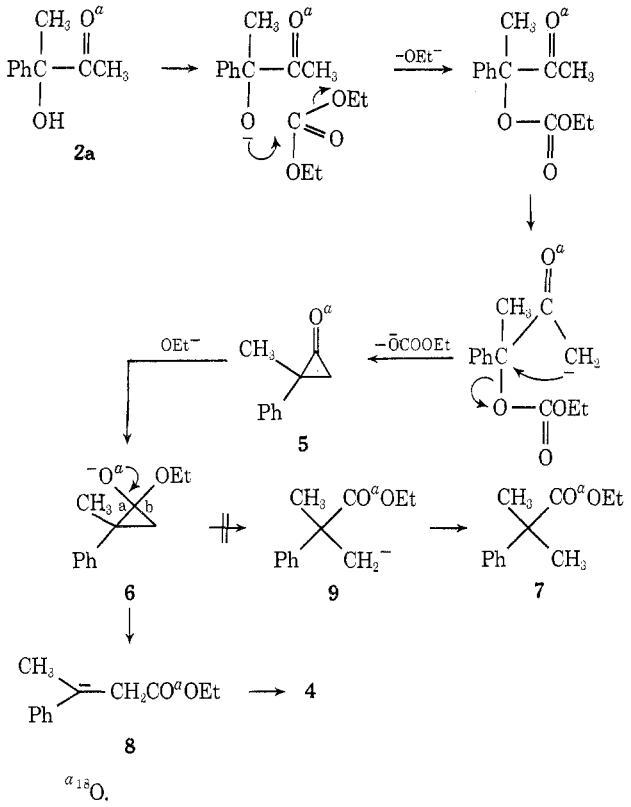
(5) R. B. Loftfield, *J. Amer. Chem. Soc.*, **72**, 632 (1950); **73**, 4707 (1951).

(6) B. Tchoubar and O. Sackur, *C. R. Acad. Sci.*, **208**, 1020 (1939).

(7) (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965. (b) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

(8) E. W. Warnhoff, C. M. Wong, and W. T. Tai, *J. Amer. Chem. Soc.*, **90**, 515 (1968).

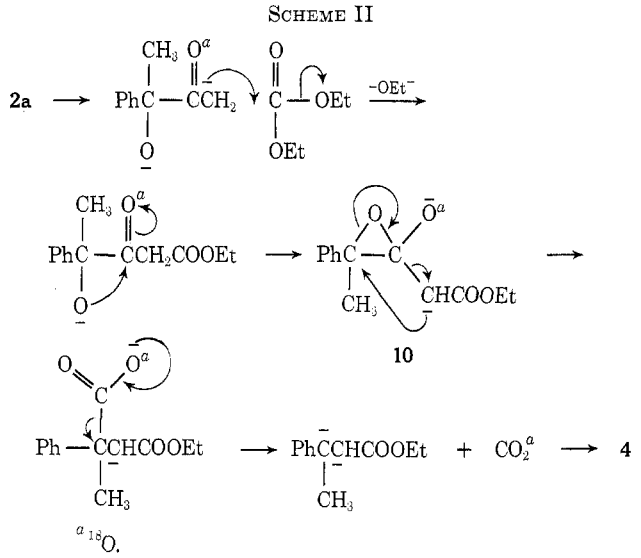
SCHEME I



α' hydrogen atom but is here excluded by reason of the product structure, and the ketene mechanism of Richard[9] is inapplicable in our instances since the tertiary carbon atom bearing the leaving group is incapable of forming the intermediate carbene.

However, an additional possibility exists of the reaction taking place *via* an epoxide mechanism, involving a Claisen condensation with formation of the

SCHEME II



epoxide dianion[10] intermediate **10,** which rearranges with loss of carbon dioxide to give **4** (Scheme II).

(9) G. Richard, *C. R. Acad. Sci.*, **197**, 1432 (1933).

(10) T. M. Harris, S. Boatman, and C. R. Hauser, *J. Amer. Chem. Soc.*, **85**, 3273 (1963).

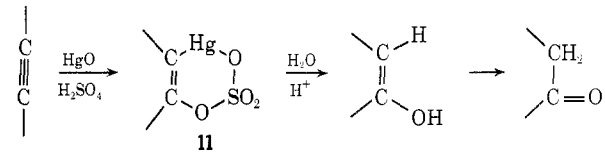
Since the epoxide mechanism cannot be excluded on the basis of product structure, and since both the cyclopropanone and the semibenzilic pathways have recently been shown[3,11] to be applicable, under different experimental conditions, to the *same* compound, it was necessary to distinguish between the two possible mechanisms in the present instance. Such a distinction can be made by the use of **2a** labeled with ^{18}O in the keto group. Mechanism I would result in retention of the isotope in **4** while mechanism II involves loss of isotope as $C^{18}O_2$.

The labeled **2a** was prepared by the hydration of 3-phenyl-3-hydroxy-1-butyne with 10 atom % $H_2{}^{18}O$ and was accompanied by a by-product identified as the corresponding methyl ether **2b**. Although the parent peak in the electron-impact mass spectrum of a tertiary alcohol is either absent or extremely weak,[12] it was possible to use chemical ionization mass spectrometry[13] to determine the amount and location of label in the starting alcohol **2a** and also in the by-product **2b**.[14]

From the differences in the ratios of the $PH^+/(PH^+ + 2)$ peaks between labeled and unlabeled **2a** and **2b,** an incorporation of 8.8 ± 0.4% ^{18}O was calculated. The use of collision-stabilized dimer and trimer peaks permitted an independent check on isotope content. Utilizing the labeled compound **2a,** the isotope peaks of the parent ion minus H_2O indicated that the ^{18}O was still completely present, whereas the isotope peaks of the parent ion minus CH_3CHO indicated total loss of unnatural ^{18}O, clearly showing that the label was all in the carbonyl oxygen.

The observed isotope content of 8.8% ^{18}O in **2a** also casts some additional light on the mechanism of hydration of alkynes.[15] The original 10 atom % ^{18}O will be diluted to 9.65% by the $H_2{}^{16}O$ formed from the reaction of the H_2SO_4 and HgO (see Experimental Section), and this in turn will be diluted to a maximum of ~8.7% by the $H_2{}^{16}O$ generated during the formation of the ether by-product **2b,** if we assume that the rates of formation of **2a** and **2b** are approximately equal.[16] From Scheme III, which shows the generally accepted sequence of

SCHEME III



events in hydrations of this type,[15] it can be seen that hydrolysis of intermediate **11** may occur *a priori* either with S–O or C–O bond cleavage. That the hydrolysis does indeed occur with C–O bond cleavage, as in the case of an alkyl sulfate,[17] is shown by the ^{18}O incorporation results. Attack of $H_2{}^{18}O$ at sulfur followed by S–O cleavage would cause additional ^{16}O incorporation into

(11) J. M. Conia and J. L. Ripoll, *Bull. Soc. Chim. Fr.*, 773 (1963).

(12) R. Silverstein and G. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1968, p 16.

(13) F. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

(14) Our thanks go to Dr. H. M. Fales and to Mr. W. Garland for these measurements, which were carried out at 25° on an MS-9 mass spectrometer.

(15) S. Matsoyan, G. Chukhadzhyan, and S. Vartanyan, *J. Gen. Chem. USSR*, **30**, 1223 (1960).

(16) Monitoring of the reaction *via* tlc showed that some **2b** was formed before all of the alkyne had reacted. Mass spectrometric analysis indicated that within experimental error both **2a** and **2b** had the same ^{18}O incorporation as would be expected if they were formed simultaneously.

(17) E. Bunel, *Chem. Rev.*, **70**, 323 (1970).

2a with dilution of the label to ~7.7% by scrambling all the oxygens of the sulfate with the $H_2{}^{18}O$. Under similar conditions no oxygen exchange between H_2SO_4 and $H_2{}^{18}O$ has been observed.[18] The experimentally found isotope content (8.8% ^{18}O) in both **2a** and **2b** is thus in agreement with a mechanism involving C–O bond cleavage of the intermediate **11**. Experiments using the ^{18}O labeled **2a** showed that the product **4** retained 91 ± 4% of its isotope label, supporting mechanism I.[19]

Experimental Section

1-Acetyl-1-hydroxy-5-methoxy-1,2,3,4-tetrahydronaphthalene (1a).—A solution of 0.50 g (2.6 mmol) of 1-ethynyl-1-hydroxy-5-methoxy-1,2,3,4-tetrahydronaphthalene in ethanol was heated to reflux with mercury *p*-toluenesulfonamide[20] (1.0 g) for 18 hr. Hydrogen sulfide gas was bubbled through the cooled solution to decompose the complex, and filtration, evaporation, and recrystallization (hexane) afforded 500 mg (90%) of white crystals: mp 54–54.5°; ir (Nujol) 3400 (OH), 1710 (C=O), 1590 cm^{-1} (OMe); nmr (CCl_4) δ 6.8 (3 H, m, aromatics), 4.1 (1 H, broad s, replaceable OH proton), 3.7 (3 H, s, OCH_3), 3.0–1.5 (6 H, m, methylenes), 1.9 (3 H, s, CH_3CO); mass spectrum peak at *m/e* 220 (M^+), exact mass 220.10989, $C_{13}H_{16}O_3$ requires 220.10994.

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.77; H,7.33.

This material was also prepared by hydrolysis of **1b** with KOH in ethanol.

1-Acetyl-1-hydroxy-5-methoxy-1,2,3,4-tetrahydronaphthalene 1-Acetate (1b).—A mixture of 20 g (0.104 mol) of 1-ethynyl-1-hydroxy-5-methoxy-1,2,3,4-tetrahydronaphthalene and 40 g of mercuric acetate was stirred at room temperature for 24 hr in 900 ml of ethyl acetate. Hydrogen sulfide gas was bubbled through the mixture to decompose the complex and filtration followed by evaporation afforded 17.0 g (61%) of the keto acetate **1b**. Distillation at 130° (0.01 mm) afforded a colorless liquid: ir (neat) 1745 and 1720 (C=O), 1570 cm^{-1} (OCH_3); nmr (CCl_4) δ 7.0 (3 H, m, aromatics), 3.8 (3 H, s, OCH_3), 2.9–1.7 (6 H, m, methylenes), 2.6 and 2.3 (3 H each, s, methyl protons).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.7; H, 6.87. Found: C, 68.89; H, 7.06.

3-Phenyl-3-hydroxy-2-butanone-^{18}O (2a).—A mixture of 0.25 g (2.5 mmol) of concentrated H_2SO_4 and 0.5 g of 10 atom % $H_2{}^{18}O$ was poured into 12.5 ml of dry methanol in a 100-ml, three-necked, round-bottom flask and heated to 55° at which time 0.30 g of red HgO was added. A solution of 7.0 g (0.048 mol) of 3-phenyl-3-hydroxy-1-butyne in 12.5 ml of dry methanol containing 0.75 g of 10 atom % $H_2{}^{18}O$ was introduced into the mixture during 1 hr. When half of the alkyne had been added, a further 0.25 g of HgO was introduced.[21] After the addition was complete, the solution was then stirred for 30 min at 55°, cooled, and poured into 200 ml of a NaCl–H_2O solution. Work-up gave 8.0 g of crude liquid. Spinning-band distillation at 60–62° (0.017 mm) gave the pure keto alcohol, 6.0 g (76%), lit.[15] bp 89–91° (2.5 mm). The nmr and ir spectra were in accord with the desired structure.

A lower boiling fraction, 1.5 g (18%) from the distillation, bp 50–52° (0.017 mm), was identified on the basis of its nmr, ir, and mass spectra as 3-phenyl-3-methoxy-2-butanone (**2b**), lit.[22] bp 92° (8 mm).

Ethyl 5-Methoxy-1,2,3,4-tetrahydronaphthalene-1-acetate (3a).—1-Acetyl-1-hydroxy-5-methoxy-1,2,3,4-tetrahydronaphthalene (**1a**) (1.1 g, 5 mmol) in diethyl carbonate (3 ml) was added over 3 hr to sodium hydride (1.2 g free from oil) in diethyl carbonate (3 ml) at 100° under N_2. The reaction mixture was stirred for a further 30 min and then cooled and diluted with HOAc (0.5 ml), H_2O (5 ml), and ether (50 ml). The ethereal layer was washed with water, dried ($MgSO_4$), filtered, and evaporated to give an oil (1.2 g, 100%). Distillation at 120° (0.01 mm) gave a colorless liquid: ir (neat) 1745 (ester C=O), 1595 cm^{-1} (OCH_3); nmr (CCl_4) δ 6.8 (3 H, m, aromatics), 4.1 (2 H, q, CH_3CH_2), 3.7 (3 H, s, OCH_3), 3.25 (1 H, broad m, benzylic H), 2.55 and 1.75 (4 H each, m, methylenes), 1.2 (3 H, t, CH_3CH_2).

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.58; H, 8.0. Found: C, 72.55; H, 8.19.

The ester was converted to 5-methoxy-1,2,3,4-tetrahydronaphthalene-1-acetic acid (**3b**) in 93% yield by hydrolysis with aqueous sodium hydroxide, mp 145.5–147°, lit.[23] mp 146–147°.

The ester was reduced with $LiAlH_4$ in ether to give 2-(5-methoxy-1,2,3,4-tetrahydronaphthyl)ethyl alcohol (**3c**), the 3,5-dinitrobenzoate of which had mp 105–106°, lit.[23] mp 107–108°.

Ethyl 3-Phenylbutyrate-^{18}O (4).—This material was prepared in 29% yield from **2a** under conditions similar to the preparation of **3a**. Its identity was confirmed by nmr and ir comparison with an authentic sample.

The labeled **4** had 8.0% more ^{18}O than a similarly prepared sample of unlabeled **4** as measured by $M^+/(M^+ + 2)$ ratios in their mass spectra. Taking into consideration the amount of ^{18}O in the starting alcohol **2a**, this means the amount of label retained in **4** is in the range of 91 ± 4%.

Registry No.—**1a**, 35031-30-2; **1b**, 35031-31-3; **2a**, 3155-01-9; **3a**, 35026-46-1.

(18) J. Halperin and H. Taube, *J. Amer. Chem. Soc.*, **74**, 375 (1952).

(19) Further support comes from the observation that the acetate **1b** is converted to **3a** with sodium ethoxide in dry benzene (60% yield), conditions under which mechanism II is inoperative.

(20) M. Goldberg, R. Aeschbacher, and E. Hardegger, *Helv. Chim. Acta*, **26**, 680 (1943).

(21) The reaction of the H_2SO_4 and HgO (2.5 mmol of each) produces 2.5 mmol of $H_2{}^{16}O$ which dilutes the $H_2{}^{18}O$ to 9.65 atom % ^{18}O.

(22) D. J. Cram and D. R. Wilson, *J. Amer. Chem. Soc.*, **85**, 1245 (1963).

(23) J. Lockett and W. Short, *J. Chem. Soc.*, 787 (1939).