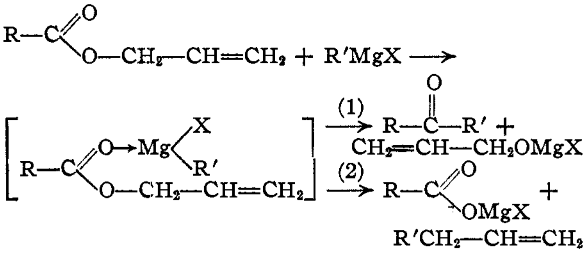
Grignard Cleavage of Allylic Esters. IV. Steric Hindrance in the Grignard Reagent

By Richard T. Arnold, R. Winston Liggett[1] and Scott Searles, Jr.[2]

A Grignard reagent may react with an allylic ester of a tertiary carboxylic acid in two ways: (1) by addition to form a ketone or an alcohol and (2) by cleavage to form an olefinic hydrocarbon and a salt of the acid. The two processes generally take place simultaneously and are the results of different modes of rearrangement of the coördination complex which is formed as the first step in the Grignard reaction.[3,4]



Unless retarded by steric hindrance the addition process (1) usually predominates over the cleavage process, as in the reaction of allyl benzoate with phenylmagnesium bromide.[5] With allylic esters of sterically hindered acids, however, it has been shown in previous communications,[4,6] that the phenyl Grignard reagent reacts chiefly by the cleavage process.[2]

It would be anticipated that the Grignard reagent may have the degree of steric hindrance required to retard the addition reaction and permit cleavage to predominate with allylic esters of unhindered acids. Actually it was found that in the reaction of mesitylmagnesium bromide with allyl benzoate, the cleavage process occurred to the extent of at least 57%,[7] while the normal addition reaction to form 2,4,6-trimethylbenzophenone proceeded to the extent of about 15%.[7] The Grignard cleavage of allylic esters due to steric hindrance in the Grignard reagent has not been reported previously.

Experimental

A Grignard solution prepared from bromomesitylene (25 g.), magnesium (3.2 g.) and ether (50 ml.) was allowed to react for eighteen hours at 25–35° with a solution of allyl benzoate (16.2 g.) in ether (50 ml.). The reaction mixture was then decomposed with slightly acidified ammonium chloride solution, and the ether solution was extracted thoroughly with sodium carbonate solution (10%). Acidification of the alkaline solution gave benzoic acid (5.1 g., 42% of theoretical); m. p. 121–121.3°.

Because of the similar boiling points of allylmesitylene and allyl benzoate, the neutral material obtained from the ether solution was saponified by refluxing four hours with alcoholic potassium hydroxide. Extraction of the mixture with water and ether and acidification of the alkaline extracts gave benzoic acid (3.2 g., corresponding to 26% recovery of unchanged allyl benzoate). Distillation of the ether layer gave allylmesitylene (5.7 g., 36%), b. p. 215–222° (737 mm.), $n^{26}\mathrm{D}$ 1.5149, and 2,4,6-trimethylbenzophenone (2.4 g., 11%), b. p. 174° (12 mm.), $n^{21}\mathrm{D}$ 1.5738, as well as some mesitylene (5.5 g.), as expected from the hydrolysis of unused Grignard reagent.

School of Chemistry
University of Minnesota
Minneapolis, Minnesota

Received July 12, 1948

---

[1] Du Pont Post-doctorate Fellow, 1941–1942.

[2] Du Pont Predoctoral Fellow, 1946–1947. Present address: Department of Chemistry, University of Illinois.

[3] Johnson, Gilman's "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1880.

[4] Arnold, Bank and Liggett, This Journal, **63**, 3444 (1941).

[5] Gilman and Robinson, *Bull. soc. chim.*, **45**, 640 (1929).

[6] Arnold and Liggett, This Journal, **64**, 2875 (1942).

[7] Actual yield adjusted for recovery of unchanged allyl benzoate.

The Osmium Tetroxide Oxidation of Some Long-Chain Unsaturated Fatty Acids

By Alfred R. Bader

As a means of extending the evidence of the configurations of the products of oxidation of oleic, elaidic, linoleic, erucic, and brassidic acid with permanganate and peracids, a study has been made of their oxidation by osmium tetroxide. Since this reacts through a cyclic ester intermediate,[1] a *cis*-ethylene must give an *erythro* diol and a *trans* ethylene a *threo* diol. In each case the oxidation products obtained were the ones obtained also in the alkaline permanganate oxidation of the same acids. Hence the 9,10-dihydroxystearic acid melting at 132° and the 13,14-dihydroxybehenic acid melting at 132° are the *erythro*-diols, the two isomers melting at 95° and 101°, respectively, are the *threo*-diols and the eight diastereoisomers of 9,10,12,13-tetrahydroxystearic acid have the configurations assigned them by McKay and Bader.[2]

This is in accord with the work of Wittcoff and co-workers[3,4] who pointed out that the criteria (*viz.*, formation of boric acid complexes, rate of oxidation with lead tetraacetate and periodate, and rate of formation of isopropylidene compounds) which characterize *cis*-glycols in cyclic structures also characterize *threo*- rather than *erythro*-diols in straight chain compounds.

Swern[5] has criticized McKay and Bader[2] for their supposed assumption that alkaline permanganate oxidation proceeds by "*trans* hydroxylation"; this criticism is due to the use[2] of the confusing designation "*trans*" glycol to describe a compound of the *erythro* series. "*trans*" was used[2] for *erythro* and "*cis*" for *threo*, because the vicinal hydroxyl groups in *threo* diols possess a closer spatial relationship than those in *erythro* diols.[4] The present work supports the actual conclusions reached[2,3,4,5] which are the opposite of those of Hilditch and co-workers[6,7,8] and of Dorée

---

[1] Criegee, *Ann.*, **522**, 75 (1936).

[2] McKay and Bader, *J. Org. Chem.*, **13**, 75 (1948).

[3] Wittcoff and Miller, This Journal, **69**, 3138 (1947).

[4] Wittcoff, Moe and Iwen, *ibid.*, **70**, 742 (1948).

[5] Swern, *ibid.*, **70**, 1239 (1948).

[6] Hilditch, *J. Chem. Soc.*, 1828 (1926).

[7] Hilditch and Lea, *ibid.*, 1576 (1928).

[8] Atherton and Hilditch, *ibid.*, 204 (1943).