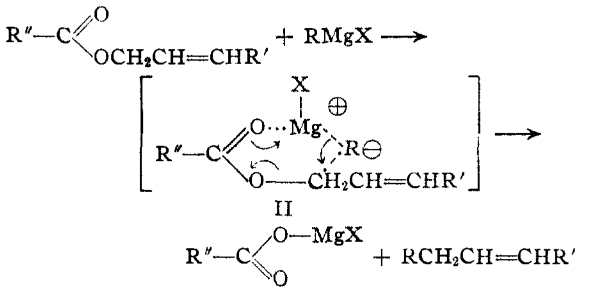
below offers an accurate description of the reaction which is under investigation in these Laboratories.



By inspection of II it can be seen that group R (from RMgX) is one element of a quasi six-membered ring and because of this fact it is geometrically in a position such that it must attack only the α-carbon atom of the allylic system $\left(-\overset{\alpha}{C}H_2-\overset{\beta}{C}H=\overset{\gamma}{C}H-R'\right)$ when the redistribution of electrons (as indicated by the arrows) is completed. We regard the breaking and formation of bonds in the decomposition of II as occurring simultaneously.

When conditions permit, a systematic investigation to prove or disprove this newly proposed mechanism will be undertaken.

Experimental

n-Crotyl Mesitoate.—This ester was prepared from pure n-crotyl alcohol, mesitoyl chloride and pyridine in cold chloroform solution as described earlier in other examples; yield 58%; b. p. 160–165° (17 mm.).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3. Found: C, 76.8; H, 8.7.

The ester on ozonolysis gave acetaldehyde as the sole volatile aldehyde.

n-Crotylbenzene.—Cleavage of n-crotyl mesitoate with phenylmagnesium bromide as described earlier[2] for other examples gave a hydrocarbon; yield 75.5%; b. p. 81–83° (22 mm.). (Reported 81–82° (18 mm.).[4])

Anal. Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.1. Found: C, 91.0; H, 9.15.

This hydrocarbon gave acetaldehyde as the only identifiable volatile aldehyde. Catalytic hydrogenation gave a non-olefinic hydrocarbon whose vapor pressure curve was identical with pure n-butylbenzene and quite different from that of s-butylbenzene.

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(4) Auwers, Roth and Eisenlohr, *Ann.*, **385**, 108 (1911).

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1,2,5,6-Diacetone d-Mannitol and 1,2,5,6-Diacetone l-Mannitol

BY ERICH BAER

The chemical synthesis of pure enantiomorphs of optically active compounds of biological interest often involves the use of difficultly accessible intermediates. The recently described syntheses of the enantiomorphs of a number of unsymmetrically substituted glycerols have been laborious because of the commercial unavailability and the lack of an efficient synthesis of the 1,2,5,6-diacetone derivatives of *d*- and *l*-mannitol. The key position of these two compounds is illustrated by the fact that they have become essential intermediates in the synthesis of *d*(+)α-glycerophosphate,[1] *l*(−)α-glycerophosphate,[2] the normal aliphatic α-monoglycerides,[3,4] α,β-diglycerides,[5] triglycerides,[3] batyl alcohol,[6] chimyl alcohol,[6] and selachyl alcohol.[7] Since the number of applications can be expected to increase, the importance of finding an improved method of preparing these mannitol derivatives is obvious when one considers the labor involved in the older methods.

The first synthesis and description of 1,2,5,6-diacetone *d*-mannitol was given by E. Fischer and Rund in 1916.[8] They obtained the substance on acetonation of *d*-mannitol with acetone and hydrochloric acid, but in a yield of 2% only. By changing the solvent used for extracting the product from the reaction mixture Fischer and Baer in 1934[9] succeeded in raising the yield of this process to approximately 6%. An entirely different procedure was reported by von Vargha,[10] who conducted the acetonation with concd. sulfuric acid in the presence of boric acid. The resulting boric acid ester (4.5) of 1,2-acetone *d*-mannitol was freed from boric acid by alcoholysis and the second acetone introduced by acetonation with copper sulfate. The yield was still very low (14%); moreover, the outcome of the synthesis was unpredictable. With the chemicals then (1934) available in Basel (Switzerland) we succeeded only twice out of many trials in obtaining any yield of diacetone *d*-mannitol. It is possible that some reactant in the successful preparations contained a contaminant which acted as a catalyst for the condensation.

The successful application of zinc chloride as catalyst in other acetonation reactions [Fischer and Taube,[11] Fischer and Baer[12]] prompted a study of its use for the preparation of the diacetone mannitols. These studies resulted in 1939 in the development of a quite satisfactory method (Baer and Fischer[13a,13b]), the yields being raised to 56%, but owing to the labor involved in the removal of large amounts of zinc chloride and solvents the method as described then was still cumbersome and only applicable to small scale preparation. The consequent necessity of repeating the synthesis at fre-

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(1) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **135**, 321 (1940).

(2) E. Baer and H. O. L. Fischer, *ibid.*, **128**, 491 (1939).

(3) E. Baer and H. O. L. Fischer, *ibid.*, **128**, 475 (1939).

(4) E. Baer and H. O. L. Fischer, communication in preparation for THIS JOURNAL.

(5) J. C. Sowden and H. O. L. Fischer, THIS JOURNAL, **63**, 3244 (1941).

(6) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **140**, 397 (1941).

(7) E. Baer, L. Rubin and H. O. L. Fischer, *ibid.*, **155**, 447 (1944).

(8) E. Fischer and C. Rund, *Ber.*, **49**, 91 (1916).

(9) H. O. L. Fischer and E. Baer, *Helv. Chim. Acta*, **17**, 622 (1934).

(10) L. von Vargha, *Ber.*, **66**, 1394 (1933).

(11) H. O. L. Fischer and C. Taube, *ibid.*, **60**, 485 (1927).

(12) H. O. L. Fischer and E. Baer, *ibid.*, **63**, 1749 (1930).

(13) (a) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **128**, 463 (1939). (b) E. Baer and H. O. L. Fischer, THIS JOURNAL, **61**, 761 (1939).

quent intervals in order to accumulate any quantity of this key intermediate compound proved very tedious.

During the past five years numerous small variations in the preparation have been given a trial. Several of the changes proved distinctly advantageous and their combination led to a procedure which is less time consuming, cheaper and which can be carried out easily on a larger scale. These improvements are the result of the following three major changes: (a) reduction of the amount of zinc chloride and acetone to one-third of the quantities originally used, (b) decrease of the reaction time from nineteen hours to approximately two hours and (c) the use of a better solvent (butyl ether instead of petroleum ether) for the isolation and crystallization of the diacetone *d*- or *l*-mannitol.

Experimental

Two hundred and seventy grams of zinc chloride sticks (Analytical reagent, Mallinckrodt) is dissolved in 1350 cc. of dry acetone. After the solution has cooled to room temperature and the insoluble matter has settled out, the slightly turbid supernatant liquid is decanted and added to 170 g. of finely powdered *d*- or *l*-mannitol which has been passed through a 200-mesh sieve. The mixture, protected against intrusion of moisture, is either shaken or vigorously stirred until most of the mannitol is dissolved. This operation usually requires about two hours at a room temperature of 19 to 20°. The solution is then filtered (recovering approximately 40 g. of unreacted mannitol) and the filtrate is immediately processed as follows.

In a 5-liter round-bottomed flask equipped with an efficient mechanical stirrer, reaching nearly to the bottom of the flask, are dissolved 340 g. of potassium carbonate (anhydrous) in 340 cc. of water; this solution is covered with 1350 cc. of dry ether.[14] The mixture is vigorously stirred while the filtered acetone-zinc chloride solution is poured in as rapidly as possible. The success of the preparation depends to a large extent upon the speed with which the reactants are brought together; thus the rate of addition and the efficiency of stirring are influential factors. The stirring is continued for a period of thirty to forty minutes, after which the ether–acetone solution is decanted and the zinc carbonate pellets are washed with several portions (totalling 300 to 400 cc.) of a 1:1 acetone–ether mixture. The combined solutions are dried by stirring with 340 g. of calcined potassium carbonate for thirty minutes. The solution is filtered and the carbonate is washed with several portions of a 1:1 acetone–ether mixture (totalling 300 cc. to 400 cc.). The combined filtrate and washings are evaporated under reduced pressure. The residue is finally dried *in vacuo* at 60 to 70° (water-bath) for two hours. The distilling flask is transferred to an oil-bath, 400 cc. of *n*-butyl ether added and the temperature of the bath raised to 135°. The hot solution is filtered rapidly, using a hot water funnel. Another 75-cc. portion of hot butyl ether is used to rinse the flask and filter. The filtrate, which solidifies immediately, is kept in ice for several hours. The precipitate is filtered with suction, washed with low boiling petroleum ether and dried *in vacuo*. The yield of 1,2,5,6-diacetone *d*- or *l*-mannitol is as high as 103 g. (55% of the theoretical amount based on the amount of mannitol in solution). The products melt from 117 to 119°. Recrystallization from water in which both acetone mannitols are very soluble occasions an appreciable loss but gives very pure products in the form of long, fine needles melting at 122°. Products, however, melting from 117 to 119° are pure enough for most purposes. Mixed melting points of 1,2,5,6-diacetone *d*- or *l*-mannitol thus prepared with corresponding enantiomorphs prepared by other methods give no depression. Both compounds on oxidation with lead tetraacetate and subsequent hydrolysis yield quantitatively *d*- or *l*-glyceraldehyde, respectively.[15,16]

Anal. 1,2,5,6-Diacetone *d*-mannitol $C_{12}H_{22}O_6$ (262.2). Calcd.: C, 54.9; H, 8.6. Found: C, 54.8; H, 8.5. 1,2,5,6-Diacetone *l*-mannitol $C_{12}H_{22}O_6$ (262.2). Calcd.: C, 54.9; H, 8.6. Found: C, 54.9; H, 8.5.

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[14] The ether was freed from ethanol and water before use.

[15] E. Baer, J. M. Grosheintz and H. O. L. Fischer, THIS JOURNAL, **61**, 2607 (1939).

[16] E. Baer and H. O. L. Fischer, *ibid.*, **61**, 761 (1939).

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On the Structure of Dimethyl Ether–Boron Trifluoride

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Brown and Adams[1] called attention to a discrepancy in the data on the dissociation of dimethyl ether–boron trifluoride.[2] We reëxamined the data in question and agree that these are not self-consistent; it is likely that the dissociations we calculated for the lower temperature range are too low. Since our experimental method was such that no direct observation of the completeness of vaporization could be made, it is possible that in this lower temperature range the sample was not entirely in the vapor phase, as was assumed in our calculations. Consequently, the percentage dissociation we assumed in interpreting our electron diffraction photographs of dimethyl ether–boron trifluoride[3] was incorrect; instead of the negligible 10% dissociation for the saturated vapor at about 40° we should have taken a value close to 57% deduced from the combined data of Brown and Adams[4] and of Laubengayer and Finlay. We have therefore reconsidered our electron diffraction results assuming more extensive dissociation.

As will be recalled, our study began with a radial distribution computation. This approach is basic, since no assumption need be made regarding the structure or composition of the diffracting sample. The interatomic distances which must occur in the diffracting sample are indicated in Fig. 1a, curve R.D. Extensive experience has shown that the peaks which lie below 1 Å. or above 4 Å. cannot be trusted, due to the fact that the incomplete integrations introduce spurious oscillations in these regions; those peaks found between 1 and 2 Å., and between 3 and 4 Å. are within 3% of the interatomic distances obtained by more extensive analysis, while the range 2 to 3 Å. is most accurately represented (to 1–2%). Since in the unassociated molecules no interatomic distances above 2.36 Å. are present, the occurrence of peaks

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[1] H. C. Brown and R. M. Adams, THIS JOURNAL, **65**, 2253 (1943).

[2] A. W. Laubengayer and G. R. Finlay, *ibid.*, **65**, 887 (1943).

[3] S. H. Bauer, G. R. Finlay and A. W. Laubengayer, *ibid.*, **65**, 889 (1943).

[4] H. C. Brown and R. M. Adams, *ibid.*, **64**, 2559 (1942).