[Contribution from the Baker Laboratory of Chemistry at Cornell University]

2-Vinyl-1,3-butadiene[1]

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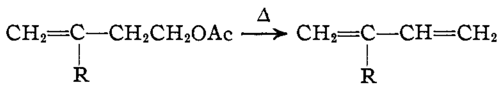
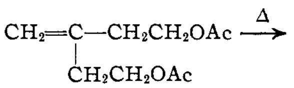
Pyrolysis of 3-methylene-1,5-pentanediol diacetate may be controlled to afford either 2-vinyl-1,3-butadiene or 2-(β-acetoxyethyl)-1,4-butadiene. The structures of the two substituted butadienes were confirmed by standard chemical and physical methods including those of infrared and ultraviolet spectrophotometry. The triene dimerizes and/or polymerizes with great ease even at −5°.

Recent studies in this Laboratory have shown that the unsaturated acetates obtained by the thermal condensation of olefins with formaldehyde in an acetic acid–acetic anhydride medium are convenient intermediates for the preparation of certain substituted 1,3-butadienes.[2] Those derived from isobutylene-type olefins are of particular interest as they afford 2-substituted-1,3-butadienes smoothly upon pyrolysis.



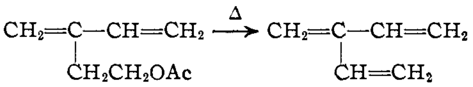
$$\mathrm{CH_2{=}\underset{\displaystyle R}{C}{-}CH_2CH_2OAc \xrightarrow{\Delta} CH_2{=}\underset{\displaystyle R}{C}{-}CH{=}CH_2}$$

In this connection, 3-methylene-1,5-pentanediol diacetate (I), a product of the thermal condensation of isobutylene with formaldehyde,[2a] appeared to be worthy of study as it should yield two butadiene derivatives by varying the pyrolysis conditions; 2-(β-acetoxyethyl)-1,3-butadiene (II) and the cross-conjugated triene 2-vinyl-1,3-butadiene (III).



$$\mathrm{CH_2{=}\underset{\displaystyle CH_2CH_2OAc}{C}{-}CH_2CH_2OAc} \xrightarrow{\Delta}$$

I



$$\mathrm{CH_2{=}\underset{\displaystyle CH_2CH_2OAc}{C}{-}CH{=}CH_2 \xrightarrow{\Delta} CH_2{=}\underset{\displaystyle CH{=}CH_2}{C}{-}CH{=}CH_2}$$

II III

Pyrolysis of I at 485° in a nitrogen atmosphere over carborundum chips gave either II or III predominately depending upon the velocity of I through the furnace (see Experimental part). Pure III, obtained after several redistillations, was a colorless volatile liquid, b.p. 44–45°, $n^{20}\mathrm{D}$ 1.4484, extremely prone to undergo dimerization and polymerization. Because of this all characterization studies were made using freshly distilled samples.

The ultraviolet spectrum of III showed one principal absorption maximum, $\lambda_{\max}^{\text{ethanol}}$ 223 mμ, log ε 4.01, in accord with the 2-vinyl-1,3-butadiene structure.[3] The infrared spectrum of III (Fig. 1) also supported the cross-conjugated triene structure; strong maxima at 6.12, 10.12, 10.97, 11.05 and 11.17 μ (characteristic of $\mathrm{RCH{=}CH_2}$ and $\mathrm{R_2C{=}CH_2}$) and a strong maximum at 6.25 μ (characteristic of $\mathrm{>C{=}C{-}C{=}C<}$).[3]

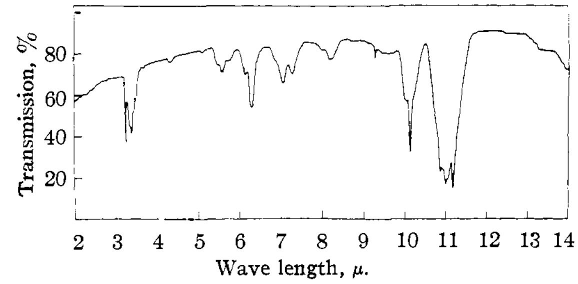
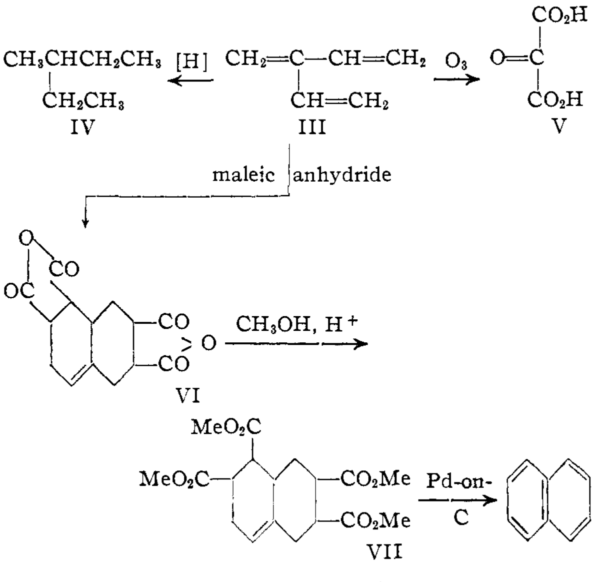


Fig. 1.—Infrared spectrum of 2-vinyl-1,3-butadiene.

Catalytic reduction of III required 96.5% of three molar equivalents of hydrogen and gave 3-methylpentane (IV), characterized by its physical properties including its infrared spectrum. Mild oxidative ozonolysis converted III to mesoxalic acid (V), characterized as its phenylhydrazone. Addition of III to a benzene solution of maleic anhydride gave a crystalline adduct VI, m.p. 238–239°, in 81% yield. Analysis of the latter indicated that it comprised one mole of III and two moles of maleic anhydride. The carbon skeleton of the adduct was indicated by aromatization and decarboxylation of its tetramethyl ester VII to naphthalene. The above transformations are illustrated in the diagram below.



The triene III dimerized and/or polymerized on standing. Upon storage at −5° it polymerized to a gelatinous mass in 36 hours. Upon standing at room temperature for a short period of time or on mild heating in the presence of hydroquinone III

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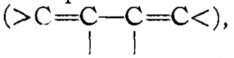
[1] The work reported here was done as part of a research program at the Baker Laboratory of Chemistry, Cornell University, sponsored by the B. F. Goodrich Company.

[2] (a) A. T. Blomquist and J. A. Verdol, This Journal, **77**, 78 (1955); (b) A. T. Blomquist and J. C. Westfahl, *ibid.*, **74**, 4073 (1952).

[3] H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., Chapt. 2.

was converted to a liquid dimer; b.p. 72–74° (8.0 mm.), $n^{20}\text{D}$ 1.5162. The dimer also was produced when distillation of III was attempted in the absence of the passage of a rapid stream of nitrogen through the distilland. Four Diels–Alder type structures for the dimer are possible and current studies are being made to establish the dimer structure.

Rapid passage of I through the pyrolysis furnace gave a 47% yield of impure II. Pure II, obtained as a colorless liquid by chromatographing through silica gel, showed b.p. 74° (18 mm.), $n^{20}\text{D}$ 1.4550.

The ultraviolet and infrared spectra of II were in accord with the 1,3-butadiene structure.[3] In the ultraviolet there was a single strong absorption maximum; $\lambda_{\text{max}}^{\text{ethanol}}$ 223 mμ, log ϵ 4.04. The infrared spectrum showed strong maxima at 6.25 μ  $(>C{=}\underset{|}{C}{-}\underset{|}{C}{=}C<)$, 6.05 and 11.25 μ ($R_2C{=}CH_2$) and 5.75 μ (RCO_2R).

Catalytic reduction of II required 99.5% of two molar equivalents of hydrogen. Upon heating II with a benzene solution of maleic anhydride some polymeric material formed together with a liquid adduct. Partial hydrolysis of the liquid adduct gave a solid crystalline 4-(β-acetoxyethyl)-1,2,3,6-tetrahydrophthalic acid, m.p. 145–146°. II reacted rapidly with 1,4-naphthoquinone to give a solid crystalline adduct, m.p. 95–96°. The structures of both adducts were supported by elemental analyses and infrared spectra measurements.

Experimental Part[4]

2-Vinyl-1,3-butadiene (III). (a) **Pyrolysis Apparatus.**—This comprised a 42.5-cm. Pyrex tube of 2.5-cm. diameter packed with 35.5 cm. of carborundum chips placed in a 13-in. electrically heated furnace having a cylindrical opening 1-in. in diameter. To the top of the tube, arranged vertically, was attached a modified Hirschberg funnel so fitted that a stream of nitrogen could be passed through the system while introducing I to the pyrolysis zone at constant rate. To the bottom of the tube were attached two receivers in series cooled with Dry Ice–trichloroethylene to collect the pyrolysate.

(b) **Distillation Apparatus.**—A pear-shaped flask fitted with a side-arm capillary tube for the introduction of a rapid stream of nitrogen through the distilland was used in all distillations of III, the distillate being collected in a series of Dry Ice traps.

With the pyrolysis tube heated to 485° and a nitrogen stream (2 bubbles per second) passing through the apparatus 50 g. (0.25 mole) of 3-methylene-1,5-pentanediol diacetate (I), n_{D}^{20} 1.4457,[2a] was added at the rate of 1 drop every two seconds. The pyrolysate containing added hydroquinone was quickly distilled using the apparatus described above until all material showing b.p. 43–44° had been collected. The still residue was recycled through the pyrolysis apparatus as above and the second pyrolysate distilled. In this manner there was obtained 9.3 g. (47%) of crude III as a colorless to straw-colored liquid. Redistillation gave 5.24 g. (26%) of III. A triply distilled sample of III showed b.p. 44–45°, n_{D}^{20} 1.4484, d_{20}^{20} 0.7356, *MR*D calcd. 28.5; found 29.1 (no correction for exhaltation due to conjugation).

Anal. Calcd. for C_6H_8: C, 89.94; H, 10.05. Found: C, 89.78, 89.96; H, 10.00, 9.95.

Quantitative hydrogenation of III in cyclohexane using Adams catalyst required 96.5% of three moles of hydrogen. Hydrogenation of 5 g. of III in a Parr apparatus gave a saturated hydrocarbon IV; b.p. 62–64°, n_{D}^{20} 1.3800, d_4^{20} 0.6759. These properties of IV correspond to those reported for 3-methylpentane.[5] The infrared spectrum of IV and 3-methylpentane were identical.

One gram of III was ozonized in chloroform for 6 hours at Dry Ice temperature and the chloroform removed *in vacuo*. The residue was treated with 40 ml. of 3% hydrogen peroxide solution and heated at 60° for 2 hours. Evaporation *in vacuo* gave 300 mg. of a white solid, m.p. 115–120°, which on recrystallization from pyridine–benzene showed m.p. 118–120°. The purified solid readily formed a phenylhydrazone derivative, m.p. 160–162.5°. The observed m.p.'s are in agreement with the values reported for mesoxalic acid.[6]

Maleic Anhydride Adduct of III. **1,2,3,5,6,7,8,9-Octahydro-1,2,6,7-naphthalenetetracarboxylic Dianhydride (VI).**—Into a previously cooled solution of benzene containing 1.29 g. (0.0137 mole) of maleic anhydride in a small Pyrex bomb was weighed 0.512 g. (0.0065 mole) of III. The bomb was then sealed and the solution became warm at once with a precipitate of adduct forming immediately. After heating the bomb to 100° for two hours, it was cooled and the white crystalline adduct VI removed. Hexane was added to precipitate the remainder of the adduct. The adduct was recrystallized from benzene to give 1.46 g. (81.5%) of VI which showed m.p. 238–239°.

Anal. Calcd. for $C_{14}H_{12}O_6$: C, 60.87; H, 4.38; sapon. no., 276. Found: C, 61.07, 60.96; H, 4.15, 4.22; sapon. no., 272, 268.

Upon quantitative hydrogenation of VI with Adams catalyst in glacial acetic acid, 0.96 molar equivalent of hydrogen were absorbed.

1,2,3,5,6,7,8,9-Octahydro-1,2,6,7-tetracarbomethoxynaphthalene (VII).—To 0.76 g. (0.0024 mole) of the adduct VI in 20.0 g. of methanol was added five drops of sulfuric acid. The mixture was heated under reflux overnight, cooled and poured into a flask containing 25 ml. of cold distilled water. Upon standing in the refrigerator VII separated as white microcrystals. Recrystallization from methanol gave 0.70 g. (79%) of VII which showed m.p. 93°.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 58.69; H, 6.57. Found: C, 58.64, 58.69; H, 6.69, 6.56.

Dehydrogenation and Degradation of VII to Naphthalene.—In a 5-ml. flask designed for the distillation of solids was placed 500 mg. of VII and 200 mg. of 10% palladium-on-charcoal. The mixture was heated slowly above the melting point of the tetraester. After 15 minutes white flakes of naphthalene began to sublime on the side-arm of the distilling flask. Heating was continued until sublimation of naphthalene ceased. Approximately 75 mg. of pure naphthalene was collected, m.p. 80°. The mixed melting point of the sublimed product and authentic sample of naphthalene was not depressed. The infrared spectrum of the sublimed product was identical with the spectrum of a pure sample of naphthalene.

Behavior of III toward Heat.—When two 2.0-g. samples of III were stored at −5° for 36 hours they polymerized into a gelatinous material. An oily substance was also present in this transformed material.

When distillation of III was effected in the absence of nitrogen, very little III could be collected. Instead, an oil formed which distilled *in vacuo*, b.p. 72–74° (8 mm.). In all cases where the triene was distilled or heated (even in the presence of inhibitor) the same hydrocarbon formed, b.p. 72–74° (8 mm.), n_{D}^{20} 1.5162. Upon quantitative hydrogenation using Adams catalyst in acetic acid the liquid hydrocarbon absorbed 99.32% of four molar equivalents of hydrogen. When the triene III was permitted to stand at room temperature for two days in a sealed tube, the same hydrocarbon also formed.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.95; H, 10.05; mol. wt., 160.25. Found: C, 89.96; H, 9.95; mol. wt., 155 (cryoscopic in benzene).

2-(β-Acetoxyethyl)-1,3-butadiene (II).—Pyrolysis was carried out in the apparatus described for III. In this case the ester I was added at a rate of 1 drop per second. One hundred grams (0.5 mole) of II was passed through the fur-

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[4] All m.p.'s were determined using a Fisher–Johns apparatus and are corrected. All b.p.'s are uncorrected. Infrared spectra were determined with a Perkin–Elmer double beam infrared spectrophotometer, model 21.

[5] F. Richter, in Beilstein's "Handbuch der organische Chemie," Vol. I, J. Springer, Berlin, Ger., 1928, p. 54.

[6] Heilbron, "Dictionary of Organic Compounds," Vol. II, Oxford University Press, N. Y., 1936, p. 604.

nace and collected in Dry Ice traps. The crude pyrolysate was washed free of acetic acid with 10% sodium carbonate solution, dried over magnesium sulfate and distilled *in vacuo*. After distilling the desired diene II, b.p. 66–69° (16 mm.), the unreacted I was recycled through the furnace. Three such passes were made to give 51.0 g. of crude II, which was redistilled to give 33.4 g. of II (46%). Purification of II was effected by chromatographing on silica gel to give II showing b.p. 73–4° (18 mm.), n^{20}_{D} 1.4550, d^{20}_{20} 0.943.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.60, 68.56; H, 8.50, 8.51.

Quantitative hydrogenation of II with Adams catalyst in glacial acetic acid required 99.5% of two molar equivalents of hydrogen.

Adduct of II with 1,4-Naphthoquinone.—When 1.40 g. (0.01 mole) of II and 1.58 g. (0.01 mole) of 1,4-naphthoquinone in 15 ml. of benzene was heated under reflux overnight, a colorless solution was obtained. Upon addition of hexane the adduct precipitated which after repeated recrystallization from hexane gave 2.06 g. (69%) of a white crystalline solid; m.p. 95–96°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 72.96; H, 5.44. Found: C, 72.82; H, 5.52.

Adduct of II with Maleic Anhydride.—When 1.66 g. (0.117 mole) of II was heated with 1.15 g. (0.117 mole) of maleic anhydride in benzene much polymeric material and an oil were formed. The oil was hydrolyzed in boiling water to give 0.8 g. of an acid. The acid was recrystallized from benzene–hexane; m.p. 145–146°. The hydrolyzed adduct strongly depressed the melting point of authentic maleic acid.

Anal. Calcd. for $C_{12}H_{16}O_6$: C, 56.22; H, 5.80; neut. equiv., 128.12. Found: C, 55.95, 55.85; H, 5.78, 5.98; neut. equiv., 127.8.

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

A Mechanism Study of the Reducing Action of Grignard Reagents on Fluorinated Carbonyl Compounds[1]

BY E. T. MCBEE, O. R. PIERCE AND D. D. MEYER

RECEIVED JULY 6, 1954

A study of the coördination of magnesium bromide with a series of compounds has shown that acetone, propionaldehyde and ethyl acetate form stable complexes in the ratio of 2:1 with magnesium bromide in phenetole, acetonitrile forms a 1:1 complex, but that methyl pentafluoroethyl ketone, heptafluorobutyraldehyde, ethyl trifluoroacetate and heptafluorobutyronitrile form no stable complexes. Possible mechanisms for the reaction of Grignard reagents with fluorinated compounds are discussed, and the effect of temperature and solvent are noted.

Discussion

Earlier papers[2,3] have reported large amounts of reduction products from the reaction of fluorinated carbonyl compounds with a series of Grignard reagents. These results were unexpected because of the absence of the large steric factor usually associated with reactions of this type, and were attributed to the inductive effect of the perfluoro alkyl group.

A mechanism for the reduction of a sterically hindered carbonyl compound by a Grignard reagent involving a six-membered cyclic intermediate was first suggested by Whitmore.[4] He postulated that a coördination compound was formed between the oxygen of the carbonyl group and the magnesium of the organometallic compound, followed by a shift of a beta hydrogen atom with its electrons. This is consistent with the fact that reduction is observed only in Grignard reagents that possess a hydrogen atom beta to the magnesium,[5] and that the predicted unsaturated hydrocarbon is formed in each reduction reaction.[6,7]

Studies were undertaken to determine the applicability of the cyclic mechanism to the reduction of perfluoro carbonyl compounds with Grignard reagents.

The ability of propiophenone and heptafluorobutyrophenone to coördinate with magnesium bromide was studied by means of infrared spectra. The carbonyl absorption peak of propiophenone was shifted from 5.90 to 6.05 μ when compared in ether and in magnesium bromide etherate, whereas that of the heptafluorobutyrophenone remained at 5.85 μ in both solvents.

A more quantitative determination of the coördination between carbonyl compounds and magnesium bromide was then carried out by measuring the vapor pressure of a series of compounds in phenetole. Henry's law constants were determined for acetone, propionaldehyde, ethyl acetate, acetonitrile, methyl pentafluoroethyl ketone, heptafluorobutyraldehyde, ethyl trifluoroacetate and heptafluorobutyronitrile. The plot of pressure as ordinate *vs.* number of millimoles of compound added (or mole fraction) gave the expected straight line curve going through the origin for all of the compounds tested, in agreement with the equation $P = kN$, Table I.

In the presence of a small amount of magnesium bromide, the curves for acetone, propionaldehyde and ethyl acetate were shifted along the abscissa

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[1] This paper represents part of a thesis submitted by D. D. Meyer to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] K. N. Campbell, J. D. Knobloch and B. K. Campbell, THIS JOURNAL, **72**, 4380 (1950).

[3] E. T. McBee, O. R. Pierce and J. F. Higgins, *ibid.*, **74**, 1736 (1952).

[4] F. C. Whitmore, paper presented before the Atlantic City meeting of the American Chemical Society, April, 1943.

[5] F. C. Whitmore and S. George, THIS JOURNAL, **64**, 1239 (1942).

[6] C. R. Noller, *ibid.*, **53**, 635 (1931).

[7] H. S. Mosher and E. LaCombe, *ibid.*, **72**, 3994 (1950), observed that partial asymmetric reduction was obtained in the reaction between methyl *t*-butyl ketone and (+)-2-methylbutylmagnesium chloride, which is further evidence for a cyclic intermediate. Swain and Boyles[8] found that the amount of addition product was increased at the expense of the reduction product if diisopropyl ketone was stirred with magnesium bromide etherate before being treated with *n*-propylmagnesium bromide. This is also in accord with the Whitmore mechanism, since the magnesium bromide is a stronger coördinating agent than the Grignard reagent and would preferentially coördinate with the carbonyl oxygen of the ketone.

[8] C. G. Swain and H. B. Boyles, *ibid.*, **73**, 870 (1951).