[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Thermal Isobutylene–Formaldehyde Condensation[1]

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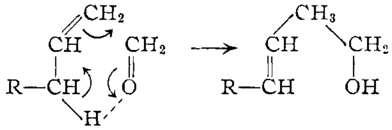
Uncatalyzed thermal condensation of isobutylene with paraformaldehyde in acetic acid–acetic anhydride affords principally 3-methyl-3-butene-1-ol acetate and 3-methylene-1,5-pentanediol diacetate. The latter is the principal product of a similar condensation of 3-methyl-3-butene-1-ol acetate with paraformaldehyde. The structure of these products was established by standard chemical and physical methods. Accessory products of the condensations which were isolated and characterized included methanol, methyl acetate and isoprene glycol diacetate. Isoprene was obtained on pyrolysis of 3-methyl-3-butene-1-ol acetate.

Recent studies of the uncatalyzed thermal condensation of olefins with formaldehyde by Bain,[2] Arnold[3] and workers in this Laboratory[4] have shown that the principal products of the reaction are unsaturated primary alcohols. Further, the carbon–carbon double bond in these alcohols has been found to occupy a position adjacent to its original location in the olefins.

$$RCH_2CH{=}CH_2 \xrightarrow[\Delta]{CH_2O\ +} RCH{=}CHCH_2CH_2OH$$

One of several possible satisfactory explanations for this shift of the unsaturation was advanced by Price[4a] and by Arnold[3] who suggested the intermediate formation of a "transient cyclic complex" as indicated below.

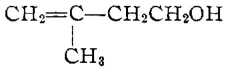


The foregoing has prompted a study of the behavior of isobutylene in its thermal condensation with formaldehyde as the expected products would be useful intermediates for the synthesis of a number of interesting simple organic compounds for polymerization reactions of the addition and condensation type.

Our experience with the thermal olefin–formaldehyde reaction had indicated that the desired products, predominately as acetates, were usually obtained in higher yields in a reaction medium of acetic acid–acetic anhydride.[4] Accordingly, such a medium was used in the present study.

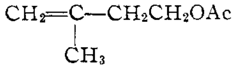
The principal products obtained upon heating paraformaldehyde with an excess of isobutylene in acetic acid–acetic anhydride for 8 hours at 190° were 3-methyl-3-buten-1-ol and its acetate, I and II (50–60%) and 3-methylene-1,5-pentanediol and its acetates, III, IV and V (13%).

A number of accessory products were also formed. Those isolated and characterized were methanol, methyl acetate and isoprene glycol diacetate, VI.



$$CH_2{=}C(CH_3){-}CH_2CH_2OH$$

I



$$CH_2{=}C(CH_3){-}CH_2CH_2OAc$$

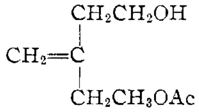
II

$CH_2{=}C(CH_2CH_2OH)_2$

III

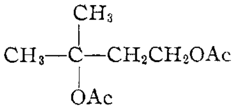
$CH_2{=}C(CH_2CH_2OAc)_2$

V



$$CH_2{=}C(CH_2CH_2OH)(CH_2CH_3OAc)$$

IV



$$CH_3{-}C(CH_3)(OAc){-}CH_2CH_2OAc$$

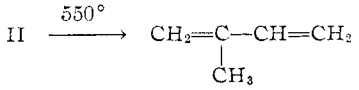
VI

Those not characterized were obtained in small amounts and included high boiling substances which presumably comprised polyhydric alcohols and their acetates resulting from formaldehyde condensations with I, II, III, IV and V.

In a second similar thermal olefin–formaldehyde condensation using pure II as the olefinic reactant the unsaturated diacetate V, containing some III and IV, was obtained in 50–60% yield. The secondary products observed here were small amounts of VI and high boiling polyhydric alcohols and their acetates.

Pure I and II were difficult to obtain by fractional distillation of the isobutylene–formaldehyde reaction mixture. Acetylation of those fractions comprising I, II and their mixtures using acetic anhydride and pyridine gave the pure acetate II, b.p. 143–144°, n^{20}_D 1.4201. Its infrared spectrum showed strong absorption at 6.05 and 11.25 μ (for $>C{=}CH_2$) and also at 5.75 μ, characteristic of an ester group.[5]

The acetate II decolorized solutions of potassium permanganate in water and bromine in carbon tetrachloride. Catalytic reduction of II required 1.05 molar equivalents of hydrogen giving a product indistinguishable from isoamyl acetate. Reductive ozonolysis of II gave formaldehyde (as its dimedon derivative) in 73% yield. Pyrolysis of II at 550° over carborundum resulted in a 73% conversion to isoprene in one pass. The isoprene obtained was characterized by its physical properties,



$$II \xrightarrow{550^\circ} CH_2{=}C(CH_3){-}CH{=}CH_2$$

including its infrared spectrum, and by its Diels–Alder adduct with maleic anhydride. Hydrolysis or methanolysis of II gave the pure unsaturated alcohol I, b.p. 131–132°, n^{20}_D 1.4340.

The pure unsaturated diacetate V was obtained

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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) J. P. Bain, THIS JOURNAL, **68**, 638 (1946).

(3) R. T. Arnold and J. F. Dowdall, *ibid.*, **70**, 2590 (1948); R. T. Arnold, R. W. Amidon and R. M. Dodson, *ibid.*, **72**, 2871 (1950).

(4) A. T. Blomquist, L. I. Diuguid, M. Passer and C. S. Schollenberger, unpublished; M. Passer, Thesis, Cornell University, 1948; C. S. Schollenberger, Thesis, Cornell University, 1947.

(4) (a) C. C. Price, "Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 45.

(5) H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., Chapt. 2.

by acetylation of a diacetate fraction having b.p. 100° (1.8 mm.) and $n^{20}\mathrm{D}$ 1.4492. The infrared spectrum of pure V, $n^{20}\mathrm{D}$ 1.4457, showed strong maxima at 6.05, 11.25 and 5.75 μ.[5] The diacetate V also decolorized solutions of potassium permanganate in water and bromine in carbon tetrachloride. Quantitative catalytic reduction of V required 1.15 molar equivalents of hydrogen and afforded the saturated diacetate VII, b.p. 98–99° (1.8 mm.), $n^{20}\mathrm{D}$ 1.4302. Reductive ozonolysis of V gave a 60% yield of formaldehyde, as its dimedone derivative.

Methanolysis or hydrolysis of V gave the pure unsaturated glycol III in 86% yield, b.p. 110–111° (0.8 mm.), $n^{20}\mathrm{D}$ 1.4785.

3-Methyl-1,5-pentanediol (VIII) was obtained in 85% yield by methanolysis of VII, b.p. 111–113° (1.0 mm.), $n^{20}\mathrm{D}$ 1.4535. The structure of VIII was confirmed by its identity with the glycol obtained by reduction of β-methylglutaric acid.

$$\begin{array}{l} \underset{\text{VII}}{\mathrm{CH_3CH((CH_2)_2OAc)_2}} \xrightarrow{\mathrm{H_2O}} \\ \qquad \underset{\text{VIII}}{\mathrm{CH_3CH((CH_2)_2OH)_2}} \xleftarrow[\mathrm{LiAlH_4}]{[\mathrm{H}]} \mathrm{CH_3CH(CH_2CO_2H)} \end{array}$$

Isoprene glycol diacetate (VI) was obtained from a mixture of products boiling between II and V. It was identified by its physical properties and its conversion to isoprene glycol, the latter being characterized by physical properties including infrared spectrum and by its phenylurethan derivative.

Experimental Part[6]

Apparatus.—Standard high pressure hydrogenation equipment fitted with a vented stainless steel liner, 3-l. capacity, was used for the olefin–formaldehyde reactions.

Thermal Condensation of Isobutylene with Formaldehyde.—In the cooled 3-l. liner containing 126.4 g. (4 moles, 95% assay) of paraformaldehyde, 240.2 g. (4 moles) of glacial acetic acid and 85.25 g. (0.8 mole) of acetic anhydride was condensed 336.0 g. (6.0 moles) of Phillips technical grade isobutylene. After placing the liner and its contents in the steel bomb, the mixture was heated with shaking for 8 hours at 190°. A maximum pressure of 525 lb./sq. in. was recorded at 190° during this period. The light straw-colored product from the cooled bomb was washed free of acetic acid and acetic anhydride with dilute aqueous sodium chloride and dilute aqueous sodium carbonate. The dried neutral mixture was distilled at atmospheric pressure through a 30-in. vacuum-jacketed column to remove the lower boiling constituents and *in vacuo* through a 30-in. Vigreux column and a 24-in. Podbielniak column to obtain higher boiling components. The following fractions were obtained: 22.0 g. of forerun, b.p. 65–110°; 271.7 g. of mixed I and II, b.p. 132–143°, $n^{20}\mathrm{D}$ 1.4347–1.4260; 20.7 g. of a mixture containing mainly VI, b.p. 84–107° (10 mm.), $n^{20}\mathrm{D}$ 1.4395–1.4435; 51.2 g. of mixed III, IV and V, b.p. 100° (1.8–2.0 mm.), $n^{20}\mathrm{D}$ 1.4492; 2.4 g. of a mixture, presumably polyhydric alcohols and their acetates, b.p. 100–130° (0.5 mm.), $n^{20}\mathrm{D}$ 1.4520–1.4550. The still residue amounted to 5.0 g.

Thermal Condensation of II with Formaldehyde.—Using the apparatus and the procedure described above, from a mixture of 128.2 g. (1.0 mole) of II, 15.8 g. (0.5 mole) of commercial paraformaldehyde, 30.25 g. (0.5 mole) of acetic acid and 16.1 g. (0.15 mole) of acetic anhydride heated at 165–170° for 8 hours the following fractions were obtained: 76.6 g. of unreacted II; 2.3 g. of VI; 51.7 g. of V, b.p. 104–105° (6 mm.), $n^{20}\mathrm{D}$ 1.4456–1.4468; and 16.0 g. showing b.p. 120–130° (0.5 mm.). The fraction comprising V gave a very weak test for the hydroxyl group with ceric nitrate. The yield of V was 51.6% based on formaldehyde and 64.3% based on II.

Acetylation of the 51.7 g. fraction of V, using the procedure subsequently described, gave V uncontaminated with any substances having free hydroxyl groups and showing b.p. 100° (1.8 mm.), $n^{20}\mathrm{D}$ 1.4457.

3-Methyl-3-buten-1-ol Acetate (II).—The fraction of mixed I and II (271.7 g., $n^{20}\mathrm{D}$ 1.4347–1.4260) was heated on a steam-bath with 102 g. of acetic acid containing 4 ml. of dry pyridine for 2 hours. The mixture, freed of excess acetic anhydride and acetic acid and dried, gave 319.2 g. of pure II on distillation, b.p. 143–144°, $n^{20}\mathrm{D}$ 1.4201. The over-all yield of pure II, based on formaldehyde, was 62.5%.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.40; sapon. no., 128. Found: C, 65.72; H, 9.49; sapon. no., 128, 129.

Reduction of 10 g. of II in ethanol at room temperature using Adams catalyst and a Parr apparatus gave 8.2 g. of distilled isoamyl acetate, b.p. 141–142°, $n^{20}\mathrm{D}$ 1.3999. The infrared spectrum of the reduced product was identical with the spectrum of authentic isoamyl acetate. The 3,5-dinitrobenzoate derivative of the product prepared by a standard method[7] showed m.p. 62° which was not depressed in a mixed m.p. determination with the 3,5-dinitrobenzoate obtained from known isoamyl acetate. Quantitative hydrogenation of II using Adams catalyst in glacial acetic acid required 1.05 molar equivalents of hydrogen.

A solution of 1.0 g. (0.0078 mole) of II in 25 ml. of methylene chloride after treatment with ozonized oxygen at Dry Ice temperature was added dropwise to a stirred refluxing solution of 0.8 g. of zinc in 25 ml. of acetic acid and heated for one hour. To the cooled filtered solution was added 4 drops of piperidine and 2 g. (0.01 mole) of dimedone. The mixture was boiled 20 minutes, cooled and water added to incipient turbidity. After standing 12 hr., 1.40 g. (60%) of the dimedone derivative was collected, m.p. 190–191°. The latter did not depress the m.p. of an authentic sample of the dimedone derivative of formaldehyde.

3-Methyl-3-buten-1-ol (I).—Hydrolysis of II was carried out in refluxing 25% ethanolic potassium hydroxide. From 12.8 g. of II there was obtained 6.0 g. of pure I, b.p. 131–132°, d^{20}_4 0.8533, $n^{20}\mathrm{D}$ 1.4340. I was also obtained easily by using the methanolysis procedure described below for preparing III.

Anal. Calcd. for $C_5H_{10}O$: C, 69.72; H, 11.90. Found: C, 69.75, 69.73; H, 11.73, 11.90.

The *p*-phenylazobenzoate of I, prepared by a standard procedure,[8] showed a m.p. of 70–71° after several recrystallizations from dilute ethanol.

Anal. Calcd. for $C_{18}H_{18}O_2N_2$: N, 9.52. Found: N, 9.60.

Pyrolysis of II to Isoprene.—Using a pyrolysis apparatus described previously,[9] 150 g. (1.21 moles) of II was pyrolyzed at 550°. With carbon dioxide passing through the furnace at a rate of one bubble per second II was added at a rate of one drop per second. The crude pyrolysate, to which hydroquinone had been added, was distilled through a 12-in. column packed with glass helices, fitted with a total reflux head cooled with ice-water, and afforded 50.1 g. of isoprene (73.5%), b.p. 33–34°, $n^{20}\mathrm{D}$ 1.4215.

From a mixture of 54.0 g. (0.55 mole) of maleic anhydride and 41.8 g. (0.614 mole) of the above isoprene in 500 ml. of benzene there was obtained in the usual way 85.6 g. (93%) of adduct showing a m.p. of 59–61°. When mixed with an authentic sample of isoprene–maleic anhydride adduct the m.p. was not depressed.

3-Methylene-1,5-pentanediol Diacetate (V).—Acetylation of 51.2 g. of the fraction showing $n^{20}\mathrm{D}$ 1.4492 and comprising a mixture of III, IV and V was carried out as described in the preparation of pure II. After fractionation through a

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[6] 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.

[7] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Ed. III, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 186.

[8] S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 193.

[9] A. T. Blomquist and J. C. Westfahl, THIS JOURNAL, **74**, 4073 (1952).

Podbielniak column, 49.5 g. (13% yield based on formaldehyde) of pure V was obtained, b.p. 100° (1.8 mm.), d^{20}_{20} 1.042, n^{20}_{D} 1.4457.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.03; H, 8.05; sapon. no., 200. Found: C, 60.07, 60.35; H, 7.99, 8.03; sapon. no., 212, 214.

Using the ozonolysis procedure described for II, 1 g. of V gave 1.07 g. (73%) of the dimedone derivative of formaldehyde.

3-Methyl-1,5-pentanediol Diacetate (VII).—Catalytic reduction of V to VII was effected in the same manner as the reduction of II. From 26.0 g. of V there was obtained 25.2 g. (95.8%) of pure VII, b.p. 98–99° (1.8 mm.), d^{20}_{20} 1.012, n^{20}_{D} 1.4308.

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97; sapon. no., 202. Found: C, 59.57; H, 9.03; sapon. no., 206, 212.

The absence of unsaturation in VII was shown by its behavior toward aqueous potassium permanganate and bromine in carbon tetrachloride. This was confirmed by its infrared spectrum.

3-Methylene-1,5-pentanediol (III).—In a flask equipped with dropping funnel, thermometer and 30-in. vacuum-jacketed column (packed with glass helices and attached to a total reflux head) was placed 328 ml. of absolute methanol. To this was added metallic sodium (0.3% by weight of the ester to be subjected to ester interchange). After the sodium had reacted, 330 g. (1.64 moles) of V was added and the mixture heated under total reflux. With the column head adjusted to a reflux ratio of 4:1 additional methanol was added to the heated mixture at a rate comparable to the distillation rate. Following the distillation with observations of b.p. and refractive index measurements, the mixture was distilled for several hours until only pure methanol was being collected. After removal of excess methanol from the mixture 165 g. (86%) of pure III was obtained on distillation; b.p. 110–111° (0.5–0.8 mm.), d^{20}_{20} 1.012, n^{20}_{D} 1.4785. The infrared spectrum of III thus obtained showed the absence of the acetate group.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found: C, 62.16, 61.93; H, 10.26, 10.35.

A sample of III prepared by saponification of V was identical with III obtained by ester interchange.

The bis-*p*-phenylazobenzoate of III, prepared by a standard method,[8] was obtained as orange plate-like crystals after several recrystallizations from dilute ethanol, m.p. 110–111°.

Anal. Calcd. for $C_{32}H_{24}O_4N_4$: C, 72.16; H, 5.29. Found: C, 72.01; H, 5.35.

3-Methyl-1,5-pentanediol (VIII). (a).—Using the methanolysis procedure described above for III, from 361 g. of VII there was obtained 188 g. (85%) of the saturated glycol VIII, b.p. 111–113° (1 mm.), d^{20}_{4} 0.9726, n^{20}_{D} 1.4535.

Anal. Calcd. for $C_6H_{14}O_2$: C, 61.01; H, 11.86. Found: C, 61.27, 61.30; H, 11.75, 11.65.

The bis-*p*-phenylazobenzoate, prepared by a standard procedure,[8] was obtained as orange plate-like crystals; m.p. 118–119°.

Anal. Calcd. for $C_{32}H_{26}O_4N_4$: N, 10.56. Found: N, 10.43.

(b).—A solution of 30.0 g. (0.2 mole) of β-methylglutaric acid in 250 ml. of anhydrous ether was added dropwise to a stirred solution of 19 g. (0.5 mole) of lithium aluminum hydride in 750 ml. of dry ether. After stirring for 4 hours, decomposing the excess hydride by the dropwise addition of the stoichiometric amount of water necessary and filtering from inorganic salts, there was obtained on distillation 9.5 g. of VIII, b.p. 128° (4.0 mm.), n^{20}_{D} 1.4535. The bis-*p*-phenylazobenzoate of this sample of VII showed m.p. 118–119° and did not depress the m.p.of the same derivative of VIII described in (a) above. The infrared spectra of the two preparations of VIII were identical.

Some Forerun Products from the Isobutylene–Formaldehyde Condensation.—A 10-g. forerun obtained on direct distillation of the unwashed isobutylene–formaldehyde reaction mixture was dried over magnesium sulfate and redistilled through a Podbielniak column affording 8 g. of material showing b.p. 62–78° and n^{20}_{D} 1.3615–1.3760. All fractions gave strong positive tests for unsaturation (permanganate solution and bromine in carbon tetrachloride). Also, positive tests for the hydroxyl group were indicated by ceric nitrate reagent. Infrared analysis of all fractions showed maxima at 2.90 μ (OH group), 5.75 μ (acetate group) and 6.02 μ (for $>C{=}C<$).[5] The foregoing indicated that a complex mixture was at hand.

Treatment of a portion of the redistilled forerun with *p*-nitrobenzoyl chloride and 3,5-dinitrobenzoyl chloride gave derivatives corresponding to those of methanol; the m.p. of the *p*-nitrobenzoate was 96° and for the 3,5-dinitrobenzoate 106–107°. Chromatographic fractionation of the redistilled forerun through alumina gave a liquid showing b.p. 57–59°, n^{20}_{D} 1.3489. The infrared spectrum and other physical properties of this liquid were identical with authentic methyl acetate.

Isoprene Glycol and its Diacetate (VI).—The fractions from the isobutylene–formaldehyde condensation showing b.p. 84–107° (10 mm.) were acetylated as described previously. This gave 18 g. of a fraction having b.p. 84° (4.0 mm.), n^{20}_{D} 1.4258. These properties correspond to those reported for authentic 3-methyl-1,3-butanediol diacetate.[10]

Methanolysis of this constant boiling fraction, using the procedure described earlier, gave a liquid showing b.p. 80° (5 mm.), n^{20}_{D} 1.4420, corresponding to the properties reported for isoprene glycol.[10] The infrared spectrum of the liquid was identical with that of authentic isoprene glycol. The phenylurethan of the methanolysis product showed m.p. 87–88° and did not depress the m.p. of the phenylurethan derivative of authentic isoprene glycol (m.p. 87–88°).

ITHACA, N. Y.

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[10] F. V. Favorsky and A. I. Lebedeva, *Bull. soc. chim.*, **6**, 1347 (1939).