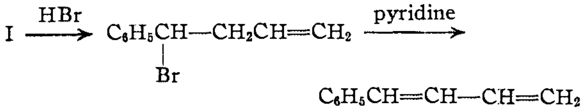
tion of the preparation of 1-phenyl-1,3-butadiene from four phenylbutenols (I–IV) has been made.

I $C_6H_5CH(OH)CH_2CH{=}CH_2$[2]
II $C_6H_5CH{=}CHCH(OH)CH_3$[3]
III $C_6H_5CH(OH)CH{=}CHCH_3$[4]
IV $C_6H_5CH_2CH(OH)CH{=}CH_2$[5]

Alcohols (I–III) were obtained by the Grignard reaction, but attempts to prepare (IV) by this reaction using the procedure of Delaby, who reported a 5% yield, gave only phenylbutadiene dimer, b. p. 250° (33 mm.),[6] and higher polymers. Alcohol (IV) is therefore probably the least stable of the four studied.

1-Phenyl-3-buten-1-ol (I) is the most stable of the alcohols (*vide infra*) and was obtained in 77% yield; it was used in preparing 1-phenyl-1,3-butadiene (46% yield from alcohol) *via* the reactions



$$\mathrm{I} \xrightarrow{\mathrm{HBr}} \underset{\substack{|\\ \mathrm{Br}}}{C_6H_5CH}{-}CH_2CH{=}CH_2 \xrightarrow{\mathrm{pyridine}} C_6H_5CH{=}CH{-}CH{=}CH_2$$

Data on the relative stability of alcohols (I–III) under dehydrating conditions were obtained by measuring the rates of water formation in solutions of each of the alcohols in benzene containing 0.1% concentrated sulfuric acid. The determined stabilities are (I) > (II) = (III). This procedure gave isolable quantities of diene monomer (6%) from (III) only.

Experimental

1-Phenyl-1,3-butadiene.—Dry hydrogen bromide was passed into a solution of 54.3 g. of 1-phenyl-3-buten-1-ol in 230 cc. C. P. benzene under reflux for five hours. Ninety per cent. of the theoretical amount of water was separated from the reaction mixture after two hours. After the benzene solution was washed free of acid with dilute aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate, it was added to 39.5 g. of pyridine and a few mg. of hydroquinone, and the resulting solution was mechanically stirred and heated under reflux for eleven hours. The supernatant liquid was decanted from the yellow, tacky precipitate which was then washed twice with benzene and was found to contain 93.5% of the theoretical amount of bromide ion; it was almost completely soluble in water. The benzene washings were combined with the decanted solution and the whole was washed seven times with water and dried over anhydrous magnesium sulfate. A small amount of hydroquinone was added and the benzene was removed *in vacuo*. The residue was a red oil which gave, upon distillation, 22 g. of 1-phenyl-1,3-butadiene [46%, based on (I)], b. p. 75–79° (6.5 mm.),[7] m. p. 1–3°.[6]

Dehydration of 1-Phenyl-3-buten-1-ol, 4-Phenyl-3-buten-2-ol and 1-Phenyl-2-buten-1-ol.—A solution of each alcohol in an equal volume of benzene containing about 0.1% concentrated sulfuric acid was heated under reflux and the returning condensate was passed over a trap from which the water was periodically withdrawn and its volume measured. Under these conditions 1-phenyl-3-buten-1-ol (I) was dehydrated only 16% in three hours while both 4-phenyl-3-buten-2-ol (II) and 1-phenyl-2-buten-1-ol (III) gave about 35% of the theoretical amount of water during the first hour and no additional water after three hours. The reaction mixtures were washed free of acid with dilute aqueous sodium bicarbonate, dried over anhydrous magnesium sulfate and distilled in the presence of hydroquinone *in vacuo*. In addition to polymeric residues which were obtained from all of the alcohols, phenylbutadiene, b. p. 96–99° (25 mm.), was obtained from the reaction with 1-phenyl-2-buten-1-ol (III) in 6% yield and 63% unchanged alcohol was recovered from the reaction with 1-phenyl-3-buten-1-ol (I).

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(2) Klimenko, *J. Russ. Phys.-Chem. Soc.*, **43**, 212 (1911).

(3) Klages, *Ber.*, **35**, 2649 (1902).

(4) Burton, *J. Chem. Soc.*, 455 (1929).

(5) Delaby, *Compt. rend.*, **194**, 1248 (1932).

(6) Liebermann and Riiber, *Ber.*, **35**, 2697 (1902).

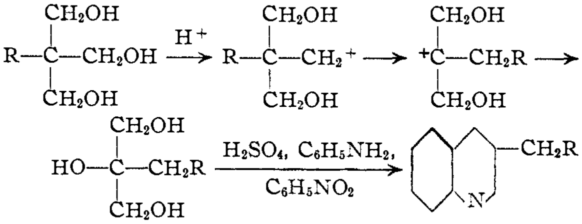
(7) Muskat and Herrman, THIS JOURNAL, **53**, 252 (1931).

Evidence of Rearrangement of Polymethylol Compounds Related to Neopentane

BY ROBERT W. BROWN[1] AND GREGG DOUGHERTY

The neopentyl system in polymethylol compounds of the type $R_2C(CH_2OH)_2$ and $RC(CH_2OH)_3$ is much more stable than it is in neopentyl alcohol, as is shown by the fact that the halides of these polyalcohols can be prepared without rearrangement by treatment with hydrogen halides.[2] The report of Fischer and Winter,[3] however, that methyl isopropyl ketone and isovaleraldehyde are formed in small amounts by the action of sulfuric acid on 2,2-dimethylpropanediol-1,3 at 200° suggests that some sort of rearrangement of the carbon skeleton takes place under sufficiently drastic conditions.

The trimethylol compounds are largely destroyed by treatment with concentrated acids at high temperatures, but as rearrangement of these compounds with migration of the alkyl group would lead to β-alkylglycerols, it appeared that the conditions of the Skraup synthesis might lead to isolable derivatives.



When 2-(hydroxymethyl)-2-methylpropanediol-1,3 was heated with aniline, nitrobenzene, and sulfuric acid, a vigorous reaction set in at about 160°. After six hours of heating at 160–170° a heavy tar was obtained, which after steam distillation and removal of primary and secondary amines by diazotization gave 10–25% yields of 3-ethylquinoline.

Under the same conditions 2-(hydroxymethyl)-2-ethylpropanediol-1,3 reacted in the same manner as the lower homolog; the product in this case being 3-propylquinoline.

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(2) Whitmore, "Organic Chemistry," D. Van Nostrand Co., New York, N. Y. 1937, pp. 368, 382.

(3) Fischer and Winter, *Monatsh.*, **21**, 301 (1900).

The quinoline derivatives were characterized by preparation of the picrates and methiodides, by analysis of the latter for iodide ion, and by oxidation to 3-quinolinecarboxylic acid.

Experimental

Materials.—The trimethylol compounds were supplied by the Heyden Corporation. A sample of 2-(hydroxymethyl)-2-methylpropanediol-1,3 was also prepared by condensation of an excess of formaldehyde with propionaldehyde in the presence of calcium hydroxide; m. p. after recrystallization from dioxane, 198–199°.

Reaction of 2-(Hydroxymethyl)-2-methylpropanediol-1,3.—A mixture of 7 g. of the alcohol, 10 g. of aniline, 11 ml. of nitrobenzene and 20 ml. of sulfuric acid was heated to 160°. A vigorous reaction set in, necessitating removal of the heating bath and external cooling of the flask. After this subsided the mixture was heated at 160–170° for six hours. The reaction mixture was made basic with 30% sodium hydroxide solution, steam distilled, the distillate acidified with dilute sulfuric acid and extracted with 30 ml. of chloroform. The acid solution was then cooled to 5° and diazotized with 10% sodium nitrite solution until an excess persisted for twenty minutes as shown by starch-iodide paper. At the end of this time the solution was heated slowly to boiling on the steam-bath. It was then made strongly basic with 30% sodium hydroxide solution and steam distilled. The distillate was extracted with three 50-ml. portions of ether and the extract dried over sodium sulfate. Removal of the ether gave 2.6 g. (28%) of crude product. Distillation at 12–13 mm. gave 2.3 g. (25%) of 3-ethylquinoline, b. p. 126–131°. The picrate was prepared by addition of a saturated solution of picric acid in alcohol to an alcoholic solution of the base; yellow needles from alcohol, m. p. 199.5–200.5°. The methiodide was prepared by reaction of the base with methyl iodide at room temperature and recrystallized from alcohol; m. p. 190–191.5°.

Anal. Calcd. for $C_{12}H_{14}NI$: I, 42.41. Found: I, 42.12.

Oxidation.—One gram of the base was dissolved in 50 ml. of 4% sulfuric acid and to it was added a solution of 4 g. of sodium dichromate in an equal volume of the same acid. The solution was heated for fifty hours on the steam-bath, then made basic with concentrated ammonium hydroxide. The hot suspension of hydrous chromic oxide was filtered off with suction and the cake washed with 30 ml. of dilute ammonia. The filtrate and washings were boiled with charcoal, filtered, acidified with acetic acid and cooled. The precipitated acid was filtered off and dried over sulfuric acid; m. p. 279–280° after recrystallization from alcohol–benzene.

Anal. Calcd. for $C_{10}H_7O_2N$: neut. equiv., 173. Found: neut. equiv., 171.

Reaction of 2-(Hydroxymethyl)-2-ethyl-propanediol-1,3.—Eight grams of the alcohol, 12 g. of aniline, 12 g. of nitrobenzene, and 25 ml. of sulfuric acid were treated as described above. The product was 1.5 g. (15%) of light yellow oil boiling at 137–140° under 11 mm. pressure. Picrate, yellow needles from alcohol, gave a m. p. 174–175°; methiodide gave a m. p. 131–132°. Oxidation with chromic acid as described above gave 3-quinolinecarboxylic acid, m. p. 279–280°.

Anal. Calcd. for $C_{13}H_{16}NI$: I, 40.52. Found: I, 40.21.

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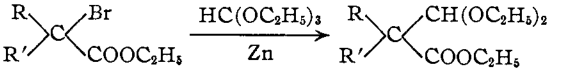
Diethyl Acetals of α-Formyl Esters

BY N. C. DENO

Tschitschibabin,[1] using a modification of the Reformatsky reaction, prepared the diethyl acetals of ethyl formylacetate and ethyl α-formylpropionate from the appropriate α-bromo ester, zinc, and ethyl orthoformate in yields of 38 and 64%, respectively. The reaction can be represented as



I

Shdanowitsch[2] reported that the reaction was successful with ethyl α-bromoisobutyrate.

In the present investigation this reaction has been applied successfully to eight α-bromo esters including the three previously investigated. Although diethyl α,α′-dibromoadipate and bromomalonic ester reacted with zinc and ethyl orthoformate, no acetal was detected.

From six of the α-bromo esters, acetal esters (I) were obtained in yields of 44–58% (Table I). On hydrolysis by alkali followed by acidification and treatment with 2,4-dinitrophenylhydrazine in 20% sulfuric acid, the acetal esters were converted to the 2,4-dinitrophenylhydrazones of simple aldehydes. Thus the derivative of isobutyraldehyde was obtained from the diethyl acetal of ethyl α-formyl isobutyrate. With the diethyl acetal of ethyl α-formyl-*n*-valerate, which was expected to give the 2,4-dinitrophenylhydrazone of *n*-valeraldehyde, only an impure product was obtained.

The acetal esters, when treated with 2,4-dinitrophenylhydrazine in 20% aqueous sulfuric acid, gave 2,4-dinitrophenylhydrazones without hydrolysis of the ester group. Their properties are listed in Table II.

Tschitschibabin[1] reported that the product from ethyl α-bromoacetate was contaminated with ethyl β-ethoxyacrylate formed by splitting out of ethanol from the acetal. Under the conditions used in the present investigation the product was about an equal mixture of ethyl β-ethoxyacrylate and the diethyl acetal of ethyl formylacetate. This mixture could be converted completely to the acrylate ester by heating at 190–200° (gentle refluxing) for one hour.

The product isolated from ethyl bromocyanoacetate was ethyl α-cyano-β-ethoxyacrylate.

This reaction constitutes a good preparative method for diethyl acetals of α-formyl esters. It is especially valuable when there are two alkyl groups in the α position, since esters such as ethyl isobutyrate undergo base-catalyzed formylation only with difficulty.[3]

Experimental

Diethyl Acetals of α-Formyl Esters.—In all runs listed in Table I the following procedure was used which gave better temperature control than the method of Tschitschibabin which did not use any solvent. About 100 g.

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[1] Tschitschibabin, *J. prakt. Chem.*, **73**, 326 (1906).

[2] Shdanowitsch, *J. Russ. Phys.-Chem. Soc.*, **42**, 1279 (1910).

[3] Hudson and Hauser (THIS JOURNAL, **63**, 3156 (1941)) obtained a 16% yield of ethyl α-formylisobutyrate using triphenylmethylsodium as the agent to condense ethyl formate and ethyl isobutyrate.