ml. of dry ether. The clear filtrate was evaporated in a dry air stream at 100° and the product crystallized from 100 ml. of acetone to produce 2.4 g. (70%) of 3,5-cholestadiene, m. p. 73–74°. Crystallization from acetone then absolute ethanol raised the m. p. to 76–77°, $[\alpha]^{22.5}\mathrm{D}$ −96.5 (109.8 mg. made up to 5 ml. with chloroform, α, −4.24°; l, 2 dm.); $\gamma_{\max}$ (obs.) 236. These values are in agreement with those of the literature, m. p. 78–79°,[13] $[\alpha]^{20}\mathrm{D}$ −97.5,[13] $\gamma_{\max}$ (obs.) mμ 235.[14] The diene gives a 20° depression in m. p. when mixed with *i*-cholestadiene[15] and its ultraviolet spectrum is clearly different from that of the *i*-diene.[16]

Isolation of 5-Cholestene.—Separate experiments generally were made to determine the extent of cholestene formation. The product resulting from the reaction of 0.026 mole of diacetyl with a mixture of 0.024 mole of cholesterylmagnesium chloride was treated so as to remove bicholesteryl. Of the remaining 8.3 g. of oil, 2 g. was dissolved in 50 ml. of petroleum ether (30–60°) and passed through a 17 by 1 cm. column packed with Brockman alumina. The eluate, 45 ml., and the first 15 ml. fraction of petroleum ether washings gave upon evaporation 1.26 g. of product, m. p. 80–84°. Crystallized once from acetone the m. p. was 85–87°, $[\alpha]^{24.5}\mathrm{D}$ −53.5°. The literature[17] values are 89–90° and −56.3°.

Acknowledgment.—We are grateful to Professor Byron Riegel for help and encouragement during the course of this work.

Summary

1. Methyl cholesteryl ketone has been prepared by the reaction of cholesteryl Grignard reagents with acetaldehyde followed by oxidation of the impure carbinol and by Grignard alkylation of cholesteryl-3-carboxylic acid chloride. Its semicarbazone is described.

2. The ketone has been degraded back to cholesteryl-3-carboxylic acid.

3. 3-Cholesteryl-5-cholestene has been identified as a by-product of the formation of cholesteryl Grignard reagents.

4. 5-Cholestene is formed in large quantity in the reaction of cholesteryl Grignard reagents with a variety of compounds.

5. 3,5-Cholestadiene is conveniently prepared by the reaction of cholesteryl *p*-toluenesulfonate with potassium cyanide.

6. Ethyl cholesteryl ketone, its semicarbazone, and dimethylcholesterylcarbinol have also been prepared.

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[13] Stavely and Bergmann, *J. Org. Chem.*, 1, 567 (1937).

[14] Woodward, THIS JOURNAL, **64**, 74 (1942).

[15] Kindly furnished by Professor Byron Riegel.

[16] We are indebted to Professor I. M. Klotz and his associates for determining this spectrum, *cf.* Klotz, *ibid.*, **66**, 88 (1944).

[17] Mauthner, *Monatsh.*, **28**, 1113 (1907).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Cleavage of Benzyl Ethers with Hydrogen

BY ROBERT H. BAKER, KATHRYN HEROLD CORNELL AND MARTIN J. CRON

Recently it has been shown that vinyl ethers and amines which are so substituted as to activate the alkyloxy or alkylamino group may be cleaved by hydrogen prior to saturation of the double bond which carries the activating effect.[1] It was hoped that the remarkable promoting effects of perchloric and sulfuric acids[2] might allow preferential cleavage of unsaturated benzyl ethers, but the results, Table I, were not promising.

Cyclic ethers bearing phenyl groups on the α carbon atom have been found to undergo hydrogenolysis. 2-Phenyltetrahydropyran[3] yields 5-phenylpentanol and since the starting materials are easily available, a convenient synthesis for 5-arylpentanols is indicated. Phenyldioxane and 2,3-diphenyldioxane[4] reacted, respectively, with one and two moles of hydrogen. The 2-(2-phenylethoxy)-ethanol produced from the former of these demonstrated that the ether linkage β to a phenyl group is quite stable under the conditions which will completely cleave a similar group in the α position.

Two isomeric compounds, m. p. 122 and 174°, to which the structure of *cis* and *trans* 2,5-diphenyldioxane have been tentatively assigned failed to behave in the expected manner.[5] Over palladium–charcoal they showed no reduction in acetic acid; with added hydrochloric acid the reduction was very slow and with added perchloric or sulfuric acids they took up three moles of hydrogen with no diminution of the rate at two moles. This can hardly be due to cleavage of 2-phenylethanol followed by its reduction to ethylbenzene because this would require four moles of hydrogen and repeated values of three would be unexpected. Further evidence against this explanation is seen in the behavior of phenethyl benzyl ether and in the fact that 2-phenylethanol takes up only 4% of one mole of hydrogen in the time and under the conditions required for complete cleavage of the phenyldioxanes.

A liquid described as 2,6-diphenyldioxane was

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[1] Baker and Weiss, THIS JOURNAL, **66**, 343 (1944); Baker and Schlesinger, *ibid.*, **68**, 2009 (1946).

[2] Karg and Marcus, *Ber.*, **75**, 1850 (1942); Kindler and Kwok, *Ann.*, **554**, 9 (1943).

[3] Paul, *Compt. rend.*, **198**, 1246 (1934).

[4] The aryldioxanes were furnished by Prof. R. K. Summerbell, *cf.* Summerbell and Bauer, THIS JOURNAL, **57**, 2364 (1935).

[5] These compounds were prepared by Aldro Bryan, Ph.D. Thesis, Northwestern University, 1945, by reaction of 2,5-dichlorodioxane with a phenyl Grignard. They were believed to contain no acetal or ketal linkage on the basis of stability to acid hydrolytic conditions. Dibromination followed by hydrolysis and treatment with phenylhydrazine produced the osazone of phenylglyoxal in poor yield. The compound referred to as 2,5-diphenyl-1,4-dioxane, m. p. 147–152°, by Smedley, U. S. Patent 2,414,982; *C. A.*, **41**, 2755 (1947), is in fact the source of these isomers.

TABLE I

HYDROGENATIONS WITH PALLADIUM–CHARCOAL

Compound	Run	Milli-moles	Cat., mg.	Solvent[a]	Moles H_2	Time, min.	% Products isolated
Benzyl allyl ether	1	1	35	AcOH	2	100	
	2	1	35	Ac–P	2	40	
	3	1	35	EtOH	1	60	
Benzyl methallyl ether	4	1	35	AcOH	2	60	
	5	1	35	Ac–P	2	50	
	6	1	35	EtOH	1	80	
Benzyl 2-phenylethyl ether	7	100	500	Ac–S	1	90	86 $C_6H_5CH_2CH_2OH$
2-Phenyltetrahydropyran	8	56	1000	Ac–P	1	35	72 $C_6H_5(CH_2)_5OH$
Phenyldioxane[4]	9	1	35	Ac–S	1	120	75 $C_6H_5CH_2CH_2OCH_2CH_2OH$
2,3-Diphenyldioxane[4]	10	1	35	Ac–P	1	180	83 $C_6H_5CH_2CH_2C_6H_5$
122°-Isomer[5]	11	1	35	Ac–S	2^b	36	[c]
	12[d]	1	100	Ac–S	3	45	40–48 $C_6H_5CH_2CH_2OH$
	13	1	35	Ac–P	3	48	[c]
	14	1	35	Ac–HCl	2^b	140	31 Starting cpd.
174°-Isomer[5]	15	1	35	Ac–S	2^b	42	[c]
Liquid isomer[6]	16	12	500	Ac–S	1.8^b	195	10 $C_6H_5CH_2CH_2OH$
Benzoin diethylacetal[7]	17	1	100	Ac–P	3	30	.. $C_6H_5CH_2CH_2C_6H_5$

[a] Ac–P and –S refer to acetic acid containing 2.5% of 60% aqueous perchloric or 2% sulfuric acid, respectively. The millimolar runs employed 4 ml. and the 0.1 molar 40 ml. of solvent. [b] These runs were stopped short of completion. [c] The unmistakable odor of 2-phenylethanol was observed but no derivatives were obtained. [d] Average values of three identical runs.

kindly furnished by Dr. W. S. Emerson.[6] Two middle fractions of it, b. p. 158–162° and 162–163° (2 mm.), n^{20}_{D} 1.5602, were combined and subjected to incomplete hydrogenation. No product corresponding to the expected diphenethyl ether could be isolated by 3-plate fractionation. The lowest boiling fraction, 75° at 2 mm., n^{20}_{D} 1.5109, was shown to contain 2-phenylethanol.

Benzoin diethylacetal was studied because of its similarity of structure to some of the other compounds in Table I. The compound is very difficult to obtain by the published method,[7] and is obtained only when very dry reagents are used and the reaction mixture is allowed to stand in the cold for twenty-one days. The oil which is obtained slowly produces crystals from petroleum ether, b. p. 60–80°, and after two more crystallizations gives the acetal, m. p. 67–68° in 3% yield. The compound could not be hydrogenated over palladium on charcoal in ethanol even at 70°.

Experimental

Preparation of Compounds.—Benzyl allyl ether has been described previously.[8] It was prepared in 65% yield by reaction of 2.1 moles of benzyl chloride with 2.1 moles of sodium allyloxide in excess allyl alcohol, b. p. 204–205°; n^{20}_{D} 1.5090; d^{25}_4 0.959.

Benzyl methallyl ether was made in a similar manner from 5.4 moles of dry methallyl alcohol, 1.56 moles of sodium and 1.56 moles of benzyl chloride. The crude ether, b. p. 110–118° at 13 mm., was subjected to 10-plate fractionation to give 33% yield, b. p. 113–114° at 12 mm.; n^{20}_{D} 1.5095; d^{25}_4 0.958; M_{D} calcd., 50.57, found 50.59.

Benzyl 2-phenylethyl ether was similarly prepared but from sodium 2-phenylethyloxide in toluene, b. p. 175–178° at 13 mm., n^{20}_{D} 1.5545.[9]

2-Phenyltetrahydropyran was prepared from dihydropyran according to the method of Paul.[3] The crude product, b. p. 110–114° at 12 mm., from the first distillation was distilled again to duplicate the published physical properties. The sources of other materials are noted in Table I.

Hydrogenations.—The millimolar reactions were carried out at one atmosphere pressure in a shaking vessel of 8-ml. capacity attached to a hydrogen buret. Palladium on charcoal (5%) obtained from Wilkens-Anderson Company, Chicago, was used in all the runs. In the small runs the catalyst was shaken with hydrogen to constant volume before dropping the sample, contained in a thimble, into the reaction mixture. Larger runs were carried out in standard size apparatus at 3 atmospheres. The data are summarized in Table I.

Isolation and Identification of Products.—No attempts to isolate products from the allyl and methallyl ethers were made. The reaction mixtures which were expected to contain alcohols were poured into 10% sodium hydroxide–ice mixtures and were refluxed for thirty minutes to saponify acetate esters which often form in the presence of noble metal catalysts. The neutral materials were extracted from the alkaline saponification mixtures with ether or tetrachloroethane. It was proved independently that tetrachloroethane could be distilled from 2-phenylethanol without loss of the latter.

An analytical procedure was used to determine the quantity of 2-phenylethanol resulting from Run 12 in dry tetrachloroethane, the procedure being standardized with known samples of the alcohol.[10] From other runs similar to 12 the alcohol was identified as its 1-naphthylcarbamate, m. p. 116–117° (lit.[11] 119°). This alcohol was otherwise identified from Run 7 by physical constants, and from Run 16 by its allophanate, m. p. 184–185°, (lit.[12] 186°).

2-(2-Phenylethoxy)-ethanol from Run 9 was also identified as its allophanate, m. p. 148–149° (from toluene), lit.[13] 150°. 1,2-Diphenylethane was purified by sublimation *in vacuo*, m. p. and mixed m. p. with an authentic sample, 51.5–52°, lit.[14] 52°.

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[6] Emerson, THIS JOURNAL, **67**, 516 (1945).

[7] Ward, *J. Chem. Soc.*, 1541 (1929).

[8] v. Braun, *Ber.*, **43**, 1350 (1910).

[9] This preparation will be the subject of a future publication.

[10] Adkins, Frank and Bloom, THIS JOURNAL, **63**, 554 (1941).

[11] McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 195.

[12] Béhal, *Bull. soc. chim.*, [4] **25**, 473 (1919).

[13] Halasz, *ibid.*, [5] **8**, 170 (1941).

[14] Ref. 11, p. 237.

5-Phenylpentanol from Run 8, b. p. 142–148° at 10 mm., d^{26}_4 0.9857, had the characteristic odor of lemons and compared favorably with the product as previously described, b. p. 140–142° at 16 mm., d^{26}_4 0.9651.[15] Since no direct derivatives were found, the alcohol was converted into crude 5-phenylpentyl bromide by refluxing with hydrobromic acid containing a trace of sulfuric acid. The bromide was refluxed in ethanol with an equivalent of ammonium dithiocarbamate[16] to produce an oil which upon crystallization from ether–petroleum ether gave 5-phenylpentyl dithiocarbamate, m. p. 72–74°, lit.[17] 75°.

Summary

1. In acid solution it is not practical to selectively hydrogenate allyl or methallylbenzyl ethers over palladium–charcoal.
2. The structures of certain aryldioxanes have been proved by hydrogenation.
3. Some compounds isomeric with 2,3-diphenyldioxane do not react with hydrogen in ways consistent with their suspected structures.
4. A convenient synthesis of 5-phenylpentanol has been described.

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[15] v. Braun, Anton and Weissbach, *Ber.*, **63**, 2847 (1930); v. Braun, *ibid.*, **44**, 2867 (1911).

[16] Mulder, *Ann.*, **168**, 228 (1873).

[17] v. Braun, *Ber.*, **45**, 1563 (1912).

[CONTRIBUTION FROM THE LABORATORY OF RADIOCHEMISTRY, UNIVERSITY OF CINCINNATI]

3-Nitrofluorenone

BY FRANCIS EARL RAY AND JAMES G. BARRICK

Mononitration of fluorene yields only 2-nitrofluorene. As this is easily oxidized to 2-nitrofluorenone the properties of both compounds are well known.[1]

4-Nitrofluorenone also seems to be well known, having first been prepared by Schmidt and Baur,[2] from the known 4-nitrophenanthraquinone by means of the benzilic acid rearrangement followed by oxidation and decarboxylation. Courtot[3] and Bell[4] have confirmed this work.

1-Nitrofluorenone has not been prepared.

3-Nitrofluorenone was first reported by Schmidt and Soll[5] who obtained it by the simultaneous nitration and oxidation of 9,10-diaminophenanthrene to 3-nitrophenanthraquinone. A benzilic acid rearrangement, followed by oxidation and decarboxylation gave a compound melting at 209–210° which was described as 3-nitrofluorenone. Its oxime melted at 240°. As the structure of 3-nitrophenanthraquinone had been proved conclusively by J. Schmidt[6] seven years previously, there seemed no reason to question the identity of Schmidt and Soll's compound. Especially was this true after the appearance of the paper by Eckert and Langecker[7] in 1928.

Using a different method, the simultaneous nitration and oxidation of 2-acetylaminofluorene to 3-nitro-2-amino-fluorenone followed by removal of the 2-amino group, Eckert and Langecker obtained identical melting points, Table I. Eckert and Langecker proved the position of the nitro group by converting their compound to the known 3-hydroxyfluorenone.[8]

Better evidence for the identity of 3-nitrofluorenone could hardly be desired. Nevertheless, in 1931 Bardout[9] reported that his preparation of this compound by essentially Eckert and Langecker's method yielded 3-nitrofluorenone melting, not at 210°, but at 239°. The oxime instead of melting at 240°, as previously reported, melted at 221°, cor. Bardout also converted his compound to the known 3-hydroxyfluorenone as well as to the known 3-bromofluorenone.[10]

In the course of his synthesis Bardout also obtained 3-nitrofluorene melting at 105°. Hayashi and Nakayama[11] repeated the synthesis of 3-nitrofluorene and found the same melting point as Bardout. They did not, however, oxidize it to the fluorenone.

With a view to resolving this difficulty, Scheer[12] attempted to repeat Bardout's synthesis but found great difficulty in isolating pure compounds. Repeating Schmidt and Soll's work, he obtained, supposedly, 3-nitrofluorenone which melted considerably higher than Schmidt and Soll's and Eckert and Langecker's compound but not quite as high as Bardout's. From the two degree range in melting point Scheer concluded that his material was still impure. The significant part remains that even the impure material melted considerably higher than the first investigators reported. A summary of these results will be found in Table I.

It seemed of interest, therefore, to attempt an entirely *new* synthesis of 3-nitrofluorenone in the hope of settling the controversy.

Our starting material was the readily available 2-aminobiphenyl. This was treated with toluenesulfonyl chloride and the product nitrated accord-

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[1] "Organic Syntheses," Coll. Vol. II, 447 (1943); Barbier, *Ann. chim. phys.*, [5] **7**, 479 (1876); Ullmann and Mallett, *Ber.*, **31**, 1694 (1898).

[2] Schmidt and Baur, *Ber.*, **38**, 3737 (1905).

[3] Courtot, *Ann. chim.*, [10] **14**, 5 (1930).

[4] Bell, *J. Chem. Soc.*, 1990 (1928).

[5] Schmidt and Soll, *Ber.*, **41**, 3691 (1908).

[6] J. Schmidt, *ibid.*, **34**, 3531 (1901).

[7] Eckert and Langecker, *J. prakt. Chem.*, **118**, 263 (1298).

[8] Ullmann and Bleier, *Ber.*, **35**, 4279 (1902); Errera and La Spada. *Gazz. chim. ital.*, **35**, 539 (1905).

[9] Bardout, *Anales asoc. quim. argentina*, **19**, 117 (1931); **22**, 123 (1934).

[10] Montagne, *Rec. trav. chim.*, **28**, 449 (1909); Montagne and van Charenti, *ibid.*, **32**, 164 (1913).

[11] Hayashi and Nakayama, *J. Soc. Chem. Ind. Japan*, **36**, 1278 (1933).

[12] Scheer, Master's Thesis, University of Cincinnati, 1942.