[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

Oxetanes. VII. Synthesis from 1,3-Diols. Reactions of Oxetanes and of 1,3-Butanediol with Hydrogen Chloride, Hydrogen Bromide and Acetyl Chloride[1,2]

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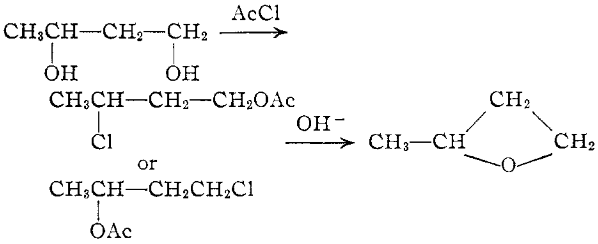
An improved synthesis of 2-methyloxetane consists of the reaction of 1,3-butanediol with acetyl chloride to form the chlorohydrin acetate, followed by reaction of the latter with hot alkali. The same general method was used to synthesize two new oxetanes, 2,3-dimethyloxetane and 3-ethyl-2-propyloxetane. The halohydrins and chlorohydrin acetate derived from 1,3-butanediol were found in every case to be mixtures of 1,3 and 2,4-isomers, the product composition being determined by infrared spectral analysis. The pure isomers were synthesized and used for reference. The composition of the products from the reactions of 2-methyloxetane with acetyl chloride, hydrogen chloride and hydrogen bromide indicated that this 4-membered cyclic ether may function as the intermediate in the acetyl chloride–diol reaction, and in the reactions with the hydrogen halides it may partially function so. The reaction of 2-phenyloxetane with hydrogen chloride or with acetyl chloride gives only the primary alcohol or acetate.

Although many 1,3-diols are readily available, their use as starting materials for the synthesis of oxetanes (1,3-epoxides) has been exploited relatively little. The conversion of the diol to the halohydrin and treatment of the latter with alkali to close the ring by an intramolecular Williamson reaction should be a simple and attractive method. In practice, however, difficulty is often experienced in the first step, so that a more complicated route is employed. For example, the reaction of 1,3-butanediol with hydrogen chloride, which is described in the patent literature,[3] was found to give only a 43% yield of the chlorohydrin.[4]

In our work a significant improvement in the synthesis of oxetanes from 1,3-diols was found in the use of the reaction of the diol with acetyl chloride, instead of with a hydrogen halide, as the first step. Not only is the yield in the first step much better, but the product is the chlorohydrin acetate, which generally reacts with alkali to form the oxetane in better yield than does the chlorohydrin. (In fact, it is usually advantageous to acetylate a chlorohydrin before closing the ring with hot alkali.[5–7])

The reaction of 1,3-butanediol with acetyl chloride has been reported previously[8] and the product stated to be 3-chloro-1-butyl acetate. The reaction has been confirmed recently and used to prepare "3-chloro-1-butanol" in 73% yield.[9] In our work an 83% yield of the chlorohydrin acetate was obtained, and treatment of this with hot alkali produced 2-methyloxetane in 52% yield—43% over-all yield from inexpensive 1,3-butanediol in two relatively simple steps. The method seems to be distinctly superior to the previously reported methods, which involve either the aforementioned diol–hydrogen chloride reaction,[3] the synthesis and reduction of 4-chloro-2-butanone[4] or the synthesis of 3-chloropropionaldehyde and its reaction with methylmagnesium bromide.[7]



This synthesis is certainly capable of extension to many other oxetanes, although no attempt has been made as yet to define its scope. With only slight modifications, however, it was used to synthesize 2,3-dimethyloxetane in 40% over-all yield from 2-methyl-1,3-butanediol, and 3-ethyl-2-propyloxetane in 29% over-all yield from 2-ethyl-1,3-hexanediol. The structure of these two new oxetanes was established by cleavage with lithium aluminum hydride to form 3-methyl-2-butanol and 3-methyl-4-heptanol, respectively.[10]

The structure of the halohydrin or chlorohydrin acetate intermediates in these syntheses of substituted oxetanes from diols is an interesting problem. Since the two hydroxyls are generally not equivalent, two isomers are possible for each product. It is somewhat surprising that 1,3-butanediol is reported to react with hydrogen chloride to give substantially pure 4-chloro-2-butanol.[3] This would appear to be a reversal of the usual order of reaction of primary and secondary carbinol groups toward halogen acids. The product of 1,3-butanediol and acetyl chloride, on the other hand, is reported to be 3-chloro-1-butyl acetate, as one might normally expect, but recently doubt has been cast on this structure.[11] Contributing to the confused picture of the relative reactivity of the primary and secondary hydroxyls in 1,3-butanediol, is the report that hydrogen bromide and hydrogen iodide react to give 4-bromo-2-butanol

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[1] This work was supported by a National Science Foundation research grant.

[2] Taken from parts of the Ph.D. dissertations of K. A. P. and F. B., Kansas State College.

[3] Celanese Corp. of America, British Patent 585,245 (Feb. 3, 1947); *C. A.*, **41**, 4167 (1947).

[4] F. Sondheimer and R. B. Woodward, THIS JOURNAL, **75**, 5438 (1953), also found that "[this] method . . . proceeded only in poor yield."

[5] R. Lespieau, *Bull. soc. chim.*, [5] **7**, 254 (1940).

[6] C. G. Derick and D. W. Bissell, THIS JOURNAL, **38**, 2478 (1916); C. R. Noller, *Org. Syntheses*, **29**, 92 (1949).

[7] N. G. Gaylord, J. H. Crowdle, W. A. Himmer and H. J. Pepe, THIS JOURNAL, **76**, 59 (1954).

[8] I. G. Farbenind, A.-G., German Patent 524,435 (April 24, 1929); *C. A.*, **25**, 3666 (1931).

[9] R. I. Meltzer and John A. King, THIS JOURNAL, **75**, 1355 (1953).

[10] S. Searles, K. A. Pollart and E. F. Lutz, *ibid.*, **79**, 948 (1957).

[11] Meltzer and King (reference 8) found that their supposed 3-chloro-1-butanol, obtained by acid-catalyzed methanolysis of the chlorohydrin acetate, reacted with a phenoxide to give a 3-hydroxy-1-butyl ether. They suspected that either the chloro ester was at least partly 4-chloro-2-butyl acetate or that a rearrangement had occurred subsequently. Later they found the chlorohydrin gave a strong iodoform test (Dr. John A. King, private communication).

and 4-iodo-2-butanol,[12] again contrary to what would normally be expected.

These "abnormal" products might conceivably arise from the diol cyclizing to 2-methyloxetane (or its conjugate acid), followed by cleavage with the hydrogen halide (or halide ion). This mechanism was suggested recently to explain the previously reported result with hydrogen iodide,[13,14] and an oxetane intermediate was postulated many years ago to explain rearrangements in the reaction of 1,3-halohydrin esters with amines.[15]

It is noteworthy, however, that no evidence has been published to support the structures of any of these products from hydrogen halides or acetyl chloride and 1,3-butanediol, except in the case of the iodohydrin. Catalytic reduction of that material gave some 2-butanol, but a considerable amount of a higher boiling fraction was also reported, which was not identified but which could well have been 1-butanol.[11] The so-called "4-iodo-2-butanol" was very likely a mixture of that substance with 3-iodo-1-butanol.

Before credence can be given to a mechanism involving an oxetane intermediate, it is certainly necessary to establish what the products are and to investigate the reaction of 2-methyloxetane with the reagents in question. This has been undertaken in this work. All of the products, except the unstable iodohydrin, had been prepared in connection with the study of the synthesis of 2-methyloxetane. It was possible to determine the compositions of these products by simply preparing for reference the pure compounds suspected of being present and by performing a quantitative infrared spectral analysis on the diol products.

The preparation of the authentic compounds was accomplished as follows: 3-Chloro-1-butanol was obtained by lithium aluminum hydride reduction of 3-chlorobutyric acid, the product of addition of hydrogen chloride to crotonic acid. The synthesis of 3-bromo-1-butanol was performed analogously, except that the ester of the bromo acid was used as the intermediate. 4-Chloro-2-butanol was made by lithium aluminum hydride reduction of 4-chloro-2-butanone, derived from methyl vinyl ketone and hydrogen chloride. 4-Bromo-2-butanol was prepared by sodium borohydride reduction of 4-bromo-2-butanone (obtained from methyl vinyl ketone and hydrogen bromide), since lithium aluminum hydride brought about dehydrobromination. The pure chlorohydrin acetates were prepared by acetylation of each pure chlorohydrin. The common physical properties of the isomers proved so similar that it was not feasible to use them for a method of analysis.

The compositions found for the various halogen products derived from 1,3-butanediol are compiled in Table I. It was observed that all are mixtures of the isomers resulting from rather non-selective reaction of the reagent with both hydroxyl groups of the diol. In the case of the chlorohydrin acetate, the secondary chloride that had been reported to be the product was present to the extent of only about 40%, the other isomer being the major constituent of the product mixture. With each of the halohydrins, however, the primary halide previously reported as the product did prove to be in slight excess over the secondary halide; addition of water and zinc chloride, though, gave predominance of the secondary chloride. It was noted that acid-catalyzed methanolysis of the chlorohydrin acetate proceeded without rearrangement, and the composition of the resulting chlorohydrin explains the results of Meltzer and King.[11]

TABLE I

HALOHYDRIN PRODUCTS FROM 1,3-BUTANEDIOL

Reagent	Product	Yield, %	I,[a,b] %	II,[a,b] %
HCl (dry, 170°)	Chlorohydrin	43	57	43
HCl (aq.)	Chlorohydrin	39	45	55
HCl + $ZnCl_2$ (aq.)	Chlorohydrin	20[c]	15	30
HBr (dry 0°)	Bromohydrin	36	60	40
$CH_3COCl + CaCl_2$	Chlorohydrin acetate	83	61	39
CH_3OH (on above ester[d])	Chlorohydrin	98	62	38

[a] I is the primary halide, $CH_3CH(OR)CH_2CH_2X$, and II, the secondary halide, $CH_3CHXCH_2CH_2OR$, where R is H or acetyl. [b] The average values of several determinations are given; the precision is about 5%. [c] This product apparently contained other materials besides I and II; their nature, however, is not known. [d] Procedure of Meltzer and King, reference 9.

The products from the reactions of 2-methyloxetane with hydrogen chloride, hydrogen bromide and acetyl chloride were analyzed by the same infrared method. The results, presented in Table II, show that the primary halide was formed predominantly from the two acids under the variety of conditions used. The proportion of secondary halide was greater in water solution than in ben-

TABLE II

HALOHYDRIN PRODUCTS FROM 2-METHYLOXETANE

Conditions	Product	Yield, %	I,[a,b] %	II,[a,b] %
HCl (dry), C_6H_6, 0°	Chlorohydrin	70	94	6
HCl (dry), C_6H_6, 80°	Chlorohydrin	26[c]	80	20
HCl (dry), $C_6H_4(CH_3)_2$, 140°	Chlorohydrin	11[c]	40	10
HCl (5% aq.), 5°	Chlorohydrin	39[d]	73	27
HCl (5% aq.), 100°	Chlorohydrin	22	71	29
HCl (37% aq.), 5°[e]	Chlorohydrin	72	79	21
CH_3COCl, C_6H_6, 5°	Chlorohydrin acetate	36	63	37
HBr (dry), C_6H_6, 5°	Bromohydrin	80	98	2
HBr, 5%, 5°	Bromohydrin	37	90	10
HBr, 5%, 99°	Bromohydrin	5	71	29

[a] I is the primary halide, $CH_3CH(OR)CH_2CH_2X$, and II is the secondary halide, $CH_3CHXCH_2CH_2OR$, with R either H or acetyl. [b] Average values of the several determinations are given; the ranges observed were 2–5%. [c] Formation of crotyl chloride and polymer observed. [d] The yield of crotyl chloride was 9%. [e] When this experiment was repeated with the reaction mixture saturated with sodium chloride, the composition of the chlorohydrin was the same, but the yield dropped to 60% and 31% of crotyl chloride was isolated.

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[12] P. A. Levene, A. Walti and H. L. Haller, *J. Biol. Chem.*, **71**, 465 (1926).

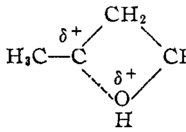
[13] W. v. E. Doering and R. W. Young, THIS JOURNAL, **74**, 2997 (1952).

[14] K. B. Wiberg, *ibid.*, **74**, 3891 (1952).

[15] E. Fourneau and P. Ramart-Lucas, *Bull. soc. chim.*, [4] **27**, 550 (1920).

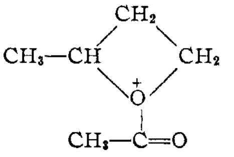
zene, though small in both cases, and was increased slightly with raise of temperature. (The temperature effect was complicated by other reactions at higher temperatures, such as crotyl halide formation.) The general picture, however, greatly resembles that for the reaction of the hydrogen halides with propylene oxide,[16] except that the proportion of the primary halide is higher under comparable conditions, and fits a predominantly SN2 mechanism.

Although it was not feasible to use 1,3-butanediol as solvent, so as to duplicate precisely the conditions of the reaction of that diol with the hydrogen halides, the small effect of solvent and temperature observed on the product composition makes it likely that the results would have been about the same. Thus, the proportion of primary halide from diol–hydrogen halide reactions is too low to admit as a reaction intermediate 2-methyloxetane or its conjugate acid; yet it seems higher than one might expect if there were no interaction between the two hydroxyls. It may be that reaction at the secondary hydroxyl gives rise to an oxetane-like intermediate (I) which, however, is more prone to react at the secondary carbon than the oxetane, since the ether linkage at that carbon is not fully formed.



I

In contrast to this, it was found that the reaction of acetyl chloride with 2-methyloxetane gave exactly the same product proportions as 1,3-butanediol. Here, then, it would appear that the diol and the oxetane were reacting *via* a common intermediate, most reasonably written as II.



Cl^-

II

The reactions of 2-phenyloxetane with hydrogen chloride and with acetyl chloride were studied to give a comparison of the effect of methyl and phenyl substitution. The only chlorohydrin isomer formed from the reaction of hydrogen chloride in both aqueous and non-aqueous solution was 3-chloro-3-phenyl-1-propanol. The yields were only 19–35%, due to its thermal instability, forming cinnamyl alcohol, etc., but no evidence for the chlorohydrin isomer with primary chlorine was obtained. Likewise, the reaction with acetyl chloride in benzene gave a 75% yield of 3-chloro-3-phenyl-1-propyl acetate. Thus, change from a methyl to a phenyl group changes the cleavage from being predominantly at the less substituted carbon to entirely at the more substituted carbon—in marked contrast to the effect of substitution on direction of reductive cleavage by lithium aluminum hydride.[10] The cleavage of styrene oxide with hydrogen iodide to form 2-iodo-2-phenyl-1-propanol furnishes an analogy in the corresponding 3-membered ring system.[17] Apparently 2-phenyloxetane can react *via* a carbonium ion when the oxygen is coördinated with a strong electron-accepting unit.

Another difference in the effect of substituents in the reactions of oxetanes with hydrogen chloride and with lithium aluminum hydride, is the lack of the pronounced deactivating effect of the *gem*-dimethyl group at position 3. 3,3-Dimethyloxetane appeared to react with hydrogen chloride in benzene approximately as rapidly as trimethylene oxide. The underlying factors here will be given further attention.

Experimental[18]

2-Methyloxetane.—The reaction of 200 g. of 1,3-butanediol with 208 g. of acetyl chloride and 38.8 g. of anhydrous calcium chloride was carried out by the procedure of Meltzer and King,[9] giving 277 g. (83%) of chloroester b.p. 88–105° (42 mm.), 60–68° (12 mm.). This product contained some hydroxyl impurity, as shown by presence of a distinct OH-absorption band in the infrared spectrum. This was removed prior to carrying out the infrared analysis by chromatographing on activated alumina, the column being washed with benzene and 3:1 benzene–ether and the purified chloroester being recovered from the eluent by distillation.

Dropwise addition of 153 g. of the crude chloroester to a vigorously stirred mixture of 250 g. of potassium hydroxide, 250 g. of sodium hydroxide and 25 ml. of water at 140–150°, removing the volatile product through a 15-in. Vigreux column, drying over potassium hydroxide pellets, and distilling from sodium metal gave 38 g. (52%) of 2-methyloxetane, b.p. 60°, $n^{20}\mathrm{D}$ 1.3913 (reported[4] b.p. 60–61, $n^{20}\mathrm{D}$ 1.3894).

2-Methyl-1,3-butanediol.—4-Hydroxy-3-methyl-2-butanone (64 g.), prepared by the method of Zimmerman and English[19] and having b.p. 95–97° (22 mm.), was hydrogenated over Raney nickel catalyst at 1250 p.s.i. initial pressure and 170–180°. After uptake of a molecular amount of hydrogen the mixture was distilled to yield 53 g. (81%) of 2-methyl-1,3-butanediol, b.p. 115–116° (20 mm.), $n^{20}\mathrm{D}$ 1.4461 (reported[20] 112–115° (20 mm.)).

2,3-Dimethyloxetane.—Acetyl chloride (99 g.) was added dropwise to a mixture of 2-methyl-1,3-butanediol (109 g.) and calcium chloride (20 g.). The reaction was carried out by the procedure described for 1,3-butanediol except that the heating period at 50° was lengthened to three hours. Distillation gave 152 g. (88.5% yield) of chloroester, b.p. 84–105° (22 mm.), $n^{20}\mathrm{D}$ 1.4318. This chloroester (77 g., 0.47 mole) was treated with a mixture of potassium hydroxide (160 g.), sodium hydroxide (160 g.) and 15 ml. of water by the procedure described for 2-methyloxetane. Distillation from sodium metal gave 18 g. (45% yield) of 2,3-dimethyloxetane, b.p. 85–86°, $n^{20}\mathrm{D}$ 1.3975.

Anal. Calcd. C, 69.70; H, 11.70. Found: C, 70.06; H, 11.76.

3-Ethyl-2-propyloxetane.—1,3-Hexanediol (67 g.) was treated with acetyl chloride (47 g.) and calcium chloride (8.9 g.) by the procedure described for 2-methyl-1,3-butanediol to give 85 g. (87%) of chloroester, b.p. 126–131° (18 mm.), $n^{20}\mathrm{D}$ 1.4407. Treatment of 84 g. of this material with 300 g. of hot sodium hydroxide–potassium hydroxide mixture, followed by purification as described for the two previous oxetanes, gave 18 g. (33%) of 3-ethyl-2-propyloxetane, b.p. 155°, $n^{20}\mathrm{D}$ 1.4216.

Anal. Calcd. for $C_{10}H_{16}O$: C, 74.93; H, 12.58. Found: C, 75.21; H, 12.50.

Reaction of Hydrogen Chloride with 1,3-Butanediol. (A).—The reaction with dry hydrogen chloride gas was carried out in a manner analogous to that described for the

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[16] C. A. Stewart and C. A. VanderWerf, THIS JOURNAL, **76**, 1259 (1954).

[17] C. Golumbic and D. L. Cottle, *ibid.*, **61**, 996 (1939).

[18] Microanalyses by Weiler and Straus, Oxford, England.

[19] H. E. Zimmerman and J. E. English, THIS JOURNAL, **76**, 2294 (1954).

[20] P. Abelmann, *Ber.*, **42**, 2500 (1909).

reaction with 1,3-propanediol.[21] A temperature of 170–180° was required to get a convenient reaction rate. The distillate was washed with saturated sodium chloride solution, dried with calcium chloride and distilled through a 3-ft. glass helices-packed, heated column to give 32 g. (28%) of chlorohydrin product, b.p. 70–74° (20 mm.), $n^{20}\mathrm{D}$ 1.4425. From the washings was recovered 30 g. of the starting diol, b.p. 100–110° (25 mm.), $n^{20}\mathrm{D}$ 1.4417, making the conversion at least 45%.

(B).—A solution of 100 g. of 1,3-butanediol and 90 ml. of concentrated hydrochloric acid was heated one hour at 140–150° and then distilled. The distillate was processed as above to give 25.5 g. (39% conversion) of chlorohydrin, b.p. 70–95° (22 mm.), and 49.5 g. of recovered diol, b.p. 95–110° (22 mm.).

(C).—When the preceding experiment was carried out with addition of 147 g. of zinc chloride, the reaction mixture got very dark and only 13 g. (20%) of rather impure chlorohydrin fraction, b.p. 75–90° (25 mm.), was obtained. The remainder of the material was not identified.

Reaction of Hydrogen Bromide with 1,3-Butanediol.—Dry hydrogen bromide (40 g.) was treated with 1,3-butanediol (45 g.) at 0° over a period of 15 hours under anhydrous conditions, as described by Levene, *et al.*[12] The product consisted of 35 g. (49%) of colorless liquid, b.p. 67–81° (14 mm.) (reported[12] 72–76° (20 mm.)).

3-Chloro-1-butanol.—To a solution of 40 g. of β-chlorobutyric acid, b.p. 110° (18 mm.), $n^{20}\mathrm{D}$ 1.4400 (reported[22] b.p. 110–113° (20 mm.), $n^{20}\mathrm{D}$ 1.4399), in 300 ml. of ether was added 11 g. of lithium aluminum hydride dissolved in 200 ml. of ether. The reaction mixture was decomposed by adding 20% sodium carbonate. The usual method of product isolation gave 12 g. (34%) of 3-chloro-1-butanol, b.p. 74° (16 mm.), $n^{20}\mathrm{D}$ 1.4398. This compound has been made previously by addition of hydrogen chloride to 3-buten-1-ol (reported[23] b.p. 67–68° (15 mm.), $n^{20}\mathrm{D}$ 1.4446). The 3,5-dinitrobenzoate melted at 71–72°.

3-Chloro-1-butyl Acetate.—3-Chloro-1-butanol (5 g.) was acetylated with 5.1 g. of acetyl chloride in 10 ml. of ether and 5.7 g. of pyridine. Obtained was 6.5 g. (93%) of the chloro ester, b.p. 74–76° (17 mm.), $n^{20}\mathrm{D}$ 1.4271.

4-Chloro-2-butanol was prepared by lithium aluminum hydride reduction of 4-chloro-2-butanone,[4] b.p. 61° (10 mm.), $n^{20}\mathrm{D}$ 1.4440 (reported[4] b.p. 67° (20 mm.), $n^{20}\mathrm{D}$ 1.4408). The 3,5-dinitrobenzoate melted at 113–114°.

4-Chloro-2-butyl acetate was prepared by acetylation of the preceding chlorohydrin as described previously,[4] b.p. 71–72° (16 mm.), $n^{20}\mathrm{D}$ 1.4273 (reported[4] b.p. 70° (16 mm.), $n^{20}\mathrm{D}$ 1.4260).

3-Bromo-1-butanol[24] was prepared in 55% yield by lithium aluminum hydride reduction of ethyl 3-bromobutyrate,[25] using inverse addition, b.p. 83° (14 mm.), $n^{20}\mathrm{D}$ 1.4772, m.p. of α-naphthylurethan 73–75°.

Anal. Calcd. for C_4H_9OBr: Br, 52.20. Found: Br, 52.10.

4-Bromo-2-butanol.—After 19 g. of methyl vinyl ketone was saturated with hydrogen bromide at 0°, nitrogen gas was bubbled in to remove unreacted hydrogen bromide, and a solution of 2.8 g. of sodium borohydride in 75 ml. of absolute alcohol was added. The mixture was stirred overnight, and then water was added. The organic layer was separated, combined with ether extracts of the aqueous layer, dried over magnesium sulfate and distilled, yielding 14.7 g. (36%) of 4-bromo-2-butanol, b.p. 75–77° (14 mm.), $n^{20}\mathrm{D}$ 1.4732, m.p. of α-naphthylurethane 70–72°.

Anal. Calcd. for C_4H_9OBr: Br, 52.20. Found: Br, 50.30. As to α-naphthylurethan, calcd. for $C_{15}H_{16}O_2NBr$: C, 55.91; H, 5.01; Br, 24.8. Found: C, 56.17; H, 4.82, Br, 23.9.

Method of infrared spectral analysis was similar to that used by Stewart and VanderWerf[16] and by Meltzer and King.[9] A Perkin-Elmer model 112 infrared spectrometer fitted with a rock salt prism, and a single standard rock salt absorption cell of about 0.03 mm. thickness was used. Bands at 8.33, 8.51, 10.54, 10.99, 11.34 and 12.13 μ were used for quantitative analyses of the chlorobutanols; at 8.42, 10.33, 10.49, 10.54, 11.86 and 12.52 μ for the chlorobutyl acetates; and at 11.32, 11.70 and 12.40 μ from the bromobutanols. The amount of each isomer was determined from a plot of concentration *vs.* transmission at the selected frequencies, made from measurements on the pure isomers and on three known mixtures of each pair of isomers.

Reactions of 2-Methyloxetane with Hydrogen Chloride and Bromide. (A) In Benzene.—2-Methyloxetane (9 g.) was dissolved in 25 ml. of benzene maintained at the temperature indicated (Table II) and dry hydrogen chloride or bromide was bubbled in until uptake was complete. The solution was washed with 5% sodium bicarbonate and water, dried over magnesium sulfate and distilled *in vacuo*. The chlorohydrin product distilled at 61–62° (11 mm.) or the equivalent, the bromohydrin at 75–78° (14 mm.).

(B) **In Xylene.**—The same procedure was used, except that the oxetane was introduced into the hot xylene as a gas simultaneously with the hydrogen chloride. A very efficient spiral condenser was used to condense as completely as possible any oxetane escaping from the reaction mixture.

(C) **In Water.**—2-Methyloxetane (9 g.) was dissolved in 10 ml. of water and added dropwise with stirring to 100 ml. of 5% hydrochloric or hydrobromic acid maintained at the desired temperature. Titration of an aliquot showed the reaction to be practically complete after one hour. The mixture was then saturated with salt and extracted with ether, and the extracts were dried and distilled. In the reactions with concentrated hydrochloric acid, the oxetane was not diluted before addition. The product composition in each case was analyzed by the infrared method described and is given in Table II.

Reaction of Acetyl Chloride with 2-Methyloxetane.—A solution of 13.5 g. of acetyl chloride in 25 ml. of benzene was added dropwise to a stirred solution of 11 g. of 2-methyloxetane in 25 ml. of benzene at 5°. Stirring was continued at this temperature for two hours, after which the mixture was washed with ice-water and 5% sodium bicarbonate and was dried and distilled. Obtained was 8.5 g. (36% yield) of chloroester, b.p. 73–78° (16 mm.), $n^{20}\mathrm{D}$ 1.4280, as well as 2 g. of a by-product, b.p. 112° (16 mm.).

Reaction of oxetane[6] and dimethyloxetane[26] with hydrogen chloride was carried out in a manner analogous to (A) for 2-methyloxetane, but the reaction was stopped after 20 minutes. The yield of 3-chloro-1-propanol from oxetane was 60%, b.p. 69–70° (20 mm.), $n^{20}\mathrm{D}$ 1.4462 (reported[6,21] b.p. 60–64° (10 mm.), $n^{20}\mathrm{D}$ 1.4469). The yield of 3-chloro-2,2-dimethyl-1-propanol was 61%, b.p. 70–71° (15 mm.), m.p. 18–19°, $n^{20}\mathrm{D}$ 1.4482 (reported[27] b.p. 78–80° (10 mm.)). The 3,5-dinitrobenzoate was prepared, m.p. 75–76° (from ligroin), and analyzed.

Anal. Calcd. for $C_{12}H_{13}O_6N_2Cl$: C, 45.51; H, 4.13. Found: C, 45.63; H, 3.96.

Reaction of 2-Phenyloxetane with Hydrogen Chloride. (A).—In benzene the same procedure as described for 2-methyloxetane was used, the temperature being 5°. From 8 g. of 2-phenyloxetane was obtained 3.5 g. (35%) of chloroalcohol, b.p. 90–100° (0.05 mm.), 0.5 g. of a fraction, b.p. 60° (0.05 mm.), having an infrared spectrum identical to that of cinnamyl alcohol and 3.5 g. of polymer. The infrared spectrum of the chloroalcohol was quite different from that of 3-chloro-1-phenyl-1-propanol[10] but was identical to that of 3-chloro-3-phenyl-1-propanol, described below, except for showing small C=C (conj.) and ether absorption bands—probably due to presence of cinnamyl ether. This impurity was removed by redistillation.

(B) **With Aqueous Hydrogen Chloride.**—Since 2-phenyloxetane is only slightly soluble in water, the reactions with aqueous hydrogen chloride were carried out in mixed solvents. The 2-phenyloxetane, in each case, was dissolved in 25 ml. of the organic solvent and added to one of the following mixtures: 25 ml. of acetone and 70 ml. of 10% HCl; 75 ml. of dioxane, 44 ml. of water and 7.3 g. of concd. HCl; 100 ml. of acetonitrile, 44 ml. of water and 7.3 g. of concd. HCl. The resulting mixture was stirred at 5–10° for 4 hours, and the product was isolated in the usual manner. In each case the chloroalcohol product was solely 3-chloro-3-phenyl-1-propanol as its infrared spectrum was identical to that of the authentic compound below and dis-

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[21] C. S. Marvel and H. O. Calvery, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 533.

[22] K. von Auwers, *Ann.*, **421**, 1 (1920).

[23] J. Verhulst, *Bull. soc. chim. Belg.*, **40**, 85 (1931).

[24] Carried out by Mr. Duncan E. Dodds.

[25] H. Burton and C. K. Ingold, *J. Chem. Soc.*, 2030 (1939).

[26] G. M. Bennett and W. G. Philip, *ibid.*, 1937 (1928).

[27] A. C. Farthing, *ibid.*, 3648 (1955).

tinctly different from that of 3-chloro-1-phenyl-1-propanol. The yields from the cleavage were: 32% in acetone–water, accompanied by a 28% yield of cinnamyl alcohol, b.p. 53–57° (0.04 mm.) and correct infrared spectrum; 27% in dioxane–water, accompanied by a 7% yield of cinnamyl alcohol and a large amount of polymer; and 19% in acetonitrile–water, accompanied by 5% of cinnamyl alcohol.

3-Chloro-3-phenyl-1-propanol.—A solution of thionyl chloride (43 g.) in 30 ml. of chloroform was added to a solution of 60 g. of methyl 3-hydroxy-4-phenylpropionate[28] and 31 g. of pyridine at 0°, and the mixture was then warmed to 50° for one-half hour. After the usual processing, 45 g. (75%) of methyl 3-chloro-3-phenylpropionate, b.p. 80–85° (0.08 mm.), was obtained. This product was infrared-spectroscopically pure of hydroxyl impurities. It was reduced then with lithium aluminum hydride (4.95 g.) in ether, inverse addition being employed, to give 10 g. (26%) of 3-chloro-3-phenyl-1-propanol, b.p. 98° (0.08 mm.). The unstable character of this compound made it difficult to purify and impossible to keep. The instability to heat caused it to decompose during careful fractional distillation, so that little material could be obtained other than an unsaturated substance and polymer (mostly the latter). It was purified best by chromatography over activated alumina in benzene solution; removal of the benzene under vacuum at 50° from a freshly chromatographed solution gave a material which had no $C{=}C$, $C{=}O$ or other unexpected infrared bonds. Unfortunately, it was not sufficiently stable to get a satisfactory elemental analysis. Its infrared differed from that of 3-chloro-1-phenyl-1-propanol in the presence of principal bands at 8.22, 9.04, 10.71 and 11.09μ and the absence of such at 8.38, 8.64 and 10.91 μ.

Reaction of Acetyl Chloride with 2-Phenyloxetane.—A solution of acetyl chloride (8.6 g., 0.11 mole) in 45 ml. of benzene was added dropwise to a stirred solution of 2-phenyloxetane (13.4 g., 0.1 mole) in 45 ml. of benzene at 5–10°. The stirring at this temperature was continued for 4 hours and then the mixture was allowed to stand overnight. The reaction mixture was washed with cold water and 5% sodium bicarbonate, dried and distilled, to give 15.9 g. (75%) of a chloroester, b.p. 82–87° (0.03 mm.). Since acid-catalyzed methanolysis of this material had been previously found to give only 17% yield of a chlorohydrin, it was cleaved with lithium aluminum hydride (1.06 g. for 9.5 g. of ester, inverse addition used). After the usual processing, distillation gave 4.8 g. of a mixture, b.p. 75–93° (0.08 mm.). Infrared spectral analysis showed this to be about 75% 3-phenyl-3-chloro-1-propanol and 25% hydrocinnamyl alcohol; there was no indication of the presence of any 3-chloro-1-phenyl-1-propanol.

MANHATTAN, KANSAS

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(28) C. R. Hauser and D. S. Breslow, *Org. Syntheses*, **21**, 51 (1941).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

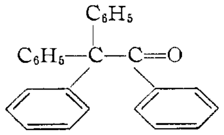
The Action of Phenylmagnesium Bromide on 10,10-Diphenyl-9,10-dihydro-9-phenanthrone[1]

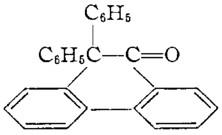
BY REYNOLD C. FUSON AND PAUL TOMBOULIAN[2]

RECEIVED AUGUST 8, 1956

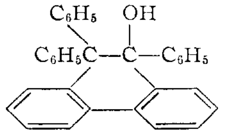
Treatment of 10,10-diphenyl-9,10-dihydro-9-phenanthrone (II) with phenylmagnesium bromide yields products formed by 1,2- and 1,4-addition. The 1,4-adduct undergoes rearrangement to form a phenanthrene derivative. Similar compounds are formed from the *p*-tolyl analog of the phenanthrone II by the action of the *p*-tolyl Grignard reagent.

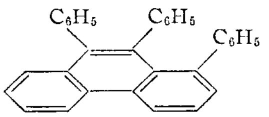
o-Phenylation of hindered ketones by the action of phenylmagnesium bromide was first realized by Schmidlin and Wohl[3] with β-benzopinacolone (I); it remained, however, for Mosher and Huber,[4] 41 years later, to interpret the experiment correctly. In the meantime a number of similar reactions had been reported.[5] In the hope of finding a more vulnerable ketone we have studied 10,10-diphenyl-9,10-dihydro-9-phenanthrone (II), the closest cyclic analog of β-benzopinacolone. It was expected that the rigidity of the fused ring system might render the phenanthrone more susceptible to nucleophilic attack than the pinacolone.


I


II

When the phenanthrone was treated with phenylmagnesium bromide in anisole at 100°, however, the reaction took an unexpected course. Chromatographic separation of the product furnished an alcohol (13% yield), which proved to be the 1,2-addition product, 9,10,10-triphenyl-9,10-dihydro-9-phenanthrol (III), and a hydrocarbon (24% yield), which was eventually identified as 1,9,10-triphenylphenanthrene (IV).


III


IV

The identity of the alcohol, clearly indicated by its elementary composition and infrared spectrum, was confirmed by comparison with an authentic sample prepared by the condensation of phenyllithium with the phenanthrone according to the method of Mosher and Huber.[4] These authors obtained the alcohol in a yield of 50% by using a reaction time of 2 hr. We found that, by extending this time to 24 hr., the alcohol could be prepared in an 83% yield. This alcohol has been synthesized also by the action of sulfuric acid on *o*-biphenylyl triphenylmethyl ketone.[3,4]

The hydrocarbon had the composition of a triphenylphenanthrene, and only the 1,9,10-isomer IV seemed to be in full agreement with the infrared and ultraviolet spectral data. This structure was confirmed by an independent synthesis. The starting material was 1-phenylphenanthrene (V), prepared by the method of Bachmann and

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(2) Du Pont Postgraduate Teaching Assistant, 1955–1956.

(3) J. Schmidlin and J. Wohl, *Ber.*, **43**, 1145 (1910).

(4) W. A. Mosher and M. L. Huber, THIS JOURNAL, **73**, 795 (1951).

(5) For references see R. C. Fuson and P. E. Wiegert, *ibid.*, **77**, 1138 (1955).