decomposed at 290–295°; recrystallized from ethanol-water, it decomposed at 295°. Both samples burned in a flame leaving a grayish residue which when moistened with distilled water tested alkaline to litmus. Both samples and acetylacetone gave the same derivatives with 2,4-dinitrophenylhydrazine, melting at 122° (lit.122°).[13]

Crude V melted at 38–40°, recrystallized from low boiling Skellysolve, m.p. 43° (lit. 43°[6]). After boiling with water, it gave the derivative of acetylacetone with 2,4-dinitrophenylhydrazine, melting at 122°.

Allylacetylacetone (VI).—Similarly, 140 g. (1 mole) of VI was treated with 3.5 moles of sodium acetylide. Fractionation of the products gave 14 g., 20% yield, of allylacetone, b.p. 69° at 100 mm., $n^{25}\text{D}$ 1.4178; 2,4-dinitrophenylhydrazone, m.p. 103–104° (lit. 104°[14]); 39 g., 36%, of unreacted VI, b.p. 82–84° at 16 mm., derivative with 2,4-dinitrophenylhydrazine, m.p. 185–186°, and a residue of 56 g., 56% yield, of crude allylacetylacetone amine (VIII), m.p. 63–66°, recrystallized from low boiling Skellysolve, m.p. 65–67°; derivative with 2,4-dinitrophenylhydrazine, m.p. 185–186°. On heating VIII with 10% sodium hydroxide, ammonia was evolved. The infrared spectrum of VIII showed a double headed absorption band having peaks at 6.22 and 6.32 μ, with no appreciable absorption from 5.7 to 6.0 μ.

Anal. Calcd. for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.07; H, 9.38; N, 10.14.

Diallylacetylacetone (VII).—When 0.47 mole (85 g.) of VII was treated with 4 moles of sodium acetylide in the usual way, the reaction mixture yielded 17 g., 34% yield, of α,α-diallylacetone, b.p. 66–67° at 15 mm., $n^{25}\text{D}$ 1.4448, semicarbazone, m.p. 109–110° (lit. 108°[15]), recrystallized from water–ethanol as the hemihydrate, m.p. 95–96° (lit. 95–96°[15]); and 19 g., 22%, of VII, b.p. 85–86° at 5 mm., $n^{25}\text{D}$ 1.4685, derivative with 2,4-dinitrophenylhydrazine decomposed at 234°.

Reaction of Diacetone Alcohol with Sodium Acetylide.—When 232 g. (2 moles) of diacetone alcohol was treated with 5 moles of sodium acetylide, the only product isolated was 107 g. (32% yield) of 3-methyl-3-hydroxy-1-butyne (IX), b.p. 103.5–104° (lit. 104°[16]), $n^{25}\text{D}$ 1.4187.

NOTRE DAME, INDIANA

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(13) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., p. 262.

(14) C. F. H. Allen, THIS JOURNAL, **52**, 2958 (1930).

(15) K. Auwers and W. Moosbrugger, *Ann.*, **387**, 196 (1912).

(16) G. F. Hennion and W. S. Murray, THIS JOURNAL, **64**, 1220 (1942).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, TULANE UNIVERSITY]

The Acid-catalyzed Reaction of Hydrogen Azide upon Certain Alicyclic Alcohols[1]

BY J. H. BOYER AND F. C. CANTER

RECEIVED JANUARY 5, 1955

The reaction between hydrogen azide and each of five alicyclic alcohols in concentrated sulfuric acid at 15–25° was investigated. The formation of ketones, cyclic Schiff bases and other products was in agreement with carbonium ion theory.

The first investigations on the acid-catalyzed action between hydrogen azide and alcohols[2] were inadequately understood and the identity of the products obtained was not rigorously established. It was later suggested that the reaction might be explained by a carbonium ion mechanism, but additional experimental data was not offered.[3] A similar explanation was demonstrated for the acid-catalyzed reaction of hydrogen azide upon olefins[4] and accounted for the formation of aniline and acetophenone from both diphenylmethylcarbinol and 1,1-diphenylethylene.[5] Benzhydrol, fluorenol and triphenylcarbinol, curiously enough, were successfully transformed into the corresponding azides by the action of hydrogen azide in sulfuric acid.[6] Azides also were obtained from a series of 1,1-diarylethanols with hydrogen azide in trichloroacetic acid. This suggested that the azides were in equilibrium with their conjugate acids.[7] Presumably a high concentration of a strong acid repressed the dissociation of the conjugate acid. Earlier work on the acid-catalyzed decomposition of alkyl azides[8] was later reinterpreted in terms of initial formation of the protonated azide.[9]

As an outgrowth of investigations on the acid-catalyzed reactions of certain secondary alicyclic azides[10] and of primary azides,[11] a comparison with the acid-catalyzed reaction of hydrogen azide upon alicyclic alcohols was undertaken. This report consists in a reinvestigation of the application of the reaction to 2-methylcyclohexanol[2] and to menthol[2] and an extension of the reaction to cyclopentanol, cyclohexanol and cycloheptanol.

Each of the three unsubstituted alicyclic alcohols apparently was transformed into the corresponding carbonium ion with no rearrangement.[12,13] Whether or not the corresponding azides could be isolated from the acid-catalyzed reactions of alicyclic alcohols and hydrogen azide was not established. Instead the reactions accompanied by the evolution of nitrogen were investigated. The attraction between the electron deficient nitrogen atom, which resulted from the elimination of molecular nitrogen from the conjugate acid of the azide, and an electron pair of an adjacent bond brought about the formation of at least two products each from cyclopentanol, cyclohexanol and cyclohep-

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(1) The financial support for this work was supplied by the Office of Ordnance Research under Contract No. DA-01-ORD-331.

(2) K. F. Schmidt and W. Klavehn, German Patent 583,565 (1933); *Frdl.*, **20**, 947 (1935).

(3) C. Schuerch and E. H. Huntress, THIS JOURNAL, **71**, 704 (1949).

(4) W. E. McEwen, M. Gilliland and B. I. Sparr, *ibid.*, **72**, 3212 (1950).

(5) L. P. Kuhn and J. DiDomenico, *ibid.*, **72**, 5777 (1950).

(6) C. L. Arcus and R. J. Mesley, *Chemistry and Industry*, 701 (1951); *J. Chem. Soc.*, 178 (1953).

(7) S. N. Ege and K. W. Sherk, THIS JOURNAL, **75**, 354 (1953).

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(9) K. W. Sherk, A. G. Haupt and A. W. Browne, THIS JOURNAL, **62**, 329 (1940).

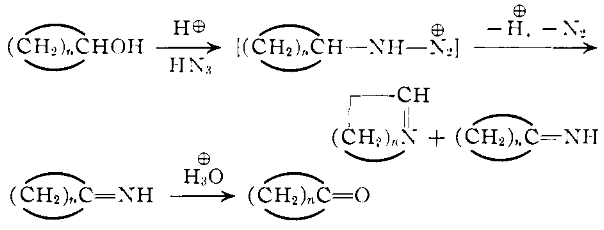
(10) J. H. Boyer, F. C. Canter, J. Hamer and R. K. Putney, unpublished work.

(11) J. H. Boyer and J. Hamer, work in progress.

(12) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 224–225.

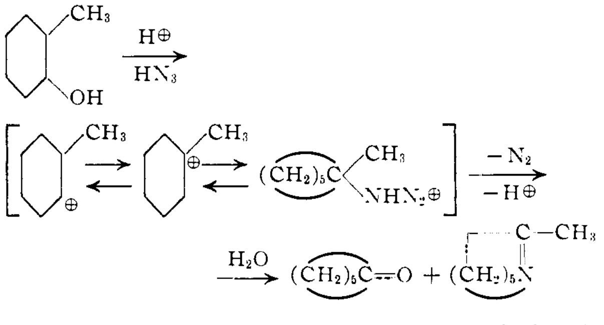
(13) R. A. Raphael, "Cycloheptane, Cycloöctane and Macrocyclic Groups" in E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IIA, Elsevier Publishing Co., Houston, Texas, 1953, p. 250.

tanol. In one case the ejection of a proton and the subsequent hydrolysis of an imine allowed the isolation of cyclopentanone (trace), cyclohexanone (7.9%) and cycloheptanone (7.3%), respectively. These cyclic ketones were isolated in yields of 2, 20 and 5%, respectively, from the action of concentrated sulfuric acid on the corresponding azides.[10] Apparently the other product in each case resulted from ring enlargement; however, piperideine (60%) from cyclopentanol was the only one identified. From cyclohexanol and cycloheptanol the extremely insoluble polymeric products resembled products obtained from cyclohexyl and cycloheptyl azides with concentrated sulfuric acid.[10] Piperideine was obtained in 80% yield from cyclopentyl azide and sulfuric acid.[10]

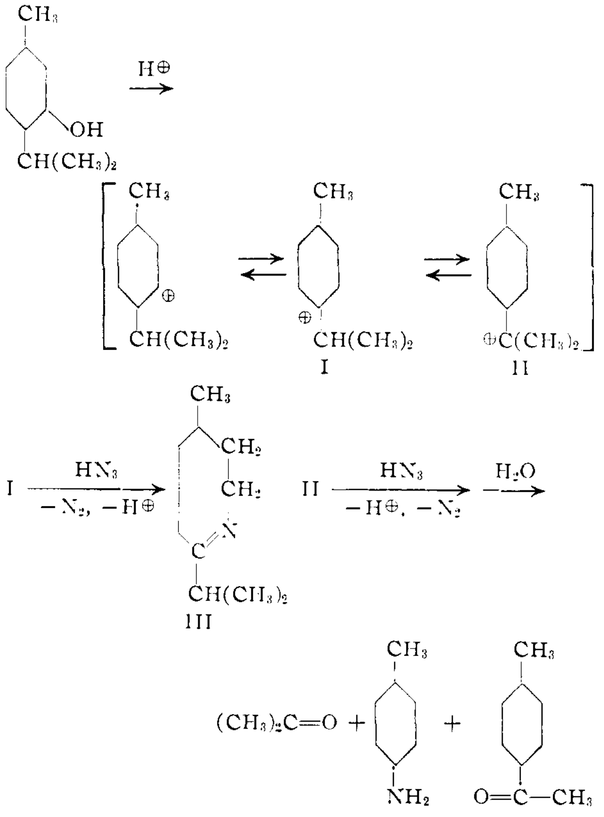


$n = 4, 5, 6$

Apparently rearrangement of the initially formed carbonium ions from 2-methylcyclohexanol and from menthol occurred prior to or simultaneously with the reaction with hydrogen azide. The presence of the more stable tertiary 1-methylcyclohexyl carbonium ion was demonstrated by the detection of cyclohexanone. In agreement with this observation it is more probable that the major product is Δ^1-2-methylazacycloheptene rather than the 7-methyl isomer which was previously considered.[2]



From menthol, four products were isolated. Schmidt and Klavehn[2] reported these to be acetone, a $C_{10}H_{20}O$ ketone, 4-methylhexamethylenimine and Δ^1-3-isopropyl-6-methylazacycloheptene. The presence of acetone in the product was verified; however, the second ketone was identified as methyl 4-methylcyclohexyl ketone ($C_9H_{16}O$). A third product was identified as 4-methylcyclohexylamine ($C_7H_{15}N$) rather than 4-methylhexamethylenimine. The identities of the $C_9H_{16}O$ ketone and the $C_7H_{15}N$ amine were thus in agreement with the predictions of Schuerch and Huntress.[3] The fourth product, $C_{10}H_{19}N$, has now been assigned the structure of Δ^1-2-isopropyl-5-methylazacycloheptene (III). Medium absorption at 1650 cm.$^{-1}$ (6.04 μ) indicated the presence of the azomethine group. In contrast with the facility with which imines of ketones are hydrolyzed,[14] the cyclic Schiff bases have shown remarkable resistance to hydrolysis. This product resembled other cyclic Schiff bases not only in this respect but also in its tendency to polymerize. The two isomeric compounds which would have involved combination of hydrogen azide and the secondary carbonium ion were considered less probable.



Experimental[15]

Cyclopentanol, cyclohexanol, 2-methylcyclohexanol and menthol were commercially available. Cycloheptanol was kindly supplied by Dr. F. F. Blicke, College of Pharmacy, University of Michigan.

Hydrogen azide was prepared according to the directions of von Braun.[16] A paste consisting of equal parts by weight of sodium azide and water was overlaid with chloroform (about 6 ml. for each gram of sodium azide), and cooled to 0°. An equivalent amount of concentrated sulfuric acid was added at such a rate that the temperature did not rise above 10°. The chloroform solution of hydrogen azide was decanted, and the concentration of the solution was determined by pipetting a 2-ml. sample into 50 ml. of water, shaking well and titrating with standard sodium hydroxide, using phenolphthalein as an indicator.

Essentially the same procedure[2] was followed in carrying out the reactions between hydrogen azide and each of the alicyclic alcohols. A solution of equimolar (0.4 to 0.8 mole) parts of hydrogen azide and alcohol in 250–350 ml. of chloroform was cooled to 10–15° in an ice-bath. With stirring, 300–320 g. of concentrated sulfuric acid was added at such a rate that the temperature of the reaction mixture did not exceed 15–20°. With stirring, the mixture was allowed to come to room temperature upon the completion of the addi-

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[14] P. L. Pickard and E. F. Engles, This Journal, **75**, 2148 (1953).

[15] Melting points are corrected; boiling points, uncorrected. Microanalyses by Micro-tech Laboratories, Skokie, Illinois. Infrared analyses by Mr. J. E. Baudean, Perkin-Elmer Corp., New Orleans, La.

[16] J. von Braun, *Ann.*, **490**, 100 (1931).

tion of sulfuric acid and was stirred at room temperature for 2–5 hours.

The chloroform layer was separated either in a separatory funnel or by steam distillation of the diluted reaction mixture. The acid aqueous layer was made basic by addition of solid sodium carbonate and 10–30% sodium hydroxide. At the stage at which the solution was still slightly acidic an organic layer separated in certain instances. This was combined with the chloroform layer. Ether extracts of the acid layer were combined with the chloroform layer. Removal of the dried organic solvents left liquid ketones: cyclopentanone (trace amounts isolated as the dinitrophenylhydrazone derivative, m.p. and mixed m.p. 144.5–145.6°) from cyclopentanol; cyclohexanone (7.9%), b.p. 150–154°, $n^{20}\mathrm{D}$ 1.4520; dinitrophenylhydrazone m.p. and mixed m.p. 162–163°, from cyclohexanol; cycloheptanone (7.3%), b.p. 68–69° (16 mm.),[17] $n^{28}\mathrm{D}$ 1.4585,[18] dinitrophenylhydrazone m.p. 146.5–148°)[18] from cycloheptanol; cyclohexanone (trace) isolated as the dinitrophenylhydrazone derivative, m.p. and mixed m.p. 162–163° from 2-methylcyclohexanol; methyl 4-methylcyclohexyl ketone, $C_9H_{16}O$ (23%), b.p. 87.5° (22 mm.),[19] $n^{21}\mathrm{D}$ 1.4445,[19,20] from menthol.

Anal. Calcd. for $C_9H_{16}O$: C, 77.11; H, 11.50. Found: C, 77.20; H, 11.20.

The semicarbazone derivative after two recrystallizations from ethanol melted 150–150.8°.[19]

Anal. Calcd. for $C_{10}H_{19}N_3O$: C, 60.86; H, 9.70; N, 21.29. Found: C, 61.24; H, 9.41; N, 21.05.

The aqueous solution was then made distinctly alkaline whereupon the basic organic products separated. The organic layer was combined with ether extracts of the aqueous basic layer, dried, ether removed and the residue worked up in various ways.

From cyclopentanol the residue consisted of 23.2 g. (60%) of piperideine isolated as its trimer, isotripiperideine, m.p. 96.2–97.0°[21] after two recrystallizations from acetone. Catalytic reduction over platinum brought about the formation of α,β-dipiperidyl (picrate m.p. 225–228°[21,22]) and piperidine isolated as its hydrochloride, m.p. 245–247°.[23]

From cyclohexanol the residue was an intractable gum which was not identified. Attempts to reduce the material both chemically and catalytically gave unsatisfactory results.

From cycloheptanol the residue was gummy polymeric material partially soluble in acetone. The insoluble portion was also insoluble in all organic solvents at hand and did not melt but charred over the range 100–300°. The material soluble in acetone was reprecipitated as an amorphous rubbery polymer upon addition of benzene and represented the major product. The analysis of a portion of the reprecipitated material was consistent with the empirical formula $C_{18}H_{32}N_2O_3$.

Anal. Calcd. for $(C_{18}H_{32}N_2O_3)_n$: C, 66.63; H, 9.94; N, 8.64. Found: C, 66.28; H, 9.55; N, 8.72.

From 2-methylcyclohexanol the residue contained 11.58 g. (30%) of Δ^1-2-methylazacycloheptene, b.p. 140–159°. Apparently polymerization occurred upon standing at room temperature since the distillate became quite viscous. Depolymerization upon distillation allowed recovery of the mobile monomer. An analytical sample was obtained from the second redistillation at 66° (34 mm.). A shift in the index of refraction from $n^{22}\mathrm{D}$ 1.4772 (not necessarily representative of pure monomer) to a constant value of $n^{22}\mathrm{D}$ 1.4880 after two days accompanied the polymerization.

Anal. Calcd. for $C_7H_{13}N$: C, 75.61; H, 11.78; N, 12.59. Found: C, 75.30; H, 12.00; N, 12.58.

From menthol the residue contained a mixture of *cis*- and *trans*-4-methylcyclohexylamine, 10.6 g. (14.3%), b.p. 149.5–150.5° (765 mm.),[24] $n^{28}\mathrm{D}$ 1.4466.[25]

Anal. Calcd. for $C_7H_{15}N$: C, 74.26; H, 13.35; N, 12.37. Found: C, 74.12; H, 12.76; N, 12.72.

A hydrochloride, m.p. 260–263°,[26] was prepared by bubbling hydrogen chloride through an ether solution of the amine. The m.p. of the hydrochloride of 4-methylhexamethylenimine, an isomer of 4-methylcyclohexylamine and previously considered to represent the product, $C_7H_{15}N$,[2] is 172–173° (F. F. Blicke, private communication). Schmidt and Klavehn[2] reported the m.p. of this hydrochloride to be 229°.

The other constituent present in the residue from the reaction with menthol has now been assigned the structure Δ^1-2-isopropyl-5-methylazacycloheptene and was collected at 198–201° (766 mm.),[2] wt. 7.0 g. (6.7%), $n^{29}\mathrm{D}$ 1.4564. Medium absorption at 1650 cm.$^{-1}$ (6.04 μ) indicated the presence of the azomethine group. The freshly distilled mobile liquid became more viscous upon standing, presumably through polymerization.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.34; H, 12.49; N, 9.14. Found: C, 78.07; H, 12.26; N, 9.40.

In one reaction with menthol, acetone was isolated in 7.2% yield as the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 125–125.8°, from the aqueous steam distillate of the reaction mixture.

Hypobromite Oxidation of Methyl 4-Methylcyclohexyl Ketone.—A solution of 12 g. (0.30 mole) of sodium hydroxide in 100 ml. of water was cooled to 0° in an ice-bath. With stirring, 17.5 g. (0.108 mole) of bromine was added at such a rate that the temperature did not rise above 10°. To this solution was added 5.0 g. (0.036 mole) of the ketone and the mixture was stirred for 90 minutes at 0–8°. The ice-bath was removed and the reaction mixture was stirred for 12 hours at room temperature. The separated aqueous layer was evaporated to about 50 ml. and acidified with concentrated hydrochloric acid. A yellow oil was extracted from the aqueous solution with three 20-ml. portions of ether; the extracts were washed with water, dried over magnesium sulfate and the ether distilled. The residue contained 4.1 g. of a mixture of *cis*- and *trans*-4-methylcyclohexanecarboxylic acid, $C_8H_{14}O_2$, b.p. 77–80° (0.05 to 2.0 mm.),[27] $n^{32}\mathrm{D}$ 1.4493, neut. equiv. calcd. 142.2, found 143.8, 144.7.

Dehydrogenation of Methyl 4-Methylcyclohexyl Ketone.—A mixture of 2.8 g. (0.02 mole) of the ketone and 1.92 g. (0.060 mole) of powdered sulfur was heated at 200–210° for 18 hours. Hydrogen sulfide gas was noted throughout this period. A moist black solid was obtained, washed with 10 ml. of ether and filtered. Five milliliters of the filtrate was added to 10 ml. of 2,4-dinitrophenylhydrazine solution and allowed to stand 15 minutes. A precipitate melted at 230–250°. After three recrystallizations from benzene and ethanol, it possessed constant melting point 254–256° (reported for the m.p. of the DNP of *p*-methylacetophenone, 253–255°[28]).

Reduction of Δ^1-2-Methylazacycloheptene.—The following procedure was previously used for the reduction of piperideine.[21] A suspension of 1.0 g. of platinum oxide in 20 ml. of water was shaken under a hydrogen pressure of three atmospheres for 10 minutes. A solution of 11.1 g. (0.10 mole) of Δ^1-2-methylazacycloheptene, in 100 ml. of 1 *N* hydrochloric acid was added to the catalyst suspension. The mixture was then shaken under a hydrogen pressure of about three atmospheres for two hours. After the reduction mixture had been filtered free of platinum, it was evaporated to dryness on a steam-bath and in a vacuum oven. The white taffy-like residue was taken up in 50 ml. of water. This solution was made basic by addition of 10% sodium hydroxide solution and then was extracted with five 25-ml. portions of ether. The extracts were dried over anhydrous magnesium sulfate. The ether was removed and the residue distilled. A yield of 4.5 g. (40%) of 2-methylhexamethylenimine, b.p. 59–61° (22 mm.),[29] $n^{27}\mathrm{D}$ 1.4569,[29] was obtained.

The hydrochloride was prepared by bubbling anhydrous hydrogen chloride into an ethereal solution of the cyclic imine. After two recrystallizations from ether and isopropyl alcohol, it melted 199–201°.[29,30]

The benzenesulfonamide after two recrystallizations from ethanol and water melted at 75–77°.[30]

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[17] I. Vogel, *J. Chem. Soc.*, **133**, 2032 (1928).

[18] O. L. Brady, *ibid.*, 756 (1931).

[19] G. Darzens, *Compt. rend.*, **144**, 1123 (1907).

[20] F. W. Semmler and C. Rimpel, *Ber.*, **39**, 2582 (1906).

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[22] C. R. Smith, THIS JOURNAL, **50**, 1936 (1928).

[23] T. B. Grave, *ibid.*, **46**, 1461 (1924).

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[25] K. von Auwers, *Chem. Zentr.*, **98**, II, 1562 (1927).

[26] J. Gutt, *Ber.*, **40**, 2061 (1907).

[27] Q. T. Chou and W. H. Perkin, Jr., *J. Chem. Soc.*, **99**, 526 (1911).

[28] S. L. Friess and R. Pinson, THIS JOURNAL, **73**, 3512 (1951).

[29] F. F. Blicke and N. J. Doorenbos, *ibid.*, **76**, 2317 (1954).

[30] S. Gabriel, *Ber.*, **42**, 1259 (1909).

Preparation of 4-Methylcyclohexanone from 4-Methylcyclohexylamine.—A solution of 1.13 g. (0.01 mole) of the amine, 1 ml. of concentrated hydrochloric acid, 2 ml. of glacial acetic acid and 2 ml. of water was cooled to 0°. With stirring, a solution of 2.6 g. (0.03 mole) of sodium nitrite in 5 ml. of water was added dropwise. The reaction mixture was stirred for 10 minutes. The brown organic layer was separated and the aqueous layer was extracted with two 2-ml. portions of ether, the extracts being added to the organic layer.

The combined organic layer was added to a solution of 0.56 g. (0.0019 mole) of potassium dichromate, 0.42 ml. (0.015 mole) of concentrated sulfuric acid and 2.5 ml. of water. This mixture was stirred and heated at 75–80° for four hours. Ten milliliters of water was added and the mixture was distilled until clear distillate came over. The distillate was extracted with two 2-ml. portions of ether. The extracts were dried over anhydrous magnesium sulfate and the ether was evaporated by a stream of dried air. There remained 0.30 g. of 4-methylcyclohexanone as a yellow oil (semicarbazone m.p. 185–190°, lit.[31] m.p. 192–193°). The dinitrophenylhydrazone of the yellow oil was prepared by dissolving the balance of the oil in 10 ml. of ethanol and adding it to 20 ml. of 2,4-dinitrophenylhydrazine solution. The solid which precipitated was filtered and recrystallized from petroleum ether. It melted at 109–116°. Four recrystallizations from ethanol and water, using the second crop of crystals from each recrystallization, gave a product which melted at 128–131°. The melting point of the dinitrophenylhydrazone of 4-methylcyclohexanone has been reported as 130°,[32] 116°[33] and 134.7–135.1°.[34]

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(31) H. E. Ungnade and A. D. McLaren, *J. Org. Chem.*, **10**, 29 (1945).

(32) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," third ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 262.

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NEW ORLEANS, LA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

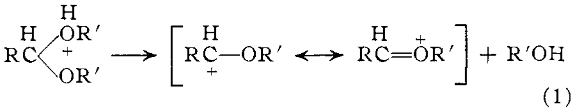
The Hydrolysis of Acetals of Methylvinylcarbinol, Phenylvinylcarbinol and α-Phenylethyl Alcohol

BY JOHN D. DRUMHELLER[1] AND LAWRENCE J. ANDREWS

RECEIVED JANUARY 26, 1955

The acetals of methylvinylcarbinol, phenylvinylcarbinol and (–)-α-phenylethyl alcohol have been synthesized. The first two are formed without allylic rearrangement, and the asymmetric centers of the third have the configuration of the parent alcohol. The acid-catalyzed hydrolysis of methylvinylcarbinyl acetal occurs without allylic rearrangement, and that of (–)α-phenylethyl alcohol takes place with complete retention of configuration at the asymmetric centers. The cinnamyl alcohol which forms during the hydrolysis of phenylvinylcarbinyl acetal is produced from isomerization of phenylvinylcarbinol, which is the immediate reaction product. Apparently no O–R′ bond fission occurs during the hydrolysis of the three acetals [$RCH(OR')_2$], even though derivatives of these alcohols (R′OH) usually undergo solvolysis through the formation of R′ carbonium ion intermediates.

The slow step in the acid-catalyzed hydrolysis of the acetal of an aliphatic alcohol is generally depicted[2] as a unimolecular dissociation (1) of the conjugate acid of the acetal.



(1)

Subsequent rapid reaction of the highly resonance stabilized cation with water to form the hemiacetal, which then decomposes by a path analogous to (1), is presumed to lead to formation of the aldehyde. This mechanism is reasonable in the light of early work[3] on the effects of changes in acetal structure on the hydrolysis rate. The recent observation[4] that the logarithm of the hydrolysis rate constant of methylal is a linear function of the acidity function of the medium strongly supports the contention that step (1) is rate determining.

It is also significant that the process of formation and subsequent hydrolysis of a simple acetal is accomplished by complete retention of configuration at the carbinol carbon of the alcohol.[5–7] This observation eliminates the possibility that R′ carbonium ion is formed as a reaction intermediate in the cases cited. It is conceivable that certain acetals, prepared from alcohols the derivatives of which readily undergo SN1 type displacements, may hydrolyze by the R′ carbonium ion path rather than by route (1).[8] The possibility has now been explored that this abnormal cleavage process might be operative during hydrolysis of acetals of methylvinylcarbinol, phenylvinylcarbinol and (–)α-phenylethyl alcohol.[9] In all three cases it appears that the normal hydrolysis path of equation (1) is preferred.

Preparation and Hydrolysis of the Acetals.—The three acetals were prepared from the reaction of acetaldehyde and the appropriate alcohol in the presence of calcium chloride with hydrogen chloride as a catalyst. That allylic configuration was maintained in the formation of methylvinylcarbinyl acetal was established through catalytic hydrogenation of the unsaturated product. The reduced acetal was identical in physical properties with those of a known sample of *sec*-butyl acetal and produced *sec*-butyl alcohol as its only alcoholic hydrolysis product.

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(1) Organic Chemicals Department, E. I. du Pont de Nemours and Co., Jackson Laboratory, Wilmington, Del.

(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 334.

(3) A. Skrabal and M. Zlatewa, *Z. physik. Chem.*, **122**, 349 (1926).

(4) D. McIntyre and F. A. Long, THIS JOURNAL, **76**, 3240 (1954).

(5) H. K. Garner and H. J. Lucas, *ibid.*, **72**, 5497 (1950).

(6) J. M. O'Gorman and H. J. Lucas, *ibid.*, **72**, 5489 (1950).

(7) E. M. Alexander, H. M. Bursch and G. L. Webster, *ibid.*, **74**, 3173 (1952).

(8) Although the acetone ketals of the *cis*-1,2-diols of tetrahydronaphthalene, hydrindene and 1-phenylcyclohexane appear to be likely candidates for such abnormal hydrolytic cleavage at the 1-position, the *trans*-diols have been isolated only as small fractions of the total glycols obtained on hydrolysis. The *trans*-diols are presumed to form by a glycol isomerization following ketal hydrolysis; *cf.* J. Böeseken and H. Derx, *Rec. trav. chim.*, **40**, 519 (1921); J. Böeseken, *Ber.*, **56B**, 2409 (1923); P. H. Hermans, *ibid.*, **57B**, 824 (1924).

(9) Esters of these types of alcohols are susceptible to acyl-oxygen fission during hydrolysis. See ref. 2, p. 760.