(88%) of a colorless liquid boiling at 132.5–133° (13 mm.), $n^{20}D$ 1.4623.

Anal. Calcd. for $C_9H_{20}O_3S$: S, 15.37. Found: S, 15.45.

β-Ethylmercaptolactaldehyde.—To 21.8 g. (0.105 mole) of β-ethylmercaptolactaldehyde diethylacetal was added 150 ml. of 0.1 *N* sulfuric acid and enough dioxane (100 ml.) to form a homogeneous solution which was allowed to stand for 10 days. The solution was exactly neutralized with 0.35 *N* barium hydroxide solution and the filtrate was concentrated under reduced pressure from a water-bath at about 40°. The residue was diluted with 300 ml. of water and extracted with ether. The ethereal extracts were dried over anhydrous magnesium sulfate and the ether removed, the last traces under reduced pressure. The semi-solid residue was triturated with *n*-hexane, filtered and recrystallized from methyl ethyl ketone. Additional material was obtained from the mother liquors by concentration and dilution with *n*-hexane for a total of about 1.0 g. of a colorless solid, m.p. 114.5° (cor.). Infrared analysis indicated that the material exists in the dimeric or polymeric form.

Anal. Calcd. for $C_5H_{10}O_2S$: C, 44.77; H, 7.52; S, 23.86. Found: C, 44.97; H, 7.55; S, 23.96.

KALAMAZOO, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

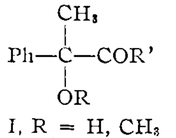
The Stereochemistry of Raney Nickel Action. VIII. Carbon–Carbon Bond Hydrogenolyses Catalyzed by Raney Nickel[1]

BY JOHN A. ZDERIC, WILLIAM A. BONNER AND THOMAS W. GREENLEE[2]

RECEIVED AUGUST 13, 1956

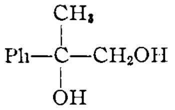
On treatment with Raney nickel in refluxing ethanol (reductive desulfuration conditions) 2-phenyl-1,2-propanediol (II) yields primarily ethylbenzene instead of the anticipated 2-phenyl-1-propanol. The main reaction thus involves carbon–carbon hydrogenolysis between C_1–C_2 of the aliphatic chain. Since reductive desulfuration is an important tool in degradative structure determination, we have investigated the carbon cleavage potentialities of 19 compounds related to II, characterizing the reaction products with the aid of vapor–liquid partition chromatography and infrared spectrophotometry. Our results permit us to conclude that the principal structural requirement for carbon–carbon hydrogenolysis is a hydroxyl or aldehyde function on a primary carbon adjacent to a carbon bearing an aromatic nucleus. In molecules where these structural features were absent, carbon–carbon hydrogenolysis failed to occur, or did so only insignificantly.

Catalytic hydrogenolyses resulting in dehydroxylation[3,4] and demethoxylation[4] have been studied recently from a stereochemical viewpoint in the 2-phenyl-2-hydroxypropionic acid series, I. Such



$$Ph\text{—}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large OR}{|}}{C}}\text{—}COR'$$

I, R = H, CH_3
R' = NH_2, OCH_3



$$Ph\text{—}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large OH}{|}}{C}}\text{—}CH_2OH$$

II

hydrogenolyses occurred with predominant retention of stereochemical configuration, an observation which was rationalized[4] by the postulation of a stereospecifically adsorbed carbonium ion intermediate. In order to assess what effect the unsaturation electrons of the carboxamide or carbalkoxyl functions in I had on determining the observed stereochemical consequences of such dehydroxylations and dealkoxylations, we recently undertook a similar study of the optically active reduced analog of I, 2-phenyl-1,2-propanediol (II), and related compounds.

When II was heated in refluxing ethanol with an excess of Raney nickel the anticipated dehydroxylation product, 2-phenyl-1-propanol, was not obtained. Instead, a hydroxyl-free oil resulted. Rectification of this oil followed by formation of a solid derivative proved the main product to be ethylbenzene. Subsequent examination of the crude hydrocarbon product with the aid of vapor–liquid partition chromatography indicated that the product was a mixture of ethylbenzene containing smaller amounts of isopropylbenzene. Traces of the anticipated 2-phenyl-1-propanol were only occasionally noted in the residues from the hydrocarbon isolation.

The main reaction thus occurring during Raney nickel treatment of II was thus one of carbon–carbon bond cleavage, presumably between carbon-1 and carbon-2 of the diol II, and probably involving the intermediate formation of 2-phenyl-1-propanol (*cf.* Table I). While such catalytic

TABLE I

PRODUCTS OBTAINED BY ACTION OF RANEY NICKEL ON VARIOUS ALCOHOLS AND RELATED COMPOUNDS UNDER REDUCTIVE DESULFURATION CONDITIONS

No.	Reactant	Products[a,b]
1	$PhC(CH_3)(OH)CH_2OH$	$PhCH(CH_3)CH_2OH$, *$PhCH_2CH_3$*(2), $PhCH(CH_3)_2$(1)
2	$PhCH(CH_3)CH_2OH$	*$PhCH_2CH_3$*(10), $PhCH(CH_3)_2$(1)
3	$PhCH(CH_3)CH{=}O$	*$PhCH_2CH_3$*(10), $PhCH(CH_3)_2$(1)
4	$PhCH(CH_3)CH_2OCH_3$	Starting material
5	$PhCH_2CH_2OH$	*$PhCH_3$* (1), $PhCH_2CH_3$(2)
6	$Ph_2CH{-}CH_2OH$	*$C_6H_{11}{-}CH_2{-}Ph$*, Ph_2CHCH_3
7	$PhC(OH)(CH_3)_2$	$PhCH(CH_3)_2$
8	$PhCH(CH_3)_2$	Starting material
9	$Ph_2C(OH)CH_3$	Ph_2CHCH_3
10	$Ph_2CHCH(OH)Ph$	Ph_2CHCH_2Ph
11	$PhCH_2CH(OH)CH_3$	$PhCH_2CH_2CH_3$
12	$PhCH(CH_3)CH(OH)CH_3$	$PhCH(CH_3)CH_2CH_3$[c,d]
13	$PhCH_2C(OH)(CH_3)_2$	$PhCH_2CH(CH_3)_2$[c,d]
14	$PhCH_2CH_2CH_2OH$	$C_6H_{11}{-}CH_2CH_2CH_2OH$[c]
15	$C_6H_{11}CH_2CH_2OH$	Starting material[c]
16	$CH_3(CH_2)_6CH_2OH$	Starting material
17	2-(1-Pyridyl)-ethanol	*1-Picoline* (2,5), by-product(1)[e]
18	$PhCH_2CH_2NH_2$	*$PhCH_3$*(1), $PhCH_2CH_3$(23)
19	$PhCH_2CH_2Cl$	$PhCH_2CH_3$
20	$PhCH_2CH_2Br$	$PhCH_2CH_3$

[a] Cleavage products are italicized. [b] Numbers in parentheses give approximate product ratios. [c] Plus traces of cleavage products; *cf.* Experimental. [d] Plus small amounts of unreacted starting material. [e] Unidentified.

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[1] We gratefully acknowledge support of a portion of this research by the Petroleum Research Fund Advisory Board.

[2] Graduate Fellow Under the American Chemical Society Petroleum Research Fund.

[3] W. A. Bonner, J. A. Zderic and G. Casaletto, THIS JOURNAL, **74**, 5086 (1952).

[4] W. A. Bonner and J. A. Zderic, *ibid.*, **78**, 3218 (1956).

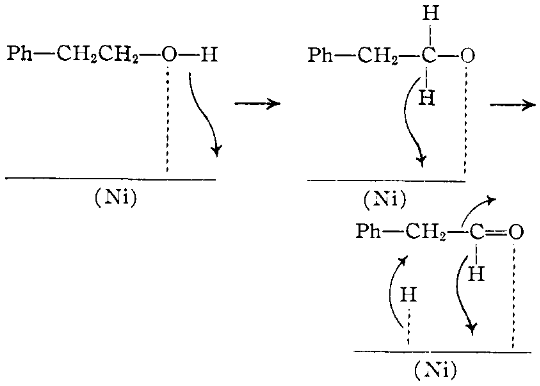
cleavage processes involving alcohols and glycols are well known at higher temperatures and pressures under the influence of nickel[5,6] or copper–chromium oxide[5] catalysts, as well as during the Raney nickel catalyzed conversion of certain alcohols into aldehydes.[7–9] they do not appear to have been noted under the present less drastic conditions prevailing during reductive desulfuration. What may be a related cleavage under desulfuration conditions has been reported[10] by Snyder and Cannon, who found that during desulfuration of 1,2-dialkylmercaptoethanes, RS–CH_2CH_2–SR, not only ethane but also methane, was evolved from the central portion of the molecule.

Reductive desulfuration is a widely employed degradative procedure for structural determination.[11] Since side reactions involving carbon–carbon fission would obviously be a serious complication in the application of this structural tool, it appeared to us highly desirable to establish what types of molecular structures would undergo carbon bond hydrogenolysis under the reaction conditions prevailing during reductive desulfuration. The present paper records preliminary observations on this question.

In Table I are recorded the results of a series of cleavage experiments with structures closely related to II. The crude products from the reactions in Table I were separated into their components by vapor–liquid partition chromatography, and each component was characterized (1) by its reflux time from the VLPC column and (2) by comparison of its infrared spectrum with that of an authentic sample. Rough estimates of the product ratios were made on the basis of the VLPC peak heights.

Examination of the data in Table I permit several empirical generalizations to be made regarding Raney nickel catalyzed carbon–carbon hydrogenolysis under reductive desulfuration conditions. The structural feature which appears to be a prerequisite for extensive occurrence of such a carbon–carbon hydrogenolysis is a hydroxyl group (1, 2, 5, 6) (or something reducible to a hydroxyl group (3)) located on a primary carbon adjacent to a carbon bearing an aromatic (or heterocyclic (17)) nucleus. In the absence of the aromatic nucleus, but with an aliphatic group present on the β-carbon (15, 16), the cleavage reaction is relatively insignificant. When the primary alcohol group is absent (8, 19, 20) or masked (4) no cleavage occurs. When the hydroxyl function is in the benzyl position (7, 9, 10) dehydroxylation occurs readily, but carbon cleavage is absent. Although the phenyl-bearing β-carbon may be branched (2, 3) or otherwise substituted (1, 6) and still constitute a molecule capable of cleavage, branching at the hydroxyl-bearing α-carbon prevents such fission. Thus the β-phenyl-bearing secondary alcohols in 10, 11 and 12 and tertiary alcohol in 13 readily undergo dehydroxylation, but fail to show any carbon–carbon hydrogenolysis. When the aromatic nucleus is located on the γ-carbon (14) rather than the β-carbon, hydrogenolysis occurs insignificantly, even though the alcohol function is primary. In this case aromatic ring reduction was the principal reaction observed. The occurrence of ring reduction simultaneously *with* carbon hydrogenolysis was noticed only in the case of 2,2-diphenylethanol (6), where it is interesting that ring reduction was observed *only* in the fission product and not in the simple dehydroxylation product. Comparison of the cleavage to dehydroxylation ratios in 2, 3 (10/1) and 1 (2/1) with that of 5 (1/2) indicates that the presence of an alkyl substituent on carbon-2 significantly facilitates cleavage.

The data in Table I strongly suggest that a preliminary dehydrogenation of the primary alcohol to an aldehyde must occur prior to carbon–carbon fission. This is indicated by the identical product ratios found in the 2-phenyl-1-propanol and 2-phenylpropanal experiments (2 and 3), as well as by the absence of cleavage products in the cases of methyl 2-phenyl-1-propyl ether (4) and the 2-phenylethyl halides (19 and 20), where an aldehyde intermediate is impossible. Similarly, secondary alcohols (*e.g.*, 10, 11, 12) would produce ketone intermediates on initial dehydrogenation, and are apparently therefore incapable of cleavage. Thus some reaction sequence similar to eq. 1 would appear a reasonable rationalization for the cleavage process, with the β-phenyl substituent being necessary to stabilize a transient radical or ionic intermediate in the final stage. Equation 1 would require the formation of carbon monoxide as a second cleavage product. While we have made no attempt to isolate this by-product, its presence has been reported[7,8] by Paul in similar reactions under comparable conditions. The small amount of cleavage noted with 2-phenylethylamine (18) might be similarly interpreted through an imine intermediate. Isotopic and stereochemical investigations designed to shed further light on the mechanism of such cleavage reactions are currently in progress.



(1)

Experimental

Raney Nickel on 2-Phenyl-1,2-propanediol.—The diol was prepared by the reduction of ethyl 2-phenyl-2-hydroxypropionate with lithium aluminum hydride in ether solution.

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[5] H. Adkins, "Reactions of Hydrogen with Organic Compounds over Copper–Chromium Oxide and Nickel Catalysts," Univ. of Wisconsin Press, Madison, Wisc., 1937, pp. 69–73, 79–83, 139–143.

[6] M. Paty and J. Deschamps, *Compt. rend.*, **234**, 2291 (1952).

[7] R. Paul, *Bull. soc. chim.*, 8, 507 (1941).

[8] R. Paul, *Compt. rend.*, **208**, 1319 (1939).

[9] L. Palfray and S. Sabetay, *ibid.*, **208**, 109 (1939).

[10] H. R. Snyder and G. W. Cannon, THIS JOURNAL, **66**, 155 (1944).

[11] *Cf.* W. A. Bonner, *ibid.*, **74**, 1034 (1952), for previous references.

The crude product was distilled, b. 97–110° (1 mm.). The viscous distillate was chilled and scratched, crystallizing readily. Recrystallization from a mixture of ether and ligroin afforded a white solid, m.p. 41–44°, in substantial agreement with the literature.[12]

The recrystallized diol (3.0 g.), Raney nickel[13] (*ca.* 12 g.) and absolute ethanol (50 ml.) were heated under reflux during six hours, whereupon the mixture was filtered and the cake rinsed with hot ethanol (100 ml.). The filtrate and washings were added to water (700 ml.), and the turbid mixture was extracted twice with ligroin. The extract was dried ($MgSO_4$) and the solvent was distilled through a small column. The residue was distilled through a semi-micro Claisen still, providing 1.2 g. of liquid, b.p. 95–134°. A small residue remained undistilled, whose infrared spectrum indicated it to be 2-phenyl-1-propanol. The distillate was redistilled and a fraction having b.p. 120–134° was collected. From this was prepared[14] a sample of 2,4-diacetylaminoethylbenzene, m.p. 224–226° (lit. 224°)[15] mixed m.p. with an authentic sample undepressed, whose infrared spectrum was identical in all respects with that of an authentic sample.

Experiments in Table I.—Each of the reactants listed in Table I was treated with Raney nickel in refluxing ethanol in the manner described above. The catalyst was filtered and washed with ethanol. The filtrate and washings were distilled approximately to dryness through a $^3/_8 \times 18''$ Stedman column. The residue was investigated for sparingly volatile materials with the aid of a vapor–liquid partition chromatographic column.[16] The distillate was treated with about a liter of water, and the mixture was continuously extracted with redistilled pentane until clear. The pentane extract was dried over phosphoric anhydride, after which the solvent was distilled through the Stedman column. The residue from this process was similarly investigated for volatile hydrocarbon components on the VLPC column.

The vapor–liquid partition column which was employed consisted of a thermostated $^1/_2 \times 48''$ glass tube with a Celite–silicone (2:1) packing. Helium at 5 p.s.i. pressure was used as a carrier gas, a tungsten lamp filament provided the detector,[17] and component efflux times were recorded on a Varian G-10 recorder. For characterization of each component two criteria were used: (1) component efflux times were compared with the efflux times under identical VLPC column conditions for authentic samples, and (2) each component from the VLPC column was isolated by chilling the exit gas stream in a Dry Ice–acetone-bath, then the infrared spectrum of the collected fraction was compared with that of an authentic sample. Rough estimates of the composition of each mixture placed on the VLPC column were obtained by comparing the recorded fraction peak-heights with the peak-heights obtained from similar mixtures of known composition.

The main products from these experiments are listed in Table I. In several reactions, notably 12–15, small amounts of additional by-products were isolated. These were characterized where possible by comparison of their efflux times on the VLPC column with those of authentic samples. Unfortunately these by-products were produced in such small quantities on the reaction scale employed that they could not be collected from the VLPC column for subsequent infrared examination. Thus in experiment 12 a trace of ethylbenzene resulted. In 13 a trace of toluene was found. In 14 the main product from the VLPC column appeared to be 3-cyclohexyl-1-propanol, $n^{20}\text{D}$ 1.4761.

Anal. Calcd. for $C_9H_{18}O$: C, 75.99; H, 12.76. Found: C, 76.05, 76.07; H, 12.00, 11.96.

In addition smaller quantities of ethylbenzene, *n*-propylbenzene, toluene, ethylcyclohexane and methylcyclohexane were formed. The former two hydrocarbons were further characterized by comparison of their infrared spectra with authentic samples. In 15 very little reaction occurred, though five products were evident in too small quantity for isolation from the VLPC column. The efflux times of two of these products corresponded to the efflux times noted for methylcyclohexane and ethylcyclohexane.

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[12] E. Eliel and J. Freeman, THIS JOURNAL, **74**, 923 (1952).

[13] R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

[14] N. Cheronis and J. Entrikin, "Semimicro Qualitative Organic Analysis," Thos. Y. Crowell Co., New York, N. Y., 1947, p. 314.

[15] G. Weisweiller, *Monatsh.*, **21**, 41 (1900).

[16] A. J. P. Martin and co-workers, *Biochem. J.*, **35**, 1358 (1941); **50**, 679 (1951).

[17] R. H. Eastman and H. S. Mosher, private communication.

STANFORD, CALIFORNIA

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Sodium-catalyzed Hydrogen Disproportionation of Phenylcyclohexene. Dehydrogenation and Condensation of Phenylcyclohexane[1]

BY HERMAN PINES AND MARJAN KOLOBIELSKI[2]

RECEIVED OCTOBER 26, 1956

1-Phenylcyclohexene on heating in the presence of sodium or sodium–benzylsodium catalyst at 200–220° undergoes a hydrogen transfer reaction resulting in the formation of two mole equivalents of phenylcyclohexane and one mole equivalent of biphenyl. When the temperature of the reaction was raised to 240°, hydrogen was evolved and the relative ratio of biphenyl to phenylcyclohexane steadily increased. The reaction also was accompanied by the formation of isomeric quaterphenyls obtained from the condensation of biphenyl with the liberation of hydrogen. 4,4′- and 3,4′-diphenylbiphenyl were isolated from the reaction product. Phenylcyclohexane underwent dehydrogenation to biphenyl when refluxed in the presence of a sodium–benzylsodium catalyst. The reaction was accompanied by the formation of quaterphenyls. 1-Cyclohexylcyclohexene under above conditions was converted to cyclohexylcyclohexane, phenylcyclohexane and biphenyl. The mechanism of hydrogen transfer and dehydrogenation reaction is discussed.

It was previously reported that both conjugated and non-conjugated monocyclic terpenes undergo double bond isomerization and dehydrogenation to *p*-cymene when refluxed in the presence of sodium and organosodium compound.[3,4] Under similar experimental conditions geminal akylcyclohexadienes, in which one of the carbon atoms on the ring has two alkyl groups attached to it, also undergo an aromatization reaction, but it is accompanied by a loss of one of the alkyl groups.[1]

Under similar condition *p*-methenes undergo only isomerization; dehydrogenation to *p*-cymene did not occur.[5] The difference in the behavior of *p*-menthadienes as compared with *p*-menthenes can be ascribed to an energy gain in passing from a cyclohexadiene to an aromatic hydrocarbon.

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[1] Paper VIII of the series of Base-catalyzed Reactions. For VII see H. Pines and H. E. Eschinazi, THIS JOURNAL, **78**, 5950 (1956).

[2] Vladimir Ipatieff Postdoctoral Fellow, 1955–1956.

[3] H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 347 (1955).

[4] H. Pines and H. E. Eschinazi, *ibid.*, **77**, 6314 (1955).

[5] H. Pines and H. E. Eschinazi, *ibid.*, **78**, 1178 (1956).