[CONTRIBUTION FROM HAVEMEYER LABORATORY, COLUMBIA UNIVERSITY]

Mechanism of the Alkoxide-catalyzed Carbinol–Carbonyl Equilibrium[1]

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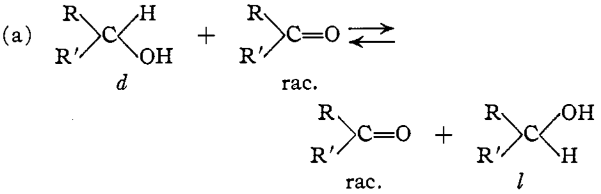
The oxidation–reduction reaction of a carbinol–carbonyl pair, investigated using racemization as tracer, is unaffected by substances which often inhibit free-radical chain reactions and does not incorporate solvent deuterium on carbon. For this reaction and its two-pair counterparts, the Meerwein–Ponndorf–Verley reduction and the Oppenauer oxidation, a mechanism involving the direct carbon to carbon transfer of hydrogen with its electrons, is indicated.

The stereochemical equilibrium of carbinols is catalyzed by aluminum alkoxide as well as by alkali alkoxides, requires initiation by carbonyl compound, and proceeds by an oxidation–reduction mechanism.[3,4] This demonstration permits the use of racemization as a tracer in the study of the oxidation–reduction process itself.

Most familiarly the oxidation–reduction involves a *pair* of carbinol–carbonyl systems, establishment of equilibrium between which[5] is accelerated by aluminum alkoxide in the Meerwein–Ponndorf–Verley reduction[6] and Oppenauer oxidation[7] and may also be catalyzed by alkoxide ion.[3,8] The simplest carbinol–carbonyl oxidation–reduction is a half-cell reaction (a) in which the equivalent forward and backward reactions are catalyzed by the same reagents and in which the presence of a dynamic equilibrium is demonstrable by the use of a stereochemical (*e.g.*, carbinol in (a) optically active) or isotopic (carbon or oxygen labeled if carbinol in (a) is racemic) tracer.



The aim of this work has been to accumulate facts relating to the half-cell reaction, the interpretation of which will impose new conditions on the mechanistic theory of the reaction. At present the theory is constrained by three conditions: (1) the structural relationship of reactants and products which is unequivocal and abundantly documented; (2) the readily reversible nature of the reaction; and (3) the catalyst requirement which recognizes the effectiveness of a wide variety of metal alkoxides in accelerating an otherwise immeasurably slow reaction. In this work there have been uncovered two new conditions which relate to the intervention of free-radical intermediates and to the origin of the reducing hydrogen atom.

The carbinol, (−)-2-methylbutanol-1, on refluxing with catalyst under a nitrogen atmosphere racemizes to the extent that molecules are oxidized to (+)-2-methylbutanal which may lose activity by enolization[9] and be reduced to racemic 2-methylbutanol-1. In Table I the results of various experiments are listed.

TABLE I

Expt.	Sodium alkoxide, mole %	Reagent, mole %	Reflux time, hr.	$[\alpha]^{27}\text{D}$ starting carbinol	$[\alpha]^{27}\text{D}$ recovered carbinol	Rac., %
1	5	None	4.5	−3.1	−3.1	0
2	5	5, IV[c]	4.5	−3.1	−0.5	84
3	5	5, IV[c] 10, V[d]	4.5	−3.1	− .2	94
4	5	5, IV[c] 6, VI[e]	4.5	−3.1	− .3	89
5	5	None	4.5	−6.0	−4.8	20
6	5	5, IV[c]	4.5	−6.6	0.0	100
7	4	3, III[a]	4.5	−6.0	−4.8	20
8	10	5, I[b]	2.5	−6.0	−5.2	12
9	7.5	5, I[b] 5, III[a]	2.5	−6.0	−5.2	12
10	5	1, IV[c]	3	−6.0	−4.6	23
11	5	1, IV[c] 5, III[a]	3	−6.0	−4.5	24
12	5	2, VII[f]	3	−5.8	−5.5	5
13	5	2, VII[f] 2, I[b]	3	−5.8	−5.5	5
14	5	5, VIII[g]	4.5	−6.7	0.0	100
15	10	5, IX[h]	7	−3.8	−3.6	5

[a] III is leuco Bindschedler's Green [bis-(*p*-dimethylaminophenyl)-amine]. [b] I is Bindschedler's Green (the oxidized form of III). [c] IV, benzophenone. [d] V, diphenylamine. [e] VI, thiophenol. [f] VII, benzhydrol. [g] VIII, benzpinacol. [h] IX, pinacol.

Experiments 1 and 5 show the extremes in variation of blank runs. A somewhat simpler procedure than the previous one[4] was used which did not avoid short exposure to air and therefore gave small but variable blanks. In expts. 2 and 6 the striking effect of adding a carbonyl oxidant is clear. Neither diphenylamine (expt. 3) nor thiophenol (expt. 4), powerful inhibitors of some free-radical reactions, exercises any retarding effect on the racemization.

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[2] Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut.

[3] W. von E. Doering, G. Cortez and L. H. Knox, THIS JOURNAL, **69**, 1700 (1947).

[4] W. von E. Doering and T. C. Aschner, *ibid.*, **71**, 838 (1949).

[5] H. Adkins, R. M. Elofson, A. G. Rossow and C. C. Robinson, *ibid.*, **71**, 3622 (1949), have determined oxidation–reduction potentials of a large number of carbinol–carbonyl systems with reference to the standard hydrogen half-cell.

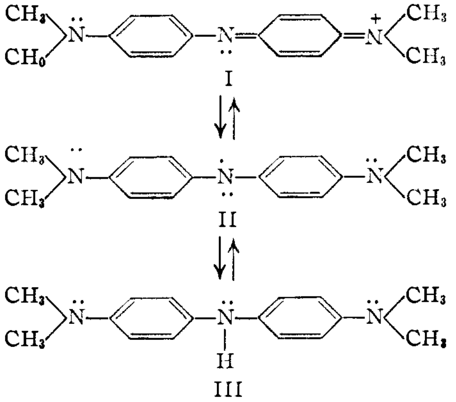
[6] A. L. Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

[7] T. Bersin, "Newer Preparative Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 125.

[8] A. Sagumeni, *Ber.*, **9**, 276 (1876); O. Diels and R. Rhodius, *ibid.*, **42**, 1072 (1909); G. Schicht, German Patent 327,510 [*C. A.*, **16**, 1434 (1922)]; P. J. Montagne, *Rec. trav. chim.*, **41**, 703 (1922); H. Meerwein and R. Schmidt, *Ann.*, **444**, 221 (1925); A. Verley, *Bull. soc. chim.*, [4] **37**, 537, 871 (1925); **41**, 788 (1927); R. V. Shankland and M. Gomberg, THIS JOURNAL, **52**, 4973 (1930); W. E. Bachmann and M. C. Kloetzel, *ibid.*, **59**, 2207 (1937); M. Rubin, *ibid.*, **66**, 2075 (1944).

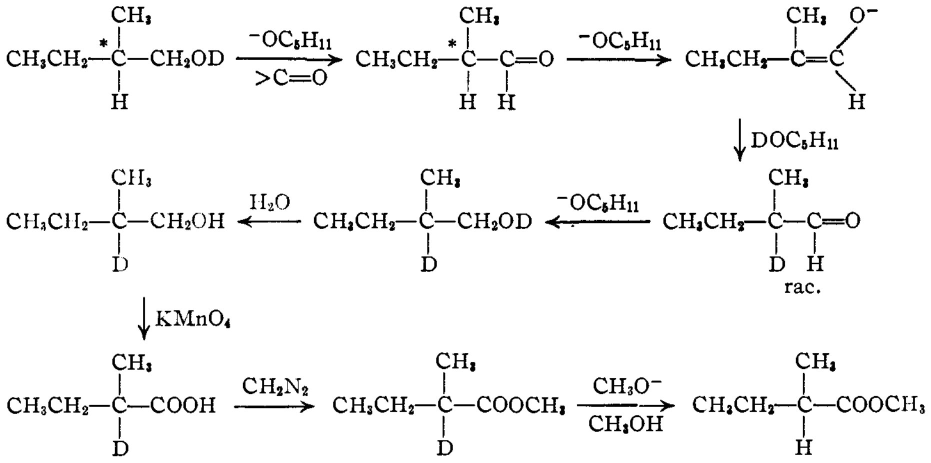
[9] E. J. Badin and E. Pacsu, *ibid.*, **67**, 1353 (1945).

The effect of the various oxidation states of *p,p'*-bis-(dimethylaminophenyl)-amine (III) was investigated. Michaelis and Schwarzenbach[10] have



discovered that equal quantities of the oxidized form (I) and the reduced form (III) disproportionate almost completely in strongly alkaline solution to the free radical (II). Accordingly this reagent should be suitable for the initiation of one-electron transfers. By way of confirmation, it has been found through spectroscopic observation that III reacts rapidly in methanolic sodium methoxide with anthraquinone, also capable of forming a stable free radical,[11] to produce the quinone imine (I). Significantly acetone produces no I. In the attempts to discover interaction between the one-electron transfer reagents and the active carbinol, all combinations were explored. The addition of I (expt. 8), II (expt. 9; equivalent quantities of I and III) or III (expt. 7) failed to initiate the racemization, as did the combination of I and benzhydrol (expt. 13). Furthermore, the addition of III to a racemization already initiated by benzophenone neither retarded nor inhibited the reaction. Benzpinacol which is known to disproportionate to benzophenone and benzhydrol[12] in the presence of alkoxide was as effective as benzophenone itself (expt. 11); but pinacol, which is stable, failed to initiate the racemization (expt. 15). Taken with the negative observation that pinacols have never been reported as by-products in the Meerwein–Ponndorf–Verley reduction, these observations make it appear improbable that free-radicals are involved in the racemization of 2-methylbutanol-1.

The origin of the hydrogen atom which becomes attached to the carbinol carbon in the reduction of the carbonyl group has been established by using racemization as a measure of the oxidation–reduction and solvent deuterium as a tracer for hydrogen. The necessary conditions for significance have been established. As expected (−)-2-methylbutanol-1-$d_{46.8\%}$ loses all deuterium in boiling water. The oxidation of $(-)_{98\%}$-2-methylbutanol-1 with alkaline permanganate to $(+)_{98\%}$-2-methylbutyric acid of undiminished optical purity demonstrates that the hydrogen atoms on carbon atom 1 in the carbinol can be removed without jeopardizing the hydrogen atom at the asymmetric center, carbon atom 2. That this latter hydrogen can be removed is shown by the fact that methyl (+)-2-methylbutyrate prepared from (+)-acid and diazomethane is racemized by methanolic sodium methoxide at the boiling point although at room temperature no racemization is observed. When $(-)_{98.5\%}$-2-methylbutanol-1-$d_{46.8\%}$ is racemized by boiling with sodium amylate, racemic carbinol is obtained which contains 20.8% deuterium after boiling with water to remove hydroxyl deuterium. Oxidation to 2-methylbutyric acid of undiminished deuterium content (21.3%) demonstrates unequivocally that no significant amount of deuterium becomes attached to carbon atom 1 during the oxidative–reductive racemization of the 2-methylbutanol-1. When this acid is esterified with diazomethane and boiled with methanolic sodium methoxide, methyl 2-methylbutyrate containing no deuterium results. As required by the proposed mechanism of racemization all the deuterium which has been introduced on carbon in the 2-methylbutanol-1 is therefore situated at carbon atom 2. These experiments are outlined in the scheme



A similar series of experiments has been conducted with aluminum alkoxide as catalyst in which $(-)_{99.0\%}$-2-methylbutanol-1-$d_{47.3\%}$ is partially racemized (52%) to $(-)_{48\%}$-2-methylbutanol-1 containing 8.9% deuterium on the asymmetric carbon atom 2.

This figure seems surprisingly low since, on the assumption of equal rates of reaction of hydrogen and deuterium, the concentration of deuterium in the solvent should have decreased from 47.3 to 31.1% corresponding to the incorporation of 16.2 to 24.6% of deuterium. Actually the solvent deuterium content decreased from 47.3 to 38.4% suggesting that between 19.9 and 24.6% deuterium

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[10] G. Schwarzenbach and L. Michaelis, This Journal, **60**, 1667 (1938).

[11] A. Geake and J. T. Lemon, *Trans. Faraday Soc.*, **34**, 1409 (1938).

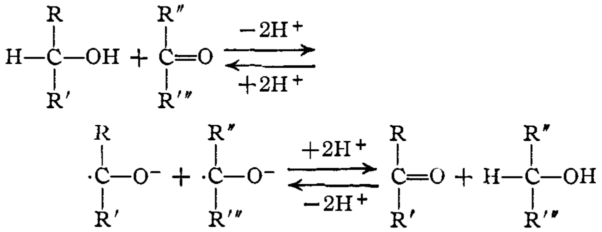
[12] J. Boëseken, *Rec. trav. chim.*, **40**, 433 (1921).

should have been incorporated (on the same assumption of equal rates of reaction of hydrogen and deuterium). As a rough approximation it follows that deuterium was incorporated about 2.5 times more slowly than hydrogen. This difference in rate of reaction between hydrogen and deuterium[13] indicates strongly that the making or breaking of a carbon–hydrogen bond has become rate-determining. It is a reasonable explanation that the rate-determining step in the racemization catalyzed by aluminum alkoxide be enolization whereas in the reaction catalyzed by sodium alkoxide it be oxidation–reduction.[14]

This change in no way detracts from the significance of the deuterium experiments which demand only that the rate of racemization be equal to or slower than the rate of oxidation–reduction. Any implication that sodium alkoxide is a more effective oxidation–reduction catalyst than aluminum alkoxide based on the relative effectiveness as catalysts for the specific racemization studied here is of course completely unwarranted.

The deuterium experiments demonstrate that solvent hydrogen does not become attached to carbinol carbon. The hypothesis is strongly supported that hydrogen is transferred directly from carbinol carbon to carbonyl carbon, irrespective of whether the catalyst is sodium or aluminum alkoxide.

Michaelis has implied for the carbinol–carbonyl oxidation–reduction system a mechanism[15] analogous to that which he has so elegantly established for the duroquinone–durohydroquinone[16] and benzil–benzoin[17] system. Only briefly formulated by Michaelis, this mechanism is based on single electron steps and dismutation and may be represented for discussion by the following scheme.

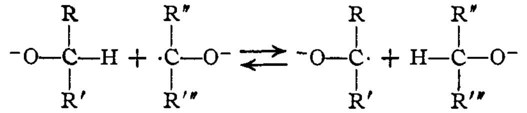


$$\mathrm{H{-}\underset{R'}{\overset{R}{C}}{-}OH + \underset{R'''}{\overset{R''}{C}}{=}O \underset{+2H^+}{\overset{-2H^+}{\rightleftharpoons}}}$$

$$\mathrm{\cdot\underset{R'}{\overset{R}{C}}{-}O^- + \cdot\underset{R'''}{\overset{R''}{C}}{-}O^- \underset{-2H^+}{\overset{+2H^+}{\rightleftharpoons}} \underset{R'}{\overset{R}{C}}{=}O + H{-}\underset{R'''}{\overset{R''}{C}}{-}OH}$$

Insofar as it applies to *aliphatic* carbinol systems, this mechanism is consistent with the structural and reversibility conditions, but accommodates only catalysis by strong bases convincingly and is in complete disaccord with the conditions of non-intervention of solvent deuterium and the apparent non-existence of free-radical intermediates. It should be emphasized, however, that this mechanism is strongly supported in those cases where structural features have greatly increased the stability of the hypothesized free radicals. In fact all systems the oxidation–reduction potential of which can be measured electrochemically (*cf.* ref. 5) presumably react by two one-electron steps. The general concept[15] that "every oxidation (or reduction) can proceed only in steps of univalent oxidations (or reductions)" seems highly questionable.

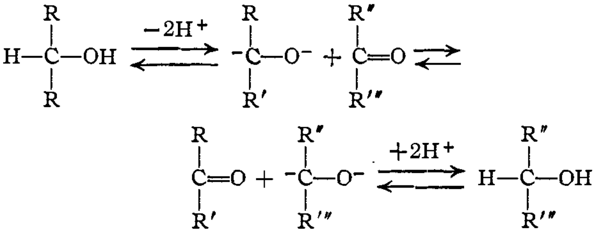
In the light of the comparatively high energy and low concentration to be expected of aliphatic ketyls, a chain mechanism may be formulated as



$$\mathrm{{}^-O{-}\underset{R'}{\overset{R}{C}}{-}H + \cdot\underset{R'''}{\overset{R''}{C}}{-}O^- \rightleftharpoons {}^-O{-}\underset{R'}{\overset{R}{C}}\cdot + H{-}\underset{R'''}{\overset{R''}{C}}{-}O^-}$$

Here very small concentrations of ketyl would carry the oxidation–reduction by a reversible chain mechanism. This mechanism is consistent not only with the same conditions as in Michaelis' mechanism but involves transfer of hydrogen directly from carbon to carbon and thus is consistent with the deuterium experiments. It seems inconsistent with the failure of Bindschedler's Green and derivatives to affect the course of the reaction and does not easily accommodate the effectiveness of *aluminum* alkoxide as catalyst.

The existence of dianions such as that indicated by the formation of benzilic acid on treating benzophenone with excess sodium[18] followed by carbon dioxide[19] suggests an ionic mechanism in which two electrons are transferred simultaneously. Once again it is mainly inconsistency with the non-intervention of solvent deuterium and the effectiveness of aluminum alkoxide which excludes this mechanism from further consideration.



$$\mathrm{H{-}\underset{R}{\overset{R}{C}}{-}OH \overset{-2H^+}{\rightleftharpoons} {}^-\underset{R'}{\overset{R}{C}}{-}O^- + \underset{R'''}{\overset{R''}{C}}{=}O \rightleftharpoons}$$

$$\mathrm{\underset{R'}{\overset{R}{C}}{=}O + {}^-\underset{R'''}{\overset{R''}{C}}{-}O^- \overset{+2H^+}{\rightleftharpoons} H{-}\underset{R'''}{\overset{R''}{C}}{-}OH}$$

In close analogy with Hammett's mechanism for the Cannizzaro reaction,[20] Woodward, Wendler and Brutschy[21] have indicated a mechanism for the carbinol–carbonyl equilibrium involving the direct transfer of hydrogen with its two bonding electrons from carbinol carbon to carbonyl carbon. Formulated in terms of the transition state, an alkoxide ion in which the negative charge is tending to expel a hydride ion[22] approaches the carbonyl compound of which the electron deficient carbon atom is a potential acceptor of a hydrogen with its pair of

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(13) For references and discussion, see F. H. Westheimer, *Chem. Revs.*, **45**, 433 (1949).

(14) This explanation is consistent with the abundant evidence that the use of aluminum alkoxide in the carbinol–carbonyl interconversions almost entirely avoids the condensations which usually prohibit the use of the strongly basic alkoxides. See reference 6, pp. 181 and 187.

(15) (a) L. Michaelis in D. Green, Ed., "Currents in Biochemical Research," Interscience Publishers, Inc., New York, N. Y., 1946, p. 213; (b) L. Michaelis and M. Schubert, *Chem. Revs.*, **22**, 437 (1938); (c) L. Michaelis, *Ann. New York Acad. Sci.*, **40**, 39 (1940).

(16) L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck and S. Granich, THIS JOURNAL, **60**, 1678 (1938).

(17) L. Michaelis and E. S. Fetcher, Jr., *ibid.*, **59**, 1246 (1937).

(18) J. B. Tingle and E. E. Gorsline, *ibid.*, **30**, 1874 (1908).

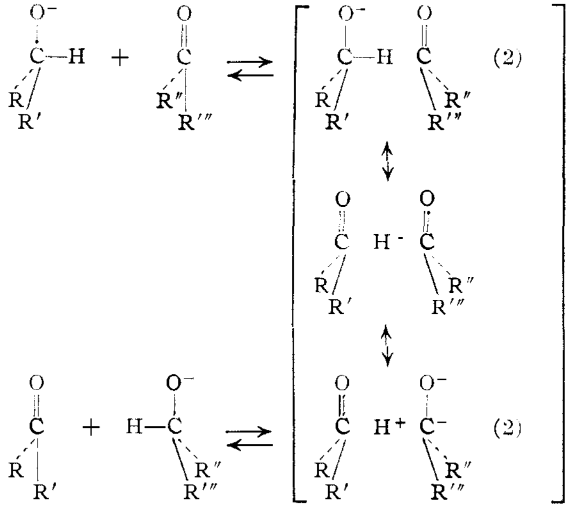
(19) E. Beckmann and T. Paul, *Ann.*, **266**, 1 (1891).

(20) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 350–353.

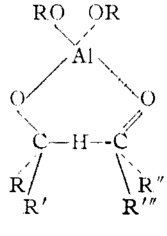
(21) R. B. Woodward, N. Wendler and F. Brutschy, THIS JOURNAL, **67**, 1426 (1945).

(22) At considerably higher temperatures alkoxide ions do in fact evolve hydrogen gas. *Cf.* W. Hückel and H. Naab, *Ber.*, **64**, 2137 (1931).

electrons. In the transition state the hydrogen being transferred is substantially equally bonded to both carbon atoms as is indicated by the several contributing resonance structures. This transition state affords a pass of lower energy for the transfer of hydrogen than the extreme alternative in which a free hydride ion is ejected and then rebonds to carbon.



This mechanism, accommodating the structural relationships and the reversible nature of the reaction, is also in accord with the apparent absence of free radical intermediates and with the non-intervention of solvent deuterium. The effectiveness of aluminum alkoxide as catalyst is equally well accommodated by the formulation[21] which permits the energy of the transition state to be lowered by partial covalent bond formation with an electron acceptor. Phrased in another way, aluminum provides less activation of the carbon–hydrogen bond, but being acidic may augment the electron-accepting character of the carbonyl group by coordination. Similar resonance structures must of



course be written for the transition state of the aluminum-catalyzed reaction as were written for the sodium.

The carbinol–carbonyl equilibrium apparently falls into a class of oxidation–reductions which have in common base-catalyzed, direct hydrogen transfer as their effective mechanisms. At the aldehyde–aldehyde level, there is the intermolecular Cannizzaro reaction,[20,23] and the intramolecular disproportionations of glyoxal[20,23] and phenylglyoxal.[24] At the carbinol–carbonyl level, there is now the intermolecular Meerwein–Ponndorf–Verley–Oppenauer interconversions and the intramolecular example of the conversion of glucose to fructose, where likewise non-intervention of solvent deuterium has been demonstrated.[25,26]

Experimental

Influence of Various Substances on the Racemization of 2-Methylbutanol-1.—In the general procedure, 1 to 10 mole % of sodium was added to 2.2 to 8.8 g. of active amyl alcohol (varying from 72–90%) in a 25-cc. flask. The flask was attached to a reflux condenser connected through a three-way stopcock either to an aspirator or to a rubber balloon filled with nitrogen. It was then evacuated and filled with nitrogen three times, and heated under positive nitrogen pressure at 120° in an oil-bath until the sodium had reacted. To the cooled, disconnected flask, the various reagents were added or, in blank runs, the flask was simply exposed to air for 30 sec. The flask was then reconnected, flushed with nitrogen as before, and heated at 120° for various periods of time. The cooled reaction mixture was made weakly acid with dilute hydrochloric acid and extracted with 50–100 cc. of ether. The organic layer was washed with water until neutral, dried over magnesium sulfate and fractionated through a 10-cm. Vigreux column. The fraction, b.p. 127–128°, was examined in methanol solution for optical activity. From blank runs it had been determined that further purification through the hydrogen phthalate was not required. Occasionally the blank runs showed some racemization, presumably due to contamination. The results of a number of experiments are compiled in Table I.

Bindschedler's Green was prepared according to Michaelis and Schwarzenbach.[27] The leuco Bindschedler's Green was obtained by reduction of the dye with alkaline, aqueous sodium bisulfite and was purified by repeated crystallization from *n*-hexane until nearly colorless crystals, m.p. 120–121°, were obtained.

Anal. Calcd. for $C_{16}H_{21}N_3$: C, 75.3; H, 8.3; N, 16.5. Found: C, 74.9; H, 8.7; N, 16.6.

Racemization of (−)-2-Methylbutanol-1-*d*. (a) Sodium Alkoxide-catalyzed.—Fractionation of 3500 g. of commercial fusel oil (17% (−)-2-methylbutanol-1 and 80% 3-methylbutanol-1) in an 8-foot column packed with $^3/_{32}$-inch metal helices afforded 565 g. of active amyl alcohol, 83% of optical purity; refractionation in the same column gave 410 g., b.p. 127.8–128.2°, $[\alpha]^{27}\text{D}$ −5.57 to −5.81° (neat), 96–99% of optical purity. Refluxing a 22-g. sample for 16 hr. with 3.0 g. of 90% deuterium oxide under nitrogen afforded on distillation 20.0 g. of $(-)_{99\%}$-2-methylbutanol-1-$d_{46.8\%}$ (A), b.p. 128°, $[\alpha]^{27}\text{D}$ −5.81°, 4.29 ± 0.02% deuterium. The analysis for deuterium involved combustion of *ca.* 50 mg. of sample, collection and purification of the water, determination of the density by the falling drop method using *o*-fluorotoluene, and calculation from a predetermined calibration curve.

When 2.0 g. of A was refluxed with 80 cc. of water for 12 hr., carbinol containing 0.3% of one deuterium atom was recovered.

A (15.0 g.) was racemized by heating at 120° with 5 mole % each of sodium and benzophenone under nitrogen for 8 hr., 12.5 g. of completely racemized carbinol being recovered. This product was refluxed for 23 hr. in 400 cc. of water to give 12.0 g. of carbinol from which water containing 1.91 ± 0.02 wt. % of deuterium oxide was obtained, corresponding to *rac*-2-methyl-2-$d_{20.6\%}$-butanol-1 (B).

A solution of 5.0 g. of B, 13 g. of potassium permanganate and 1.5 g. of potassium hydroxide in 250 cc. of water was stirred for 40 min., extracted with 50 cc. of ether, acidified with hydrochloric acid and extracted with chloroform. The chloroform extract was washed with 50 cc. of water, dried with magnesium sulfate, concentrated and fractionated in a 10-cm. Vigreux column to give 3.0 g. of *rac*-α-methyl-α-$d_{21.2\%}$-butyric acid (C), b.p. 173–174°, giving on combustion water containing 2.36 ± 0.02 wt. % of deuterium oxide.

Reaction of 1.6 g. of C with excess diazomethane in ether,

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(23) H. Fredenhagen and K. F. Bonhoeffer, *Z. physik. Chem.*, **A181**, 379 (1938).

(24) W. v. E. Doering, T. I. Taylor and E. Schoenewaldt, This Journal, **70**, 455 (1948).

(25) H. Fredenhagen and K. F. Bonhoeffer, *Z. physik. Chem.*, **A181**, 392 (1938).

(26) K. Goto, *J. Chem. Soc. Japan.*, **63**, 217 (1942).

(27) L. Michaelis and G. Schwarzenbach, This Journal, **60**, 1667 (1938).

removal of solvent and fractional distillation yielded 0.6 g. of the methyl ester of C, b.p. 110–116°, which was refluxed for 36 hr. in a solution of 0.06 g. of sodium in 20 cc. of methanol. The cooled mixture was neutralized with gaseous hydrogen chloride, filtered from sodium chloride and freed of solvent by distillation. Evaporative distillation of the residue afforded 0.2 g. of *rac*-methyl α-methylbutyrate from which water containing 0.04 ± 0.01 wt. % of deuterium oxide was obtained.

When 10.0 g. of optically pure carbinol, $[\alpha]^{27}\mathrm{D}$ −5.81° (neat), is oxidized by the procedure applied to B, 6.0 g. of α-methylbutyric acid, $[\alpha]^{27}\mathrm{D}$ +17.75° (neat), 98% optically pure, was obtained. Reaction of 3.6 g. of this acid with excess diazomethane and fractional distillation of the product gave 1.22 g. of methyl α-methylbutyrate, b.p. 112–115°, $[\alpha]^{27}\mathrm{D}$ +21.1° (*c* 1.7, methanol). A solution of 1.2 g. of this ester in 25 cc. of methanol containing 0.1 g. of sodium was not racemized on standing 24 hr. at room temperature, but was completely racemized on refluxing for 30 hr.

(**b**) **Aluminum Alkoxide-catalyzed.**—By a procedure similar to the previous one, 15.0 g. of $(-)_{99\%}$-2-methylbutanol-1-$d_{47.3\%}$ was heated at 120° for 40 hr., with 5 mole % each of aluminum isopropoxide and benzophenone. Carbinol was isolated, refluxed with 400 cc. of water for 24 hr. and purified by distillation to give 10.0 g. of $(-)_{48\%}$-2-methyl-2-$d_{8.9\%}$-butanol-1. Five grams of this material was oxidized with alkaline permanganate to 2.7 g. of α-methyl-α-$d_{8.9\%}$-butyric acid, b.p. 173–174°, $[\alpha]^{27}\mathrm{D}$ +10.4° (methanol), from which water of combustion containing 0.98 ± 0.02 wt. % of deuterium oxide was obtained.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Studies in the Wagner Rearrangement.[1-3] III. Chrysene-5,6-C_1^{14}

BY CLAIR J. COLLINS, DANIEL N. HESS, ROWLAND H. MAYOR,[4] GEORGE M. TOFFEL[5] AND A. RUSSELL JONES

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Chrysene-5,6-C_1^{14} was produced in quantitative yield through the dehydration–rearrangement of 11H-benzo[a]fluorene-11-methanol-C^{14}. The distribution of radioactivity between the 5- and 6-positions of the chrysene so prepared has been shown to be in the ratio 76:24. These results are discussed in terms of the presumed carbonium ion intermediates. The over-all yield of chrysene-5,6-C_1^{14}, in the four-step synthesis from carbon-C^{14} dioxide, was 93%.

Introduction

The synthetic method used for incorporating carbon-14 into phenanthrene[1a] and benz[a]anthracene[1b] has now been extended to the preparation of labeled chrysene V. Although the radioactivity was nearly equally divided between the two labeled positions of benz[a]anthracene-5,6-C_1^{14} (48% in the 5-position and 52% in the 6-position), the chrysene V contains more than three times as much carbon-14 in the 5- as in the 6-position.

The compounds involved in the synthesis of chrysene-5,6-C_1^{14} are shown in the reaction sequence I → V; the degradative scheme used to establish the partition of radioactivity between the two labeled positions is indicated by structures V → XIII. The former sequence parallels those employed for phenanthrene[1a] and benz[a]anthracene,[1b] and requires no further discussion. The latter scheme is noteworthy however, both because it provides two separate checks on the carbon-14 distribution in hydrocarbon V, and because it clears up the confusion which previously existed[6,7] concerning the structures of keto acids VIII and XI.

Labeled chrysene V was oxidized to chrysenequinone VI with chromic acid.[6] The quinone VI was then converted to the dicarboxylic acid VII either through the Beckmann rearrangement of the quinone monoöxime and hydrolysis of the resulting amides,[7] or by its direct oxidation with hydrogen peroxide. Graebe and co-workers[6,7] reported that a keto acid melting at 283° and corresponding to structure VIII was obtained either when the monoöxime of the quinone was subjected to a Beckmann rearrangement at 130–140°, or when the dicarboxylic acid VII was treated with sulfuric acid for periods of 12 to 24 hours at room temperature. Structure VIII was assigned this compound on the basis of its failure according to "von Meyer's rule," to form a methyl ester when heated for 24 hours with methanol saturated with hydrogen chloride. Graebe and Gnehm[8] reported also that this keto acid on being heated with soda lime yielded 11H-benzo[a]fluorene-11-one (XIII) while, when distilled with zinc dust, it was converted to 11H-benzo[a]fluorene (I). These authors said, "It was not possible for us to solve this paradox."[8]

We have now shown that the action of sulfuric acid on compound VII causes the formation of two keto acids, VIII and XI. Further, the keto acid which melts at 283° possesses structure XI rather than structure VIII. Contrary to the observations of Graebe and Gnehm, keto acid XI is easily esterified when heated in methanol containing a trace of acetyl chloride, while keto acid VIII remains unesterified; this difference in ease of esterification was used in fact to separate these two compounds. There can be no doubt of these structures since, on decarboxylation, the two compounds yielded the known ketones X and XIII, respectively. Structures VIII and XI are also confirmed by the radiochemical data.

Radioactivities are shown by the appropriate

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[1] Previous papers: (a) I, C. J. Collins, THIS JOURNAL, **70**, 2418 (1948); (b) II, C. J. Collins, J. G. Burr and D. N. Hess, *ibid.*, **73**, 5176 (1951).

[2] This paper is based upon work performed under contract Number W-7405-eng-26 for the Atomic Energy Commission at Oak Ridge National Laboratory.

[3] Presented in part before the Division of Organic Chemistry at the 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950.

[4] Visiting Consultant to Oak Ridge National Laboratory, June–September, 1950.

[5] Member of the Research Participation Program jointly sponsored by the Oak Ridge Institute of Nuclear Studies and the Oak Ridge National Laboratory, March–June, 1950.

[6] C. Graebe and F. Honigsberger, *Ann.*, **311**, 257 (1900).

[7] C. Graebe and R. Gnehm, Jr., *ibid.*, **335**, 113 (1904).

[8] Reference 7, p. 120.