Tebbe for certain chemical intermediates, and of A. M. Ribley for analytical data.

Summary

Alkylthio-(trifluoromethyl)-benzenes containing one, two and three trifluoromethyl groups have been prepared by the action of a sodium or potassium alkyl sulfide on a trifluoromethyl-substituted bromo- or chlorobenzene in an alcoholic solvent.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Rearrangements of Carbon Atoms in *t*-Butyl and *t*-Amyl Derivatives[1,2]

BY JOHN D. ROBERTS, ROBERT E. MCMAHON AND JACK S. HINE

Rearrangements of the Wagner–Meerwein type of alkyl derivatives with polar catalysts are commonly considered to proceed through carbonium ion intermediates.[3] Where such rearrangements may lead to several products, it is often possible to predict which product will be formed most readily by postulating that the most favorable sequence of carbonium ion intermediates should involve ions of maximum stability formed by successive 1,2-shifts of hydride or alkide ions.[4] The order of carbonium ion stability (tertiary≫ secondary > primary) is usually inferred from the solvolytic reactivities of alkyl halides in ionizing (but weakly nucleophilic) solvents such as formic acid.[5]

Despite the very considerable work which has been done on carbonium ion rearrangement reactions a number of important problems have not yet been solved. Among these is the question of carbonium ion structure in circumstances where at least two isomeric forms might be expected, each of comparable energy and obtainable from the others by simple 1,2-shifts. Such ions may be represented as a mixture of forms with energy barriers to interconversion depending on their structures and environment or else as single species of intermediate structure.[6] Little concrete experimental evidence bearing on this point is available except for the elegant study made by Winstein and Trifan[6b] of the solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate.[7] The magnitudes of the energy barriers to interconversion of isomeric carbonium ions have not been adequately evaluated and the present investigation is concerned with the ease of rearrangements of the following type in reactions which are commonly considered to involve either stepwise carbonium ion or direct concerted mechanisms. These rearrangements involving substances of identical carbon skeletons and nearly identical energies[8] were studied using C-14 as a tracer. It is expected that investigation of rearrangements between substances of identical energies

$$\underset{\text{I}}{(CH_3)_3C^{14}\text{—}X} \rightleftarrows \underset{\text{II}}{(CH_3)_2(C^{14}H_3)C\text{—}X}$$

$$\underset{\text{III}}{(CH_3)_2C^{14}XCH_2CH_3} \rightleftarrows \underset{\text{IV}}{CH_3(C^{14}H_3)CXCH_2CH_3} \rightleftarrows$$

$$\underset{\text{V}}{(CH_3)_2CXC^{14}H_2CH_3} \rightleftarrows \underset{\text{VI}}{(CH_3)_2CXCH_2C^{14}H_3}$$

should enable determination of the magnitude of interconversion energy barriers free of complications resulting from differences in energy between starting materials and products. This advantage is well exemplified by the behavior of the neopentyl cation which when generated in any irreversible reaction undergoes rapid and complete rearrangement to a *t*-amyl cation.[9] It is not known to what degree this ease of rearrangement is generally characteristic of carbonium ions since it is possible that the isomerization transition state is stabilized by contributions of resonance forms resembling the (more stable)

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[1] Supported in part by the joint program of the Office of Naval Research and the Atomic Energy Commission.

[2] Preliminary communication, THIS JOURNAL, **71**, 1896 (1949).

[3] (a) Whitmore, *ibid.*, **54**, 3274 (1932); *Chem. Eng. News*, **26**, 668 (1947). (b) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, pp. 317–325.

[4] Mosher and Cox (Abstracts of September 1949 meeting of the American Chemical Society) have presented evidence for 1,3-shifts of methyl groups in the dehydration of 4,4-dimethyl-3-ethyl-2-pentanol.

[5] Bateman and Hughes, *J. Chem. Soc.*, 945 (1940); Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[6] (a) Dewar, "The Electronic Theory of Organic Chemistry," The Oxford University Press, London, 1949, pp. 211–213; (b) *cf.* also references cited by Winstein and Trifan, THIS JOURNAL, **71**, 2953 (1949).

[7] It should be noted that the existence of a carbonium ion of intermediate structure is not unequivocally demonstrated by the experiments of Winstein and Trifan since the racemization accompanying the solvolysis could be produced by processes other than rearrangement of carbon skeleton. Work on the establishment of the structure of the norbornyl cation using C-14 as tracer has been in progress in this laboratory since 1947.

[8] It is recognized that the bond energies of C^{12}–C^{12} bonds are not identical with those of C^{12}–C^{14} bonds. The experimental findings with regard to the magnitude of "isotope effects" arising from such bond energy differences are confusing and, at present, no quantitative evaluation appears to be possible. We believe that isotope effects in our work should be small but there is no assurance that this is actually the case. See Beeck, Otvos, Stevenson and Wagner, *J. Chem. Phys.*, **16**, 255, 993 (1948); Meyerson and Daniels, *Science*, **108**, 676 (1948); Bigeleisen, *ibid.*, **110**, 14 (1949); Yankwich and Calvin, *J. Chem. Phys.*, **17**, 109 (1949); Bigeleisen and Friedman, *ibid.*, **17**, 998 (1949); Stevens and Attree, *Can. J. Research*, **27B**, 807 (1949); *J. Chem. Phys.*, **18**, 574 (1950) for isotope effects in other reactions.

[9] (a) Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932). (b) Whitmore, Wittle and Popkin, *ibid.*, **61**, 1586 (1939). (c) Dostrovsky and Hughes, *J. Chem. Soc.*, 166 (1946).

product. In fact, the neopentyl cation may have no separate existence, the *t*-amyl ion being formed essentially directly from neopentyl derivatives in those reactions usually expected to proceed by carbonium ion intermediates.[3a,10]

Synthetic and Degradative Methods

The starting compounds for the rearrangement studies were 2-methyl-2-propanol-2-C^{14} (I, X = OH), 2-methyl-2-butanol-2-C^{14} (III, X = OH) and 2-methyl-2-butanol-1-C^{14} (IV, X = OH). These substances were prepared from methanol-C^{14} and barium carbonate-C^{14} as the isotopic raw materials[11] by the reactions shown below.

$$C^{14}O_2 \xrightarrow[(2)\ HCl]{(1)\ CH_3MgCl} CH_3C^{14}O_2H \xrightarrow{PCl_3}$$

$$CH_3C^{14}OCl \xrightarrow[(2)\ NH_4Cl]{(1)\ CH_3MgCl} I\ (X = OH)$$

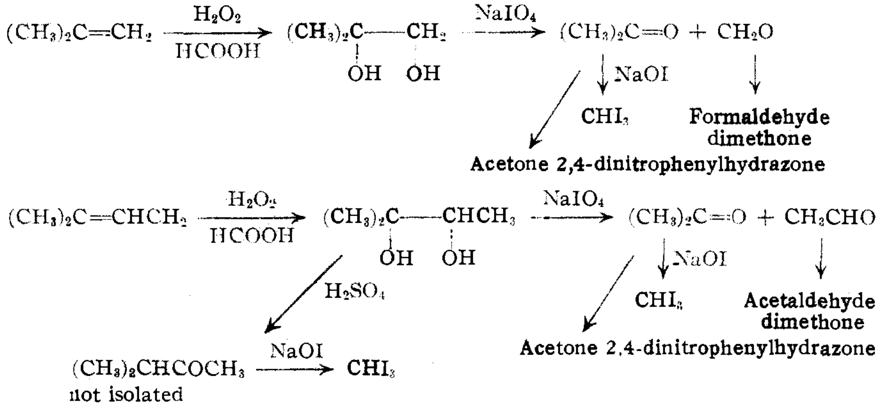
$$C^{14}O_2 \xrightarrow[(2)\ HCl]{(1)\ C_2H_5MgCl} CH_3CH_2C^{14}O_2H \xrightarrow{PCl_3}$$

$$CH_3CH_2C^{14}OCl \xrightarrow[(2)\ NH_4Cl]{(1)\ CH_3MgCl} III\ (X = OH)$$

$$C^{14}H_3OH \xrightarrow{HI} C^{14}H_3I \xrightarrow{Mg}$$

$$C^{14}H_3MgI \xrightarrow[(2)\ NH_4Cl]{(1)\ CH_3COCH_2CH_3} IV\ (X = OH)$$

The degradation procedures for location of the C^{14} atoms in the isobutane and isopentane skeletons involved conversion of the final products of the reactions studied for possible rearrangements into isobutylene or trimethylethylene. In each case it was demonstrated that the reactions used for alkene formation gave no carbon skeleton rearrangements. The alkenes were then degraded by hydroxylation with performic acid[12] and cleavage of the resulting glycols with sodium periodate solution. The over-all degradative sequences follow.



The **bold-face type** substances were analyzed for C^{14} by the method previously described.[13] The measured activities were corrected for self-absorption. The specific activities corresponding to each carbon of the isobutane or isopentane chains were obtained from the following equations in which A_n refers to the specific activity of the n^{th} carbon of the chain and k is a correction for self-absorption. In our work, chemically *equivalent* positions, such as the three methyl groups

Isobutane chain:

$A_1 = 3 \times 17k \times$ activity of formaldehyde dimethone $= 3k \times$ activity of iodoform

$A_2 = 9k \times$ activity of acetone 2,4-dinitrophenylhydrazone $- 2/3\ A_1$

Isopentane chain:

$A_1 = 2k \times$ activity of iodoform (from acetone)

$A_2 = 9k \times$ activity of acetone 2,4-dinitrophenylhydrazone $- A_1$

$A_4 = k \times$ activity of iodoform (from methyl isopropyl ketone)

$A_3 = 18k \times$ activity of the acetaldehyde dimethone $- A_4$

of II, are treated as a unit and the reported activity is the sum of the specific activities of the equivalent positions.[14]

It is to be noted that pinacol-type rearrangement of 2-methyl-2,3-butanediol to methyl isopropyl ketone with sulfuric acid may proceed either with hydrogen or methyl shift to give the same final product. Since the utility of the reaction in the degradative scheme depends on which process actually occurs this point was checked using 2-methyl-2,3-butanediol-1-C^{14}. The iodoform obtained from sodium hypoiodite oxidation of the rearrangement product was completely inactive and it may be concluded that the rearrangement proceeds exclusively with hydrogen shift. It is probable that the exclusive migration of hydrogen in this reaction may be ascribed more to the relative ease of loss of the tertiary hydroxyl as compared with the secondary hydroxyl than to a large difference between the migratory aptitudes of hydrogen and methyl.

Results and Discussion

The reactions studied for rearrangements of type I ⇄ II or III ⇄ IV, etc., were of varieties generally considered to involve carbonium ion intermediates with *t*-alkyl compounds and were selected with the

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[10] *Cf.* Swain, THIS JOURNAL, **70**, 1119 (1946).

[11] The C^{14}-containing methanol and barium carbonate were supplied by the Clinton Laboratories, Oak Ridge, Tenn., on allocation from the U. S. Atomic Energy Commission.

[12] Swern, Billen and Scanlan, THIS JOURNAL, **68**, 1504 (1946).

[13] Roberts, Bennett, Holroyd and Fugitt, *Anal. Chem.*, **20**, 904 (1948).

[14] This method of expressing the activity of chemically equivalent positions obviates direct assignment of activity to carbons which are actually not labeled. For further discussion see Calvin, Heidelberger, Reid, Tolbert and Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. xi–xii.

TABLE I

RADIOACTIVITY ANALYSES

R	Starting C^{14} position	Reaction sequence	Glycol[a]	Iodoform (C-1)[a]	Acetone 2,4-dinitrophenylhydrazone[a]	Aldehyde dimethone[a]	Iodoform (C-4)[a]	A_1[b]	A_2[b]	A_3[b]	A_4[b]
t-C_4H_9	2	ROH with HCl, RCl with $NaOC_2H_5$	1672 ± 13	....	735 ± 5	0.2 ± 2[c]	.....	3	2283	...	...
t-C_4H_9	2	RCl with $AlCl_3$, RCl with $NaOC_2H_5$	1376 ± 12	19 ± 1	607 ± 3	3.6 ± 1[c]	.....	42	1858	...	...
t-C_5H_{11}	1	ROH with HCl, RCl with H_2O	325 ± 6	....	167 ± 2	−0.5 ± 1[d]	.....	518[e]		0[f]	
t-C_5H_{11}	1	Dehydration of ROH with H_2SO_4	261 ± 3	....	144 ± 1	1.3 ± 0.5[d]	.....	448[e]		8[f]	
t-C_5H_{11}	2		228 ± 1	....	135 ± 1	0.4 ± 1[d]	.....	418[e]		2.5[f]	
t-C_5H_{11}	1	RCl with $AlCl_3$, RCl with H_2O	576 ± 5	1013 ± 10	217 ± 2	56.2 ± 0.5[d]	956 ± 8	700	(−18)	20	330
t-C_5H_{11}	2	Same	913 ± 10	2 ± 1	311 ± 4	88 ± 4	45 ± 1	2	961	529	16
t-C_5H_{11}	1 + 2	Same	871 ± 1	883 ± 10	327 ± 4	82 ± 1	654 ± 6	610	406	283	226

[a] Measured activities of barium carbonate precipitates (*cf.* Ref. 13) corrected for background with standard deviations. [b] Corrected activities in counts/min./mg. of barium carbonate. [c] Formaldehyde dimethone. [d] Acetaldehyde dimethone. [e] A_1 plus A_2. [f] A_3 plus A_4.

TABLE II

ACTIVITY DISTRIBUTIONS OF STARTING MATERIALS AND PRODUCTS

R	Reaction sequence	% Activity of starting materials C-1	C-2	% Activity of products C-1	C-2	C-3	C-4
t-C_4H_9	ROH with HCl, RCl with $NaOC_2H_5$	....	100	0.13	99.87	..	..
t-C_4H_9	RCl with $AlCl_3$, RCl with $NaOC_2H_5$	....	100	3.1	96.9	..	..
t-C_5H_{11}	ROH with HCl, RCl with H_2O	100	....	100[a]		0[b]	
t-C_5H_{11}	Dehydration of ROH, H_2SO_4, 140°	100	....	98.2[a]		1.8[b]	
t-C_5H_{11}	Dehydration of ROH, H_2SO_4, 140°	....	100	99.4[a]		0.6[b]	
t-C_5H_{11}	RCl with $AlCl_3$, RCl with H_2O	100	....	66.3	0	1.9	31.8
t-C_5H_{11}	RCl with $AlCl_3$, RCl with H_2O	....	100	0.1	63.7	35.1	1.1
t-C_5H_{11}	RCl with $AlCl_3$, RCl with H_2O	54.8[c]	45.2[c]	40.0	26.6	18.6	14.8

[a] C-1 plus C-2. [b] C-3 plus C-4. [c] Not measured directly, calculated from activities of positions of products on the assumption that no exchange took place between C-1 (or C-4) and C-2 (or C-3).

object of having a graded sequence with increasing severity of conditions. The first reactions investigated were the formation of *t*-alkyl chlorides from the alcohols with hydrochloric acid and the conversions of the chlorides to the corresponding alkenes. A carbonium ion mechanism seems probable for the reaction of tertiary alcohols with hydrochloric acid on the basis of the ease of reaction of tertiary alcohols as compared with primary alcohols and the rearrangements which often accompany the reaction.[15] The reaction sequence, *t*-butyl alcohol $\xrightarrow{HCl}$ *t*-butyl chloride $\xrightarrow{NaOC_2H_5}$ isobutylene was carried out with 2-methyl-2-propanol-2-C^{14} (I, X = OH) and no rearrangement to II or the corresponding alkene could be detected.[16] The experimental data are given in Table I and the calculated activities of the various positions of the carbon chain in Table II. A similar sequence of reactions, *t*-amyl alcohol $\xrightarrow{HCl}$ *t*-amyl chloride $\xrightarrow{H_2O}$ trimethylethylene, gave no rearrangement (see Tables I and II) starting with 2-methyl-2-butanol-1-C^{14} (IV, X = OH).

The dehydration of alcohols in sulfuric acid solution often leads to rearranged products and is customarily regarded as proceeding through carbonium ion intermediates.[3] The conditions of this reaction are usually more drastic than those used for the preparation of *t*-alkyl chlorides. However, the dehydration of III (X = OH) and IV (X = OH) gave trimethylethylene with less than 2% change in the isotopic distributions of the carbon chains (Tables I and II) in 18 *N* sulfuric acid at 140°. It is apparent from these results and those mentioned earlier that rearrangements of the type I ⇄ II and III ⇄ IV, etc., do not seem to be important in the usual essentially non-reversible metathetical carbonium ion reactions of *t*-butyl and *t*-amyl derivatives. This finding is not unexpected as these rearrangements would involve sequences of relatively unstable primary or secondary cations such as those shown in Equations (1), (2) and (3).

The energy difference between tertiary and secondary cations is considered to be about 11 kcal./mole[17] and this difference represents the minimum energy of activation for rearrangement. Accordingly, it should be clear that the activation energy for reaction of the tertiary cation with electron-pairing reagents to give non-rearranged products must be rather high (on the order of 8 kcal./mole[18]) if a detectable ratio of rearrangement to normal reaction is to result. It is note-

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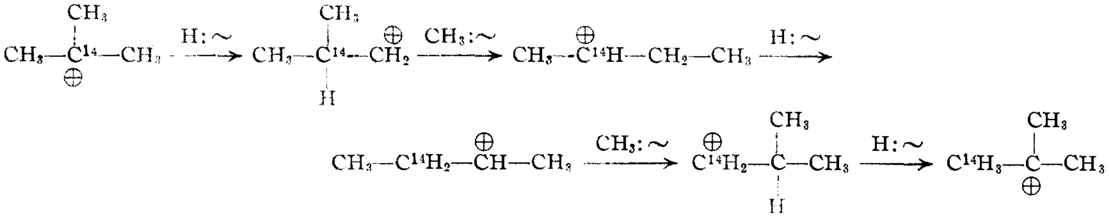
(15) (a) Lucas, THIS JOURNAL, **52**, 802 (1930). (b) Brown and Fletcher, *ibid.*, **71**, 1845 (1949).

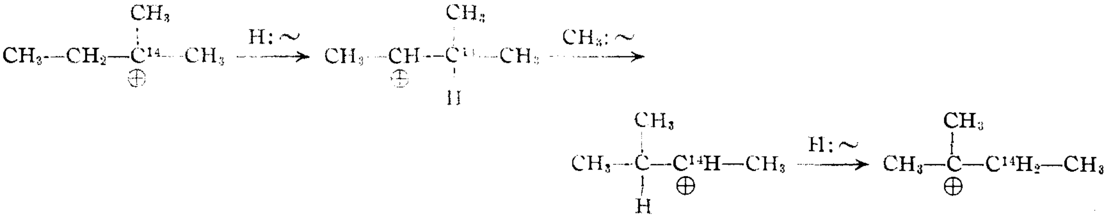
(16) No rearrangement is likely in the dehydrohalogenation step since under these conditions the reaction probably does not involve a carbonium ion intermediate, *cf.* Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(17) Evans, "The Reactions of Organic Halides in Solution," The Manchester University Press, Manchester, 1946, p. 15.

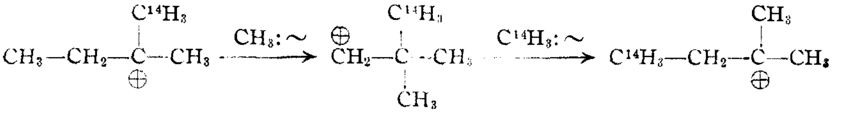
(18) Neglecting differences in entropy of activation.

(1) 

$$CH_3-\overset{CH_3}{\underset{\oplus}{C^{14}}}-CH_3 \xrightarrow{H:\sim} CH_3-\overset{CH_3}{\underset{H}{C^{14}}}-\overset{\oplus}{C}H_2 \xrightarrow{CH_3:\sim} CH_3-\overset{\oplus}{C^{14}}H-CH_2-CH_3 \xrightarrow{H:\sim} CH_3-C^{14}H_2-\overset{\oplus}{C}H-CH_3 \xrightarrow{CH_3:\sim} \overset{\oplus}{C^{14}}H_2-\overset{CH_3}{\underset{H}{C}}-CH_3 \xrightarrow{H:\sim} C^{14}H_3-\overset{CH_3}{\underset{\oplus}{C}}-CH_3$$

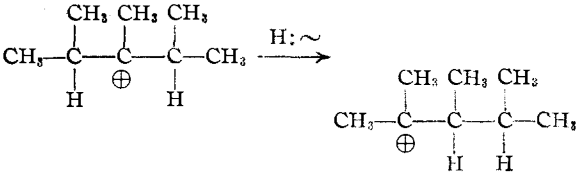
(2) 

$$CH_3-CH_2-\overset{CH_3}{\underset{\oplus}{C^{14}}}-CH_3 \xrightarrow{H:\sim} CH_3-\underset{\oplus}{C}H-\overset{CH_3}{\underset{H}{C^{14}}}-CH_3 \xrightarrow{CH_3:\sim} CH_3-\overset{CH_3}{\underset{H}{C}}-\underset{\oplus}{C^{14}}H-CH_3 \xrightarrow{H:\sim} CH_3-\overset{CH_3}{\underset{\oplus}{C}}-C^{14}H_2-CH_3$$

(3) 

$$CH_3-CH_2-\overset{C^{14}H_3}{\underset{\oplus}{C}}-CH_3 \xrightarrow{CH_3:\sim} \overset{\oplus}{C}H_2-\overset{C^{14}H_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{C^{14}H_3:\sim} C^{14}H_3-CH_2-\overset{CH_3}{\underset{\oplus}{C}}-CH_3$$

worthy that the rearrangements which have been detected in the metathetical reactions of tertiary alcohols involve *direct* interconversions of tertiary cations of comparable energy as in the following example.[15b]



$$CH_3-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{\oplus}{C}}-\overset{CH_3}{\underset{H}{C}}-CH_3 \xrightarrow{H:\sim} CH_3-\overset{CH_3}{\underset{\oplus}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-CH_3$$

Furthermore, the rearrangements which appear to involve the conversion of tertiary to secondary or primary cations, *e. g.*, the rearrangement of camphene hydrochloride to isobornyl chloride, under conditions where the process is reversible and the relative stability of the intermediate carbonium ions is less important in determining the direction of the reaction than the dissociability of the products. These considerations and the observation by Bartlett, Condon and Schneider[19] that *t*-amyl bromide is isomerized to 2-methyl-3-bromobutane by aluminum bromide indicated that rearrangements of type I ⇄ II or III ⇄ IV, etc., might occur under the influence of strong electrophilic agents in the absence of substances which can react rapidly and essentially irreversibly with carbonium ions. Consequently, the behavior of labeled *t*-butyl and *t*-amyl chlorides with aluminum chloride was investigated.

Treatment of 2-methyl-2-chlorobutane-1-C^{14} (IV, X = Cl) with aluminum chloride at 0° resulted in the evolution of hydrogen chloride and the formation of a lower layer of polymer.[20] After a few moments, the unpolymerized chloride was removed by distillation under reduced pressure (20% recovery) and converted to trimethylethylene by boiling with water. The trimethylethylene was degraded as described earlier. The results of the isotopic assay (Tables I and II) indicate that in this experiment essentially complete isotopic equilibrium was established between C-1 and C-4. A small amount of the total activity (1.7%) is indicated at C-3 but it is felt that this is probably illusory since the C-3 activity is obtained as the difference between the large activities of the iodoform (from the methyl isopropyl ketone) and acetaldehyde dimethone and there was no detectable activity at C-2.

Treatment of 2-methyl-2-chlorobutane-2-C^{14} (III, X = Cl) with aluminum chloride under conditions where 57% of the chloride was recovered gave a partially rearranged product (Tables I and II) with about 70% of the statistically possible exchange between C-2 and C-3 and feeble activities at C-1 and C-4. These results, as well as those obtained with 2-methyl-2-chlorobutane-1-C^{14}, demonstrate that little, if any, exchange occurs between the methyl groups and the carbons in the center of the chain during the isotopic equilibration between C-2 and C-3 or between C-1 and C-4.

The aluminum chloride catalyzed rearrangement of 2-methyl-2-chloropropane-2-C^{14} (I, X = Cl) occurred considerably less readily than the

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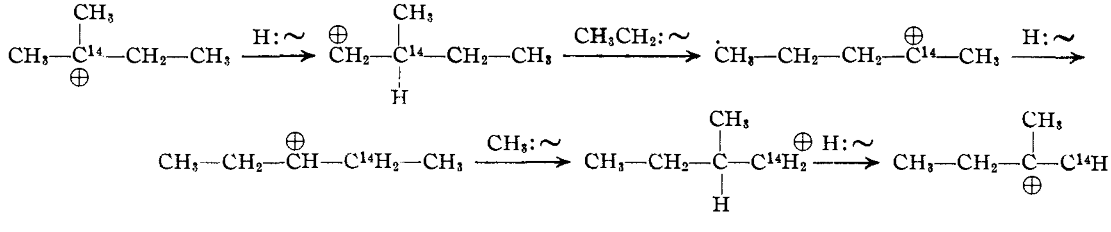
(19) Bartlett, Condon and Schneider, This Journal, **66**, 1531 (1944).

(20) In some experiments with labeled *t*-amyl chlorides the reaction did not begin at once and additional catalyst was required before the reaction would proceed. This behavior must be due to either the absence of a "promoter" or the presence of an "inhibitor." Pines and Wackher have found that the isomerization of alkanes in the presence of aluminum chloride–hydrogen chloride catalyst is promoted by olefins, oxygen or water [This Journal, **68**, 595, 599, 1642, 2518 (1946)] and inhibited by benzene [*ibid.*, **71**, 749 (1949)]. In the present work, xylene was used as a distillation base in the purification of the labeled *t*-amyl chlorides and may have been present to some extent in the starting material. The extent of rearrangement appeared to be related to the extent of production of hydrogen chloride and polymer since a sample of *t*-amyl chloride which reacted vigorously was completely rearranged in ninety seconds while a different sample, which was in contact with aluminum chloride for six minutes and only appeared to react slightly, was rearranged but 6%.

rearrangement of *t*-amyl chlorides and, under conditions sufficiently drastic so that much of the starting material was converted to polymer, the recovered chloride (48% recovery) contained only 1–3% of 2-methyl-2-chloropropane-1-C^{14} (II, X = Cl). The activity data for this experiment are summarized in Tables I and II.

The rearrangements of *t*-butyl and *t*-amyl chlorides induced by aluminum chloride which result in the shift of labeled carbon atoms (isotope-position rearrangements) appear to be most satisfactorily interpreted on the basis of carbonium ion intermediates as shown in Reactions (1), (2) and (3)[21] with the catalyst facilitating the ionization processes by acting as an acceptor of chloride ion from the organic halides. While the "freeness" of carbonium ions produced under these conditions is open to question, there can be no doubt that the intermediates are extremely reactive[19] and on this score warrant at least the title of "virtual" carbonium ions. For obvious reasons, we symbolize the intermediates as simple free ions but it is not to be inferred that in so doing we are assuming that it is correct to consider them wholly apart from their environment.

If the relative rates of formation of the possible isomerization products depends on the relative stabilities of the ions through which each is formed, it is expected that labeled *t*-butyl chloride should undergo isotope-position rearrangement considerably less readily than *t*-amyl chloride. This conclusion follows from the fact that the simplest reaction sequence (1) for *t*-butyl chloride involves two primary and two secondary cations while with *t*-amyl chloride the simplest sequences have either two secondary (2) or one primary (3) cations as intermediates. The lack of significant isotope exchange between the methyl groups and C-2 and C-3 of the *t*-amyl halides is easily predictable from the following possible sequence (4) for such a process which involves two primary and two secondary cationic intermediates.

(4) 

$$CH_3-\overset{CH_3}{\underset{\oplus}{C^{14}}}-CH_2-CH_3 \xrightarrow{H:\sim} \overset{\oplus}{C}H_2-\overset{CH_3}{\underset{H}{C^{14}}}-CH_2-CH_3 \xrightarrow{CH_3CH_2:\sim} CH_3-CH_2-CH_2-\overset{\oplus}{C^{14}}-CH_3 \xrightarrow{H:\sim}$$

$$CH_3-CH_2-\overset{\oplus}{C}H-C^{14}H_2-CH_3 \xrightarrow{CH_3:\sim} CH_3-CH_2-\overset{CH_3}{\underset{H}{C}}-\overset{\oplus}{C^{14}}H_2 \xrightarrow{H:\sim} CH_3-CH_2-\overset{CH_3}{\underset{\oplus}{C}}-C^{14}H_3$$

As a consequence, isomerization by (4) or similar paths is expected to be much slower than by either (2) or (3).

The relative rates of Reactions (2) and (3) are of particular interest since, by the considerations already mentioned, (2) would be expected to be more likely. An experimental determination of the relative rates of (2) and (3) is possible since every molecule which isomerizes by path (2) exchanges not only C-2 and C-3 but C-1 and C-4 as well. Isomerization by (3) results *only* in exchange between C-1 and C-4. If we let k_{14} represent the rate constant for exchange between C-1 and C-4; k'_{14}, the rate constant of the reverse reaction; A_{1_0}, the initial activity at C-1; and A_1, the activity at C-1 at time t, then

$$-\mathrm{d}A_1/\mathrm{d}t = k_{14}A_1 - k'_{14}(A_{1_0} - A_1)$$

Since, at equilibrium, $A_1 = 2/3\ A_{1_0}$,[22] then $2k_{14} = k'_{14}$

$$(5)\quad k_{14}t = -1/3 \log (3A_1 - 2A_{1_0})/A_{1_0}$$

The corresponding rate expression for exchange between C-2 and C-3 is similarly obtained.

$$-\mathrm{d}A_2/\mathrm{d}t = k_{23}A_2 - k'_{23}(A_{2_0} - A_2)$$

At equilibrium $A_2 = A_{2_0}$[23]$/2$ and hence $k_{23} = k'_{23}$

$$(6)\quad k_{23}t = -\frac{1}{2}\log\frac{2A_2 - A_{2_0}}{A_{2_0}}$$

For reasons mentioned earlier,[21] it would be very difficult to determine k_{14} and k_{23} accurately in separate experiments starting with III (X = Cl) and IV (X = Cl). However, the demonstrated slowness of exchange between the methyl groups and the carbons in the center of the chain permits the relative rates to be determined in a single experiment using double-labeled *t*-amyl chloride or a mixture of III (X = Cl) and IV (X = Cl) which for all practical purposes is the equivalent of double-labeled material.[23] The results of such an experiment using a mixture of III (X = Cl) and IV (X = Cl) are summarized in Tables I and II. The calculated value of k_{23}/k_{14} obtained from equations (5) and (6) was 1.55. If only sequence (2) operates k_{23}/k_{14} should be 2.00 and the experimental value of 1.55 corresponds to 87% reaction by (2) and 13% reaction by (3). These figures are rather sensitive to variations in the measured activities and if A_1 and A_2 are each uncertain by 5 c./min. (corresponding to about 15 c./min. in the measured activities of the iodoforms) k_{23}/k_{14} is uncertain by ±0.14 and the fraction proceeding *via* (2) by ±5%. Unquestionably, the data indicate that sequence (2) is considerably more favorable than sequence (3).[24] That the difference is not

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(21) It is recognized that the intermediates depicted in (1), (2) and (3) may be converted to the corresponding halides or olefins. Separate consideration of these substances has been omitted since they are expected to be in equilibrium with the carbonium ions in the presence of aluminum chloride (and hydrogen chloride).

(22) The isotope effect is neglected in this equation, *cf.* ref. 8.

(23) *Cf.* Calvin, *Science*, **104**, 470 (1946).

(24) It is probable that a carbonium ion isomerization mechanism similar to (2) is also more likely to obtain in the interesting rearrangement observed in the degradation of triethylacetic acid by the Schmidt reaction than the sequence analogous to (3) proposed by Schuerch and Huntress, THIS JOURNAL, **71**, 2238 (1949).

larger than was actually observed may be due to experimental error or may indicate that, other things being equal, the process with the fewest number of steps will be much more favored.

Inasmuch as the low temperature alkylation of isoalkanes proceeds under conditions[25] similar to those employed in the present work for the isotope-position rearrangements of *t*-alkyl halides, it is likely that similar intermediates and rearrangements are to be expected in each. Mechanisms have been proposed for aluminum chloride catalyzed alkane isomerizations which involve equilibria between carbonium ions.[3a,26] However, these reactions are probably not as closely related to the *t*-alkyl chloride isomerization as the low-temperature alkylation since they are not ordinarily carried out in the liquid phase. Indeed, it has been reported[27] that the gas-phase isomerization of C^{13} labeled butanes over moisture-promoted aluminum bromide is accompanied by a deep-seated "scrambling" of isotopic atoms, altogether different from the selective rearrangements found in the present study. Conventional carbonium ions are considered to be inadequate to account for the butane isomerization and instead an alkane-catalyst complex is suggested in which the isotopic butanes are sufficiently activated to form all of the possible mono-C^{13}-butanes in proportion to their statistical weights.[27] Irrespective of the merits of such intermediates for the interpretation of the course of vapor-phase alkane isomerizations, the Whitmore[8] carbonium ion, which undergoes more selective rearrangements, appears to give a better explanation of liquid-phase isomerizations and alkylations.[19]

Acknowledgment.—We are indebted to Miss Winifred Bennett for the radioactivity determinations and to Mrs. Hildegarde Harris and Mrs. Rose Armstrong for help with some of the experimental work.

Experimental

Methyl-C^{14} Iodide.[28]—A mixture of 100 ml. of concentrated hydriodic acid and 16 g. of methanol[11] (containing about 200 microcuries of C^{14}) was refluxed for thirty minutes. The halide was distilled into a flask containing calcium chloride and then under reduced pressure into a Dry Ice-cooled round-bottomed flask. The flask was attached to a 50 cm. glass helix-packed fractionating column and the product distilled. The yield of methyl-C^{14} iodide, b. p. 40.5–41° (740 mm.) was 66.5 g. (93%).

2-Methyl-2-butanol-1-C^{14}.—A solution of methyl-C^{14}-magnesium iodide was prepared from 43.5 g. (0.31 mole) of methyl-C^{14} iodide (about 90 microcuries) and 7.5 g. (0.31 g. atom) of magnesium in 100 ml. of dry ether under an atmosphere of nitrogen. A solution of 22.4 g. (0.31 mole) of methyl ethyl ketone in 100 ml. of ether was added dropwise. The reaction mixture was allowed to stand overnight and then treated with a solution of 35 g. of ammonium chloride in 215 ml. of water. The organic products were removed by continuous extraction with ether. The ether extract was dried over calcium sulfate and fractionated through a 50-cm. glass helix-packed column using 20 ml. of dry xylene as a distillation base. The yield of 2-methyl-2-butanol-1-C^{14} was 20.1 g. (75%); b. p. 96–100° (720 mm.).

Propionic-1-C^{14} Acid.—This preparation was designed to give an anhydrous product of relatively low specific activity. A solution of ethylmagnesium chloride prepared from 1.5 g. (0.063 g. atom) of magnesium turnings and excess ethyl chloride in 75 ml. of ether was treated with C^{14}-carbon dioxide using a procedure similar to the one described by Dauben, Reid and Yankwich.[29] The carbon dioxide was generated from 10.2 g. of barium carbonate[11] containing 210 microcuries of C^{14} by treatment with perchloric acid. After the reaction was complete, 77 ml. of a 0.68 *N* solution of hydrogen chloride in ether was added, followed by 10 g. of redistilled inactive propionic acid and 1 g. of inactive propionic anhydride. The volatile materials were distilled into a Dry Ice-cooled flask under reduced pressure. The residue was mixed with 10 g. of inactive propionic acid and then distilled under reduced pressure until nothing further came over on heating the distillation flask in a boiling water-bath at 4 mm. The residue was treated with an additional 10 g. of propionic acid and the distillation process repeated. The combined distillates were fractionated through a 50-cm. glass helix-packed column. The yield of propionic acid was 23.5 g. (64%) b. p. 100.5–101.5° (205 mm.). An additional 8.5 g. (23%) was recovered as sodium propionate by acidification and steam distillation of the residue from the Grignard reaction. The sodium propionate contained 37 microcuries (17%) of the total C^{14} activity.

Propionyl-1-C^{14} Chloride.—One procedure was that of Clark and Bell.[30] The yield of propionyl-1-C^{14} chloride, b. p. 74–75° (693 mm.), from 15 g. of propionic acid containing about 70 microcuries of C^{14} was 17.4 g. (93%). Another preparation was made by the method of Brown[31] and from 20 g. of propionic-1-C^{14} acid (about 70 microcuries of C^{14}) and 63 ml. of benzoyl chloride there was obtained 20.3 g. (81%) of propionyl-1-C^{14} chloride, b. p. 76–77° (740 mm.).

2-Methyl-2-butanol-2-C^{14}.—Propionyl-1-C^{14} chloride (20 g., 0.22 mole, about 58 microcuries of C^{14}) dissolved in 100 ml. of dry ether was added dropwise to an ice-cooled, stirred solution of methylmagnesium chloride prepared from 17.1 g. (0.70 g. atom) of magnesium in 900 ml. of dry ether. The reaction was carried out in a nitrogen atmosphere. The mixture was stirred for several hours and then allowed to stand overnight. Saturated ammonium chloride solution (130 ml.) was added to decompose the Grignard complexes. The ether layer was siphoned into another flask and the solid cake was washed several times with ether. The combined ethereal solutions were dried over calcium sulfate and distilled through a 50-cm. glass helix-packed column using xylene as a distillation base. The yield of 2-methyl-2-butanol-2-C^{14}, b. p. 100–102° (750 mm.), was 16.1 g. (81%).

Acetic-1-C^{14} Acid.[32]—The procedure was similar to that given above for propionic-1-C^{14} acid. From 0.063 mole of methylmagnesium chloride and 10.2 g. of barium C^{14}-carbonate[11] (270 microcuries of C^{14}) using 50 g. of inactive acetic acid as carrier there was obtained 44 g. of acetic-1-C^{14} acid, b. p. 102–102.3° (490 mm.), and 22 g. of sodium acetate-1-C^{14}. The total radioactivity accounted for was 98%, 10% as sodium acetate.

Acetyl-1-C^{14} chloride was prepared by the procedure of Clark and Bell.[31] The yield from 42 g. (230 microcuries of C^{14}) of acetic-1-C^{14} acid was 52 g. (95%), b. p. 48–54°.

2-Methyl-2-propanol-2-C^{14}.—Acetyl-1-C^{14} chloride (52.0 g., 0.66 mole, 220 microcuries of C^{14}) was added to a stirred, ice-cooled solution of 1.60 mole of methylmagnesium chloride in 1 l. of dry ether. The products were isolated as described for 2-methyl-2-butanol-2-C^{14}

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(25) Egloff and Hulla, *Chem. Rev.*, **37**, 323 (1945).

(26) Bloch, Pines and Schmerling, THIS JOURNAL, **68**, 153 (1946).

(27) Otvos, Stevenson, Wagner and Beeck, *J. Chem. Phys.*, **16**, 745 (1948).

(28) The procedure is based on that of Norris, *Am. Chem. J.* **38**, 639 (1907).

(29) Dauben, Reid and Yankwich, *Anal. Chem.*, **19**, 828 (1947).

(30) Clark and Bell, *Trans. Roy. Soc. Canada*, [3] **27**, 97 (1933).

(31) Brown, THIS JOURNAL, **60**, 1325 (1938).

(32) This preparation was made by Dr. D. R. Smith.

The yield of 2-methyl-2-propanol-2-C^{14}, b. p. 78–82.5°, was 29.0 g. (59%).

2-Methyl-2-chlorobutane-1(or 2)-C^{14}.—The labeled 2-methyl-2-butanols were converted to the corresponding chlorides by distillation with concentrated hydrochloric acid.[33] In each preparation, the organic portion of the distillate was washed with cold water, saturated salt solution, dried over calcium sulfate and distilled through a 50-cm. glass helix-packed column to give 85–95% yields of labeled *t*-amyl chloride, b. p. 41–43° (180 mm.), n^{25}D 1.4012. It was found helpful to add a few ml. of dimethylaniline to the distillation flask to prevent decomposition[34] during distillation.

2-Methyl-2-chloropropane-2-C^{14}.—2-Methyl-2-propanol-2-C^{14} was converted to the corresponding chloride by the procedure of Norris and Olmstead[35] in 73% yield; b. p. 50–50.5°, n^{25}D 1.3818.

2-Methyl-2-chlorobutane-1(or 2)-C^{14} with Aluminum Chloride.—The details of a typical experiment are given. Labeled *t*-amyl chloride (15 g.) was placed in a 200-ml. three-necked flask having standard-taper joints and equipped with a magnetic stirrer, solid addition tube and a connection to a series of three Dry Ice-cooled traps. Aluminum chloride (0.1 g., Baker and Adamson Reagent Grade) was placed in the addition tube which was so arranged that by rotation of the tube 180° about its connection to the reaction flask the solid could be added to the *t*-amyl chloride in the flask. The flask was cooled in an ice-bath and the aluminum chloride added to the stirred contents. Reaction usually began at once[20] with hydrogen chloride evolution and formation of a red-brown lower layer. After about ninety seconds the system was evacuated through the Dry Ice traps and within about two minutes all of the volatile material in the reaction flask had collected in the traps. The distillate was transferred to a flask containing 10 ml. of dry xylene (distillation base) and 3 ml. of dimethylaniline and fractionated through a 50 cm. glass helix-packed column. The recovery of labeled *t*-amyl chloride was 10.0 g. (67%); b. p. 39–40° (175 mm.), n^{25}D 1.4012.

2-Methyl-2-chloropropane-2-C^{14} with Aluminum Chloride.—The procedure was similar to that used for the labeled *t*-amyl chlorides. From the reaction of 12.2 g. of 2-methyl-2-chloropropane-2-C^{14} with 1.0 g. of aluminum chloride over a ten-minute period at room temperature there was obtained 5.9 g. (48% recovery) of labeled *t*-butyl chloride; b. p. 49.5–50°, n^{25}D 1.3812. About 4 g. of a thick red oil (polyisobutylenes?) remained in the reaction flask.

Dehydrohalogenation of C^{14}-Labeled *t*-Amyl Chlorides.—The following procedure is illustrative. 2-Methyl-2-chlorobutane-1-C^{14} (11.7 g.) was refluxed for ten hours with 50 ml. of water in a flask equipped with a water-cooled reflux condenser surmounted by a Dry Ice-cooled reflux condenser. The organic material was distilled under reduced pressure into a Dry Ice-cooled flask containing 10 g. of anhydrous calcium sulfate and 10 ml. of isoöctane. After the distillation was complete the flask was attached to a 50-cm. glass helix-packed column and the material fractionated. The yield of 2-methyl-2-butene was 3.2 g. (42%); b. p. 36–36.5° (725 mm.), n^{25}D 1.3838 (lit., b. p. 38.6° (760 mm.)[36], n^{20}D 1.3878,[36] n^{30}D 1.3814[37]).

This method of dehydrohalogenation was preferred since substantially pure trimethylethylene is formed.[38] Dehydrohalogenation with sodium ethoxide gives considerable 2-methyl-1-butene.

Dehydration of 2-Methyl-2-butanol-1(or 2)-C^{14}.—The procedure was a modification of that reported by Norris and Joubert,[39] and is illustrated by the dehydration of 2-methyl-2-butanol-2-C^{14}. A mixture of 11.1 g. of 2-methyl-2-butanol-2-C^{14} and 35 ml. of 18 *N* sulfuric acid contained in a flask equipped with a short Vigreux column connected to a condenser set for downward distillation was heated in an oil-bath at 140° until no further material distilled. The distillate which was collected in a Dry Ice-cooled flask containing 2 g. of solid potassium hydroxide was distilled under reduced pressure into a flask containing 10 ml. of isoöctane and the mixture fractionated through a 50-cm. glass helix-packed column. The yield of labeled 2-methyl-2-butene, b. p. 36–37° (740 mm.), was 5.2 g. (59%). About 1.2 g. of forerun, b. p. 30–36°, was obtained which probably consisted largely of 2-methyl-1-butene.

2-Methyl-2,3-butanediol.—The following procedure is typical of the many preparations from isotopic 2-methyl-2-butene by hydroxylation with performic acid.[12] In a 200-ml. three-necked flask fitted with a dropping funnel, an ice water-cooled reflux condenser surmounted by a Dry Ice-cooled condenser, a magnetic stirrer and a thermometer which dipped below the liquid level was placed 25 ml. of 87% formic acid and 5 ml. of 35% hydrogen peroxide. 2-Methyl-2-butene (2.0 g.) was added dropwise to the stirred mixture at a slow enough rate to keep the temperature from rising above 30°. After the addition of the alkene was complete the mixture was stirred at room temperature for several hours. The larger part of the formic acid was removed by distillation and the residue refluxed with a solution of 10 g. of potassium hydroxide in 35 ml. of water for thirty minutes. The mixture was cooled, saturated with potassium carbonate and extracted continuously with ether. The ether extract was dried over magnesium sulfate and the ether removed by distillation. The residue was mixed with 5 ml. of dry benzene and any traces of moisture removed by azeotropic distillation with the benzene. The residual glycol was distilled under reduced pressure. The yield of pure 2-methyl-2,3-butanediol was 1.8 g. (61%); b. p. 96–97° (30 mm.), n^{25}D 1.4360 (lit., b. p. 75–76° (14 mm.), n^{25}D 1.4375[40]).

2-Methyl-1,2-propanediol.—2-Methyl-2-chloropropane-2(or 1)-C^{14} was converted to the glycol by the following illustrative procedure without isolation of the intermediate alkene. A mixture of 6.6 g. of isotopic 2-methyl-2-chloropropane with a solution of sodium ethoxide (2.3 g. of sodium in 50 ml. of ethanol) was heated in a flask equipped with a reflux condenser and nitrogen inlet tube. The top of the condenser was connected through an ice-cooled trap to an inlet to a second flask containing 7.5 ml. of 35% hydrogen peroxide and 30 ml. of 87% formic acid and equipped with a magnetic stirrer and an ice water cooled reflux condenser surmounted by a Dry Ice cooled reflux condenser. The isobutylene formed in the dehydrohalogenation reaction distilled directly into the performic acid hydroxylation solution. The dehydrohalogenation reaction was carried out over a ten-hour period, at the end of which time the system was flushed with nitrogen to carry any remaining alkene into the hydroxylation flask. The performic acid reaction mixture was allowed to stand for several hours and then was worked up as described for 2-methyl-2,3-butanediol. The yield of 2-methyl-1,2-propanediol, b. p. 96–98° (30 mm.), was 2.5 g. (39%).

Degradation of Isotopic 2-Methyl-2,3-butanediol.—A typical experiment is described. A mixture of 0.52 g. of C^{14}-containing 2-methyl-2,3-butanediol, 1.07 g. of sodium metaperiodate and 50 ml. of water was shaken in a stoppered flask until all of the salt had dissolved. The solution was then allowed to stand overnight. About 80% of the liquid in the flask was distilled into a Dry Ice-cooled receiver under reduced pressure. The distillate was mixed and about one-third of it added to a filtered solution of 0.40 g. of methone in 100 ml. of water. The resulting acetaldehyde dimethone (0.20 g.) was collected and recrystallized from a methanol–water mixture; m. p. 142–143°.

The remainder of the distillate was treated with dilute potassium permanganate solution until the permanganate

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[33] Norris, Watt and Thomas, THIS JOURNAL, **38**, 1076 (1916).

[34] *Cf.* Corson, Thomas and Waugh, *ibid.*, **51**, 1950 (1929).

[35] "Organic Syntheses," Coll. Vol. 1, p. 144.

[36] Egloff, "Physical Constants of Hydrocarbon," Vol. I, Reinhold Publishing Corporation, New York, N. Y., 1939, p. 181.

[37] Norris and Reuter, THIS JOURNAL, **49**, 2633 (1927).

[38] Woodburn and Whitmore, *ibid.*, **56**, 1394 (1934).

[39] Norris and Joubert, *ibid.*, **49**, 884 (1927).

[40] Suter and Zook, *ibid.*, **66**, 738 (1944).

color persisted for an hour. The excess permanganate was destroyed with a few drops of 4% sodium bisulfite and the manganese dioxide removed by gravity filtration. The filtrate was divided into two equal portions and to one portion was added a filtered solution of 0.40 g. of 2,4-dinitrophenylhydrazine in 100 ml. of 2 *N* hydrochloric acid. The resulting acetone 2,4-dinitrophenylhydrazone (0.37 g.) was collected, dried and purified by several crystallizations from methanol–water, m. p. 123–124°.

Potassium hydroxide (3 g.) was dissolved in the remaining portion of the filtrate and to the resulting solution was added an excess of iodine–potassium iodide solution. The iodoform precipitate amounted to 0.60 g., m. p. 118–121° (dec.).

Iodoform from C-4 of the glycol was obtained by the following procedure. A mixture of 0.31 g. of 2-methyl-2,3-butanediol, 20 ml. of water and 1.5 ml. of concentrated sulfuric acid was distilled through a short Vigreux column until about 15 ml. of distillate were obtained. The distillate was diluted to 50 ml. and then made alkaline with a solution of 2 g. of potassium hydroxide in 5 ml. of water. Excess iodine–potassium iodide solution was added dropwise and the resulting iodoform removed by filtration. The yield was 0.42 g.; m. p. 119–121° (dec.).

Degradation of Isotopic 2-Methyl-1,2-propanediol.—The procedure for the degradation of 2-methyl-1,2-propanediol paralleled that used for degradation of 2-methyl-1,2-butanediol. The portion of the distillate from the sodium metaperiodate which was treated with methone in water afforded formaldehyde dimethone, m. p. 190.5–191°. The remaining distillate was treated with permanganate and divided into two portions for the preparation of acetone 2,4-dinitrophenylhydrazone and iodoform as described for 2-methyl-1,2-butanediol.

Summary

Several carbonium ion reactions of C^{14}-labeled *t*-butyl and *t*-amyl derivatives have been investigated to determine the ease of rearrangement in such processes to substances with identical carbon skeletons but different locations of the isotopic atoms. This type of rearrangement does not appear to be important in the usual essentially non-reversible metathetical and elimination reactions of *t*-butyl and *t*-amyl alcohols and chlorides.

Isotope-position rearrangements occur in *t*-amyl chloride and less readily in *t*-butyl chloride under the influence of aluminum chloride. The relative rates of formation of the various products are in accord with the accepted order of carbonium ion stabilities.

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[CONTRIBUTION FROM THE EXPERIMENT STATION OF THE HERCULES POWDER COMPANY]

The Synthesis of Acid-soluble Derivatives of Cellulose

BY DAVID S. BRESLOW

Since carboxymethylcellulose, a commercially available cellulose derivative, is soluble in dilute alkali but not in dilute acid, it was considered of interest to prepare a cellulose derivative which would be soluble in dilute acid but not in dilute alkali.

Although there are numerous references in the literature to the preparation of derivatives of cellulose containing basic nitrogen, the great majority of the derivatives prepared were insoluble in dilute acids. The two reactions used most frequently were the reaction of an arylsulfonate ester of cellulose or a cellulose derivative with ammonia or an amine,[1] and the reaction of cellulose or its derivatives with an aminoalkyl halide[1d,2] or sulfate.[3] Hardy[1d] prepared derivatives soluble in dilute acetic acid by treating the *p*-toluenesulfonate ester of a hydroxyalkylcellulose with a secondary alkylamine. Haskins[1e] showed that an acid-soluble derivative was obtained when a *p*-toluenesulfonate ester of cellulose or one of its derivatives which was soluble in organic solvents reacted with a primary or secondary alkylamine. The only successful synthesis of an acid-soluble derivative involving an aminoalkyl halide was that of Hardy,[1d] who prepared sodium cellulosate using sodium in liquid ammonia and treated it with a monohalogen amine salt, such as bromoethylamine hydrobromide.

In recent years it has been shown[4] that cellulose derivatives react readily with aromatic isocyanates to give cellulose aryl carbamates which are soluble in organic solvents. Since little degradation of the cellulose derivatives takes place during this reaction[4b] and since the carbamates are highly resistant to acid hydrolysis,[5] this appeared to be an excellent reaction for preparing cellulose derivatives soluble in dilute acid.

It has been found that the reaction of nicotinyl azide with ethylcellulose and cellulose acetate and the reaction of *p*-dimethylaminophenyl isocyanate with hydroxyethylcellulose give cellulose derivatives soluble in dilute acid. The general procedure for the preparation of the cellulose carbamates involved drying the cellulose derivative by azeotropic distillation of the water with benzene, then the azide or isocyanate plus dry pyridine were added and the reaction mixture was heated at 60–100° until the reaction was com-

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[1] (a) Karrer and Wehrli, *Helv. Chim. Acta*, **9**, 591 (1926); (b) British Patent 279,801 (1926); (c) Hagedorn and Ossenbrunner, U. S. Patent 1,833,286 (1931); (d) Hardy, U. S. Patent 2,136,296 (1938); (e) Haskins, U. S. Patent 2,136,299 (1938); (f) Dreyfus, U. S. Patent 2,241,542 (1941); (g) Kenyon and Reynolds, U. S. Patent 2,360,238 (1944).

[2] (a) Hartmann, U. S. Patent 1,777,970 (1930); (b) German Patent 719,241 (1942).

[3] Guthrie, *Textile Research Journal*, **17**, 625 (1947); U. S. Patent 2,459,222 (1949).

[4] (a) Hearon, Hiatt and Fordyce, THIS JOURNAL, **65**, 829 (1943); (b) Dyer and McCormick, *ibid.*, **68**, 986 (1946); (c) Hearon and Lobsitz, *ibid.*, **70**, 296 (1948).

[5] Hearon, Hiatt and Fordyce, *ibid.*, **65**, 833 (1943).