TABLE I

ISOTOPE DISTRIBUTION IN SUCCINYL CoA DERIVED FROM 2-C^{14}-METHYLMALONYL COA

Carbon		Cpm./μatom
1	COSCoA	0
2	CH_2	14
3	CH_2	54
4	COOH	0

Ten ml. of reaction mixture containing 0.4 μmole of 2-C^{14}-methylmalonyl CoA (1.9 × 10^5 cpm.), 0.035 μmole of dimethylbenzimidazole—cobamide-coenzyme (supplied by H. A. Barker), 2.6 units of avidin,[12] 200 μmoles of histidine-HCl buffer (*p*H 6.2), and an isomerase preparation from *P. shermanii* (700 μg. protein) were incubated at 25° for 10 minutes. The mixture was then treated with concentrated NH_4OH to convert the acyl CoA compounds to their acid amide derivatives. This and three similar reaction mixtures containing a total of 1.8 μmoles of 2-C^{14} D,L-methylmalonyl CoA (7.3 × 10^5 cpm.) were pooled and the succinic acid amide was isolated and degraded as described in the text.

established that isomerization involves rearrangement of the thiolester group.

Although the data do not eliminate the possibility that isomerization occurs by an intermolecular transfer of the thiolester group, a much more reasonable mechanism is suggested by analogy to the intramolecular rearrangement of phenylneopentyl radical discovered by Urry and Kharasch.[13] In the proposed mechanism (Fig. 1) the role of the cobamide coenzyme is to produce a radical by the one electron oxidation of methylmalonyl-CoA. The radical then could isomerize by the mechanism of Urry and Kharasch and the succinic acid derivative could be stabilized by interaction with reduced cobamide coenzyme.

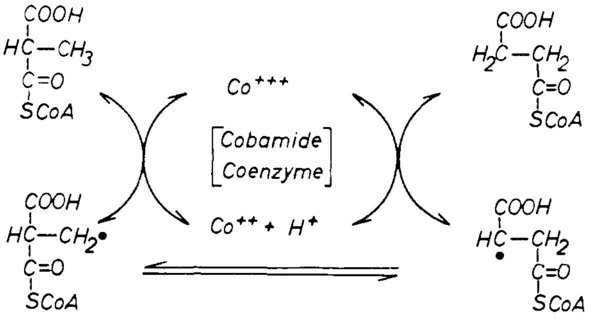

Fig. 1.

In view of the fact that the cobalt in cobamide coenzyme has a valence of +3 it is of further significance for the proposed mechanism, that Co^{+3} is known to produce radicals by reaction with a variety of organic compounds.[14]

MAX-PLANCK-INSTITUT FÜR ZELLCHEMIE
MÜNCHEN, GERMANY
H. EGGERER
P. OVERATH
F. LYNEN
NATIONAL HEART INSTITUTE
BETHESDA, MARYLAND
E. R. STADTMAN

RECEIVED APRIL 6, 1960

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for randomization of the carbon atoms was obtained by showing that, under otherwise identical conditions, the isomerization of unlabeled methylmalonyl CoA in the presence of added trace amounts of 1,4-C^{14}-succinate led to the formation of C^{14}-succinyl CoA which was isolated as the succinic amide derivative.

(12) Avidin was added to prevent the decarboxylation of methylmalonyl CoA to propionyl CoA (4).

(13) W. H. Urry and M. S. Kharasch, THIS JOURNAL, **66**, 1438 (1944).

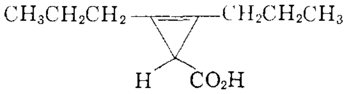
(14) A. F. Trotman-Dickenson, "Free Radicals," John Wiley and Sons, New York, N. Y., 1959, p. 10.

THE SYNTHESIS OF THE DIPROPYLCYCLOPROPENIUM ION

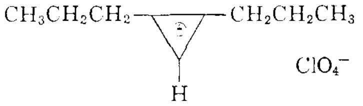
Sir:

Although the properties of the triphenylcyclopropenium ion[1] strongly support the idea that the cyclopropenyl cation is a fundamental aromatic system, it seemed desirable to prepare a derivative free of phenyl groups. The properties of the diphenylcyclopropenyl cation[2,3] suggested that a simple alkylated cation might well be stable, and we wish to report that this is indeed the case.

Reaction of dipropylcyclopropene carboxylic acid (I)[4] with acetyl perchlorate in acetic anhydride,[3,5] and then ether precipitation, led to dipropylcyclopropenium perchlorate (II), m.p. ~80° (dec.), which was recrystallized from ethyl acetate and ether. Found: C, 48.7; H, 6.6. The compound is insoluble in ether, hexane, or other non-polar solvents, but is soluble in acetone and other polar organic solvents and in 1 *N* HCl. It gives a positive perchlorate test with potassium nitrate, and the infrared spectrum also reveals the presence of perchlorate ion. In strong acid the compound has only end absorption in the ultraviolet.



I



II

The n.m.r. spectrum, in 50% aqueous sulfuric acid, is as expected, with a sharp band at −4.15 p.p.m., shifted to very low field for the proton on a positive carbon, and the characteristic pattern of two equivalent propyl groups also strongly shifted, with a 4 proton triplet centered at +3.12, a four proton sextuplet at +4.43, and a six proton triplet at +5.30 p.p.m. relative to a benzene capillary; the absence of any further hidden bands was established by dilution of the solvent, with consequent shift of its absorption.

Although the cation is soluble and stable in 1 *N* acid, its solution in 0.1 *N* acid or water becomes turbid. This reaction of the carbonium ion with water gives a complex mixture of products, but at least some of the components are cyclopropene derivatives, as evidenced by their characteristic double-bond stretching absorption in the infrared at 5.3μ. From this it can be estimated that the pK_a of the cation is greater than 0 and probably is less than 1. For comparison, the diphenylcyclopropenyl cation has a pK_a of 0.3.[2] That these two are so close is certainly a chance coincidence,

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[1] R. Breslow and C. Yuan, THIS JOURNAL, **80**, 5991 (1958).

[2] The diphenylcyclopropenyl cation has been prepared by Dr. Joyce Lockhart, unpublished work, by the reaction of phenylchlorocarbene with phenylacetylene.

[3] Prepared independently by Dr. Donald Farnum by the use of acetyl perchlorate on the appropriate acid. We wish to thank Dr. Farnum for making his results available prior to publication.

[4] I. A. Dyakonov, *et al.*, *Zhur. Obshchei Khim.*, **29**, 3848 (1959).

[5] A similar reaction with acetyl fluoroborate, to form the tropylium ion, has been reported by M. Dewar and C. Ganellin, *J. Chem. Soc.*, 2438 (1959).

considering the many factors which are involved, but it is of interest that the qualitative idea that phenyl groups should stabilize the cation more than alkyl groups do apparently is incorrect. This result is predicted by simple L.C.A.O. calculations,[6] which show that the ΔD.E. of ionization for our cation should be 2β compared to only 1.9β for the diphenyl cation, the explanation of this apparent anomaly being that the phenyl groups stabilize the covalent cyclopropene even more than they stabilize the cation. Our results furnish strong support for this striking prediction.

[6] *Cf.* J. D. Roberts and S. L. Manatt, *J. Org. Chem.*, **24**, 1336 (1959).

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK
RONALD BRESLOW
HERMANN HÖVER

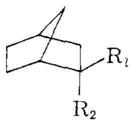
RECEIVED MARCH 30, 1960

GENERATION OF CATIONIC CARBON BY ANODIC OXIDATION OF CARBOXYLIC ACIDS

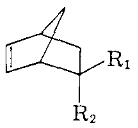
Sir:

The sequence involved in the Kolbe synthesis of hydrocarbons from carboxylate ions, $\text{RCOO}^- \rightarrow \text{RCOO}\cdot \rightarrow \text{R}\cdot$ can be extended by another stage of electron transfer to the generation of species which behave like carbonium ions. The anodic synthesis of such ionic species becomes more important with increasing voltage and seems to be especially favorable with those structures which give rise to relatively stable carbonium ions. In fact, the cases in which the Kolbe coupling reaction has been reported to fail usually are such instances.[1]

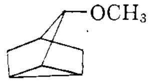
Anodic oxidation[2] of *exo*- or *endo*-norbornane-2-carboxylic acid (I or II) in methanol (50 volts, 10°) produced *exo*-norbornyl methyl ether (III)[3] in 35–40% yield and a very small amount of norcamphor as the only volatile materials; no *endo* methyl ether could be detected by vapor chromatography or infrared analysis. *The methyl ether III obtained from optically active II was racemic,* $[\alpha]^{25}_{\text{D}}$ 0.00 ± 0.09° ($[\alpha]^{25}_{\text{D}} \cong \pm 10.6°$ for optically pure III). Electrolysis of *exo*- or *endo*-5-norbornene-2-carboxylic acid (IV or V) gave 3-methoxynortricyclene (VI)[4] (56%).



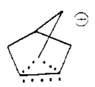
I, R_1 = COOH, R_2 = H
II, R_1 = H, R_2 = COOH
III, R_1 = OCH_3, R_2 = H



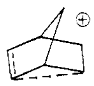
IV, R_1 = COOH, R_2 = H
V, R_1 = H, R_2 = COOH



VI



VII



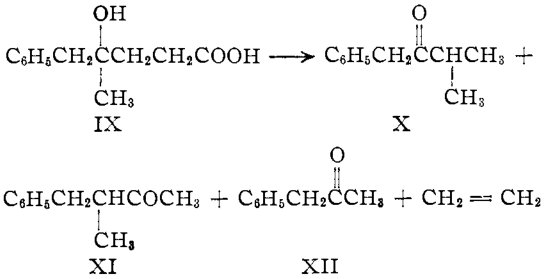
VIII

The formation of methyl ethers in these cases is inconsistent with radial attack on solvent (which should produce hydrocarbon by hydrogen atom abstraction[5]), but suggestive of cationic intermediates. Further, the particular ethers produced correspond *exactly* to the products obtained via bridged ions VII[6] and VIII[7] in solvolysis.

Anodic oxidation of cyclobutanecarboxylic acid in water (20 volts, 100°) afforded mainly cyclobutanol and cyclopropylcarbinol (ratio 1.1 to 1) and a small amount of allylcarbinol, a mixture identical with that resulting from deamination of cyclobutylamine.[8]

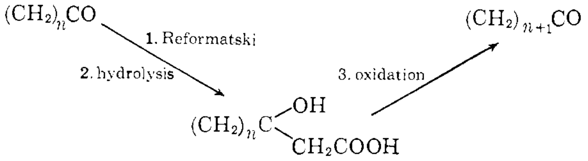
Electrolysis of cholesteryl-3β-carboxylic acid[9] in methanol (150 volts) produced 6β-methoxy-3,5-cyclocholestane, the characteristic methanolysis product of cholesteryl tosylate,[10] and a mixture of 6β-methoxy-Δ^4-cholestene and 4β-methoxy-Δ^6-cholestene, previously obtained from methanolysis of epicholesteryl tosylate.[10]

Electrolysis of γ-benzyl-γ-hydroxyvaleric acid (IX) (methanol, 100 volts) gave two products resulting from double 1,2-migration, X and XI (ratio 1 to 2.5), whose formation is most readily explicable on the basis of cation intervention. In addition, methyl benzyl ketone (XII) and ethylene were formed (30–85% yield depending on temperature) by a cleavage process analogous to that observed earlier.[11]



$$\underset{\text{IX}}{C_6H_5CH_2\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_2COOH} \longrightarrow \underset{\text{X}}{C_6H_5CH_2\overset{\overset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_3} + \underset{\text{XI}}{C_6H_5CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCOCH_3} + \underset{\text{XII}}{C_6H_5CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3} + CH_2{=}CH_2$$

The generation of cations by anodic decarboxylation can be of value in synthesis, as illustrated by its application to the ring expansion of cyclic ketones via the operations



Electrolysis of 1-hydroxycyclohexylacetic acid in acetonitrile (175 volts, 10°) afforded cycloheptanone (45–53%); 1-hydroxycyclopentylacetic acid yielded cyclohexanone (54–63%). Cyclooctanone and α-methylcycloheptanone have been obtained similarly.

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[1] See for example J. Walker and M. Carmack, *J. Chem. Soc.*, **77**, 374 (1900); R. P. Linstead, B. R. Shephard and B. C. L. Weedon, *ibid.*, 2854 (1951); M. Finkelstein and R. C. Peterson, *J. Org. Chem.*, **25**, 136 (1960).

[2] Smooth platinum electrodes were used throughout. Triethylamine was added to increase carboxylate ion concentration.

[3] T. G. Traylor and A. W. Baker, *Tetrahedron Letters*, **19**, 14 (1959).

[4] Shell Co., Technical Information Bulletin MD-101.

[5] W. H. Urry, F. W. Stacey, E. S. Huyser and O. O. Juveland, THIS JOURNAL, **76**, 450 (1954).

[6] S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952).

[7] J. D. Roberts, E. R. Trumbull, W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

[8] R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[9] E. J. Corey and R. A. Sneen, *ibid.*, **75**, 6234 (1953).

[10] D. D. Evans and C. W. Shoppee, *J. Chem. Soc.*, 540 (1953); E. M. Kosower and S. Winstein, THIS JOURNAL, **78**, 4354 (1956).

[11] E. J. Corey and R. R. Sauers, *ibid.*, **81**, 1743 (1959).