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).

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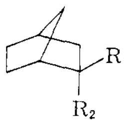
RECEIVED MARCH 30, 1960

GENERATION OF CATIONIC CARBON BY ANODIC OXIDATION OF CARBOXYLIC ACIDS

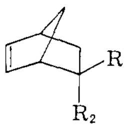
Sir:

The sequence involved in the Kolbe synthesis of hydrocarbons from carboxylate ions, $RCOO^- \rightarrow RCOO\cdot \rightarrow R\cdot$ 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]

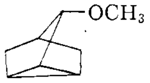
Anodic oxidation[2] of *exo*- or *endo*-norbornane-2-carboxylic acid (I or II) in methanol (50 volts, 10°) produced *exo*-norbornyl methyl ether (III)[3] in 35–40% yield and a very small amount of norcamphor as the only volatile materials; no *endo* methyl ether could be detected by vapor chromatography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



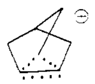
I, R_1 = COOH,R_2 = H
II, R_1 = H, R_2 = COOH
III, R_1 = OCH_3, R_2 = H



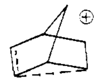
IV, R_1 = COOH, R_2 = H
V, R_1 = H, R_2 = COOH



VI



VII



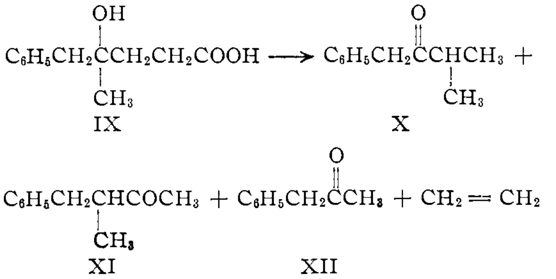
VIII

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]

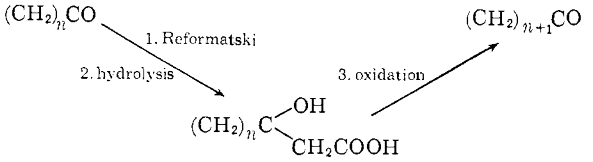
Electrolysis of γ-benzyl-γ-hydroxyvaleric acid (IX) (methanol, 100 volts) gave two products resulting from double 1,2-migration, X and XI (ratio 1 to 2.5), whose formation is most readily explicable on the basis of cation intervention. In addition, methyl benzyl ketone (XII) and ethylene



$$\underset{\text{IX}}{C_6H_5CH_2\overset{OH}{\underset{CH_3}{C}}CH_2CH_2COOH} \longrightarrow \underset{\text{X}}{C_6H_5CH_2\overset{O}{\overset{\|}{C}}\underset{CH_3}{CH}CH_3} + \underset{\text{XI}}{C_6H_5CH_2\underset{CH_3}{CH}COCH_3} + \underset{\text{XII}}{C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_3} + CH_2{=}CH_2$$

were formed (30–85% yield depending on temperature) by a cleavage process analogous to that observed earlier.[11]

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).

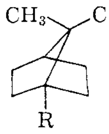
[8] R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[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).

The possibility that relatively unstable carbonium ions can be generated from carboxylic acids at high voltages is indicated by the formation of apocamphyl methyl ether (XIII) from the acid (XIV) (methanol, 150 volts).[12,13]



XIII, R = OCH_3
XIV, R = COOH

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(12) Data of H. J. Dauben and M. A. Muhs quoted by D. E. Applequist and J. D. Roberts in *Chem. Rev.*, **54**, 1079 (1954).

(13) Joint contribution from Harvard University (a) and the University of Illinois (b). We are indebted to Drs. T. Traylor, J. Berson and H. Schmid for samples and to the National Science Foundation and U. S. Public Health Service for support.

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RECEIVED APRIL 4, 1960

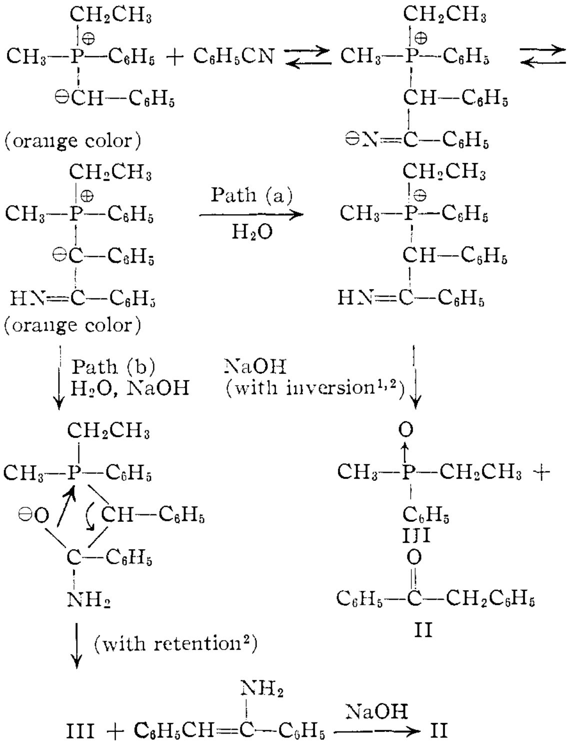
REACTION OF METHYLETHYLPHENYLBENZYLIDENEPHOSPHORANE WITH BENZONITRILE

Sir:

The typical orange color of a solution of racemic methylethylphenylbenzylidenephosphorane (I) in ether is not discharged when 1.45 equivalents of benzonitrile is added and the mixture stirred at 25° for 12 hours. However, removal of the ether and treatment of the residue with a solution of potassium hydroxide in aqueous methanol under reflux gives desoxybenzoin (II) in 78% yield and racemic methylethylphenylphosphine oxide (III) in 71% yield. This appears to be the first recorded example of the reaction of a methylenephosphorane with a nitrile.

When optically active I, prepared by the action of phenyllithium on levorotatory methylethylphenylbenzylphosphonium iodide,[1,2] is treated in the same manner as cited above for racemic I, the phosphine oxide, III, obtained is optically active, $[\alpha]^{25}\text{D}$ +8.3° (*c*, 3.856 in water). Inasmuch as optically pure dextrorotatory III has a specific rotation of 22.8°,[3,4] and since it has been demonstrated[2] that levorotatory methylethylphenylbenzylphosphonium iodide belongs to the same configurational family as levorotatory III, it follows that the reaction of I with benzonitrile and the subsequent treatment with alkali gave III with 68% inversion.

These observations suggest that two competing reactions are taking place, the major path (a) giving III with inversion of configuration of the phosphorus atom, and the minor path (b) giving III with retention.



Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. We also acknowledge research support from the Pan American Petroleum Corporation and the Banco de México, S. A., of Mexico City in the form of fellowships to A. B.-F.

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RECEIVED APRIL 8, 1960

(1) K. F. Kumli, W. E. McEwen and C. A. VanderWerf, THIS JOURNAL, **81**, 248 (1959).

(2) A. Bladé-Font, C. A. VanderWerf and W. E. McEwen, *ibid.*, **82**, 2396 (1960).

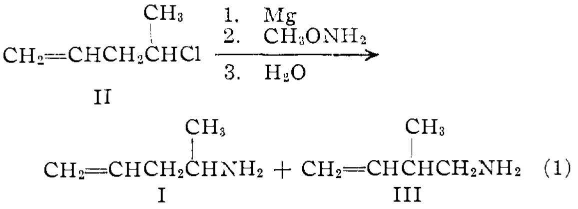
(3) K. F. Kumli, W. E. McEwen and C. A. VanderWerf, *ibid.*, **81**, 3805 (1959).

(4) (a) J. Meisenheimer and L. Lichtenstadt, *Ber.*, **44**, 356 (1911); (b) J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt and W. Samuel, *Ann.*, **449**, 213 (1926).

SMALL-RING COMPOUNDS. XXVIII. ISOTOPE-POSITION REARRANGEMENTS OF ALLYLCARBINYL GRIGNARD REAGENTS[1]

Sir:

We have observed a remarkable rearrangement while attempting to prepare 4-penten-2-ylamine (I) through the reaction of the Grignard reagent derived from 4-penten-2-yl chloride (II) with methoxylamine,[2] in that part of the amine formed appeared to be 2-methyl-3-butenylamine (III).



$$\underset{\text{II}}{CH_2{=}CHCH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCl} \xrightarrow[\text{3. } H_2O]{\text{1. Mg} \quad \text{2. } CH_3ONH_2}$$

$$\underset{\text{I}}{CH_2{=}CHCH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HNH_2} + \underset{\text{III}}{CH_2{=}CH\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2NH_2} \quad (1)$$

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(1) (a) Supported in part by the Office of Naval Research and the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund. (b) Presented in part at the Sixteenth National Organic Symposium, Seattle, Washington, June 15, 1959.

(2) R. Brown and W. E. Jones, *J. Chem. Soc.*, 781 (1946).