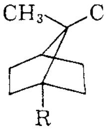
The possibility that relatively unstable carbonium ions can be generated from carboxylic acids at high voltages is indicated by the formation of apocamphyl methyl ether (XIII) from the acid (XIV) (methanol, 150 volts).[12,13]



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

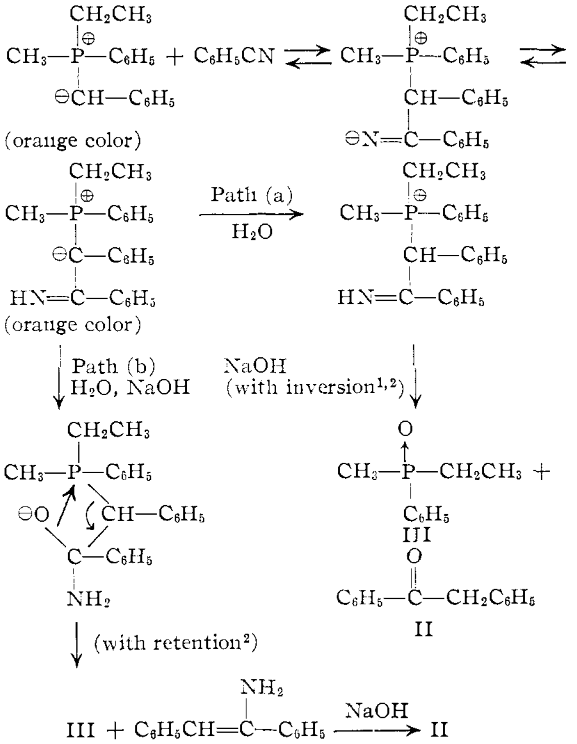
REACTION OF METHYLETHYLPHENYLBENZYLIDENEPHOSPHORANE WITH BENZONITRILE

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, $[\alpha]^{25}D$ +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

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[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).

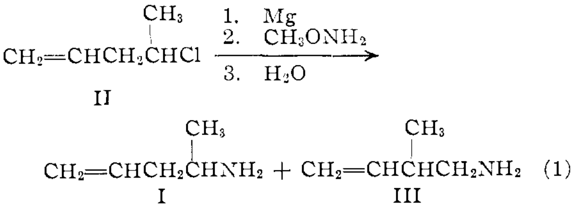
[3] K. F. Kumli, W. E. McEwen and C. A. VanderWerf, *ibid.*, **81**, 3805 (1959).

[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).

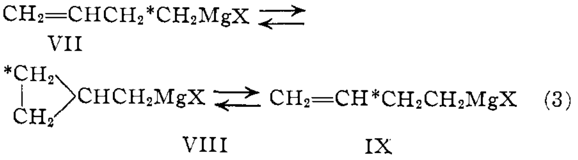
This fact suggested that similar rearrangements might be observed in the Grignard reactions of isotope-labeled 3-butenyl halides. Indeed, when the Grignard reagent prepared from the ^{14}C-labeled chloride IV[3] was oxygenated some 24 hours after formation, *equal amounts* of the normal (V) and rearranged[4] (VI) alcohols were formed.

$$\underset{\mathrm{IV}}{\mathrm{CH_2{=}CHCH_2{}^{14}CH_2Cl}} \xrightarrow[\text{3. } \mathrm{H_2O}]{\text{1. Mg} \quad \text{2. } \mathrm{O_2}}$$

$$\underset{\mathrm{V}}{\mathrm{CH_2{=}CHCH_2{}^{14}CH_2OH}} + \underset{\mathrm{VI}}{\mathrm{CH_2{=}CH^{14}CH_2CH_2OH}} \qquad (2)$$

These results are consistent with the intervention of cyclopropylcarbinyl intermediates somewhere between formation of the Grignard reagent and the final products. Product analysis alone does not establish at which stage(s) rearrangement occurs. Nuclear magnetic resonance (n.m.r.) spectroscopy, however, has been decisive in determining the structures of the carbon radicals of the Grignard reagents and in demonstrating that it is only the reagents themselves which rearrange (Eq. 3), there being no detectable rearrangement during their formation or reaction.

First, n.m.r. spectra clearly show that $\gtrsim 99\%$ of the Grignard reagent from allylcarbinyl chloride (or bromide) has the allylcarbinyl structure. Furthermore, the observation of two discrete aliphatic CH$_2$ resonances (separation 163.3 cps.) implies that the mean lifetimes of VII and IX are



a, $^*\mathrm{CH_2} = \mathrm{CH_2}$, X = Cl
b, $^*\mathrm{CH_2} = {}^{14}\mathrm{CH_2}$, X = Cl
c, $^*\mathrm{CH_2} = \mathrm{CD_2}$, X = Br

$\geq 10^{-2}$ sec.[5] Second, the n.m.r. spectrum of the Grignard reagent prepared from cyclopropylcarbinyl chloride shows only the allylcarbinyl structure, as might be expected from prior chemical evidence that this reagent affords exclusively allylcarbinyl products.[6]

An n.m.r. study of the rearrangement of 3-butenyl-1,1-^{2}H$_2$-magnesium bromide (VIIc) to 3-butenyl-2,2-^{2}H$_2$-magnesium bromide (IXc) in concentrated ethereal solution and of the products of oxygenation and of carbonation of VIIc has demonstrated unequivocally that the Grignard reagent rearranges after its formation and prior to conversion to final products. The Grignard reagent prepared from 3-butenyl-1,1-^{2}H$_2$ bromide[7] was 97% VIIc[8] as evidenced by the relative areas of the CH$_2$ doublet at 7.82 (VIIc) and singlet at 10.54 (IXc) (*cf.* Fig. 1). When the Grignard solution is allowed to stand, VIIc is converted slowly to IXc and, at equilibrium, the characteristic CH$_2$ peaks of each have equal areas (Fig. 1). The half-times for equilibration are thirty hours at 27° and forty minutes at 55.5°, corresponding to an activation energy of about 23 kcal.

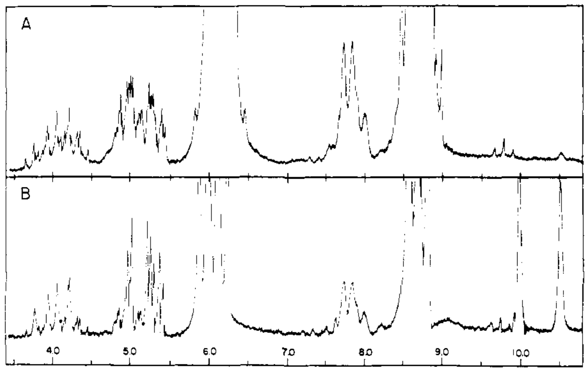


Fig. 1.—N.m.r. spectra at 60 mc.: curve A is VIIc and curve **B** is VIIc + IXc at equilibrium. **B** shows the internal standard, Si(CH$_3$)$_4$ ($\equiv$10.00 τ units). The ether bands are 6.1 (CH$_2$), 8.7 (CH$_3$) and 9.8 (^{13}CH$_3$).

The n.m.r. spectra of the products isolated after oxygenation and carbonation of VIIc (at least 97% pure[8]) showed no evidence of further rearrangement as judged by location and areas of the CH$_2$ peaks and of the multiplet structure of the vinyl lines.

The details of these and other results regarding the interconversion of allylcarbinyl and cyclopropylcarbinyl Grignard reagents will be published later.

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[3] Prepared from 3-butenonitrile-1-^{14}C (allyl bromide and cuprous cyanide-^{14}C) by hydrolysis, hydride reduction and reaction with thionyl chloride.

[4] The product ^{14}C distribution was determined by conversion to butyric acid and then Curtius rearrangement to the isocyanate, which with phenylmagnesium bromide gave N-propylbenzamide, the ^{14}C activity of which (0.0418 ± 0.0003 mc./mmole) was taken as 100%. Hydrolysis gave benzoic acid (0.0205 ± 0.0002 mc./mmole) and *n*-propylamine (0.0206 ± 0.0002 mc./mmole as N-propylbenzamide). Successive oxidations of the labeled allylcarbinol with performic acid and periodate gave formaldehyde (C-4) with no ^{14}C activity.

[5] *Cf.* J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, N. Y., 1959, Chap. IV; compare with allylmagnesium bromide, J. E. Nordlander and J. D. Roberts, THIS JOURNAL, **81**, 1769 (1959).

[6] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

[7] Prepared from methyl 3-butenoate by deuteride reduction and conversion of the deuterioalcohol to the bromide via the benzenesulfonate and reaction with lithium bromide. The purity of both the alcohol and the bromide was determined by n.m.r. and vapor-phase chromatography to be >98.5%.

[8] The preparation and concentration of the n.m.r. sample at 20° required about six hours; consequently, on the basis of the rate data above, it is likely that no rearrangement takes place in the reaction of the halide with magnesium.

CONTRIBUTION NO. 2570 MARC S. SILVER
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RECEIVED APRIL 9, 1960

PHOSPHONITRILIC BROMIDES[1]

Sir:

The paucity of available information on the bromine analogs of the phosphonitrilic chlorides probably is due to the general beliefs that substantial thermal decomposition of phosphorus-

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[1] This research was supported by Contract AF 33(616)5486 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. Reproduction of this communication in whole or in part is permitted for any purpose of the United States Government.