Similar considerations lead to the conclusion that osmocene is protonated in boron trifluoride hydrate to a lesser extent than either ferrocene or ruthenocene.

It is attractive to consider that bonding of the type proposed here involves utilization of the electron pair in the metallocene ha_g molecular orbital which is of correct symmetry, and which the calculations of Moffitt[7] suggest is localized in the equatorial plane between the cyclopentadienyl rings.

Though the importance of similar "d-orbital" complexes in general processes of electrophilic substitution of metallocenes remains at present unresolved, their intervention as essential intermediates in such reactions appears quite plausible. For example, deuteration of ferrocene takes place in the presence of $BF_3 \cdot D_2O$.[8] Furthermore, it is of interest to note the correspondence between those properties associated with direct participation of the metal atom of the metallocenes, such as basicity and ease of oxidation,[9] with the relative reactivities of these substances in Friedel–Crafts acylation reactions.[10]

Acknowledgment.—This research was supported by grants from the National Science Foundation and the National Institutes of Health (RG-5978-C1).

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(8) Unpublished observations of J. O. Santer.

(9) D. E. Bublitz, G. Hoh and T. Kuwana, *Chemistry and Industry*, 635 (1959).

(10) M. D. Rausch, E. O. Fischer and H. Grubert, THIS JOURNAL, **82**, 76 (1960).

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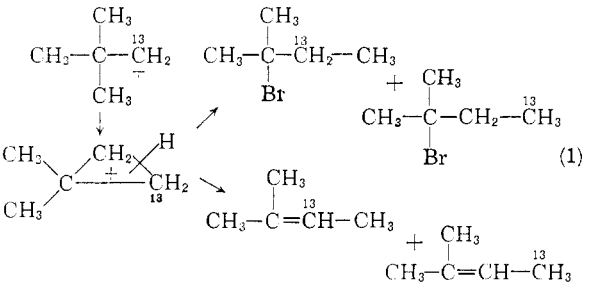
RECEIVED AUGUST 10, 1960

CARBONIUM ION REARRANGEMENT OF THE NEOPENTYL SYSTEM

Sir:

The role of protonated cyclopropanes as intermediates in carbonium ion reactions has aroused recent interest[1]; we wish to report some of our work which seems relevant to the subject of carbonium ion rearrangements.

Preparation of *tert*-amyl chlorides and bromides labeled with carbon-13 at the various carbon atoms of the *t*-amyl skeleton has been in progress in our laboratories for mechanistic studies on carbonium ion rearrangements. The attempted preparation of 2-bromo-2-methylbutane-3-C^{13} by two hour reflux and subsequent distillation of neopentyl alcohol-1-C^{13} (30% excess C^{13}) with concentrated hydrobromic acid led to a product which was shown by vapor phase chromatography to consist mainly of unreacted alcohol, 2-methyl-2-butene, and some *tert*-amyl bromide and 2-methyl-1-butene. Our interest in spin-spin coupling constants between C^{13} and hydrogen[2] led to examination of the proton n.m.r. spectrum (60 Mc.) of the product; the findings bear some relevance to the question of protonated cyclopropanes as intermediates in carbonium ion rearrangements. According to mechanism (1)—disregarding isotope effects—a one to one mixture of products labeled at carbon-3 and carbon-



(1)

4 should be obtained. Such products are distinguishable from each other by proton n.m.r. spectroscopy because of the large difference in spin-spin coupling constants between C^{13} and hydrogens attached to it (about 130 c.p.s.) and between C^{13} and hydrogens on carbons removed from C^{13} by one or two bonds (4–6 c.p.s.)[2]; thus, a distinction between mechanism (1) and mechanisms involving rearrangements of open carbonium ions, the latter leading to products not labeled at carbon-4, is possible.

The 60 Mc. proton n.m.r. spectrum of neopentyl alcohol-1-C^{13} (neat) shows peaks—benzene was used as the external reference standard—at 97 c.p.s. (–OH), at 206 c.p.s. ($-CH_2-$) with side bands 139 c.p.s. and 271 c.p.s. due to the presence of 30% excess C^{13} (J_{C-H} = 132 c.p.s.), and at 344 c.p.s. [$-C(CH_3)_3$] with side bands around 341.6 c.p.s. and 346.4 c.p.s. from the splitting of methyl hydrogens by C^{13} ($J_{C^{13}-C(CH_3)_3}$ = 4.8 c.p.s.). The spectrum of the product (carbon tetrachloride solution) shows the C^{13} distribution in neopentyl alcohol unchanged, and the methyl protons of methylbutene at 294 c.p.s. These protons are split by C^{13}, side bands at 291.6 c.p.s. and 296.4 c.p.s., with a $J_{C^{13}-CH_3}$ = 4.8 c.p.s. The observations listed suggest that mechanism (1) is not the main path of the reaction: First, the ratio of the sum of the areas under side bands 291.6 c.p.s. and 296.4 c.p.s. to the area under 294 c.p.s. is approximately the same as the corresponding ratio of the sum of areas under side bands 341.6 c.p.s. and 346.4 c.p.s. to the area under 344 c.p.s. This is an indication that carbon-3 of 2-methyl-2-butene contains as much excess C^{13} as carbon-1 of neopentyl alcohol[3]; mechanism (1) predicts the former ratio to be only one-half of the latter. Second, if carbon-4 contained any C^{13}, side bands in the vicinity 255 ± 20 c.p.s. and 365 ± 20 c.p.s. should appear; no such bands appear in the spectrum.[4] The iso-

(1) (a) P. S. Skell and I. Starer, THIS JOURNAL, **82**, 2971 (1960); (b) M. S. Silver, *ibid.*, **82**, 2971 (1960).

(2) A detailed presentation of the proton n.m.r. spectra of compounds discussed in this communication as well as those of related ones will be published later.

(3) The possibility that some C^{13} might be at carbon-2 of the pentene cannot be ruled out, because the spin–spin coupling constants between the methyl hydrogens and carbon-2 or carbon-3 are comparable in magnitude.[2]

(4) Availability of samples in only small quantities prevented component separation and spectrum amplification for accurate measurements of vinyl hydrogen and *t*-amyl bromide.

topic enrichment of the alcohol (30% excess C^{13}) suggests that detection of C^{13} in carbon-4 would have been achieved, had mechanism (1) occurred to the extent of 20% or more.

The above arguments lead to the conclusion that under strong acid conditions carbonium ion rearrangements of the neopentyl system do not occur mainly *via* protonated cyclopropanes.[5]

(5) Since our interests when we started this work were not centered around the intermediacy of protonated cyclopropanes in carbonium ion rearrangements, no attempt was made to identify any product of cyclopropane skeleton. We wish to emphasize that our arguments do not necessarily apply to reactions done under basic conditions,[1a] nor do they exclude protonated cyclopropanes as intermediates in the formation of cyclopropane compounds.[1b] In addition we wish to point out that the work of J. D. Roberts and J. A. Yancy, THIS JOURNAL, **77**, 5558 (1955), on the reaction of 2,3,3-trimethyl-2-butanol-1-C^{14} with concentrated hydrochloric acid also excludes any protonated cyclopropane intermediates prior to formation of classical carbonium ions, or before reaction of classical carbonium ions with chloride ions.

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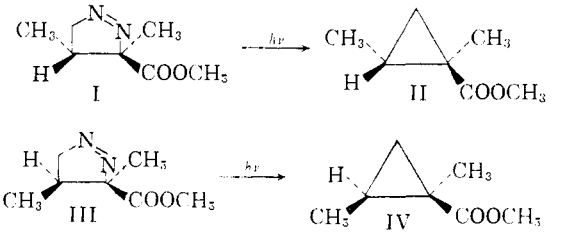
RECEIVED AUGUST 10, 1960

LIGHT-INDUCED DECOMPOSITION OF PYRAZOLINES. AN IMPROVED ENTRY INTO THE CYCLOPROPANE SERIES

Sir:

Thermal decomposition of pyrazolines is a well-known route to cyclopropanes.[1,2,3,4] The synthetic value of the reaction is reduced considerably, however, by the extensive formation of olefinic products,[2,3,4,5,6] by a lack of stereospecificity,[5] and often by extensive tar formation.[2] We now wish to report that light-induced decomposition of stereoisomeric pyrazolines has led to the formation of cyclopropanes stereospecifically, and without olefin formation.

When 3-carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline (I), prepared by treatment of methyl tiglate with diazomethane,[5,7] was irradiated with a sunlamp at *ca.* 15°, the sole product (by gas-liquid chromatographic analysis) was methyl *cis*-1,2-dimethylcyclopropane - 1 - carboxylate (II), $n^{25}D$ 1.4289 [*Anal.* Found: C, 65.26; H, 9.44].



Irradiation at *ca.* 30–35° of 3-carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (III),[5] prepared from methyl angelate and diazomethane, gave a mixture of esters which gas chromatographic analysis showed to consist of 87% methyl *trans*-1,2-dimethylcyclopropane - 1 - carboxylate (IV), $n^{25}D$ 1.4218 [*Anal.* Found: C, 65.86; H, 9.50], 2% II, 7% methyl 2,3-dimethyl-2-butenoate (V) (identified by infrared spectrum and gas chromatographic retention time identical with those of an authentic sample), and 4% methyl angelate (identified in the same manner as V). At 33–35° irradiation of I gave a mixture of esters found by gas chromatography to consist of 73% II, 3% V, and 20% methyl tiglate (identified in the same manner as V). The methyl angelate and methyl tiglate formed in these irradiations resulted from the apparent reversal of pyrazoline formation, a reaction which has not been previously observed.

The structures of the products were established as cyclopropanes by their infrared, ultraviolet, and n.m.r. spectra. The infrared spectra of II and IV (in carbon tetrachloride) contain no olefinic bands in the 1700–1600 or 950–880 $cm.^{-1}$ regions,[8] while their ultraviolet spectra show only weak end absorption (ϵ *ca.* 200). Olefinic hydrogen peaks are absent from their n.m.r. spectra, while cyclopropane hydrogens appear in the region τ[9] = 8.6–9.8.[10]

Steric assignments of II and IV were made on the basis of (a) competitive saponification of a mixture of II and IV in which the less hindered ester moiety of II was hydrolyzed more rapidly than that of IV, and (b) their formation from pyrazolines, in which stereospecific inversion is considered to be unlikely.

Acknowledgment.—This investigation was supported in part by a grant (No. RG-5883) from the Division of Research Grants, National Institutes of Health.

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(11) Lubrizol Fellow, 1959–1960.

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RECEIVED AUGUST 22, 1960

THE METABOLISM OF ALDOSTERONE: ISOLATION AND CHARACTERIZATION OF TWO NEW METABOLITES[1]

Sir:

In this report we describe the isolation of two new metabolites of *d*-aldosterone, 5α-(4,5)-dihydroaldosterone (Ia) and 3βOH,5α-(4,5)-tetrahydroaldosterone (IIa), from the incubate of *d*-aldosterone with rat liver homogenates. In addition, the synthetic preparation of 5α-(4,5)-dihydroaldosterone 21-acetate (IIIb), 3βOH,5α-(4,5)-tetrahydroaldosterone (IIb), the 3-keto etiolactone (IVb), and the 3-hydroxy etiolactone (VIb) are recorded. Romani, *et al.*,[2] have suggested the formation of

(1) This work was supported in part by a grant (P. H. S. A-1156) from the National Institute of Arthritis and Metabolic Diseases of the National Institutes of Health, Education and Welfare.
(2) J. D. Romani, C. Bessard, J. Sosa-Castellanos and A. Keller, *Ann. Endocrinol.*, **20**, 209 (1959).