mole of fluorobenzene, the reaction being quenched while incomplete. The relative yields of chlorate and fluoride ions were as 8:1 (ClO_3^-, *ca.* 32%; $F^- < 4\%$). As is evident from these Wittig reactions the perchlorylbenzenes did not undergo reactivity reversal (relative to the other halogenobenzenes) with change in the mode of benzyne synthesis.

We ascribe the dominance of the perchloryl moiety in these elimination processes to a combination of its high electronegativity[6] (and consequent acidity of proximate aryl hydrogens) and its excellent anionic leaving group ability.[6]

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PROTONATION OF METALLOCENES BY STRONG ACIDS. STRUCTURE OF THE CATION

Sir:

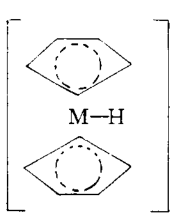
Ferrocene recently has been shown to form a stable complex salt of composition ($C_{10}H_{10}Fe \cdot HAlCl_4$) in the presence of aluminum chloride and hydrogen chloride.[1] This finding, together with the suggestion[2] that the transition state for electrophilic substitution of ferrocene, ruthenocene and osmocene may involve initial interaction of the electrophile with the metal atom, prompted us to examine the n.m.r. spectra of these metallocenes in media of high acidity.

We now wish to report preliminary results of these studies which demonstrate that, in solutions of boron trifluoride hydrate, the cation resulting from protonation of the metallocene possesses structure I. These data are summarized in the table.

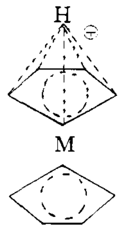
The absence of complex unsymmetrical multiplet absorption for the cyclopentadienyl ring protons, together with the appearance of resonance absorption at unusually high magnetic fields are not consistent with a formulation such as III for the protonated metallocenes.[3]

Although the presence of a highly shielded proton may be accounted for in terms of the pi-complex structure II, the apparent magnetic equivalence of protons on each of the cyclopentadienyl rings is not in accord with such a formulation. Symmetrically diprotonated structures of this type are eliminated on the basis of the relative integrated intensities of the magnetically non-equivalent protons.

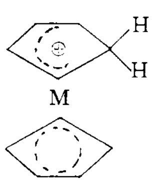
Structure I for the protonated species is in accord with the appearance of very high field absorption characteristic of a proton bonded directly to the metal atom.[4] The field independent doublet splitting of ring protons in the spectrum of the ferrocene cation readily is assigned to spin coupling of these nuclei with the metal bound proton. The magnitude of this coupling ($J = 1.3 \pm 0.2$ c.p.s.) is similar to that reported by Green, Pratt and Wilkinson for bis-cyclopentadienylrhenium hydride[4] ($J = 1.0_5$ cps.). Furthermore, the magnetic equivalence of all ring protons implies that in the protonated metallocenes, the two cyclopentadienyl rings are relatively free to rotate, as they are in ferrocene.[5]



I



II



III

FERROCENE

Solvent	Peak position[a]	Relative intensity
$BF_3 \cdot H_2O$	4.99 (sym. doublet; $J = 1.2 \pm 0.2$)[b]	11 ± 2
	12.07 (broad)[b]	1
$BF_3 \cdot H_2O$	5.05 (sym. doublet; $J = 1.3 \pm 0.2$)[c]	15 ± 2
	12.10 (broad)[c]	1
$BF_3 \cdot H_2O-CF_3CO_2H$ (1:2)	4.97 (sym. doublet; $J = 1.5 \pm 0.2$)[c]	12.5 ± 2
	11.89	1
$BF_3 \cdot H_2O-CF_3CO_2H$ (2:1)	5.02 (sym. doublet; $J = 1.8 \pm 0.2$)[c]	13 ± 2
	11.91	1
CF_3CO_2H	5.33 (singlet)[c]	...
CCl_4	5.958 (singlet)[d]	...
	RUTHENOCENE	
$BF_3 \cdot H_2O$	4.67 (singlet)[c]	16 ± 2
	17.2[c]	1
CCl_4	5.58 (singlet)[c]	...
	OSMOCENE	
$BF_3 \cdot H_2O$	4.88 (singlet)[c]	...
$CDCl_3$	5.29 (singlet)[c]	...

[a] Peak positions are given in ppm. relative to tetramethylsilane having an assigned value of 10 [*cf.* G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958)]. Internal standard in acid media, $(CH_3)_3CCO_2H$ ($\tau = 8.77$); in neutral media, $[(CH_3)_3Si]_2O$ ($\tau = 9.95$). [b] Determined at 60 mc. [c] Determined at 40 mc. [d] Value reported by G. V. D. Tiers, abstracts of the 137th Meeting of the American Chemical Society, April 1960, p. 4-O.

Ruthenocene is apparently a somewhat weaker base in $BF_3 \cdot H_2O$ than is ferrocene, judging by the relative peak intensities of the high and low field absorptions for the two substances. The absence of spin splitting of ring protons in the spectrum of the ruthenocene cation, as well as the sharp appearance of the high field absorption peak, is attributable to a rapid exchange of the acid proton.[6]

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(1) M. Rosenblum and J. O. Santer, THIS JOURNAL, **81**, 5517 (1959).

(2) J. H. Richards, presented at the 135th Meeting of the American Chemical Society, April 1959; *cf.* abstracts, p. 86-O.

(3) For comparison, *cf.* M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959), for the n.m.r. spectra of $(C_5H_6)(C_5H_5)Co$ and $(C_5H_6)(C_5H_5)Rh$; *cf.* also C. MacLean, J. H. van der Waals and E. L. Mackor, *Mol. Phys.*, **1**, 247 (1958).

(4) *Cf.*, for example, J. Chatt and R. G. Hayter, *Proc. Chem. Soc.* 153 (1959); G. Wilkinson, *Angew. Chem.*, 35 (1960); M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).

(5) Yu. T. Struchkov, *Zhur. Obshchei Khim.*, **27**, 2039 (1957); L. N. Mulay, E. G. Rochow and E. O. Fischer, *J. Inorg. and Nucl. Chem.*, **4**, 231 (1957); M. Rosenblum and R. B. Woodward, THIS JOURNAL, **80**, 5443 (1958).

(6) For a discussion of the dependence of rates of protolysis of amine salts on their basicity, *cf.* A. Lowenstein and S. Meiboom, *J. Chem. Phys.*, **27**, 1067 (1957), and C. G. Swain, J. T. McKnight and V. P. Kreiter, THIS JOURNAL, **79**, 1088 (1957).

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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(7) W. Moffitt, THIS JOURNAL, **76**, 3386 (1954).

(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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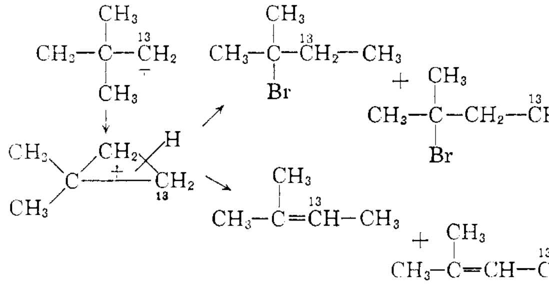
CARBONIUM ION REARRANGEMENT OF THE NEOPENTYL SYSTEM

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-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.



(1)

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-

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(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.

CONTRIBUTION NO. 2610
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