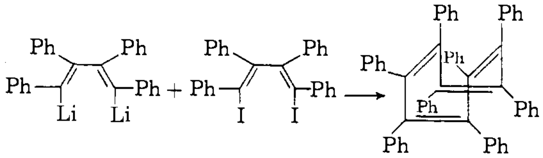
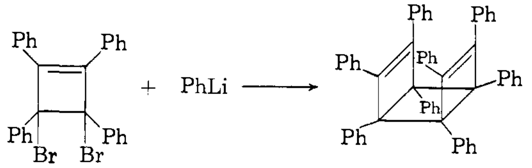
(2)) reasonably could be expected to produce the octaphenyltricyclooctadiene (IIIa, written as the *exo* isomer), there was obtained in 40 and 80% yield, respectively, the same new colorless hydrocarbon.



(1)

IIa



(2)

IIIa

This new compound is distinguished by its tendency to isomerize to I even in the solid state at room temperature, and preliminary attempts at its characterization have led only to the quantitative recovery of I. However, it is stable at −25° and is readily distinguished from I by the X-ray powder pattern and by the solid state infrared and, in particular, the Raman spectrum, which has a strong band at 1650 cm.$^{-1}$. This latter band is assignable only to a C=C stretching mode and could fit equally well for IIa or IIIa.[11]

Though the exact identity of this unstable compound must be deferred pending the completion of studies now in progress, it is clear that a choice between IIa and IIIa cannot be made by analogy with the established chemistry of similar compounds. Structural considerations suggest that IIIa would be the logical precursor of I, but the production of IIIa by route (1) is unlikely and the isomerization of a cycloöctatetraene to a tricyclooctadiene (in contrast to the reverse isomerization[4]) is unknown. It has been calculated that unsubstituted cycloöctatetraene is more stable than its cubic tautomer by about 80 cal.[12]; based on their thermal behavior, the reverse seems to be true for the octaphenyl derivatives and it is tempting to explain this remarkable reversal of thermal stability as a consequence of the steric requirements of the eight phenyl groups.

**Acknowledgments.**—H. H. F. is indebted to Dr. Frederick Leavitt for the initial preparation of the unstable dimer and to Angus Frantz, Jr., for experimental assistance.

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[11] 3,4-Dibromotetraphenylcyclobutene has a strong band at 1627 cm.$^{-1}$ in the Raman. Steric interference between the opposing phenyls on the double bonds of IIIa might well raise this stretching frequency to 1650 cm.$^{-1}$.

[12] W. Weltner, Jr., *J. Am. Chem. Soc.*, **75**, 4224 (1953).

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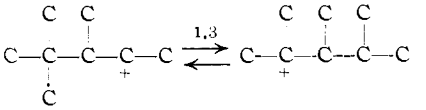
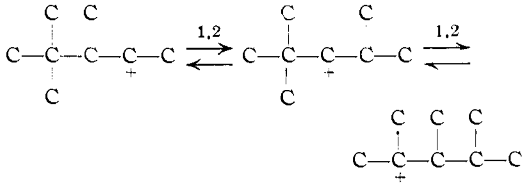
## CARBONIUM ION REARRANGEMENTS. V.[1] 1,3-HYDRIDE SHIFTS IN THE 1-PROPYL CATION

*Sir:*

The occurrence of Wagner–Meerwein 1,3-shifts in *open chain systems* has eluded unambiguous confirmation. Such shifts have been proposed[2] in mechanistic interpretations of product formation in carbonium ion reactions, *e.g.*, (1) has been suggested.[2a] However, the products can always be rationalized equally well by postulating successive 1,2-shifts, *e.g.* (2), and the acceptance or rejection of 1,3-shifts in open chain systems remains at best a matter of personal taste.[3]



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}\overset{C}{C}{-}\underset{+}{C}{-}C} \underset{}{\overset{1,3}{\rightleftarrows}} \mathrm{C{-}\underset{+}{\overset{C}{C}}{-}\overset{C}{C}{-}\overset{C}{C}{-}C} \qquad (1)$$



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}\overset{C}{C}{-}\underset{+}{C}{-}C} \overset{1,2}{\rightleftarrows} \mathrm{C{-}\underset{C}{\overset{C}{C}}{-}\underset{+}{C}{-}\overset{C}{C}{-}C} \overset{1,2}{\rightleftarrows} \mathrm{C{-}\underset{+}{\overset{C}{C}}{-}\overset{C}{C}{-}\overset{C}{C}{-}C} \qquad (2)$$

Our interests in carbonium ion rearrangements and, from a mechanistic point of view, the obvious importance of settling unambiguously the question of 1,3-shifts have led us to undertake a thorough examination of the problem. We shall discuss in this communication 1,3-hydride shifts.

It has been shown[4,5] that the nitrous acid deamination of the perchlorate salt of 1-propylamine-1-$C^{14}$ leads to labeled 1-propanol and 2-propanol, the label in 1-propanol being at C-1 and C-3 only.[5] As pointed out[5] the formation of 1-propanol-3-$C^{14}$ can result from either a 1,3-hydride shift, according to (3), or from successive 1,2-shifts, according to (4). We wish to present evidence that (3) represents the correct mechanism of the rearrangement.[6]

$$\mathrm{CH_3{-}CH_2{-}\underset{+}{\overset{14}{C}}H_2} \xrightarrow{1,3} \mathrm{\underset{+}{C}H_2{-}CH_2{-}\overset{14}{C}H_3} \qquad (3)$$

$$\mathrm{CH_3{-}CH_2{-}\underset{+}{\overset{14}{C}}H_2} \overset{1,2}{\rightleftarrows} \mathrm{CH_3{-}\underset{+}{C}H{-}\overset{14}{C}H_3} \overset{1,2}{\rightleftarrows} \mathrm{\underset{+}{C}H_2{-}CH_2{-}\overset{14}{C}H_3} \qquad (4)$$

Differentiation between (3) and (4) is possible by use of the perchlorate salt of 1-propylamine-1,1,2,2-$d_4$, since (3) leads to I and (4) to II. Proton n.m.r. can distinguish between I and II as follows: I should show a broad singlet or quintet around 6.6

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[1] Papers III and IV in this series, in press.

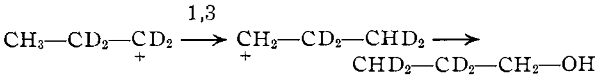
[2] (a) F. C. Whitmore, K. C. Laughlin, J. F. Matuszeski and J. D. Surmatis, *J. Am. Chem. Soc.*, **63**, 756 (1941); (*b*) F. C. Whitmore and W. A. Mosher, *ibid.*, **68**, 281 (1946); (c) W. A. Mosher and J. C. Cox, *ibid.*, **72**, 3701 (1950).

[3] W. H. Saunders and C. J. Carges, *ibid.*, **82**, 3582 (1960), have shown that during the dehydration of 3,4,4-trimethyl-2-pentanol, under irreversible conditions, no appreciable 1,3-shifts occur.

[4] J. D. Roberts and M. Halman, *ibid.*, **75**, 5759 (1953).

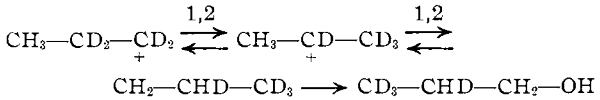
[5] O. A. Reutov and T. N. Shatkina, *Dokl. Akad. Nauk S.S.S.R.*, **133**, 606 (1960); *Tetrahedron*, **18**, 237 (1962).

[6] The assumption is made that the carbonium ion is the intermediate and that the products do not arise from direct reactions of the diazonium salt with solvent.



$$CH_3—CD_2—\underset{+}{C}D_2 \xrightarrow{1,3} \underset{+}{C}H_2—CD_2—CHD_2 \longrightarrow CHD_2—CD_2—CH_2—OH$$

I



$$CH_3—CD_2—\underset{+}{C}D_2 \overset{1,2}{\rightleftarrows} CH_3—\underset{+}{C}D—CD_3 \overset{1,2}{\rightleftarrows} \underset{+}{C}H_2—CHD—CD_3 \longrightarrow CD_3—CHD—CH_2—OH$$

II

$\tau$ for $\alpha$-hydrogens and no signal around 8.5 $\tau$ for $\beta$-hydrogens. II should show a broad doublet ($J \sim 7.4$ c.p.s.) or two triplets around 6.6 $\tau$ and a multiplet around 8.5 $\tau$, the ratio of 6.6 $\tau$ to 8.5 $\tau$ signals being 2.

A solution of 29.58 g. (0.181 mole) of 97.5% 1-propylammonium-1,1,2,2-$d_4$ perchlorate and 2.5% 1-propylammonium-1,1,2-$d_3$ perchlorate[7] (m.p. 168–169°; lit. value 167°) in 26 ml. of 35% aqueous perchloric acid was treated with a solution of 27.6 g. (0.4 mole) sodium nitrite in 40 ml of water, at room temperature. The product was treated as before[4] yielding 4.21 g. (36.4%) propanols. The mixture consisted of 30% 1-propanol and 70% 2-propanol (v.p.c. determination). The two propanols were separated and purified with a Beckman Megachrom, and analyzed with a Varian Associates A-60 n.m.r. spectrometer.

The 1-propanol (40% solution in carbon tetrachloride) gave signals at 9.14 $\tau$ (methyl), 6.58 $\tau$ ($\alpha$-hydrogens) and 5.41 $\tau$ (hydroxyl). The 6.58 $\tau$ signal is a single broad peak with a half-width of about 6 c.p.s. A weak signal (multiplet) appears at 8.5 $\tau$ with an integrated area corresponding to about 20% of the area of the 6.58 $\tau$; however, because of the interference of spinning bands from the methyl signal in this area the 20% value is considered to be a maximum value.

On the basis of the above results we conclude that the rearrangement is mainly, if not exclusively,[8] due to a 1,3-hydride shift. The amount of I in 1-propanol is 11.8%. Corroborative evidence that the rearrangement occurs *via* a 1,3-shift and not *via* successive 1,2-shifts is obtained by examining the spectrum of 2-propanol. Successive 1,2-shifts should introduce hydrogen at C-2 of 2-propanol. The amount of hydrogen at C-2 was found to be 1% (originally there was 2.5% hydrogen at C-2 as indicated previously). The less than 2.5% found probably is due to a kinetic isotope effect ($k_H/k_D$ 1). That the 2-propyl cation does not rearrange to the 1-propyl cation is supported further by the fact that 2-propylamine gave 2-propanol without a trace of 1-propanol.

In summary, the above and previous data[5] suggest the following with respect to the rearrangements of the 1-propyl cation under the experimental conditions: The 1-propyl cation rearranges irreversibly to the 2-propyl cation; it undergoes a 1,3-hydride shift; protonated cyclopropanes are not intermediates in the formation of the propanols; methyl migration does not occur.[5]

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[7] The labeled perchlorate was prepared from the corresponding amine which in turn was prepared by reduction of propionitrile-2,2-$d_2$ with lithium aluminum deuteride. The propionitrile-2,2-$d_2$ was prepared according to L. C. Leitch, *Can. J. Chem.*, **35**, 345 (1957), and was found by n.m.r. (integration of the methylene signal at 7.67 $\tau$ against the natural abundance $C^{13}$-satellites of the methyl group) to be 97.5% dideuterated species and 2.5% monodeuterated species. All integrations involving weak signals were made against natural abundance $C^{13}$-satellites of strong signals. Details will be published later.

[8] The 20% value of the 8.5 $\tau$ signal could be construed as indicative of the fact that the rearrangement occurs 60% *via* a 1,3-shift and 40% *via* successive 1,2-shifts. If such were the case the 6.58 $\tau$ signal would not have been a clean singlet. We could easily detect from the 6.58 $\tau$ signal a 10% rearrangement *via* successive 1,2-shifts.

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## VIBRONIC INTERACTION IN POTASSIUM *o*-XYLENIDE[1]

*Sir:*

The possibility of vibronic mixing in paramagnetic negative ions with nearly degenerate ground states has been discussed recently in connection with apparent positive spin densities around para carbon atoms in monoalkylated benzenides.[2] This discussion further pointed to the possibility of observing a temperature dependence in the proton hyperfine splittings in the electron spin resonance (e.s.r.) absorption spectra of these compounds. Such a temperature dependence has been reported in the e.s.r. absorption spectra of a series of monoalkylated benzenides.[3] We present evidence here to support the contention that vibronic mixing is also important in alkylated benzenides.

The e.s.r. absorption spectrum of potassium *o*-xylenide in 1,2-dimethoxyethane solution at −80° has been observed to consist of three groups of seven lines. Each of these twenty-one lines is further split into six. The corresponding spectrum of potassium *o*-xylenide-$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-$d_6$ also has three main lines each made up of at least fifteen components. The data on these spectra are summarized in Table I. In comparing the data for the two spectra we see that the substitution of six deuteriums on the methyl groups has the expected effect of collapsing the seven line structure on each of the three main components, but we also see an unexpected amplification of about 11% in the large proton splitting. Considering the evidence previously presented for near degeneracy in the ground states of closely allied compounds, this redistribution of electron spin, on changing essentially nothing but mass through

TABLE I

HYPERFINE COUPLINGS IN POTASSIUM *o*-XYLENIDE

| | A[a] | B[b] |
|---|---|---|
| Two ring protons | 6.95 | 7.75 |
| Methyl protons | 2.01 | 0.41[c] |
| Two ring protons | *ca.* 0.2 | ... |
| Potassium | *ca.* 0.2 | ... |

[a] Potassium *o*-xylenide hyperfine couplings. [b] Potassium *o*-xylenide-$d_6$ hyperfine couplings. [c] Smaller coupling for *o*-xylenide-$d_6$.

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[1] This work has been supported in part by the National Science Foundation.

[2] J. R. Bolton, A. Carrington, A. Forman and J. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

[3] T. R. Tuttle, Jr., *J. Am. Chem. Soc.*, **84**, 1492 (1962).