

The biosynthesis of 3'-methylnicotine (**10**) from 1,3-dimethyl-1-pyrrolinium salt **1** demonstrates that the enzyme system which catalyzes the biosynthesis of nicotine from 1-methyl-1-pyrrolinium salt **2** and a nicotinic acid derivative is not completely specific, and its requirements may become definable through experiments such as these. In addition the formation of unnatural products from unnatural precursors *in vivo* should be useful in the preparation of analogs of biologically active natural products (with high specific activity if desired) and in the study of metabolism and interrelationships among alkaloids.

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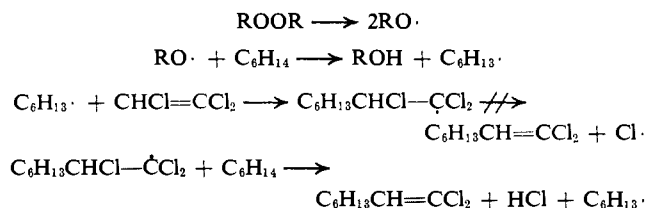
Some Highly Selective Radicals. The Chlorovinylation of Hexane

Sir:

Early investigations of product distributions following chlorinations, brominations, or oxidations of linear paraffin hydrocarbons indicated a nearly equal reactivity of all methylene hydrogen atoms. However, Asinger and Fell¹ and Fell and Kung² have demonstrated that a number of free radicals attack the methylene groups of a linear hydrocarbon in a significantly selective manner. Russell³ made the important finding that the selectivity of chlorine atoms in the chlorination of dimethylbutane could be greatly accentuated by a

should be derivable from molecules already containing bound chlorine. Just such highly selective radicals are indicated to be intermediates in the production of chlorovinyl derivatives by the peroxide-catalyzed combination of polychloroethylenes and paraffin hydrocarbons discovered by Schmerling and West.⁴ Unfortunately, these authors did not have the benefit of gas chromatography; otherwise it is doubtful that they would have hypothesized a chlorine atom intermediate as the reaction chain carrier because the isomer distributions in no way correspond to those that would be predicted from chlorine atom attack. We have treated *cis*-1,2-dichloroethylene, trichloroethylene, and tetrachloroethylene with hexane (1:6 *M* ratio) in sealed Pyrex bomb tubes at 125° with di-*tert*-butyl peroxide (1-2 mol %) as the reaction initiator (reaction times, *ca.* 16 hr). The product isomers were separated by glc and the reactivities of the hydrogen atoms in the various systems are compared with the reactivities of those same hydrogen atoms toward chlorine (photochlorination of hexane at 65°). The results are summarized in Table I.

The Schmerling-West mechanism as modified (for the case of trichloroethylene-hexane) then becomes



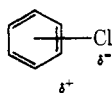
where $\text{C}_6\text{H}_{13}\cdot = \text{CH}_3\dot{\text{C}}\text{HCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3\text{CH}_2-\dot{\text{C}}\text{HCH}_2\text{CH}_2\text{CH}_3$.

Table I. Relative Reactivities of the Hydrogens in Hexane

Hexane	$h\nu$, 65° Cl ₂ -hexane	<i>cis</i> -CHCl=CHCl + hexane	CHCl=CCl ₂ + hexane	CCl ₂ =CCl ₂ + hexane	CHCl=CCl ₂ + CCl ₄ + hexane	CCl ₄ + hexane
CH ₃	0.35	0.06	0.04	Trace	<0.03	Trace
CH ₂	1.15	1.97 ^a	1.68	4.24	1.19	1.63
CH ₂	1.0	1.0	1.0	1.0	1.0	1.0

^a The product contains two *cis* and two *trans* isomers. The two *cis* isomers did not resolve on glc. Therefore, the value 1.97 is the ratio of *trans*-C₆H₉CHCH₃CH=CHCl to *trans*-C₆H₇CHC₂H₅CH=CHCl. The ratio of total *cis* to total *trans* was 1.44.

solvent such as benzene or carbon disulfide. Fell and Kung chlorinated *n*-heptane and *n*-octane in these solvents and showed that in these systems the methylene hydrogens were far from equivalent in reactivity. The rationale for the remarkable effect of benzene, for example, presupposes a polarized reaction intermediate or loose complex between the chlorine atom and the benzene solvent. Whatever the formalized description of this intermediate, it seems probable that this same



radical is the first step in the addition of chlorine to benzene. If this is so, then highly selective radicals

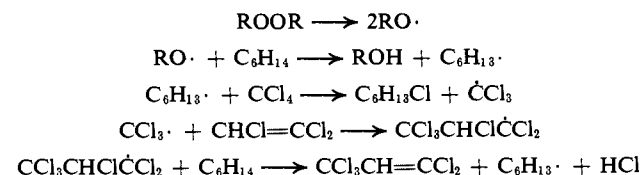
(1) F. Asinger and B. Fell, *Erdoel Kohle, Erdgas, Petrochem.*, **17**, 74 (1964).

(2) B. Fell and L. Kung, *Chem. Ber.*, **98**, 2871 (1965).

(3) G. A. Russell, *J. Amer. Chem. Soc.*, **80**, 4987 (1958).

Most noteworthy is the unusual selectivity of the chain-carrying radical from tetrachloroethylene and hexane. Over 80% of the reaction is at the 2 position.

A system which possesses its own unique pattern of selectivity and at the same time produces chlorohexane instead of vinylic chloro derivatives is a mixture of carbon tetrachloride, trichloroethylene, and hexane. In this case the reaction system proposed is



Referring to Table I where the results of this reaction can be compared with halogenation of hexane by chlorine and by carbon tetrachloride, it seems obvious from

(4) L. Schmerling and J. P. West, *ibid.*, **71**, 2015 (1949).

the isomer distribution that chlorine atoms are not involved—there is almost no reaction at the methyl group—nor is CCl_3 attack involved; there is neither CHCl_3 in the product nor an isomer distribution characteristic of CCl_3 attack.

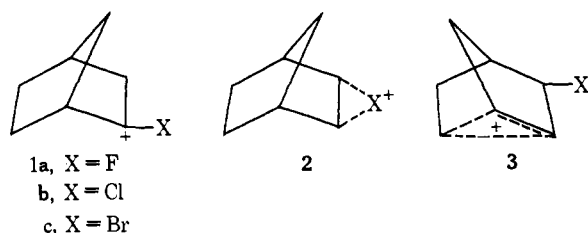
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Stable Carbonium Ions. CXIII.¹ 2-Halonorbornyl Cations and Protonated 4-Halonortricyclenes

Sir:

2-Alkylnorbornyl cations have been demonstrated to be partially delocalized tertiary ions, whereas the unsubstituted norbornyl cation in superacids is symmetrically delocalized (corner-protonated nortricyclene).² In view of this difference in structure, we felt it would be of interest to study the 2-halonorbornyl cations (**1a-c**) which also could yield ions such as **2** and



3.³ We wish to report now our work in this regard

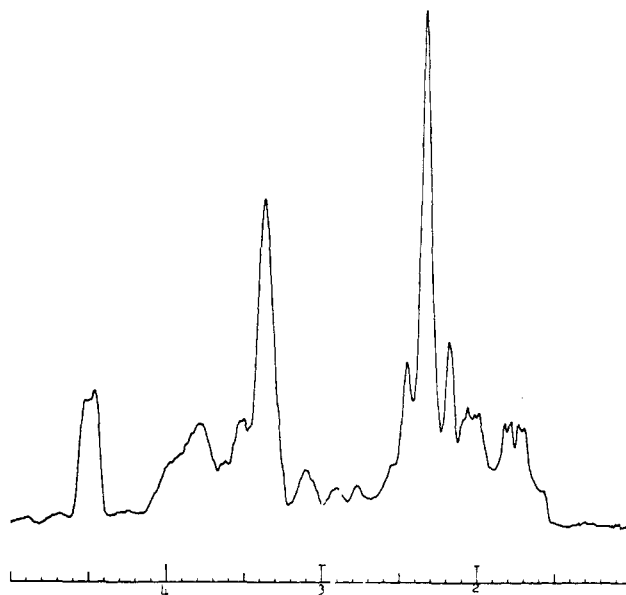


Figure 1. PMR spectrum of 2-fluoronorbornyl cation in SO_2 at -70° (100 MHz).

cation (**1b**) and protonated 4-chloronortricyclene (**5b**). Ion **5b** was identified by comparison of its proton (pmr) and ^{13}C (cmr) chemical shifts with those of protonated nortricyclene (Table II). Warming the solution to -25° produces no change in the distribution of the ions. Ion **1b** may be produced alone by treating **4b** with SbF_5 in SO_2/ClF . Warming this solution to -15° does not produce any **5b**. Local heating during ion formation may be responsible for the formation of **5b** from

Table I. Nmr Parameters of 2-Halo- and 2-Methylnorbornyl Cations in $\text{SbF}_5\text{-SO}_2$ Solution at -70°

Ion	PMR chemical shifts (δ) ^a								Cmr shift ^b C ₂
	CH ₃	H ₁	exo-H ₆	exo,endo-H ₃	H ₄	H ₇	exo,endo-H ₅	endo-H ₆	
1a		4.50	3.68	3.38 (br)	3.38 (br)	2.34	2.00	1.76	-80.1
1b		4.91	3.56 (br)	3.56 (br)	3.34	2.24	1.97	1.65	-92.1
1d	3.37	5.01	3.54	3.20	3.12	2.05	1.83	1.49	-76.1

^a In ppm from capillary TMS. ^b In ppm from CS_2 .

and the observation of 2-halonorbornyl cations. In the course of this work we have observed a rearrangement which leads to 4-substituted nortricyclenes.

2,2-Difluoronorbornane (**4a**) when treated with $\text{SbF}_5\text{-SO}_2$ forms the 2-fluoronorbornyl cation (**1a**). The pmr spectrum of this cation is shown in Figure 1. The assignment of the pmr chemical shifts was made by comparison with those found for the 2-methylnorbornyl cation (**1d**) (Table I).² The cmr shift of C₂ in ion **1a** is -80.1 ppm (from CS_2), while the fluorine at C₂ has an ^{19}F resonance at $\phi -71.6$ (from CCl_3F).

2,2-Dichloronorbornane (**4b**) in $\text{SbF}_5\text{-SO}_2$ solution at -78° gives a mixture of the 2-chloronorbornyl

1b. Ion **5b** is also obtained from 4-chloronortricyclene⁴ (**6**) in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ solution at -78° .

When 3-bromonortricyclene (**7**) in SO_2 is added to $\text{FSO}_3\text{H-SO}_2$ and the resulting solution is treated with SbF_5 , protonated 4-bromonortricyclene (**5c**) is obtained. The proton magnetic resonance spectrum at -70° is shown in Figure 2. As may be seen from Table II, both the pmr and the cmr chemical shifts compare favorably with those of protonated nortricyclene.²

On quenching ion **5c** with pyridine, 4-bromonortricyclene (**8**) is obtained. Ion **1c** is also obtained by treating 2,7-dibromonorbornane (**9**) and 2,3-dibromonorbornane (**10**) with SbF_5 in SO_2 .

Both the 2-fluoronorbornyl cation (**1a**) and the 2-chloronorbornyl cation (**1b**) are stable partially delocalized norbornyl cations. Back-donation from fluorine and chlorine is sufficient to stabilize the 2-halonorbornyl cations. That the 2-fluoro substituent bears

(4) We wish to thank Dr. G. Dunn for a sample of 4-chloronortricyclene.

(1) Part CXII: G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, submitted for publication.

(2) (a) G. A. Olah and A. M. White, *ibid.*, **91**, 3954 (1969); (b) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *ibid.*, **91**, 3958 (1969); (c) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, **92**, 4627 (1970).

(3) Ions **2** and **3** have been postulated as intermediates in electrophilic additions to norbornene: T. F. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969), and references therein.