

TABLE I  
N<sup>14</sup> COUPLING CONSTANTS

Negative ion radical <sup>a</sup>	a <sub>N</sub>  , gauss
Nitroethane	25.2
1-Nitropropane	24.8
2-Nitropropane	25.4
1-Nitrobutane	24.3
2-Nitrobutane	24.5

<sup>a</sup> All generated in background electrolyte of 0.4 M KCl with 10% 1-propanol for solubility.

diphenylamine and several derivatives of chloro-promazine has been carried out in aqueous buffers.

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DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF KANSAS  
LAWRENCE, KANSAS

L. H. PIETTE  
P. LUDWIG  
R. N. ADAMS

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#### ON THE MECHANISM FOR LONG RANGE PROTON SPIN COUPLINGS

Sir:

In a recent paper, Kreevoy, *et al.*,<sup>1</sup> question the evidence for hyperconjugation as a mechanism for long range coupling in unsaturated compounds<sup>2</sup> such as propargyl derivatives and suggest that  $\alpha$ -hydrogen bonding<sup>3</sup> should be involved instead. They refer to recent theoretical work by Karplus<sup>4</sup> which, they claim, utilized essentially the  $\alpha$ -hydrogen bonding model. This latter assertion is not valid. Though Karplus states explicitly<sup>4</sup> that "the orbitals on the protons H and H' whose coupling is being determined are taken to be part of the sigma-electron system, this does not imply that hyperconjugation is not involved in his theory, since the proton spin coupling, as calculated by Karplus, is expressed in terms of hyperfine coupling constants and triplet state energies. Now the hyperfine coupling constants are obtained from e.s.r. data on related free radicals and insofar as the fragments

$\text{H}-\overset{\cdot}{\text{C}}-\overset{\cdot}{\text{C}}$  are concerned all theoretical interpretations<sup>5,6</sup> involve hyperconjugation either in its molecular orbital<sup>5</sup> or valence bond<sup>6</sup> formulation.

Thus the successful theoretical treatment of long range coupling<sup>4</sup> depends ultimately on hyperconjugation, rather than on the use of the  $\alpha$ -hydrogen bonding model.

(1) M. M. Kreevoy, H. B. Charman and D. R. Vinard, *J. Am. Chem. Soc.*, **83**, 1978 (1961).

(2) (a) R. A. Hoffman, *Mol. Phys.*, **1**, 326 (1958); (b) E. B. Whipple, J. H. Goldstein and L. Mandell, *J. Chem. Phys.*, **30**, 1109 (1959); (c) E. B. Whipple, J. H. Goldstein and W. E. Stewart, *J. Am. Chem. Soc.*, **81**, 4761 (1959); (d) A. D. Cohen and N. Sheppard, *Proc. Roy. Soc. (London)*, **A252**, 488 (1959); (e) P. L. Corlo and I. Weinberg, *J. Chem. Phys.*, **31**, 569 (1959); (f) R. A. Hoffman and S. Gronowitz, *Acta Chem. Scand.*, **13**, 1477 (1959).

(3) M. M. Kreevoy and H. Eyring, *J. Am. Chem. Soc.*, **79**, 5121 (1957).

(4) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(5) (a) R. Bersohn, *ibid.*, **24**, 1066 (1956); (b) D. B. Chesnut, *ibid.*, **29**, 43 (1958).

(6) (a) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958); (b) P. G. Lykos, *J. Chem. Phys.*, **32**, 625 (1960).

Apparently<sup>7</sup> the fundamental difference between hyperconjugation and  $\alpha$ -hydrogen bonding is that whereas hyperconjugation depends upon a non-vanishing magnitude for the exchange integral between a carbon  $p\pi$ -orbital and the tetrahedral hybrid on an  $\alpha$ -carbon,  $\alpha$ -hydrogen bonding requires a non-vanishing magnitude for the exchange integral between the  $p\pi$ -orbital and an  $\alpha$ -hydrogen  $1s$ -orbital.

Until calculations have demonstrated that acceptable estimates of the latter integral can account for the magnitudes and signs of observed long range couplings, it seems more reasonable to interpret these couplings in terms of hyperconjugation. More elaborate arguments and evidence in support of this view may be found in some recent works.<sup>8</sup>

(7) M. M. Kreevoy, *Tetrahedron*, **5**, 233 (1959).

(8) (a) R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, **16**, 471 (1960); (b) R. A. Hoffman, *ibid.*, **17**, 1 (1960).

INSTITUTE OF PHYSICS  
INSTITUTE OF CHEMISTRY  
UNIVERSITY OF UPPSALA  
UPPSALA, SWEDEN

RAGNAR A. HOFFMAN  
SALO GRONOWITZ

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#### ON d HYBRIDIZATION IN CHLORINE

Sir:

The use of hybridization in valence bond theory in order to explain observed molecular geometries is well known. The classic example is of  $sp^3$  hybridization in the group IV elements. In this case the bonding configuration (valence state) is considerably above the ground state in energy. The necessary promotion energy is regained upon bond formation yielding, of course, a stable molecule.

It is known that compounds of fluorine and chlorine exhibit many differences in structural properties. These differences frequently have been attributed to d hybridization in chlorine. Since chlorine has valence electrons in the 3s and 3p shells, excitation of these electrons to the 3d orbital has been assumed to be relatively easy in contradistinction to fluorine where the necessary excitation is 2s and 2p to 3d. The argument of easy orbital excitation when the principal quantum number remains unchanged is based in essence upon the assumption that the field in which the valence electrons move is reasonably close to coulombic.

In fluorine the energy of the center of gravity of states arising from  $2s^2 2p^4 (^3P) 3d$  is 15.9 e.v.<sup>1</sup> Until recently the energy location of states arising from the configuration  $3s^2 3p^4 3d$  in chlorine was unknown. Humphreys and Paul<sup>2</sup> and Minnhagen<sup>3</sup> have analyzed the chlorine spectrum. From their assignments the center of gravity of states arising from  $3s^2 3p^4 (^3P) 3d$  is 11.2 e.v.

In both fluorine and chlorine the excitation energy is large, in each instance being slightly less than 2 e.v. below the ionization limit. It would thus appear arbitrary to select the configuration of chlorine involving 3d electrons from the wealth of configurations near the ionization limit. In view of

(1) Charlotte E. Moore, "Atomic Energy Levels," Vol. I, United States Department of Commerce, 1949, Washington, D. C.

(2) C. J. Humphreys and E. Paul, Jr., *J. Opt. Soc. Am.*, **49**, 1186 (1959).

(3) L. Minnhagen, *ibid.*, **51**, 298 (1961).

the similarity in magnitude of 3d excitation in chlorine and fluorine it seems unreasonable to base gross differences in structural properties on these relatively small differences in energy.

In view of the fact that most modern calculations require an extensive linear combination of atomic orbitals for a basis set, the selection of a single excited configuration as predominant for qualitative discussion would appear useful only if this configuration lies uniquely lower in energy than the remaining member of the set. It appears that the differences in chemical bonding of chlorine and fluorine cannot be naturally explained simply in terms of 3d hybridization.

DEPARTMENT OF CHEMISTRY  
HARVARD UNIVERSITY  
CAMBRIDGE 38, MASS.

WILLIAM KLEMPERER

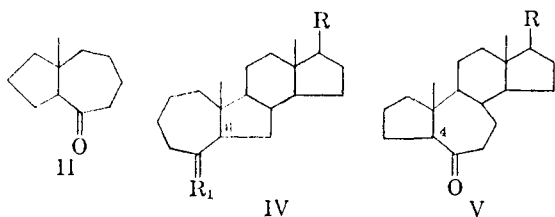
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### SYNTHESIS OF PERHYDROAZULENES

Sir:

We wish to report a facile stereospecific conversion of bicyclo[4,4,0]decanes to bicyclo[5,3,0]decanes. This conversion involves a pinacolic type rearrangement of vicinal *cis*-glycol monotosylates.<sup>1</sup>

10-Methyl- $\Delta^{1,9}$ -octalin<sup>2</sup> in pyridine was treated with osmium tetroxide to give 10-methyl-decal-1,9-diol, m.p. 96–98°, which with tosyl chloride in pyridine at room temperature yielded 10-methyl-decal-1,9-diol 1-tosylate (I). Treatment of I with potassium *t*-butoxide in *t*-butyl alcohol or with alumina (Alcoa F-20) gave 10-methylbicyclo[5,3,0]decan-1-one (II), b.p. 110° (25 mm.); dinitrophenylhydrazone, m.p. 118°,  $\lambda_{\max}$  366 m $\mu$  ( $\epsilon$  25,900); semicarbazone, m.p. 169–171°,  $\lambda_{\max}$  226 m $\mu$  ( $\epsilon$  11,800).<sup>3</sup> The stereochemistry and exact conditions of this rearrangement were studied on a more convenient system, on the steroidal nucleus.



Cholestane-5 $\alpha$ ,6 $\alpha$ -diol 6-tosylate (III, m.p. 122–123°;  $[\alpha]_D +18^\circ$ ) on treatment at 25° with 1 mole equiv. of potassium *t*-butoxide in *t*-butyl alcohol or at 100° with dimethylformamide and calcium carbonate (for 8 hr.), gave a quantitative yield of *cis*-ketone (IV, R = C<sub>8</sub>H<sub>17</sub>, R<sub>1</sub> = O, 6  $\beta$  H; m.p. 125–126°;  $[\alpha]_D +19^\circ$ ;  $[\alpha]_{310} +1105^\circ$ , positive Cotton effect). Heating with aqueous sulfuric acid-dioxane for 2 hr. yielded an equilibrium mix-

(1) Cf., *inter al.*, P. D. Bartlett and R. H. Rosenwald, *J. Am. Chem. Soc.*, **56**, 1990 (1934); R. B. Bates, G. Büchi, T. Matsuura and R. R. Shaffer, *ibid.*, **82**, 2327 (1960); E. J. Corey, M. Ohno, P. A. Vatakencherry and R. B. Mitra, *ibid.*, **83**, 1251 (1961); N. L. Wendler, *Tetrahedron*, **11**, 213 (1960).

(2) F. Sondheimer and D. Rosenthal, *J. Am. Chem. Soc.*, **80**, 3995 (1958).

(3) All the compounds described gave analytical results, infrared and ultraviolet spectra compatible with the assigned structures. Rotations were taken in chloroform and rotatory dispersion measurements in dioxane.

ture,  $[\alpha]_{310} +534^\circ$ , from which the *trans*-ketone (IV, R = C<sub>8</sub>H<sub>17</sub>, R<sub>1</sub> = O, 6  $\alpha$  H; m.p. 136–137°;  $[\alpha]_D -10^\circ$ ;  $[\alpha]_{310} -1017^\circ$ , negative Cotton effect) was isolated.<sup>4</sup> This thermodynamic equilibrium corresponds to 77% *cis*  $\rightleftharpoons$  23% *trans* (as calculated from  $[\alpha]_{310}$ ). The two ketones also were formed by passing III through alumina (Merck, acid washed). The structure and stereochemistry of the *cis*-ketone was proved through its conversion (65%) by Wolff-Kishner reduction to the hydrocarbon (IV, R = C<sub>8</sub>H<sub>17</sub>, R<sub>1</sub> = H<sub>2</sub>, 6  $\beta$  H; m.p. 71–72°;  $[\alpha]_D +29.5^\circ$ ) which was identical with the one obtained by conversion of B-norcoprostan-3-one<sup>5</sup> with diazomethane *in situ* to A-homo-B-nor-6 $\beta$ H-cholestan-4-one (m.p. 78–80°;  $[\alpha]_D +21^\circ$ ) and subsequent reduction.

Similarly, androstane-5 $\alpha$ ,6 $\alpha$ ,17 $\beta$ -triol 6-tosylate 17-benzoate (m.p. 129–130°;  $[\alpha]_D +34^\circ$ ) was converted to (IV, R = OBz, R<sub>1</sub> = O, 6 $\beta$ H; m.p. 120–122°;  $[\alpha]_D +51^\circ$ ). The corresponding alcohol (IV, R = OH, R<sub>1</sub> = O, 6 $\beta$ H; m.p. 152–153°;  $[\alpha]_D +5^\circ$ ;  $[\alpha]_{320} +275^\circ$ , positive Cotton effect) was stable to acid and base.

Cholestane-4 $\alpha$ ,5 $\alpha$ -diol 4-tosylate (m.p. 135–136°;  $[\alpha]_D +8^\circ$ ), stable on alumina (Merck acid washed), was rearranged to the ketone (V, R = C<sub>8</sub>H<sub>17</sub>, 4 $\beta$ H; m.p. 87–88°;  $[\alpha]_D +125^\circ$ ;  $[\alpha]_{310} +1945^\circ$ , positive Cotton effect) with 1 mole equiv. of potassium *t*-butoxide or by boiling with dimethylformamide-calcium carbonate for 24 hr. This ketone was converted to the equilibrium mixture,  $[\alpha]_{310} +1520^\circ$  (85% *cis*  $\rightleftharpoons$  15% *trans*) from which (V, R = C<sub>8</sub>H<sub>17</sub>, 4 $\alpha$ H; m.p. 136–137°;  $[\alpha]_D -27^\circ$ ;  $[\alpha]_{310} -717^\circ$ , negative Cotton effect) was isolated. In the same way androstane-4 $\alpha$ ,5 $\alpha$ ,17 $\beta$ -triol-4-tosylate 17-benzoate (m.p. 138–139°;  $[\alpha]_D +53^\circ$ ) was rearranged to (V, R = OBz, 4 $\beta$ H; m.p. 166–168°;  $[\alpha]_D +33^\circ$ ). The equilibrium mixture of the two corresponding ketoalcohols (V, R = OH, 4 $\beta$ H; m.p. 126–128°;  $[\alpha]_D +20^\circ$ ;  $[\alpha]_{320} +100^\circ$ , positive Cotton effect), and (V, R = OH, 4 $\alpha$ H; m.p. 162–163°;  $[\alpha]_D +155^\circ$ ;  $[\alpha]_{320} +2375^\circ$ , positive Cotton effect) corresponds to 15% *cis*  $\rightleftharpoons$  85% *trans*.

The transition state for this rearrangement demands coplanarity of the four centers involved, which together with the concerted electron shift, causes retention of configuration at the bridgehead of the product.<sup>6</sup>

It is of particular interest that there are marked variations in the relative stabilities of the *cis*  $\rightleftharpoons$  *trans* ketones in the systems studied. Differences in the substitution in these systems may change the conformation of the cycloheptane ring as inferred from the directions of the respective Cotton effects. This is in accord with the flexibilities

(4) This is compatible with the Cotton effect of similar systems: D. N. Kirk and V. Petrow, *J. Chem. Soc.*, 4057 (1960); G. Büchi, S. W. Chow, T. Matsuura, T. L. Popper, H. H. Rennhard and M. Schach von Wittenau, *Tetrahedron Letters*, **6**, 14 (1959).

(5) J. Joska, J. Fajkos and F. Šorm, *Coll. Czech. Chem. Comm.*, **25**, 2341 (1960).

(6) Cf., *inter al.*, R. J. W. Cremllyn, D. L. Garmalse and C. W. Shoppee, *J. Chem. Soc.*, 1847 (1953); J. Elks, G. H. Phillips, D. A. H. Taylor and L. J. Wyman, *ibid.*, 1739 (1954); R. Hirschmann, C. S. Snoddy, C. F. Hiskey and N. L. Wendler, *J. Am. Chem. Soc.*, **76**, 4013 (1954); R. Anliker, O. Rohr and H. Heusser, *Helv. Chim. Acta*, **38**, 1171 (1955).