

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.

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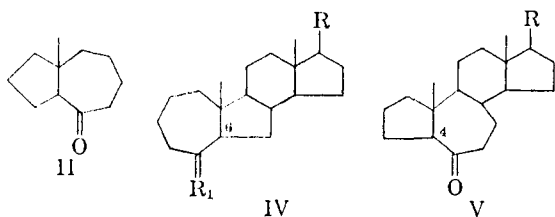
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SYNTHESIS OF PERHYDROAZULENES

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 pinacol type rearrangement of vicinal *cis*-glycol monotosylates.¹

10-Methyl- $\Delta^{1,9}$ -octalin² 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°, λ_{\max} 366 m μ (ϵ 25,900); semicarbazone, m.p. 169–171°, λ_{\max} 226 m μ (ϵ 11,800).³ The stereochemistry and exact conditions of this rearrangement were studied on a more convenient system, on the steroidal nucleus.



Cholestane-5 α ,6 α -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 = C₈H₁₇, R₁ = O, 6 β 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 = C₈H₁₇, R₁ = O, 6 α H; m.p. 136–137°; $[\alpha]_D -10^\circ$; $[\alpha]_{310} -1017^\circ$, negative Cotton effect) was isolated.⁴ 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 = C₈H₁₇, R₁ = H₂, 6 β H; m.p. 71–72°; $[\alpha]_D +29.5^\circ$) which was identical with the one obtained by conversion of B-norcoprostan-3-one⁵ with diazomethane *in situ* to A-homo-B-nor-6 β H-cholestan-4-one (m.p. 78–80°; $[\alpha]_D +21^\circ$) and subsequent reduction.

Similarly, androstane-5 α ,6 α ,17 β -triol 6-tosylate 17-benzoate (m.p. 129–130°; $[\alpha]_D +34^\circ$) was converted to (IV, R = OBz, R₁ = O, 6 β H; m.p. 120–122°; $[\alpha]_D +51^\circ$). The corresponding alcohol (IV, R = OH, R₁ = O, 6 β H; m.p. 152–153°; $[\alpha]_D +5^\circ$; $[\alpha]_{320} +275^\circ$, positive Cotton effect) was stable to acid and base.

Cholestane-4 α ,5 α -diol 4-tosylate (m.p. 135–136°; $[\alpha]_D +8^\circ$), stable on alumina (Merck acid washed), was rearranged to the ketone (V, R = C₈H₁₇, 4 β 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 = C₈H₁₇, 4 α H; m.p. 136–137°; $[\alpha]_D -27^\circ$; $[\alpha]_{310} -717^\circ$, negative Cotton effect) was isolated. In the same way androstane-4 α ,5 α ,17 β -triol-4-tosylate 17-benzoate (m.p. 138–139°; $[\alpha]_D +53^\circ$) was rearranged to (V, R = OBz, 4 β H; m.p. 166–168°; $[\alpha]_D +33^\circ$). The equilibrium mixture of the two corresponding ketoalcohols (V, R = OH, 4 β H; m.p. 126–128°; $[\alpha]_D +20^\circ$; $[\alpha]_{320} +100^\circ$, positive Cotton effect), and (V, R = OH, 4 α 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.⁶

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. Rennbard 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. Cremling, D. L. Garmale 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).

of substituted cycloheptanes⁷ observed in perhydroazulenes.⁸ The application of this rearrangement to the synthesis of seven-membered aromatic compounds is now in progress.

We are indebted to Prof. F. Sondheimer for his interest and encouragement, and to Syntex S.A., Mexico, for a generous gift of starting materials, and optical rotatory dispersion measurements.

(7) H. J. E. Loewenthal and R. Rona, *J. Chem. Soc.*, 1429 (1961), and refs. cited therein.

(8) N. L. Allinger and V. B. Zalkow, *J. Am. Chem. Soc.*, **83**, 1144 (1961).

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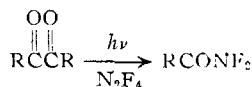
TETRAFLUOROHYDRAZINE: A VERSATILE INTERMEDIATE FOR THE SYNTHESIS OF N-FLUORO COMPOUNDS

Sir:

We have found tetrafluorohydrazine,¹ N₂F₄, to be a versatile intermediate for the synthesis of both organic and inorganic compounds containing the difluoramino group, NF₂. N₂F₄ participates in a variety of free radical reactions as might be expected from its low N-N bond strength.²

N₂F₄ and chlorine react under the influence of ultraviolet light in Pyrex to produce chlorodifluoramino,³ ClNF₂. This is an equilibrium reaction in which the formation of chlorodifluoramino is favored by a large excess of chlorine and a relatively high temperature (80°). The synthesis of difluoramino, HNF₂, by the hydrogen abstraction reaction between N₂F₄ and thiophenol has been reported.⁴

The photolysis of diketones in the presence of N₂F₄ at room temperature in Pyrex caused the formation of N,N-difluoroamides in good yield.



The reaction has been applied successfully to biacetyl, glyoxal and benzil. For example, 0.06 mole of biacetyl and 0.06 mole of N₂F₄ irradiated for sixteen hours with a Hanovia EH-4 lamp yielded 0.077 mole of N,N-difluoroacetamide (IV), b.p. 45–47°; yield 80% based on N₂F₄ consumed. *Anal.* Calcd. for C₂H₃F₂NO: N, 14.74. Found; N, 14.40. The material was characterized by its infrared spectrum ($\nu_{\text{C=O}}$ 1820 cm.⁻¹), n.m.r. spectrum⁵ (F¹⁹ resonance at -4270 c.p.s. and H¹ resonance at +190 c.p.s.), and by its solvolysis in ethanol to ethyl acetate and difluoramino.

Alkyl radicals⁶ generated by the decomposition of

(1) C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1958).

(2) C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

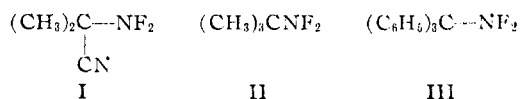
(3) R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

(4) J. P. Freeman, A. Kennedy and C. B. Colburn, *ibid.*, **82**, 5304 (1960).

(5) F¹⁹ resonances are recorded in cycles from external CF₃CO₂H and H¹ resonances from external C₆H₆. Negative values indicate resonance at lower field than the standard.

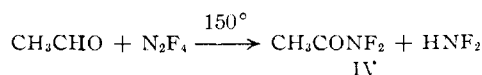
(6) The photochemical reaction between alkyl iodides and N₂F₄ presumably involves alkyl radicals; J. W. Frazer, *J. Inorg. Nucl. Chem.*, **16**, 63 (1960).

azoisobutyronitrile, azoisobutane, and hexaphenyl-ethane also reacted with N₂F₄ to produce the corresponding difluoramines, I, b.p. 71–72° (150 mm.), II, b.p. 54–55° and III, m.p. 81–82°.



Satisfactory analyses were obtained for all these compounds. Their F¹⁹ n.m.r. spectra⁵ all show signals from the NF₂ groups at -4724, -4224, and -4430 c.p.s., respectively. These compounds resist hydrolysis.

N,N-Difluoroamides also may be obtained by the reaction of aldehydes with N₂F₄. N,N-Difluoroacetamide and difluoramino were produced when acet-aldehyde and N₂F₄ were heated at 150° in a Pyrex bulb. This reaction may be compared to the conversion of benzaldehyde to benzoyl chloride by chlorine.⁷



N₂F₄ must be handled cautiously. Oxygen must be excluded rigorously from mixtures of N₂F₄ and organic compounds or explosions are likely to result. The difluoramino compounds themselves should also be handled with care.

Acknowledgment.—This work was conducted under Army Ordnance Contract DA-01-021 ORD-5135. The support and encouragement of Dr. Warren D. Niederhauser is gratefully acknowledged.

(7) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 369.

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CARBONIUM ION SALTS. II. REACTION OF CYCLOHEPTATRIENE WITH INORGANIC HALIDES; TROPENIUM CHLOROBORATE¹

There is much interest in compounds of the chloroborate anion^{2a–i}; however, their preparation has required high temperature and pressure,^{2d} long milling of solids,^{2h} or liquid hydrogen chloride solvent,^{2g} and the products often give unsatisfactory analyses. The only easily prepared, stoichiometric chloroborate reported is cesium chloroborate.^{2i,3}

We find that the reaction of boron chloride with cycloheptatriene⁴ in methylene chloride (dry conditions under nitrogen, room temp. for 24 hr., mole ratio BCl₃/C₇H₈ of 1.4/1) gives 12.6% tropenium

(1) Supported by the Petroleum Research Fund, Grant 443-A.

(2) (a) D. R. Martin, *Chem. Rev.*, **42**, 581 (1948); (b) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1527 (1956); (c) M. F. Lappert, *Proc. Chem. Soc.*, 121 (1957); (d) E. L. Muettterties, *J. Am. Chem. Soc.*, **79**, 6563 (1957); (e) A. B. Burg and E. R. Birnbaum, *J. Inorg. Nucl. Chem.*, **7**, 146 (1958); (f) D. E. Burge, H. Freund and T. H. Norris, *J. Phys. Chem.*, **63**, 1069 (1959); (g) T. C. Waddington and F. Klanberg, *Naturwiss.*, **20**, 578 (1959); *J. Chem. Soc.*, 2329, 2332 (1960); (h) W. Kynaston, B. E. Larcombe and H. S. Turner, *ibid.*, 1772 (1960); (i) E. L. Muettterties, *J. Inorg. Nucl. Chem.*, **12**, 355 (1960).

(3) Lappert^{2c} has reported the preparation of pyridinium chloroborate but does not give experimental or analytical details.

(4) Generously supplied by the Shell Chemical Company.