or *d-trans* acid with *l*-allethrolone plus *l-trans* acid with *d*-allethrolone; the *β-dl-trans* isomer consists of the other pair.

Entomological tests[5] on house flies indicate the *α-dl-trans* isomer to be less effective and the *β-dl-trans* isomer to be more effective than allethrin.

The pure, crystalline *α-dl-trans* isomer of allethrin should serve as a useful reference standard in Peet-Grady, Campbell turntable, and other insecticide test methods, and for checking chemical analytical methods for substances of the pyrethrin or allethrin type.

(5) By W. A. Gersdorff, N. Mitlin, and J. H. Fales, Bureau of Entomology and Plant Quarantine.

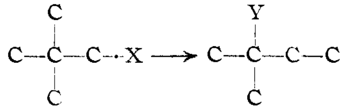
BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
AGRICULTURAL RESEARCH ADMINISTRATION
U. S. DEPARTMENT OF AGRICULTURE MILTON S. SCHECHTER
BELTSVILLE, MARYLAND F. B. LAFORGE
BENZOL PRODUCTS CO. A. ZIMMERLI
NEWARK, N. J. J. M. THOMAS

RECEIVED JUNE 19, 1951

NON-REARRANGEMENT REACTIONS OF THE NEOPENTYL-OXYGEN BOND. NEW SYNTHESES OF NEOPENTYL HALIDES

Sir:

Anionoid substitution reactions of neopentyl compounds have long been known to proceed with rearrangement of the carbon skeleton.[1] Indeed,



these changes are often cited in textbooks as classical simple examples of the Wagner-Meerwein rearrangement.

In a recent elegant series of papers, however, I. Dostrovsky, E. D. Hughes and C. K. Ingold[2] have demonstrated rearrangement for neopentyl bromide in S_N1 reactions and non-rearrangement in S_N2 reactions. This suggested to us that similar non-rearrangement reactions of the neopentyl-oxygen bond might be isolated by appropriate structural variations in neopentyl alcohol (which did not disturb the neopentyl-oxygen configuration) or by reaction conditions unfavorable to reaction of the alcohol by an S_N1 mechanism.

In this communication we wish to report what we believe to be the first unequivocal examples of reactions of the neopentyl-oxygen bond proceeding without rearrangement.

$$Me_3CCH_2OSiEt_3 + PBr_3 \xrightarrow{C_9H_7N\cdot HX} Me_3CCH_2Br + Et_3SiBr$$

$$Me_3CCH_2OSiEt_3 + SOCl_2 \xrightarrow{C_9H_7\cdot HX} Me_3CCH_2Cl + Et_3SiCl$$

$$Me_3CCH_2OH + PBr_3 + C_9H_7N \longrightarrow Me_3CCH_2Br + C_9H_7N\cdot HBr$$

Triethylneopentoxysilane, b.p. 67° (10 mm.), n^{20}D 1.4189 (calcd. for $C_{11}H_{26}OSi$: Si, 13.84. Found: Si, 13.78) was prepared by the method of R. O. Sauer[3] using neopentyl alcohol, triethylchlorosilane, and quinoline, in a benzene solvent. Pure neopentyl bromide, b. 104° (733 mm.), n^{20}D 1.4371, d^{20} 1.200, lit.[1c] b.p. 105°, n^{20}D 1.4370, d^{20} 1.199; anilide, m.p. and mixed m.p. 130°; less than 0.5% reaction with NaOEt in EtOH at reflux for four hours; (calcd. for $C_5H_{11}Br$: Br, 52.9. Found: Br, 52.9) was formed in 85% yield by heating 2 moles of triethylneopentoxysilane with four moles of phosphorus tribromide at 173° for 16 hours in the presence of 3 g. of quinoline hydrochloride.[4]

A similar reaction using thionyl chloride and carried out at 115° for 23 hours gave a 61% yield of pure neopentyl chloride, b.p. 83° (725 mm.), n^{20}D 1.4043, d^{20} 0.8659, lit.[1c] b.p. 83.5° (740 mm.), n^{22}D 1.4043, d^{20} 0.865; completely inert to NaOEt in EtOH; anilide, m.p. and mixed m.p. 130° (calcd. for $C_5H_{11}Cl$: Cl, 33.27. Found: Cl, 32.58).

Neopentyl bromide, b.p. 104.5° (728 mm.), n^{20}D 1.4370, d^{20} 1.200, was also prepared in 47% yield by heating a mixture of neopentyl alcohol (2 moles), quinoline (2.43 moles) and bromobenzene (900 cc.) at 181° for 24 hours.

From the above data it is now clear that use of neopentyl as a critical group in experiments aimed at determining the mechanism of cleavage of a carbon-oxygen bond in a given reaction[5] (based on the postulate[1a] that neopentyl-oxygen fission invariably gives rearrangement) are of little absolute value in the elucidation of such mechanisms.

A further consequence of the present work is that neopentyl bromide is now as readily available as other aliphatic bromides from reaction of the alcohol with phosphorus tribromide and quinoline.

The mechanisms and possible extensions of the above reactions are under investigation.

(1) (a) F. C. Whitmore, THIS JOURNAL, **54**, 3274 (1932); (b) F. C. Whitmore and H. S. Rothrock, *ibid.*, **54**, 3431 (1932); (c) F. C. Whitmore, E. L. Wittle and B. R. Harriman, *ibid.*, **61**, 1586 (1939).

(2) Hughes and Ingold, *J. Chem. Soc.*, 157 (1946).

(3) Sauer, THIS JOURNAL, **66**, 1707 (1944).

(4) The latter is a necessary catalyst whose broad function probably involves action as a good source of halide ions and in addition includes a labilizing effect on the Si-O-C grouping *via* electrophilic attack by quinolinium ions; *cf.* W. Gerrard and A. French, *Nature*, **159**, 263 (1947).

(5) *Cf.* A. Scattergood, W. H. Miller and J. Gammon, THIS JOURNAL, **67**, 2150 (1945); N. C. Deno and M. S. Newman, *ibid.*, **72**, 3852 (1950).

THE WHITMORE LABORATORY
THE PENNSYLVANIA STATE LEO H. SOMMER
COLLEGE HERBERT D. BLANKMAN
STATE COLLEGE, PA. PAUL C. MILLER

RECEIVED APRIL 11, 1951

THE NATURE OF THE INTERMEDIATE IN CARBONIUM ION-TYPE INTERCONVERSION REACTIONS OF CYCLOBUTYL, CYCLOPROPYLCARBINYL AND ALLYLCARBINYL DERIVATIVES[1]

Sir:

The striking ease of interconversion of cyclobutyl and cyclopropylcarbinyl derivatives in carbonium ion-type reactions[2] and the abnormally large solvolytic reactivities of cyclobutyl and cyclopropylcarbinyl halides[2] and sulfonate esters[3,4] have led to a

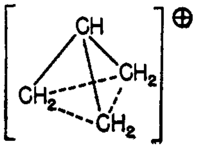
(1) Supported by the program of research of the U. S. Atomic Energy Commission.

(2) J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951).

(3) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 3176 (1951).

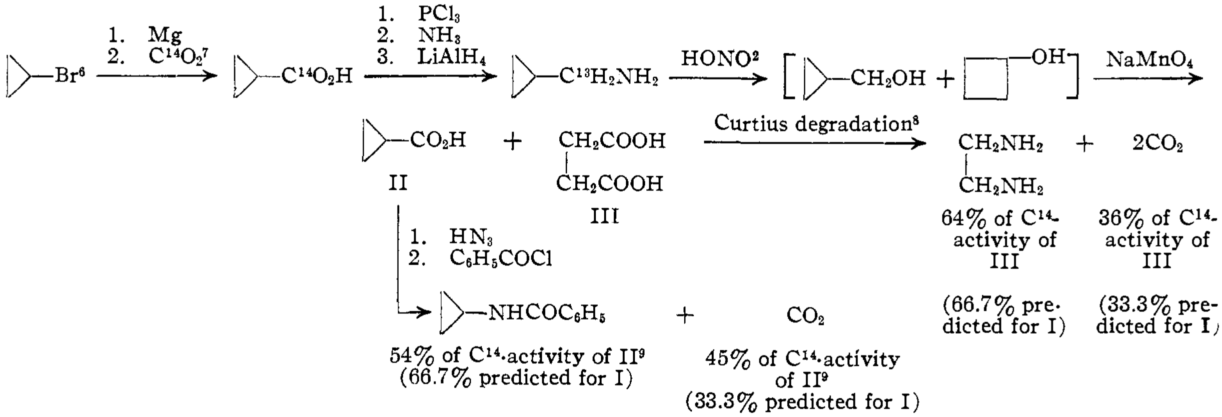
(4) C. G. Bergstrom and S. Siegel, Abstracts of the 119th Meeting of the American Chemical Society, Boston, Mass., April 4, 1951, p. 33M.

number of suggestions[2,4,5] regarding the nature of the cationic intermediate (or intermediates) which might be involved. Investigation of the course of the reactions using C^{14}-labeled cyclopropylcarbinyl derivatives reveals that the three methylene groups of the starting material achieve a degree of equivalence at some point between reactants and products which is well (although not uniquely) accounted for by a "non-classical" cationic intermediate of structure I.[4,5]

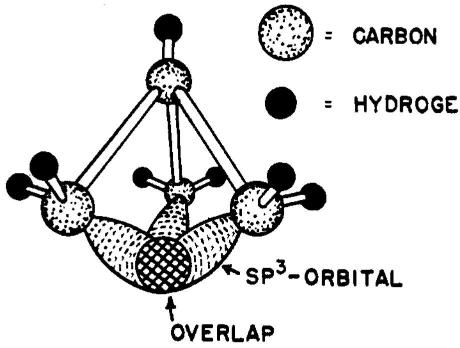


I

The main features of the experimental evidence for attainment of substantial equivalence between the methylene groups in the reaction of cyclopropylcarbinylamine with nitrous acid follow.



Dr. M. J. S. Dewar (private communication) suggests that I can be very reasonably formulated by the molecular orbital theory if it is considered that all of the carbon atoms use the customary sp^3 orbitals and that the methinyl (CH) group is attached to the three methylene groups by the customary σ-bonds. The three extra sp^3 orbitals of each of the methylene groups are then positioned to overlap as shown in IV and can form one stable molecular orbital holding two electrons[10] and two vacant, considerably-less stable orbitals. This formulation is especially attractive since it permits prediction that structures analogous to II for the corresponding anion or free radical would be unfavorable because the extra electrons would have to go into less stable orbitals. It is significant that the experimental data, so far available,[2] indicate that cyclopropylcarbinyl and cyclobutyl derivatives are not interconverted in anion or free-radical reactions.



IV

A full report of this and related work will be presented in later papers.

Department of Chemistry and Laboratory for
Nuclear Science and Engineering John D. Roberts
Massachusetts Institute of Technology
Cambridge 39, Mass. Robert H. Mazur

Received May 25, 1951

---

(5) (a) V. C. Chambers, Ph.D. Thesis, M.I.T., October, 1950; (b) R. H. Mazur, Ph.D. Thesis, M.I.T., January, 1951; (c) R. B. Woodward (Harvard University), private communication.

(6) J. D. Roberts and V. C. Chambers, This Journal, **73**, 3176 (1951).

(7) The carbon dioxide was prepared from barium carbonate-C^{14} supplied by the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission. The radioactivity analyses were made by Miss Winifred Bennett and Miss Clare M. McGinnis.

(8) A. A. Benson and J. A. Bassham, This Journal, **70**, 3939 (1948).

(9) The difference between predicted and found is likely to be due to some direct (non-carbonium ion) replacement of $-NH_2$ by $-OH$.

(10) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); T. M. Sugden, *Nature*, **160**, 367 (1947); R. S. Mulliken, *J. Chem. Phys.*, **1**, 492 (1933). It is to be noted that the argument here is not rigorous since the three orbitals do not have D_{3h} symmetry.

THE VALENCE OF PRECIPITATING RABBIT ANTIBODY

Sir:

In the course of a quantitative ultracentrifugal and electrophoretic investigation of the soluble complexes formed between antigen and antibody in the region of antigen excess, we have obtained evidence that precipitating antibody to bovine serum albumin (BSA) is largely bivalent. Crystalline BSA was iodinated to an average degree of 5.1 I atoms per molecule (BSA-5I), and rabbit antisera were prepared against the un-iodinated BSA. The γ-globulin fraction of the pooled antisera was first purified by precipitation with $^1/_3$ saturated $(NH_4)_2SO_4$, and then a specific antigen-antibody precipitate was formed in the equivalence zone using BSA-5I as antigen. The precipitate was washed with cold saline and then was redissolved in antigen excess. Treatment of this solution with $^1/_2$ saturated $(NH_4)_2SO_4$ resulted in a precipitate that completely redissolved in buffered saline.