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.

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

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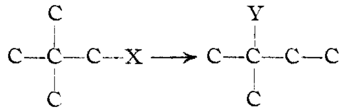
NON-REARRANGEMENT REACTIONS OF THE NEOPENTYL-OXYGEN BOND. NEW SYNTHESES OF NEOPENTYL HALIDES

Sir:

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



$$\mathrm{C{-}C(C)_2{-}C{-}X \longrightarrow C{-}C(Y)(C){-}C{-}C}$$

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.

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

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

$$\mathrm{Me_3CCH_2OH + PBr_3 + C_9H_7N \longrightarrow Me_3CCH_2Br + C_9H_7N\cdot HBr}$$

Triethylneopentoxysilane, b.p. 67° (10 mm.), $n^{20}\mathrm{D}$ 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.), $n^{20}\mathrm{D}$ 1.4371, d^{20} 1.200, lit.[1c] b.p. 105°, $n^{20}\mathrm{D}$ 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.), $n^{20}\mathrm{D}$ 1.4043, d^{20} 0.8659, lit.[1c] b.p. 83.5° (740 mm.), $n^{22}\mathrm{D}$ 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.), $n^{20}\mathrm{D}$ 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.

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(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).

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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

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(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.