therefore with Taft's σ^* values.[10] This reflects an entirely different balance of inductive, steric and solvation forces in oxygen bases than in their nitrogen analogues.[4,11] Very likely solvation is the reason for the large disparity between our measurement of the pK_a of dioxane in water and that estimated for the same compound (−4) by Lemaire and Lucas[12] using perchloric acid titration in glacial acetic acid.

Acknowledgment. We are grateful for a very helpful discussion of solvent extraction with Professor Quintus Fernando of this department. This work was made possible by a research grant from the Public Health Service, A-3643 B.B.C. of the National Institutes of Health.

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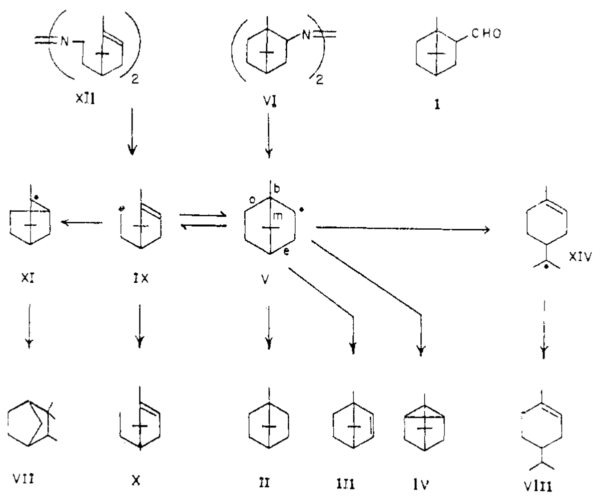
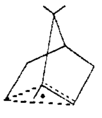
A FREE RADICAL WAGNER-MEERWEIN REARRANGEMENT

Sir:

The failure of alkyl groups to migrate to adjacent free radical centers has been demonstrated repeatedly.[1] In most of the cases investigated,[2] alkyl group rearrangements do not compete observably with such processes as hydrogen abstraction, aryl group migration, dimerization, and disproportionation. We now report a study of a system in which alkyl group migration is observed. The results demonstrate the occurrence of a *formal* free radical analog of the Wagner–Meerwein carbonium ion rearrangement.

Decarbonylation of camphane-2-carboxaldehyde (I) with *t*-butyl peroxide at 140–150° gives mainly the unrearranged product camphane (II). Small amounts of the disproportionation products bornylene (III) and tricyclene (IV) also are observed. Under these conditions, the bornyl radical (V), which is the proximate product of the decarbonylation, does not rearrange. Generation of the radical by decomposition of 2,2′-bis-azocamphane VI at higher temperatures (255–290°), however, gives, among other products, some isocamphane (VII), which is structurally related to II in the Wagner–Meerwein sense.




XIII

Among the other products of the decomposition of VI are camphane (II) and *p*-menthene (VIII). The formation of VIII suggests that at high temperatures the bornyl radical V suffers ring-opening by β-elimination; cleavage of bond m would then lead to an unsaturated monocyclic radical (XIV) which would give VIII by hydrogen abstraction. Of the three remaining formally possible β-eliminations of V, the one involving bond b is prohibited by Bredt's rule; the one involving bond e is not thus prohibited, and although we have not yet found the olefin that would result, it presumably is present among the several still unidentified reaction products. Cleavage at bond o would lead to radical IX, which could give olefin X by hydrogen abstraction, radical V by re-cyclization at the original position of attachment of the two-carbon chain, *or radical XI by cyclization in the alternative sense.*

Direct evidence that cyclization of IX to V and XI occurs is provided by the decomposition of the azo compound XII. The latter is prepared by the route α-pinene oxide → (2,2,3-trimethyl-Δ^3-cyclopentenyl)-acetaldehyde (campholenaldehyde)[3] → *campholenaldehyde azine*, b. p. 164–166°(1.5 mm.), n^{25}_D 1.5028, *Anal.* Found: C, 79.69; H, 10.75; N, 9.21) → the corresponding hydrazine → XII, b.p. 150–152° (1.5 mm.), n^{25}_D 1.4858, λ_{max} 360 mμ, log ϵ 1.47, *Anal.* Found: C, 79.37; H, 11.39; N, 9.20. Wolff-Kishner reduction of campholenaldehyde gives *1,5,5-trimethyl-4-ethyl-1-cyclopentene (X)*, b.p. 68–68.5° (43 mm.), n^{25}_D 1.4429, *Anal.* Found: C, 86.68; H, 13.21, which forms two *nitrosochlorides*, m.p. 95–96° and 122.5–123°. *Anal.* Found (for the 123° form): C, 58.85; H, 8.85; N, 6.96. The thermal decomposition of XII gives qualitatively the same products that are obtained from VI, namely, VIII, II, VII, III, IV and X.

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Identification and quantitative estimation is achieved by gas–liquid chromatography using a Trend[4] (a commerical detergent) column and three different silicone oil-on-firebrick columns, infrared examination of fractions from preparative gas-liquid chromatography, and separation of olefinic materials by solution chromatography on silica gel.

Different ratios of products are obtained from VI and XII, large quantities of hydrocarbon with unaltered carbon skeleton resulting from each starting material. In *n*-hexadecane at 287°, for example, the relative product distribution (on a weight basis) from XII at 0.172 *M* initial concentration is II, 1.0: X, 2.1: VII, 0.50: VIII, 0.34: IV, 0.29: III, trace. Under the same conditions, the distribution from VI is II, 1.0: X, present (>0.01)[5]: VII, 0.035: VIII, 0.17: IV, ~ 0.01: III, 0.02. Further, isocamphane (VII) is formed from either VI or XII as a mixture of both stereoisomers in a ratio that is essentially the same as that produced by the catalytic hydrogenation of camphene. The dependence of the product distribution on the starting material and the non-stereospecificity of hydrogen abstraction by the radical precursor of VII are evidence against a mesomeric bridged radical (XIII) as the sole intermediate and in favor of a cleavage–re-cyclization mechanism for the rearrangement. From what is known of the behavior of simple alkyl radicals,[6] it is reasonable to assume that the activation energy for β-elimination in the radical V should be substantially higher than those for disproportionation or hydrogen abstraction. The observation that products of β-elimination (VIII and the rearrangement product VII) occur only at high temperatures is thus also consistent with the cleavage–re-cyclization mechanism.

The formation of VII from VI is the first clearly intramolecular example of a free radical alkyl group rearrangement.[7]

(4) We are indebted to Dr. Robert Petterson of Purex Corporation for a sample of this material and to Dr. A. Hussey of Northwestern University for an authentic sample of *p*-menthene.

(5) Olefin X is not well resolved from IV and II on our columns and can therefore be determined readily only when present in substantial quantity, as in the mixture of products from XII.

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(8) Richfield Oil Fellow, 1956–1957.

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THE REACTIVITY OF METHYLENE FROM PHOTOLYSIS OF DIAZOMETHANE

Sir:

Differences have been reported in the recent literature concerning the reactivity of methylene generated by photolysis of diazomethane. Doering, Buttery, Laughlin and Chaudhuri[1] found that the methylene produced by solution photolysis in alkanes reacted randomly with primary, secondary and tertiary carbon–hydrogen bonds. Frey,[2] on the other hand, reported that gas-phase photolysis gave a methylene which reacted selectively with carbon–hydrogen bonds in the approximate reactivity ratio $k_{\text{tert}}/k_{\text{sec}}/k_{\text{prim}}$ of 1.5/1.2/1.0. We wish to report results confirming and extending the evidence for random reactivity of methylene in alkane solution and to rationalize the difference noted above.

We have carried out the solution photolysis of diazomethane in fourteen C_7, C_8, and C_9 alkanes in the usual manner.[1] The reaction mixtures were analyzed directly by capillary gas chromatography with a squalane-coated column coupled to an argon ionization detector.[3,4] The results obtained with the four trimethylpentanes are given in Table I.

TABLE I

METHYLENE INSERTION PRODUCTS FROM THE TRIMETHYLPENTANES

Parent	Product	Precursor bond Type	Precursor bond Number	Calcd. Dist., %	Obs. Dist., %[a]
2,2,4-Trimethylpentane	2,4,4-Me_3C_6	1	9	50.0	51
	2,2,3,4-Me_4C_5	2	2	11.1	10
	2,2,4,4-Me_4C_5	3	1	5.6	4
	2,2,4-Me_3C_6	1	6	33.3	35
2,2,3-Trimethylpentane	2,2,3,4-Me_4C_5	2	2	11.1	9
	[2,2,3-Me_3C_6	1	3][b]	33.3	35
	2,2-Me_2-3-EtC_5]	1	3][b]		
	2,2,3,3-Me_4C_5	3	1	5.6	4
	3,3,4-Me_3C_6	1	9	50.0	52
2,3,3-Trimethylpentane	2,3,3-Me_3C_6	1	3	16.7	18
	2,2,3,3-Me_4C_5	3	1	5.6	5
	3,3,4-Me_3C_6	1	6	33.3	34
	2,3,3,4-Me_4C_5	2	2	11.1	11
	2,3-Me_2-3-EtC_5[c]	1	6	33.3	32
2,3,4-Trimethylpentane	2,2,3,4-Me_4C_5	3	2	11.1	10
	2,4-Me_2-3-EtC_5	1	3	16.7	16
	2,3,4-Me_3C_6[d]	1	12	66.7	69
	2,3,3,4-Me_4C_5	3	1	5.6	5

[a] Each product, with two noted exceptions,[c,d] was identified by comparison of its column retention time with that of an authentic sample (American Petroleum Institute Research Project 6B). The variation in isomer detector sensitivity in this molecular weight range is of the order of errors in peak area measurements; sensitivity corrections were not applied. [b] Incomplete resolution. [c] The identity of this compound was assumed. [d] The identity of this product was confirmed through alternate synthesis from 2,4-dimethylhexane by methylene insertion.

The observed product compositions are in good agreement with those expected from random insertion of methylene into carbon–hydrogen bonds. Equally good agreement between observed and calculated product distribution was obtained with ten other C_7-C_9 alkanes as solvents for the diazomethane

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