A crude mechanism for the isomerizations of the butenes may be written as

$$\begin{tikzcd}
\text{1-butene} + H^+ \arrow[r, shift left, "k_{-1}"] & \text{intermediate} \arrow[l, shift left, "k_1"] \arrow[r, shift left, "k_2"] \arrow[d, shift left, "k_3"] & trans\text{-2-butene} + H^+ \arrow[l, shift left, "k_{-2}"] \\
& cis\text{-2-butene} + H^+ \arrow[u, shift left, "k_{-3}"] &
\end{tikzcd}$$

By determining the initial rates of formation of the two products from a given starting olefin one may compute the ratios k_2/k_3, k_3/k_1 and k_2/k_1 unhindered by considerations of the reversibilities of the above steps since at t_0 the reverse reactions will not have been established. Plots of the data for the isomerization of each of these olefins were linear over the first 150–200 minutes of reaction time. The ratios of rates of formation of the various butenes calculated from these slopes are given in Table I. It should be remembered for future discussion that the rates of production of *trans*- and *cis*-2-butene from the reaction intermediate were nearly equal.

Haag and Pines[5] have reported a higher initial rate of conversion of 1-butene to *cis*-2-butene than to *trans*-2-butene on bubbling the gas through phosphoric acid. The ratio of *cis* to *trans* was found to increase at higher temperatures and with shorter contact times with the acid. Since these results ran counter to our observations with sulfuric acid, we have attempted to repeat these experiments using 85% phosphoric acid at about 100°. The details of the experiments are given in the Experimental section. Even at very short contact times (1 sec. or less) the amounts of the two 2-butene isomers were nearly the same with the *trans* isomer slightly in excess (Table II). The concentration of the phosphoric acid in the work of Haag and Pines was not given.

The classical picture of the acid-catalyzed isomerization of the *n*-butenes involves the 2-butyl cation as a common intermediate. On repeated formation, the ultimate result should be the thermodynamic equilibrium mixture of butene isomers. However, by studying the acid-catalyzed isomerization at short reaction times before the various reversible steps have assumed importance it has been shown that the formation of *trans*- and *cis*-2-butenes occurs at equal rates in either sulfuric acid or phosphoric acid. Clearly no special hydrogen-bridged structures or protonium ions need be evoked, and the reaction can be described as simply proceeding through a 2-butyl cation.

Both Pines and co-workers[5,6] and Lucchesi, *et al.*,[4] have proposed non-classical bridged structures to explain the greater rate of formation of *cis*-2-butene than *trans*-2-butene in various isomerization and elimination reactions of the 2-butyl system over alumina and silica–alumina catalysts, respectively. In none of these studies was the question of the role of the catalyst surface raised. In view of results and reasoning given above, it seems most unlikely that non-classical hydrogen bridged ions play any important role in E_1 reactions in the 2-butyl system. There is no evidence that they would be formed in a high temperature heterogeneous reaction, nor is there any *ad hoc* line of thought which suggests that they would occur more readily under these conditions than in the reactions studied here. Keeping in mind our present inexact knowledge of heterogeneous reactions, one may readily imagine several possible surface effects which could explain the results reported.

Acknowledgment.—Part of the research reported here was supported by a grant from the Robert A. Welch Foundation (W. H. W.). Grateful acknowledgment for this support is hereby given. The authors also wish to acknowledge the help of Mr. Charles Wall (National Science Foundation Undergraduate Research Participant) in determining the isomerization rates of the butenes over sulfuric acid.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

Reactions of the 2-Bornyl Radical. I. The Decarbonylation of 2-Formylbornane[1]

BY JEROME A. BERSON AND CARL J. OLSEN[2]

RECEIVED MARCH 2, 1962

The di-*t*-butyl peroxide-induced decarbonylation of 2-formylbornane in the liquid phase at 138° gives mainly bornane and traces of bornene and tricyclene as the sole C_{10}-hydrocarbon products. The hypothetical rearrangement product 2,3,3-trimethylnorbornane (isocamphane) is not observed and cannot be present to an extent greater than about 0.1% of the total volatile hydrocarbon formed. The chain length for carbon monoxide production in the decarbonylation varies with the ratio of peroxide to aldehyde used and ranges from about 0.4 to about 4.8 as the ratio changes from about unity to about 0.1. At high initial ratios, the yields of disproportionation products (bornene and tricyclene) increase at the expense of bornane, suggesting an increased importance of radical–radical reactions relative to hydrogen abstraction.

As part of a study of the reactions of the bornyl free radical, we report here on the *t*-butyl peroxide-induced decarbonylation of 2-formylbornane (2-formylcamphane)[3] (I). The radical is of potential

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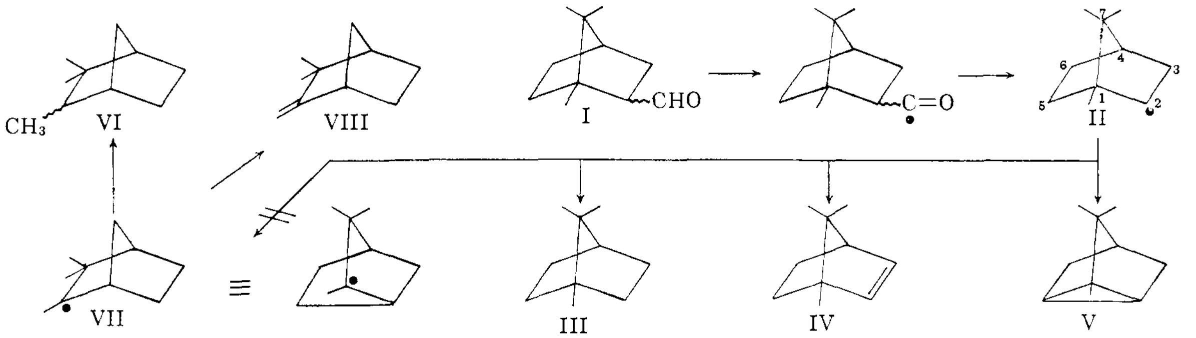
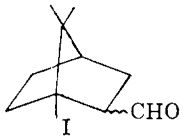
[1] (a) This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF18-(600)-1544. Reproduction in whole or in part is permitted for any purpose of the United States Government. Also supported in part by the Office of Ordnance Research under Contract No. DA-04-495-ORD-532. We are indebted to these agencies and to the Alfred P. Sloan Foundation and the Richfield Oil Corporation for support. (b) Taken from a portion of the dissertation submitted by C. J. Olsen in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) For a preliminary report, see J. A. Berson, C. J. Olsen and J. S. Walia, *J. Am. Chem. Soc.*, **82**, 5000 (1960).

[2] Richfield Oil Corporation Fellow, 1956–1957.

[3] The nomenclature used in this and the following paper[4] is con-



theoretical interest because of its formal structural relationship to the bornyl cation,[6] the archetypical Wagner–Meerwein rearrangement system.



I

Racemic 2-formylbornane is prepared by the reaction of racemic 2-bornylmagnesium chloride and N-methylformanilide.[7] The aldehyde thus obtained is probably a mixture of epimers and is used without an attempt to separate these. Decarbonylation[8–13] is effected by adding di-*t*-butyl peroxide to the aldehyde at 138° in the absence of any solvent other than the reactants. Analysis of the products is carried out by a preliminary separation into gases and liquids, vacuum-line fractionation of the liquid product into volatile and difficultly volatile portions, and gas–liquid chromatography of the volatile portion. The data for experiments carried out under varying conditions are shown in Table I. The C_{10}-hydrocarbon product, which consists mainly of bornane (III) and contains small quantities of the disproportionation products bornene (IV) and tricyclene (V), apparently is derived entirely from the proximate product of the decarbonylation, the 2-bornyl radical II. The rearranged saturated product, 2,3,3-trimethylnorbornane (isocamphane) (VI), derivable in principle from hydrogen abstraction by the Wagner–Meerwein-related 2,3,3-trimethyl-2-norbornyl radical VII, is not observed and would be detectable if it were present to the extent of 0.1% of the bornane formed. The corresponding rearranged disproportionation product camphene VIII is not detected either, although the analytical column used for gas–liquid chromatography does not separate VIII and III sufficiently well to disclose the presence of a small amount of VIII.

TABLE I

STOICHIOMETRY OF THE DECARBONYLATION OF 2-FORMYLBORNANE AT 138 ± 1°

Compound	Quantity in expt. no. (mmoles) 1	2	3
2-Formylbornane, init.	30.0	7.39	19.50
(t-BuO)$_2$, init.	3.45[a]	2.00[b]	20.11[c]
(t-BuO)$_2$, recovd.	1.30	0.68	9.18
(t-BuO)$_2$, reacted	2.15	1.314	10.93
Products			
Acetone	0.109	0.178	2.61
t-BuOH	3.11	1.27	16.20
Bornane	15.55	4.21	8.26
Bornene + tricyclene	<0.03	0.032[d]	2.40[e]
Total gas	15.82	5.67	16.60
CO[f]	15.71	5.49	14.00

[a] Peroxide added in two portions; reaction times 7 and 7.5 hr. [b] Peroxide added in three portions; reaction times 2.8, 4.5 and 4.5 hr. [c] Peroxide added in two portions; reaction times 2.9 and 4.5 hr. [d] 94.1% bornene and 5.9% tricyclene. [e] 90.8% bornene and 9.2% tricyclene. [f] Mmoles of total gas minus mmoles of methane; methane assumed equal to acetone.

The formation of tricyclene (V) is of interest as an example of a reaction that is, as far as we are aware, without precedent: namely the formation of a cyclopropane by disproportionation of a free radical. Although both bornene (IV) and tricyclene (V) are likely products from several imaginable side reactions of the bornyl chloride used as starting material for the synthesis of the aldehyde I, their presence in the reaction products from the decarbonylation cannot have the trivial explanation that they are carried along from the aldehyde as contaminants: The aldehyde is prepared from carefully recrystallized semicarbazone and, furthermore, the amount of IV and V in the products should increase as the initial charge of aldehyde is increased if they were merely contaminants in the aldehyde. That this is not the case is evident from Table I. The exact details of the conversion of the radical II to tricyclene (V) are not yet clear. Abstraction of a hydrogen at C.6 and establishment of a covalent bond at C.6–C.2, or abstraction of a hydrogen at C.2 followed by an intramolecular insertion reaction of the derived carbene are the

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sistent with the 1957 Rules[5] of the International Union of Pure and Applied Chemistry with the single exception that the name *tricyclene* is used for ease of reference rather than the suggested[5] name 1,7,7-trimethyltricyclo[2.2.1.0′]heptane. The more familiar trivial names frequently are given in parentheses.

(4) J. A. Berson, C. J. Olsen and J. S. Walia, *J. Am. Chem. Soc.*, **84**, Sept. 5 (1962).

(5) International Union of Pure and Applied Chemistry, 1957 Report of the Commission on the Nomenclature of Organic Chemistry, *ibid.*, **82**, 5545 (1960).

(6) H. Meerwein and K. van Emster, *Ber.*, (a) **53**, 1815 (1920); (b) **55**, 2500 (1922).

(7) J. Houben and H. Doescher, *ibid.*, **40**, 4576 (1907); **43**, 3435 (1910).

(8) (a) S. Winstein and F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **69**, 2916 (1947); (b) F. H. Seubold, Jr., *ibid.*, **75**, 2532 (1953).

(9) W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).

(10) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952).

(11) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960).

(12) S. Winstein, R. Heck, S. Lapporte and R. Baird, *Experientia*, **12**, 138 (1956).

(13) J. W. Wilt and Br. Herbert Phillip, F.S.C., *J. Org. Chem.*, **25**, 891 (1960).

two processes that seem most attractive at present. We hope to be able to report subsequently on the results of experiments designed to distinguish between these two possibilities. The hypothetical carbene intermediate in the second mechanism above would be identical with or at least closely related to the intermediate presumably involved in the synthesis of tricyclene by mercuric oxide oxidation of camphor hydrazone.[6,14] There is no experimentally established precedent for α-hydrogen abstraction from a free radical to give a carbene, although this process has been postulated[15] to account for the formation of stilbene in the decomposition of ω,ω'-azotoluene.

The mechanism of the decarbonylation is conveniently discussed in terms of eq. 1–7, a scheme formulated to conform to the general outlines established[8–13,16] for di-*t*-butyl peroxide-induced reactions of this type.

$$(t\text{-BuO})_2 \longrightarrow 2\ t\text{-BuO}\cdot \qquad (1)$$

$$t\text{-BuO}\cdot \longrightarrow CH_3\cdot + CH_3COCH_3 \qquad (2)$$

$$t\text{-BuO}\cdot + RCHO \longrightarrow t\text{-BuOH} + R\dot{C}O \qquad (3)$$

$$CH_3\cdot + RCHO \longrightarrow CH_4 + R\dot{C}O \qquad (3a)$$

$$R\underset{\cdot}{C}O \longrightarrow R\cdot + CO \qquad (4)$$

$$R\cdot + RCHO \longrightarrow RH + R\dot{C}O \qquad (5)$$

$$2R\cdot \longrightarrow R_2 \qquad (6)$$

$$2R\cdot \longrightarrow \text{disproportionation} \qquad (7)$$

$$R = \text{2-bornyl}$$

Decarbonylation is a chain process, initiation being effected by 3 or 3a, propagation by 4 and 5, and termination by 6 and 7. The scheme is incomplete in the sense that all of the possible chain-termination steps are not shown.

Decomposition of a mole of peroxide produces two moles of radicals (either *t*-BuO. or $CH_3\cdot$); the yield of product per mole of radical produced (*F*) is therefore obtained by dividing the number of moles of each product by twice the number of moles of peroxide consumed. These *F*-values are collected in Table II. If each *t*-butoxy or methyl radical produced started a chain, the sum of the *F*-values for methane (assumed to be the same as that for acetone) and *t*-butyl alcohol would be unity. Since this sum is less than unity in all three experiments, some of the radicals produced by decomposition of the peroxide (eq. 1 and 2) must be involved in chain termination or in some side reaction.

TABLE II

CHAIN LENGTHS AND YIELDS OF PRODUCTS PER MOLE OF RADICALS IN THE DECARBONYLATION OF 2-FORMYLBORNANE

	Experiment no.					
	1		2		3	
Initial ratio $(t\text{-BuO})_2$/RCHO	0.115		0.271		1.03	
Compound	F^a	F'^b	F	F'	F	F'
Acetone	0.0254	..	0.0678	..	0.119	...
t-BuOH	0.724	..	0.484	..	.740	...
Bornane	3.62	4.83	1.60	2.91	.378	0.439
Bornene + tricyclene[c]	..	..	0.012	0.022	.109	.128
CO	3.66	4.88	2.08	3.79	.639	.882
Bornane + $C_{10}H_{16}$	3.62	4.83	1.62	2.93	.487	.567

[a] F = (mmoles cpd.)/(2 × mmoles peroxide reacted) = yield per mole of radicals produced from peroxide. [b] F' = (mmoles cpd.)/(mmoles *t*-BuOH + mmoles CH_4) = chain length per mole of chain-initiating radicals produced from peroxide. [c] $C_{10}H_{16}$.

In experiment 1, with a low initial ratio of peroxide to aldehyde, the *F*-values for carbon monoxide and for the C_{10}-hydrocarbon product (essentially pure bornane) are identical within experimental error. This can only mean that the 2-bornyl radicals are not involved in chain termination to any significant extent, for if they were, the *F*-value for bornane would be smaller than that for carbon monoxide. With an increased initial ratio of peroxide to aldehyde (experiments 2 and 3), the *F*-value for the C_{10}-product (bornane, bornene and tricyclene) falls well below that for carbon monoxide. This result is expected, since the reaction conditions ensure a higher instantaneous concentration of radicals than in experiment 1, thereby increasing the relative probability of reactions of the initiating or propagating radicals with bornyl radicals.

To estimate the chain length, it is necessary to know the number of moles of product per mole of radicals actually initiating chains. The latter figure is evaluated on the assumption that the aldehyde is the sole source of hydrogen for the conversion of *t*-butoxy and methyl radicals to *t*-butyl alcohol and methane. Although other hydrogen sources may be imagined (*e.g.*, the peroxide itself undergoes[17] an induced decomposition in the absence of other hydrogen donors), the aldehyde hydrogen is much the most reactive[18] hydrogen source in the system and is expected to play the predominant role except when its concentration is extremely low. The chain length is thus given to a good approximation by *F'*, the number of moles of product per mole of *t*-butoxy radicals accounted for as *t*-butyl alcohol and methane. The *F'*-value for carbon monoxide production (Table II) falls from 4.88 at a low initial peroxide/aldehyde ratio to less than unity at an initial ratio near unity, suggesting that the higher concentration of radicals ensured by the higher proportion of peroxide in the latter experiment increases the probability of termination by radical–radical reactions. Consistent with this interpretation is the observed (Table I) increased fraction of the total C_{10}-hydrocarbon product represented by disproportionation products bornene (IV) and tricyclene (V).

The ratio $F_{\text{acetone}}/F_{t\text{-BuOH}}$ represents the fraction of *t*-butoxy radicals that survive long enough to suffer fragmentation (eq. 2). That this ratio should

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(14) Several other examples of intramolecular insertion reactions of carbenes are now available; see *inter alia* (a) W. R. Moore, H. R. Ward and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961); (b) L. Friedman and J. G. Berger, *ibid.*, **83**, 492 (1961); (c) W. Kirmse and W. von E. Doering, *Tetrahedron*, **11**, 266 (1960); (d) G. Closs, Abstracts of Papers, 138th Meeting of the American Chemical Society, New York, N. Y., Sept., 1960, p. 9-P; (e) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959). (f) α-Elimination may also provide a path for the observed formation of bornene (see ref. 14c for an analogy), although the more conventional β-elimination is a plausible alternative. (g) Although the olefin bornene (IV) cannot yet be formally eliminated as a possible source of tricyclene (*e.g.*, by hydrogen abstraction from C.5 of IV), its concentration at any time is so low that one may doubt that it could function as a hydrogen source in competition with the much more reactive aldehyde I.

(15) A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 312 (1950).

(16) J. H. Raley, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948).

(17) J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 2767 (1948).

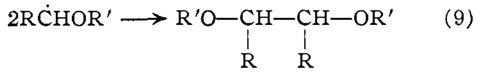
(18) R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, **20**, 1053 (1952).

increase as the initial relative concentration of aldehyde decreases (Table II) is reasonable if the aldehyde is the most active source of hydrogen.

One possible mode of reaction of the methyl radicals produced by fragmentation of *t*-butoxy radicals is disclosed in a preliminary experiment (not analyzed gas chromatographically and not listed in Table I or II) with optically active 2-formylbornane. Decarbonylation with di-*t*-butyl peroxide under conditions somewhat different from those of experiments 1, 2, and 3 gives a saturated volatile hydrocarbon mixture from which a fraction of molecular weight 154 ± 3 ($C_{11}H_{20}$) is isolated by bulb-to-bulb vacuum line manipulation. By preferential precipitation of thiourea inclusion complexes, the mixture can be fractionated to give pure bornane and two *levorotatory* fractions. The latter two fractions must contain some substance other than bornane and tricyclene (both optically inactive), other than bornene (unsaturated) and other than the rearrangement product 2,3,3-trimethylnorbornane (which would have been dextrorotatory[19]). It seems probable that the unknown product is 2- or 3-methylbornane (or both). In the more carefully controlled experiments of Tables I and II, we are unable to observe any substance corresponding in retention time to a mixture of synthetic 2-methylbornanes. The formation of methylbornanes must then require very special conditions, which would be the case if they arise by addition of methyl radicals to bornene. This could occur only late in the decarbonylation, after the bornene concentration has built up and the aldehyde concentration has decreased to a sufficient level to allow the addition to compete with the more facile[13] hydrogen abstraction from the aldehyde. The aldehyde concentration, however, would still have to be high enough to supply an ample hydrogen source, or else the methylbornyl radicals resulting from addition would end their careers as disproportionation or combination products rather than as methylbornanes. It is therefore not surprising that the formation of methylbornanes is not reproduced in experiments 1–3. The absence of methylbornanes from the products in the latter experiments is additional support for the assumption that the methyl radicals show up as methane and therefore that the methane and acetone yields are identical.

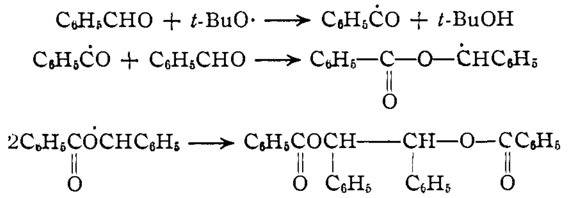
Despite the complete consumption of the aldehyde in all the experiments of Table I, evidenced by the cessation of carbon monoxide evolution, the yields of carbon monoxide are never quantitative but vary between 52 and 74%. Apparently, either the aldehyde itself or the acyl radical RCO derived from it (or both) are directly or indirectly involved in chain termination. Although we have no direct evidence for the exact nature of such chain termination steps, they may include reactions such as those of eq. 8 and 9, where $R'\cdot$ is any radical in the system, including 2-bornyl.

$$R'\cdot + RCHO \longrightarrow R\dot{C}HOR' \qquad (8)$$



$$2R\dot{C}HOR' \longrightarrow R'O-\underset{R}{CH}-\underset{R}{CH}-OR' \qquad (9)$$

A parallel to these processes has been observed[22] in the formation of *meso*-hydrobenzoin dibenzoate from the decarbonylation of benzaldehyde, by the sequence



$$C_6H_5CHO + t\text{-BuO}\cdot \longrightarrow C_6H_5\dot{C}O + t\text{-BuOH}$$

$$C_6H_5\dot{C}O + C_6H_5CHO \longrightarrow C_6H_5-\underset{\underset{O}{\|}}{C}-O-\dot{C}HC_6H_5$$

$$2C_6H_5\underset{\underset{O}{\|}}{C}O\dot{C}HC_6H_5 \longrightarrow C_6H_5\underset{\underset{O}{\|}}{C}O\underset{C_6H_5}{CH}-\underset{C_6H_5}{CH}-O-\underset{\underset{O}{\|}}{C}C_6H_5$$

Experimental[23]

Procedure for Decarbonylations.—The reaction vessel was a 15 ×100 mm. glass tube fitted with a short side-arm near the upper end. The side arm was capped with a serum rubber septum. The upper end of the vessel was connected through a jacketed 200-mm. Vigreux column and two cold traps to a jacketed gas buret filled with brine. The vessel was charged with a sample of aldehyde and brought to 138 ± 1° by immersion in a heated oil-bath. The two traps were cooled in acetone–solid carbon dioxide baths, and steam was passed through the jacket of the Vigreux column. Di-*t*-butyl peroxide, freshly distilled *in vacuo* immediately before use, was added through the rubber septum with a hypodermic syringe, and reaction was allowed to proceed. Steam was passed through the Vigreux jacket throughout the reaction to facilitate removal of the volatile products. If this was not done, there were erratic temperature variations in the reaction mixture. After completion of the reaction, the volatile, non-gaseous products were passed into a vacuum line at 10^{-4}–10^{-5} mm. and trapped in a liquid nitrogen-cooled U-tube. In some experiments, the entire volatile fraction was analyzed by gas–liquid partition chromatography. In others, a partial fractionation was first effected by bulb-to-bulb distillation in the vacuum line, followed by gas chromatographic analysis of each fraction.

Racemic 2-formylbornane was prepared by a modification of the method of Houben and Doescher[7] in which a solution of bornylmagnesium chloride from 59 g. of racemic *endo*-2-chlorobornane (bornyl chloride) in 400 ml. of anhydrous ether was treated with 57.5 g. of N-methylformanilide during 1 hour while stirring. The mixture was heated at reflux for 14 hours, chilled, hydrolyzed with 10% sulfuric acid, and steam distilled. The ether layer was separated from the distillate, the aqueous layer was twice extracted with fresh ether and the combined ether solutions were dried over calcium sulfate. The ether was evaporated, and the residue was freed of bornene and bornane by sublimation of the hydrocarbons under vacuum (8.0 g. of hydrocarbon was recovered). The non-volatile residue was taken up in 300 ml. of boiling methanol and treated with a solution of 49.2 g. of sodium acetate and 36.3 g. of semicarbazide hydrochloride in 85 ml. of water. The solution was heated on the steam-bath for a few minutes until crystals began to form, allowed to cool slowly to room temperature and finally stored in a refrigerator overnight. The crystals then were filtered with suction, washed repeatedly with water, and dried in a vacuum desiccator over sulfuric acid to give 35.4 g. (45%) of 2-formylbornane semicarbazone, m.p. 198–202°.

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[19] (−)-*endo*-2-Chlorobornane (bornyl chloride) gives (−)-camphene,[20] which can be catalytically hydrogenated to (+)-2,3,3-trimethylnorbornane.[21] Since (−)-bornyl chloride was also used to prepare the 2-formylbornane used in our studies, we should have obtained (+)-2,3,3-trimethylnorbornane (isocamphane) provided *either* of the following two sufficient conditions are satisfied (i) the *endo* and *exo* epimers of isocamphane have the same sign of rotation in a given configurational series; (ii) hydrogen atom abstraction by the radical precursor of isocamphane gives about the same ratio of *endo* and *exo* isomers as does catalytic hydrogenation. That condition (ii) above is satisfied, at least at somewhat higher temperature, is established.[4]

[20] M. Berthelot, *Compt. rend.*, **47**, 266 (1858).

[21] P. Lipp, *Ann.*, **382**, 265 (1911).

[22] F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 3258 (1948).

[23] Melting points and boiling points are corrected. Melting points of hydrocarbons were determined in sealed capillaries. The microanalyses are by Drs. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, Calif., and Joseph Alicino, Metuchen, N. J.

Two recrystallizations from 95% ethanol gave material of m.p. 204.5–206°.

Anal. Calcd. for $C_{12}H_{21}ON_3$: C, 64.54; H, 9.48; N, 18.82. Found: C, 64.33; H, 9.50; N, 18.80.

The semicarbazone was suspended in 20% sulfuric acid and the mixture subjected to steam distillation. The distillate was extracted with hexane, and the hexane solution was evaporated, leaving crude 2-formylbornane. Two sublimations in high vacuum (trap at 0° to avoid condensing volatile impurities) gave material of m.p. 115–119°. In this way, 10.0 g. of semicarbazone gave 3.5 g. (47%) of 2-formylbornane.

Optically active 2-formylbornane, m.p. 130–134°, semicarbazone m.p. 203.5–204°, was obtained in the same manner from bornyl chloride of $[\alpha]_D$ −31.8° (*c* 10, ethanol), 95% optically pure.[24] Houben and Doescher[7] report 2-formylbornane prepared from bornyl chloride of unspecified optical purity to have m.p. 131°; semicarbazone, m.p. 220°.

Analysis of the Decarbonylation Products (Experiments 1-3, Tables I and II).—Carbon monoxide and methane were qualitatively identified in the permanent gases from the decarbonylation by their retention times on the Perkin-Elmer "I" column (molecular sieve) at a helium flow rate of 20 ml./min. at 100°. This and all subsequent gas chromatographic analyses employed the Perkin-Elmer model 154C instrument. Chemical confirmation of the presence of carbon monoxide was afforded when the gas reduced palladium chloride to the metal.

Bornane, bornene and tricyclene were identified by cochromatography of the volatile hydrocarbon fraction with authentic samples of these compounds. The authentic samples were prepared by literature procedures: bornane by hydrolysis of bornylmagnesium chloride,[25] bornene by dehydrohalogenation of bornyl chloride with potassium amylate,[26] tricyclene by oxidation of camphor hydrazone.[6] Each of the standard samples was purified by preparative gas chromatography. Analyses for the hydrocarbons, peroxide and acetone were performed with the Perkin-Elmer "K" column (polypropylene glycol) at a helium flow rate of 80 ml./min. at 60°. Analyses[4] of known mixtures of bornane, bornene and tricyclene showed that relative peak areas were so nearly proportional to weight fraction that no correction for differing thermal conductivities was required.

Decarbonylation of Optically Active 2-Formylbornane.—The sample of optically active aldehyde (8.2 g., 49 mmoles) contained in a 100-ml. 3-neck flask equipped with dropping funnel, thermometer and condenser was heated to 140° with a heating mantle (after having been flushed with oxygen-free nitrogen for 1 hr.) and treated with *t*-butyl peroxide (0.73 g., 5.0 mmoles) while steam was passed through the condenser jacket. Gas, which was evolved after a short induction period, was collected and measured over water. The reaction was allowed to continue until gas evolution had almost ceased, whereupon another 0.73-g. portion of peroxide was added. This procedure was repeated until 5 portions (total of 25 mmoles) of peroxide had been added. The last addition of peroxide caused no further evolution of gas during 1.5 hours. Throughout the reaction, the temperature was held at 140 ± 2° and a flow of steam was maintained in the condenser jacket. The reaction required 8 hours, and 430 ml. (corrected to standard conditions) of gas was evolved. Calculated as carbon monoxide, this corresponds to 39% of theory, based on starting aldehyde.

The decarbonylation mixture was dissolved in acetone and added to a solution of 16 g. of potassium permanganate in 400 ml. of acetone. After 12 hr. at room temperature, the solution was filtered and added to 1 liter of water. Sulfur dioxide was passed into the solution to destroy the excess permanganate, and the mixture was extracted with 200 ml. of pentane. The pentane solution was washed successively with three 50-ml. portions of 5% sodium hydroxide, three 50-ml. portions of water and repeatedly with 30-ml. portions of concentrated sulfuric acid until the aqueous phase was colorless. After a final washing with two 50-ml. portions of water and drying over calcium sulfate, the solution was concentrated to a volume of about 10 ml. and examined polarimetrically: α_D −5.8° in a 2-dcm. tube. Most of the remaining pentane was removed through a short fractionating column, and the residue was cooled in ice, whereupon it partially solidified. A portion of the liquid layer was introduced into a vacuum line, and the last traces of pentane were removed by repeatedly trapping the sample at −45°. The portion that trapped at −45° was then further fractionated by trapping at −20°. The latter material was a white solid, m.p. 125–135°. Its molecular weight by vapor volume was 154 ± 3.

The solid and remaining liquid portions of the original pentane extract were sublimed to give 1.62 g. of material of m.p. 120–130°. A trace (0.04 g.) of non-volatile residue remained. To 0.43 g. of the volatile material was added 8.5 ml. of a saturated solution of thiourea in methanol. The mixture was shaken vigorously, and white needles of inclusion compound appeared almost immediately. After 12 hours at room temperature, the mixture was filtered. A second crop of crystals was obtained by cooling the filtrate in ice for 12 hours. Each of the crops was worked up separately as follows. The inclusion compound was added to 10 ml. of water and 5 ml. of ether and the mixture was stirred until no solid was left. The ether was separated, the aqueous phase was extracted with more ether, and the combined ether layers were dried over calcium sulfate and evaporated. From the first crop there was thus obtained fraction I and from the second fraction II. The filtrate from the second crop was decomposed with 100 ml. of water and 200 ml. of ether, and the ether layer was worked up as above to give fraction III. Each of the three fractions was sublimed. Fraction I, 36.1 mg., m.p. 145–150°, $[\alpha]_D$ 0.00° (*c* 0.3 in pentane); fraction II, 38.5 mg., m.p. 125–138°, $[\alpha]_D$ −13.4° (*c* 0.3 in pentane); fraction III, 34.3 mg., m.p. 103–115°, $[\alpha]_D$ −17.3° (*c* 0.3 in pentane). Fraction I was further purified by recrystallization from methanol and sublimation to give material of m.p. 158–159°, alone or mixed with authentic bornane (reported[27] m.p. 158–159°).

Preparation of Racemic 2-Methylbornanes (Predominantly *endo*).—Carbonation[28] of racemic bornylmagnesium chloride gave a mixture of bornane-2-carboxylic acids. A solution of 91.1 g. of this material in 1 liter of anhydrous ether was added with stirring during 3 hours to a suspension of 56.9 g. of lithium aluminum hydride in 1 liter of ether. After the mixture had been stirred under reflux for 5.5 days, water was added with cooling, the resulting suspension was filtered, and the ether was removed to give 73.0 g. of mixed 2-hydroxymethylbornanes. An additional 6.2 g. of product was obtained by working up the filter cake with chloroform and hydrochloric acid. Gas chromatography ("K" column at 80 ml./min. of helium, 190°) showed the product to be a mixture of two isomers: isomer A, 6.5%, which emerged first from the column; isomer B, 93.5%. Isomer A is assigned the *exo* configuration, B the *endo*, on the grounds that lithium aluminum hydride reduction of a sample of acid that had been converted to methyl ester, stereochemically equilibrated with boiling methanolic sodium methoxide, and then hydrolyzed gave on reduction as above a mixture of 4.5% of A and 95.5% of B. On steric grounds, the *endo* isomers in this series are expected to be the more stable.

The 6.5:93.5 mixture of carbinols (16.8 g.) was converted to *p*-bromobenzenesulfonate with 28.0 g. of *p*-bromobenzenesulfonyl chloride and 200 ml. of dry pyridine. After 20 hours at room temperature, the mixture was poured into 3 liters of ice-water. Three hours of occasional stirring sufficed to induce crystallization, whereupon the mixture was filtered, the solid was thoroughly washed with ice-water and dried over sulfuric acid *in vacuo* to give 37.1 g. (96%) of crude ester, m.p. 59–62°. Two recrystallizations from pentane and three from absolute methanol gave material of m.p. 64–65.5°.

Anal. Calcd. for $C_{17}H_{23}O_3BrS$: C, 52.70; H, 5.98. Found: C, 52.75; H, 5.94.

A solution of 10.3 g. of the purified *p*-bromobenzenesulfonate in 100 ml. of ether was added to a stirred suspension of 1.54 g. of lithium aluminum hydride in 50 ml. of ether. After having been stirred at room temperature for 8 hours and then at reflux for 12 hours under a solid carbon dioxide-acetone cold finger condenser, the solution was concentrated by distillation of the ether through a fractionating column. The product was sublimed from the residue at 20 mm. to

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(24) See F. H. Thurber and R. C. Thielke, *J. Am. Chem. Soc.*, **53**, 1030 (1931).

(25) A. Hesse, *Ber.*, **39**, 1127 (1906).

(26) H. Meerwein and J. Joussen, *ibid.*, **55**, 2529 (1922).

(27) N. Kizhner, *J. Russ. Phys. Chem. Soc.*, **43**, 582 (1911); *C. A.*, **6**, 347 (1912).

(28) *Cf.* M. de Botton, *Bull. soc. chim. France*, 816 (1955); 372 (1958).

give 2.7 g. (66%) of hydrocarbon, m.p. 85–87°. Recrystallization from methanol did not change the m.p. Gas-liquid chromatography (2.7 m. × 6 mm. column packed with 20 weight % Dow Corning 702 silicone fluid on 40–60 mesh fire brick at 120 ml./min. and 85°) showed this material to be 4 ± 2% *exo* and 96 ± 2% *endo*-2-methylbornane.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.56; H, 13.24.

A second preparation of predominantly *endo* racemic 2-methylbornane was effected by heating at reflux for 20 hours a mixture of 42.6 g. of methyl iodide and ethereal bornylmagnesium chloride (from 17.3 g. of *endo*-2-chlorobornane). The solvent was evaporated and the residue, after sublimation, was subjected to preparative gas chromatography (3.6 m. × 2.2 cm. column packed with 15 weight % Dow Corning High Vacuum grease on 40–60 mesh fire brick at 500 ml./min. and 95°) to give 1.29 g. of bornene, 2.60 g. of bornane and 1.29 g. (8.5%) of mixed 2-methylbornanes, m.p. 91–93.5°, consisting of 81 ± 2% *endo* and 19 ± 2% *exo* isomers.

Predominantly *exo*-2-Methylbornane.—A modification of the method of Zeiss and Zwanzig[29] was used for the preparation of 2-methylenebornane (1-methyl-α-fenchene). Acetylation of racemic 2-hydroxymethylbornane with acetic anhydride in pyridine gave 2-acetoxymethylbornane, b.p. 111.5–112.5° (7.5 mm.), n^{25}_{D} 1.4673; reported[29] b.p. 90–92° (1.5 mm.), n^{26}_{D} 1.4672. Pyrolysis of the acetate according to a general procedure[30] (dripping the ester through a Vycor tube containing a packed section 20 cm. long and packed with 5-mm. Pyrex helices at 500–520° in a nitrogen atmosphere) gave 65% (based on recovered acetate) of 2-methylenebornane, m.p. 86–86.5° after two recrystallizations from methanol. Zeiss and Zwanzig[28] report m.p. 62.5–64° for partially optically active material. The infrared spectrum of our racemic material was identical with that of the optically active sample prepared by these workers. We are indebted to Dr. H. H. Zeiss for a copy of the infrared spectrum of his material.

Catalytic hydrogenation (platinum oxide, methanol) of 1.16 g. of the above racemic olefin resulted in the absorption of one molar equivalent of hydrogen in 1 hour. The filtered solution was poured into water, the product was extracted with pentane, and the pentane solution, after having been washed with water and dried over calcium sulfate, was filtered, concentrated to a volume of 15 ml., and chromatographed on 70 g. of silica gel. The hydrocarbon was eluted with pentane, the solution concentrated to a small volume, and the remaining pentane was removed in the vacuum line to give 0.77 g. (66%) of white solid, m.p. 101–106°. Two recrystallizations from methanol gave 2-methylbornane, m.p. 107–108°. This material consisted of 29 ± 2% *endo* and 71 ± 2% *exo* isomer (by gas chromatography).

Anal. Calcd. for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.59; H, 13.36.

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[29] H. H. Zeiss and F. R. Zwanzig, *J. Am. Chem. Soc.*, **79**, 1733 (1957).

[30] W. J. Bailey and W. B. Lawson, *ibid.*, **77**, 1606 (1955).

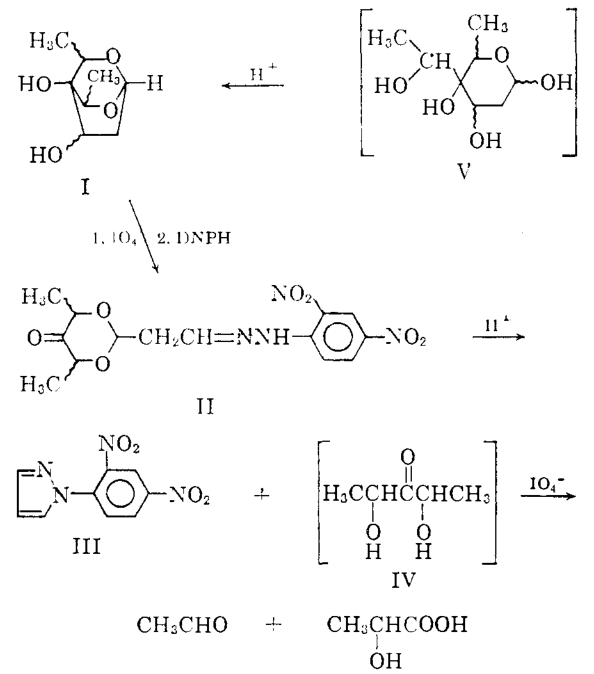
COMMUNICATIONS TO THE EDITOR

A NEW ANHYDRO C_8 SUGAR FROM AN ANTIBIOTIC

Sir:

We wish to describe studies establishing structure I, Chart A, for a product resulting from mild acid hydrolysis of the *Streptomyces aureofaciens* antibiotic previously designated as "γ-Activity X."[1] It is believed that I has been derived from a branched chain trideoxyoctose, structure V, a representative of a new class of sugars.

The new anhydro sugar was obtained by hydrolyzing a 5% solution of "γ-activity X" in 1 *N* HCl at room temperature for 24 hours. After removal of the insoluble aglycone by filtration, the hydrolysate was adjusted to pH 6.5–7.0 with silver carbonate, clarified, and concentrated under reduced pressure. The syrupy residue was redissolved in water and extracted into ethyl acetate. Evaporation of the combined extracts left an amorphous residue which was taken up in ether, filtered, and concentrated to yield a syrup which partially crystallized on standing. The white crystals were collected, recrystallized from ethyl acetate and found to have the following properties: m.p. 153–154° (with slow sublimation at 120°); $[\alpha]^{25}_{D}$ −144° (*c* 2, water). *Anal.* Calcd. for $C_8H_{14}O_4$ (174): C, 55.16; H, 8.10. Found: C, 55.1; H, 8.1; mol. wt.,[2] 171. In addition the new compound was non-reducing, showed neither absorption in the ultraviolet nor carbonyl band in the infrared, gave a positive iodoform test and contained two C-methyl groups by Kuhn-Roth (Calcd. for: 1-CH_3, 8.64; 2-CH_3, 17.3. Found: 10.7,



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[1] J. H. Martin, *et al.*, in H. Welch and F. Marti-Ibañez, "Antibiotics Annual 1954–1955," Medical Encyclopedia, Inc., New York, N. Y., 1955, pp. 1020–1024.

[2] Micro Menzies–Wright method in methanol: D. Ketchum, *Anal. Chem.*, **19**, 504 (1947).