

formed (48%) with the evolution of carbon monoxide (52%). The heretofore unreported benzyldiphenylsilane (2),⁴ a possible rearrangement product (synthesized by reaction of benzylmagnesium chloride with diphenylsilane), was not detected in the reaction product even though 2 was not destroyed under the reaction conditions used. Control studies indicated that ca. 5% rearrangement was detectable via infrared and n.m.r. spectroscopy.

Furthermore, no rearrangement of 1 was detected when decarbonylation was achieved in refluxing chlorobenzene under dilute conditions Methyltriphenylsilane again resulted (35%). No evidence was found in this reaction for silyl radical intervention via attack on either chlorobenzene⁵ or the peroxide.

In striking contrast to the above results, decarbonylation of β,β,β -triphenylpropionaldehyde (3) with di-tbutyl peroxide at 140° has been shown⁶ to afford essentially completely rearranged hydrocarbon products.

$$(C_{6}H_{5})_{3}CCH_{2}CHO \xrightarrow{DTBP}_{\Delta} + CO$$
3
$$(C_{6}H_{5})_{3}CCH_{2}C_{6}H_{5}$$

On the plausible assumption that the decarbonylation reactions of 1 and 3 do not differ mechanistically, the following course for the reactions may be written.

$$[(CH_3)_3CO]_2 \longrightarrow 2(CH_3)_3CO \cdot$$
(1)

 $(C_{\delta}H_{\delta})_{3}GCH_{2}CHO + (CH_{\delta})_{3}CO \cdot \longrightarrow (CH_{\delta}H_{\delta})_{3}GCH_{2}CO \cdot +$ (CH₃)₃COH (2)

$$(C_{6}H_{b})_{3}GCH_{2}CO \cdot \longrightarrow (C_{6}H_{b})_{3}GCH_{2} \cdot + CO$$
(3)

$$(C_{6}H_{\delta})_{3}GCH_{2}\cdot + (C_{6}H_{\delta})_{3}GCH_{2}CHO \longrightarrow (C_{6}H_{\delta})_{3}GCH_{3} + (C_{6}H_{\delta})_{3}GCH_{2}CO \cdot (4)$$

$$(C_{\theta}H_{\mathfrak{z}})_{\mathfrak{z}}GCH_{2} \cdot \longrightarrow (C_{\theta}H_{\mathfrak{z}})_{\mathfrak{z}}\dot{G}CH_{2}C_{\theta}H_{\mathfrak{z}}$$
(5)

$$(C_{6}H_{\delta})_{2}GCH_{2}C_{6}H_{\delta} + (C_{6}H_{\delta})_{3}GCH_{2}CHO \longrightarrow (C_{6}H_{\delta})_{2}GHCH_{2}C_{6}H_{\delta} + (C_{6}H_{\delta})_{3}GCH_{2}CO \cdot (6)$$

The results indicate clearly that process 5 does not occur under the conditions studied when G is silicon. When G is carbon, process 5 not only occurs but it occurs to the virtual exclusion of process 4.6

Several factors may be involved in the lack of rearrangement of the triphenylsilylmethyl radical (4). A type of "back bonding"⁷ of the unpaired electron on carbon through delocalization into an adjacent dorbital of silicon could stabilize 4 and remove some of the driving force associated with the rearrangement of 3. Also, the decreased steric compression of the phenyls in 4 (because of the larger size of silicon) may be important.8 In addition, the "push-pull" mechanism9

(6) D. Y. Curtin and M. J. Hurwitz, *ibid.*, 74, 5381 (1952); D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, 25, 880 (1960). In the latter paper the authors report some spectral evidence for perhaps 10% unrearranged product in the hydrocarbon fraction.

(7) C. Eaborn, pp. 91–103 of ref. 2.
(8) E. S. Gould, "Mechanism and Structure in Organic Chemistry," H. Holt and Co., New York, N. Y., 1959, p. 756. Such compression used to explain the *ionic* migration of phenyl from silicon to carbon may be needed in its radical migration also. If so, such a process is not readily achieved in decarbonylation.

Present work is aimed at determining which of these (or other) factors are really involved in the decarbonylation of 1. In addition, other organosilicon substrates (presumably) prone to radical rearrangement are being investigated.

- increases rearrangement but is not necessary for it to occur. Cf. L. H. Slaugh, J. Am. Chem. Soc., 81, 2262 (1959), and W. A. Bonner and F. D. Mango, J. Org. Chem., 29, 29 (1964). (9) A. G. Brook, K. H. Pannell, G. E. LeGrow, and J. J. Sheeto, L. Orgenwentel (Chem. 2 (102) (102))
- J. Organometal. Chem., 2, 493 (1964).

J. W. Wilt, O. Kolewe Department of Chemistry, Loyola University Chicago, Illinois 60626 Received March 24, 1965

Bimolecular Reactions in Frozen Organic Solutions¹

Sir:

In organic solutions the base-catalyzed decomposition of *t*-butylperoxy formate (TBF) proceeds with pseudo-first-order formation of t-butyl alcohol and carbon dioxide.² This bimolecular reaction involves attack by base on the formate hydrogen with concerted development of carbon dioxide in the ratedetermining step.³

$$\begin{array}{c} O \\ H \longrightarrow C \longrightarrow O \longrightarrow C(CH_{3})_{3} + B : \longrightarrow \begin{bmatrix} O \\ BH^{+}C \longrightarrow C(CH_{3})_{3} \\ O \\ B : + CO_{2} + HO \longrightarrow C(CH_{3})_{3} \end{bmatrix} \rightarrow \\ \end{array}$$

In liquid *p*-xylene at 70°, samples of a solution 0.031M in TBF and 0.012 M in 2,6-lutidine gave an observed pseudo-first-order rate constant of 28.2 \times 10^{-5} sec.⁻¹. If identical samples were first frozen at -70° then held at 0° and defrosted at various times, the peroxide disappeared in the frozen samples with a first-order rate constant of 50.2 \times 10⁻⁵ sec.⁻¹.

In frozen p-xylene (m.p. 13.25°) solutions, the reaction was quenched simply by defrosting the individual samples of a run. Except at high base concentrations there was little loss of peroxide at room temperature and samples were analyzed for TBF as previously described.² Comparisons of frozen samples with identical, but unfrozen (i.e., supercooled), samples held at the temperature of the run also double-checked that loss of TBF occurred only in frozen samples. The 2,6-lutidine-catalyzed pseudo-first-order decomposition of TBF occurs at 0° and with accelerated rates in frozen dioxane, benzene, nitrobenzene, pchlorotoluene, and diphenylmethane solutions.

Reactions catalyzed by pyridine and by 2,6-lutidine in *p*-xylene have been extensively investigated and show the following features as illustrated by the data in Table I. (A) All runs gave good straight plots of log

⁽⁵⁾ J. Curtice, H. Gilman, and G. S. Hammond, J. Am. Chem. Soc., 79, 4754 (1957).

⁽¹⁾ This research was supported by grants from the National Research Council of Canada and the Petroleum Research Fund of the American Chemical Society. A research fellowship to T. K. from the Research Committee of the University of British Columbia is also gratefully acknowledged.

⁽²⁾ R. E. Pincock, J. Am. Chem. Soc., 86, 1820 (1964).

⁽³⁾ R. E. Pincock, ibid., 87, 1274 (1965).

 Table I.
 Decomposition of t-Butylperoxy Formate

 by 2,6-Lutidine in Frozen p-Xylene Solutions

Run	Concn. TBF, $M \times 10^2$	Concn. base, $M \times 10^2$	Temp., °C.	$k_{\text{obsd.}}$ $\times 10^{5}$ sec. ⁻¹
1ª	2.92	1.12	0.0	46.2
26	2.92	1.12	0.0	50.2
3°	2.57	0.0386	0.0	2.69
4ª	2.88	0.0773	0.0	4.82
5	3,08	1.16	11.0	8.56
6	3.08	1.19	6.0	33.5
7	3.08	1.19	2.0	52.4
8	3.05	1.16	-10.0	36.1
9	3.09	1.25	-20.0	19.3
10	3.05	1.16	-30.0	7.61
11°	3.0	1.2	0.0	0.23
12	3.05	2.06	0.0	62.4
13	3.05	4.98	0.0	77.0
14	2.82	7.50	0.0	85.7
15	2.93	1.63	0.0	60.8
16	29.2	1.49	0.0	9.09
17	3.02	1.19	0.0	45.3
18 ⁷	3.02	1.19	0.0	24.1
19 <i>ª</i>	3.01	1.19	0.0	10.3
20 ^h	3.05	1.19	0.0	11.1
211	3.05	1.19	0.0	10.2

^a Samples, ca. 2 ml., frozen slowly by seeding at $+8^{\circ}$. ^b Samples, ca. 0.5 ml., frozen at -195° . ^c Followed to 60% decomposition. ^d Followed to 87% decomposition. ^e Calculated for reaction at the given concentration of 2,6-lutidine in *p*-xylene from $\Delta H^* = 12.3 \text{ kcal.}$, $\Delta S^* = -30.5 \text{ e.u.}$, obtained for second-order rate constants measured at 90, 70, and 50°. ^f Solution contains 0.0149 *M* benzene. ^a 0.0571 *M* benzene. ^b 0.0473 *M* carbon tetrachloride. ⁱ 0.0368 *M* heptane.

(relative concentration) against time, followed usually to 90% decomposition. (B) Observed rate constants were independent of the method of freezing samples (see runs 1 and 2). (C) Even 2.6 % 2,6-lutidine relative to the initial TBF concentration resulted in complete loss of the peroxide (runs 3 and 4). (D) The rate of reaction in frozen p-xylene solutions is a maximum at ca. $+2^{\circ}$ but reaction occurs at $+12^{\circ}$ and at -30° (however not at -70°) at greater rates than those calculated for the reaction in liquid at the given lutidine concentrations (see runs 5-10). (E) For constant initial peroxide concentration and low 2,6-lutidine concentrations the observed rate constants at 0° are approximately proportional to the lutidine concentration; however, at high concentrations of lutidine the observed rate constants reach a maximum (runs 3, 4, 2, 12–14). (F) Although the decomposition is first order in TBF, the observed first-order rate constants decrease with greater initial concentrations of TBF (runs 15 and 16). (G) At low concentrations of TBF and 2,6-lutidine the observed first-order rate constants are greatly sensitive to the presence of "inert" impurities (e.g., 0.16 mole % benzene in pxylene decreases the observed rate by one-half; see runs 17 and 18). Within certain limits⁴ the nature of the impurity is unimportant; similar concentrations of different substances decrease the rate to the same extent (runs 19-21).

These results indicate that the reaction proceeds in liquid⁵ holes, present among the crystalline solid, which

contain high concentrations of the reactants.⁶ If ideal behavior for the solutes is assumed then the following relationship is expected

$$k_{\rm obsd} = k_{\rm z} C \, \frac{M_{\rm b}}{M_{\rm b} + M_{\rm p} + M_{\rm i}}$$

where k_{obsd} is the observed first-order rate constant, k_2 is the second-order rate constant for liquid phase reaction, C is the total constant concentration of solutes in the liquid holes, and $M_{\rm b}$, $M_{\rm p}$, and $M_{\rm i}$ are the initial concentrations of base, peroxide, and impurities, respectively. This relationship reproduces, from experimental measurements of C for 2,6-lutidine in pxylene (*i.e.*, from the freezing point-composition phase diagram) and from the calculated k_2 extrapolated from higher temperatures, the form of the observed temperature dependence of k_{obsd} (see D above). For low and high concentrations of 2,6-lutic ine or of pyridine the experimentally observed change in k_{obsd} with base concentration is correctly predicted (see E above). At high TBF concentrations or in the presence of impurities which follow ideal behavior at 0° in p-xylene the predicted decrease in rate constant is experimentally found (see F and G above). These variations in k_{obsd} , which are related by the above equation to measurable solution concentrations, may be visualized in terms of changes in the total volume and in the relative reactant concentrations of the liquid regions.

Many of the features reported here for the TBFbase reactions in frozen organic solutions are similar to results reported by Bruice and Butler⁷ for several bimolecular reactions in ice. It may be generally expected that, if the reactants of a bimolecular reaction are sufficiently soluble at temperatures below the freezing point of the solvent, and the reaction has a low activation energy, an acceleration due to the concentration effect will be observed when the system is frozen. Experiments on the reaction of methyl iodide with triethylamine in benzene and the Diels-Alder reaction of cyclopentadiene with methyl acrylate in *p*-xylene at 0° show that freezing accelerates the formation of products.

close to the expected ratio for liquid phase reaction as estimated from the known isotope effects at 90°, $^{\rm 3}$

(6) A concentration of 2.35 M 2,6-lutidine in *p*-xylene is required to prevent freezing at 0°. From this the maximum total volume of "holes" for most of the runs of Table I may be estimated to be *ca.* 2% of the volume of the original solution before freezing. (7) T. C. Bruice and A. R. Butler, *J. Am. Chem. Soc.*, 86, 313, 4104

(1) 1. C. Bruice and A. R. Butler, J. Am. Chem. Soc., 86, 313, 4104 (1964).

Richard E. Pincock, Thomas E. Kiovsky

Department of Chemistry, University of British Columbia Vancouver 8, British Columbia, Canada Received February 19, 1965

The Total Synthesis of (\pm) -Ibogamine and of (\pm) -Epiibogamine

Sir:

Ibogamine $(1)^{1,2}$ is the least substituted member of a large group of natural bases structurally characterized by the presence of an isoquinuclidine ring and a sevenmembered ring C. We have now completed the first total synthesis of an iboga alkaloid.

 M. F. Bartlett, D. F. Dickel, and W. I. Taylor, J. Am. Chem. Soc., 80, 126 (1958).
 G. A. Jeffrey, G. Arai, and J. Coppola, Acta Cryst., 13, 553 (1960).

Communications to the Editor 2073

⁽⁴⁾ Anthracene, 0.015 M, has no effect on the rate while *t*-butyl alcohol, 0.033 M, is less than half as effective in decreasing the rate as benzene, carbon tetrachloride, or heptane at the same concentration.

⁽⁵⁾ The deuterium isotope effect for reaction of *t*-butylperoxy formate-*d* with pyridine in frozen *p*-xylene at 0° is $k_{\rm H}/k_{\rm D} = ca.$ 9,