Figure 1. CD spectra of the benzoate of presqualene alcohol (A, curve 1) and of *trans-(R)*-chrysanthemum alcohol (A, curve 2), of the dibenzoate of *trans-(R)*-caronic alcohol[14] (B, curve 3), and of the tribenzoate of an ozonolysis product 2a of presqualene alcohol (B, curve 4). The spectra were taken in ethanol in a Cary 60 spectropolarimeter fitted with a CD attachment. The CD spectrum of presqualene benzoate shown appears to represent one-half of the split Cotton effect resulting from the interaction of the primary benzoate with a cyclopropyl olefinic chromophore, whereas for all other compounds the effects of isolated "chiral" benzoate groups are seen. The measurements could not be extended to below 215 nm on account of the strong uv absorption of the specimens even in very dilute solutions.

A full account of this work will be presented elsewhere.

G. Popják,* John Edmond, Siu-May Wong

Departments of Biological Chemistry and Psychiatry
Mental Retardation Center and Brain Research Institute
School of Medicine, University of California
Los Angeles, California 90024

Photochemical Reactions of Benzoic Acid. Cycloaddition, Hydrogen Abstraction, and Reverse Type II Elimination

Sir:

The photochemistry of aromatic aldehydes and ketones has received intensive study, especially during the past decade, and the behavior of the n → π* triplet excited states of these molecules is now fairly well understood.[1,2] On the other hand, the photochemical behavior of carboxylic acids has been scarcely investigated. Aliphatic α,β-unsaturated acids are known to undergo cis–trans isomerization and addition of alcohols to the double bond.[3-5] Aliphatic acids are reported to decarboxylate when irradiated with light of short

(1) P. J. Wagner, *Advan. Photochem.*, 5, 23 (1968).
(2) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Wiley-Interscience, New York, N. Y., 1969, Chapter 3.
(3) M. J. Jorgenson, *Chem. Commun.*, 137 (1965).
(4) P. J. Kropp and H. J. Krauss, *J. Org. Chem.*, 32, 3222 (1967).
(5) C. H. Nicholls and P. A. Leermakers, *ibid.*, 35, 2754 (1970).

wavelength.[6] We report here our results on the solution photochemistry of benzoic acid, which we have observed to undergo the several processes mentioned in the title.

Irradiation[7] of a 1% solution of benzoic acid (1) and excess 2,3-dimethyl-2-butene in hexane until 35% of 1 was consumed (~2 hr) led to the isolation of four products: (a) 2,3-dimethyl-2-butyl benzoate (2, 46%), bp 73–75° (0.1 mm) [ir (film) 1711 cm⁻¹; nmr τ 2.3 (2 H, m), 2.8 (3 H, m), 6.7 (1 H, septet, J = 6.8 Hz), 8.53 (6 H, s), and 9.00 (6 H, d, J = 6.8 Hz)], identified by comparison with an authentic sample;[8] (b) isobutyrophenone (3, 22%); (c) 1-benzoyl-2,3-dimethyl-2-butene (4, 7%) [ir (film) 1681 cm⁻¹; nmr τ 2.3–2.8 (5 H, m), 6.5 (2 H, s, br) 8.3 (6 H, s, br), and 8.4 (3 H, s, br); m/e 188 (P, 11), 173 (13), 106 (28), 105 (80), and 84 (100)]; and (d) diene 5[9] (25%) [τ 7.9 (4 H, s, br) and
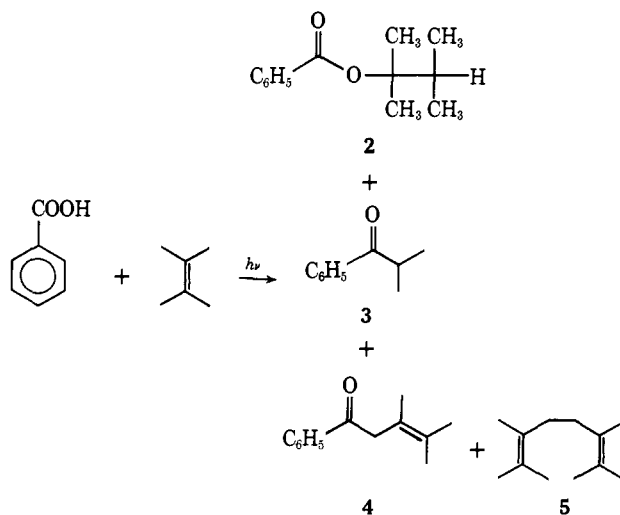
8.4 (18 H, s, br)]. Ester 2, the major product, is evidently formed by a process which is the reverse of the well-known type II elimination so often observed with alkyl and aryl alkyl ketones,[10] and which has recently been observed in esters of simple aromatic acids.[11] Evidence for this mechanism was provided by the observation that irradiation of C₆H₅COOD in excess olefin gave a monodeuterated ester 2 with the deuterium located at C-3 of the 2,3-dimethyl-2-butyl group as shown by its nmr spectrum. Irradiation of 2 itself gave benzoic acid and 2,3-dimethyl-2-butene; the position of equilibrium between the forward and reverse reactions could not be determined because of competing reactions of both 1 and 2, such as formation of 3. Irradiation of solutions of 1 and olefin until 1 was entirely consumed gave mainly 3. Compound 3, isobutyrophenone, is most simply rationalized as arising *via* retro 2 + 2 cleavage of an intermediate oxetane, a sequence which has analogy in some cases of ketone-derived oxetanes.[12]

(6) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, 33, 1530 (1955).
(7) Preparative irradiations were performed with a 15-fold excess of olefin, using light from a Hanovia 450-W medium-pressure mercury arc.
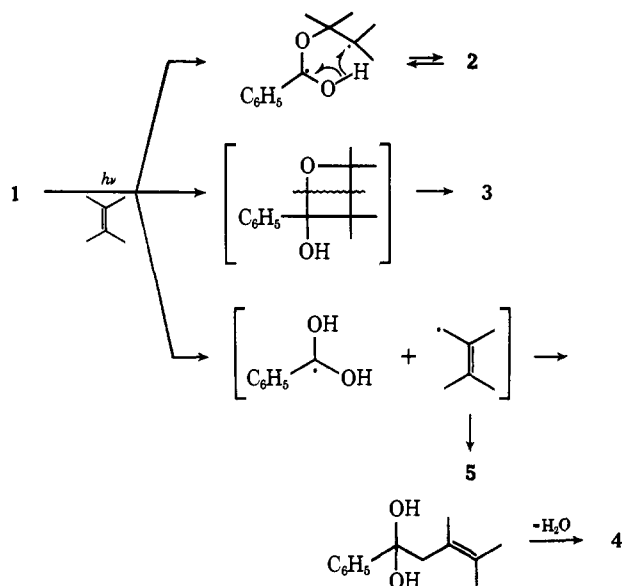(8) The authentic material was prepared by sequential treatment of 2,3-dimethyl-2-butanol with 1 equiv of butyllithium and 1 equiv of benzoyl chloride.
(9) T. Midgely and A. L. Henne, *J. Amer. Chem. Soc.*, 52, 2078 (1930).
(10) P. J. Wagner, *Accounts Chem. Res.*, 4, 168 (1971).
(11) J. A. Barltrop and J. D. Coyle, *J. Chem. Soc. B*, 251 (1971).
(12) D. R. Arnold, *Advan. Photochem.*, 6, 301 (1968), and references given therein.

C₆H₅ [structure] ⇌ 2

1 —hv→ [structure] → 3

[structure with C₆H₅, OH + olefin] →

↓

5

C₆H₅ [structure] -H₂O→ 4

Irradiation of **1** in excess 2-methyl-2-butene until 50% of **1** was consumed gave a single ester, 3-methyl-2-butyl benzoate (**6**, 37%), the ketones isobutyrophenone (**3**) and propiophenone (**7**) (14 and 20%, respectively), a ketone believed to be 1-benzoyl-2-methyl-2-butene (**8**, 5%), as well as a mixture of C_{10} hydrocarbons derived from the olefin. Irradiation of mixtures of **1** and excess cyclohexene gave cyclohexyl benzoate (**9**, 55% based on unrecovered **1**), 3,3'-bicyclohexenyl (**10**, 20%), and 3-cyclohexylcyclohexene (**11**, 29%), as well as a complex mixture of C_{18} hydrocarbons derived from cyclohexenyl radicals. The quantum yields measured at 2537 Å[13] for the formation of **2** and **3** are 0.22 and 0.05, respectively. Those for **6**, **3**, and **7**, the products from 2-methyl-2-butene, are 0.12, 0.04, and 0.06.

The high triplet energy of **1** (78 kcal)[14] made meaningful sensitization experiments impractical. However, added 1,3-pentadiene at concentrations up to 0.5 M caused no reduction in the rate of formation of **2** and **3**; these results imply that the reactions of **1** with olefin occur *via* excited singlet states of **1**, or perhaps *via* very short-lived triplets. The high reactivity of **1** at the carbonyl group would imply that the reactive excited state is of predominantly n → π* character. This behavior is similar to that which we recently observed with benzonitrile, which reacts with electron-rich olefins at the nitrile group, apparently *via* an excited singlet state.[15] We hope to resolve this matter by fluorescence studies of benzoic acid and its derivatives. We have not thus far observed products of photochemical reaction of **1** at the benzene ring. Our study of the photochemical behavior of this and related compounds with lowest π → π* triplet excited states is continuing.

Acknowledgments. The author gratefully thanks Mr. William Landis of the National Institutes of Health for the mass spectral data reported and Professor Stuart Staley for the loan of facilities. This work was

(13) These experiments were performed on solutions flushed with argon in runs carried to 6–10% conversion; a correction was made for light absorbed by the products.
(14) Y. Kanda, R. Shimada, and Y. Takenoshita, *Spectrochim. Acta*, **19**, 1249 (1963).
(15) T. S. Cantrell, *J. Amer. Chem. Soc.*, **94**, 5929 (1972).

Thomas S. Cantrell
*Department of Chemistry, American University
Washington, D. C. 20016*

### Formation and Reactions of Boron-Stabilized Carbanions Derived from Vinylboranes

Sir:

We recently reported that reaction of *B*-methyl-9-borabicyclononane with the hindered base lithium 2,2,6,6-tetramethylpiperidide (LiTMP) produces a boron-stabilized carbanion (I, eq 1).[1] With stoichio-

[structure] BCH₃ + [structure] NLi —benzene 25°→

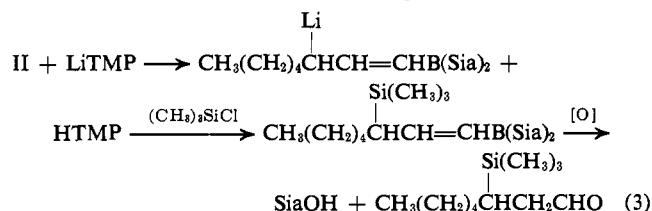[structure] BCH₂Li + [structure] NH (1)

I
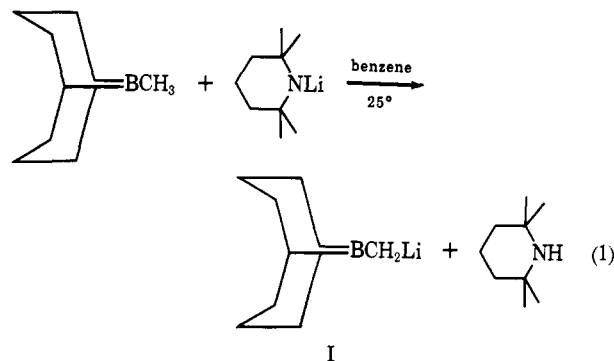
metric quantities of base, the conversion to I is approximately 65%; however, other trialkylboranes give much smaller conversions to the corresponding anions.

We now report results obtained with vinylboron compounds, prepared by the monohydroboration of alkynes with disiamylborane (eq 2).[2]

$$(Sia)_2BH + 1\text{-octyne} \xrightarrow[25°]{THF} CH_3(CH_2)_5CH=CHB(Sia)_2 \quad (2)$$

II
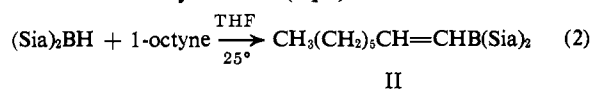
Addition of vinylborane II to tetrahydrofuran solutions of a base of moderate steric requirements, such as lithium diisopropylamide or lithium *N*-isopropylcyclohexylamide, followed sequentially by treatment with trimethylchlorosilane and alkaline hydrogen peroxide gives only siamyl alcohol and octanal (60–85% yields), the normal oxidation products of II.[2] No silylated derivatives of the alkyl groupings were detected.

Addition of II to equivalent amounts of LiTMP in tetrahydrofuran produces a light red solution. Addition of trimethylchlorosilane to the reaction mixture gives an immediate precipitate of lithium chloride and subsequent peroxide oxidation furnishes 3-trimethylsilyloctanal in overall yields (from 1-octyne) of 75%. This result is rationalized by the formation of a boron-stabilized carbanion as shown in eq 3.

Li
|
II + LiTMP —→ CH₃(CH₂)₄CHCH=CHB(Sia)₂ +

Si(CH₃)₃
|
HTMP —(CH₃)₃SiCl→ CH₃(CH₂)₄CHCH=CHB(Sia)₂ —[O]→

Si(CH₃)₃
|
SiaOH + CH₃(CH₂)₄CHCH₂CHO (3)

(1) M. W. Rathke and R. Kow, *J. Amer. Chem. Soc.*, **94**, 6854 (1972).
(2) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 3834 (1961).