in the case of the conversion of **2** to **4**. This enhancement in the rate of hydrolysis is attributed to the +I effect of the cyclopropenyl methyl group in **5**.

Reaction of difluorocarbene with the cyclopropenone **4** under strictly anhydrous conditions provided, besides some starting material, 50% of the ethynyl derivative **1**. However, in the presence of water this transformation took a different course to yield (in 20%) the unsaturated ester **8** [mp 111–112°; $[\alpha]_D$ +58°; λ_{max} 222–224, 278, and 287 mμ (log ε 4.23, 3.24, and 3.20); ν_{max} 1760 and 1750 cm^{-1}; pmr 1.00 (18-H), 2.05 (acetate), 5.74 (d, J_{trans} = 16 cps, 21-H), 7.19 (d, J_{trans} = 16 cps, 20-H), and 7.09 ppm (t, $J_{H,F}$ = 71 cps, O–CHF_2). *Anal.* Found: C, 66.47; H, 6.72; F, 8.37]. The ethynyl derivative **1** is probably formed by simple thermal decomposition of the cyclopropenone since, when heated in diglyme in the absence of sodium chlorodifluoroacetate, the cyclopropenone **4** affords compound **1** in 49% yield.[6,7]

Ester **8** formation probably proceeds *via* attack by difluorocarbene[8] on the free α,β-unsaturated acid **9** [mp 175–177°; $[\alpha]_D$ +73°; λ_{max} 278 and 287 mμ (log ε 3.31 and 3.27); ν_{max} 3420, 3190, 1732, and 1713 cm^{-1}; pmr 1.00 (18-H), 2.06 (acetate), 5.78 (d, J_{trans} = 16 cps, 21-H), 7.15 (d, J_{trans} = 16 cps, 20-H), and 9.83 ppm (carboxyl H, exchanged with D_2O). *Anal.* Found: C, 71.78; H, 7.59]. When this reaction is run in the presence of water the yield of difluoromethyl ester[8] rises to 48%.

Reaction of **3** with sodium hydride in benzene solution afforded the difluoromethylene cyclopropene **10** [mp 109–111°; $[\alpha]_D$ +31°; λ_{max} 232, 278, and 287 mμ (log ε 4.46, 3.33, and 3.29); ν_{max} 1855 and 1775 cm^{-1}; pmr 0.95 (18-H) and 2.20 (acetate); ^{19}F nmr 92.4 (dd, $J_{4'F,4'F}$ = 117 cps, $J_{2'F,4'F}$ = 43 cps), 94 (dd, $J_{4'F,4'F}$ = 117 cps, $J_{2'F,4'F}$ = 43 cps, 4,4′-difluoromethylene), 140 ppm (*t*, $J_{2'F,4'cF} = J_{21F,4'tF}$ = 43 cps, 2′F), *m/e* 432 (M^+). *Anal.* Found: C, 69.49; H, 6.43; F, 14.00]. The structure of **10** is supported by its physical properties[9] and represents the first example of a methylenecyclopropene not stabilized by electron-delocalizing substituents.

The formation of **10** can be rationalized as resulting from the C-21 anion[10] which undergoes bond cleavage and expulsion of fluoride ion as indicated in **11**.

Acknowledgment. We wish to thank Miss J. Tremble and Drs. T. Toube, L. Throop, and L. T kes for the determination of physical properties of compounds here reported.

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(7) This observation has some precedent; *cf.* R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965); R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965).

(8) R. A. Mitsch and J. E. Robertson, *J. Heterocyclic Chem.*, **2**, 152 (1965).

(9) A. S. Kende, *J. Am. Chem. Soc.*, **85**, 1882 (1963); M. A. Battiste, *ibid.*, **86**, 942 (1964); W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964); E. D. Bergmann and I. Agronat, *ibid.*, **86**, 3587 (1964); A. S. Kende and P. T. Izzo, *ibid.*, **86**, 3587 (1964); T. Eicher and A. Loschner, *Z. Naturforsch.*, **21b**, 899 (1966), and references cited.

(10) It was neither possible to exchange the C-21 proton with D_2O nor to intercept this anion with methyl iodide, since attempted alkylation afforded **10**. These observations support the concerted mechanism shown in **11**.

(11) Syntex Postdoctoral Fellow, 1966–1967.

(12) Institute of Steroid Chemistry, Syntex Research, Palo Alto, Calif.

(13) Deceased, Jan 6, 1966.

P. Anderson,[11] P. Crabbé, A. D. Cross,[12] J. H. Fried[12]
L. H. Knox,[13] J. Murphy,[12] E. Velarde
Research Laboratories, Syntex, S.A.
México, D. F., Mexico

Received February 6, 1968

The Formation and Reactivity of Benzocyclobutenone Anion

Sir:

The benzocyclobutadiene character of the enolate anion of benzocyclobutenone (**1a**) might lead to the prediction of an unusually low acidity of the methylene hydrogens of this compound. An unsuccessful attempt to observe base-catalyzed hydrogen–deuterium exchange as a probe in evaluating this prediction has been reported.[1,2] These data have demonstrated that the carbonyl of benzocyclobutenone is highly reactive toward nucleophiles and that the four-membered ring cleaves with great facility, but have not provided an answer to this interesting question. Since the acidity of the methylene hydrogens of benzocyclobutenone is of interest from both a synthetic as well as theoretical standpoint, we have investigated some base-catalyzed reactions of this compound.

Addition of **1a**[3] or **1b**[1] to a suspension of NaH in DMF results in a moderately rapid evolution of hydrogen gas (reaction time ~30 min at 25°). Acidic workup of the reaction mixture yields as the major products (~50%) dimers **2a**[4] and **2b** derived from the original ketones. The dimeric nature of these products could be verified by their mass spectral molecular weights (**2a** *m/e* 236 ($C_{16}H_{12}O_2$), **2b**, *m/e* 292 ($C_{20}H_{20}O_2$)). The infrared spectra of **2a** and **2b** show carbonyl bands at 1690 cm^{-1} characteristic of an open-chain or nonstrained ketone. Both products contain four enolizable hydrogens, as evidenced by rapid acid-catalyzed hydrogen–deuterium exchange which could be detected by nmr spectroscopy. The nmr spectrum of **2a** (τ 2.15–3.0 m and 5.41 s; relative intensities 2:1) and **2b** (τ 3.1 s, 3.22 s, 6.0 s, and 7.79 s; relative intensities 1:1:2:6) combined with the above data are consistent with the dibenzo[*a*,*e*]cycloocta-3,7-dione and 3′,5′,8′,10′-tetramethyldibenzo[*a*,*e*]cycloocta-3,7-dione[5] structures indicated. The structure of **2a** can be conclusively demonstrated by comparison of its physical properties to those reported for this compound.[6] The origin of **2a** and **2b** can readily be accounted for according to Scheme I.[7]

Addition of **1a** or **1b** to a suspension of NaH in DMF containing 1 equiv of benzaldehyde yields as the major

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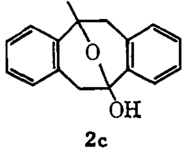
(1) An initial successful report of base-catalyzed exchange for this compound (H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 749 (1960)) has recently proven to be incorrect: H. Hart, J. A. Hartlage, R. W. Fish, and R. R. Rafos, *J. Org. Chem.*, **31**, 2244 (1966).

(2) M. P. Cava (unpublished work) has observed partial base-catalyzed hydrogen–deuterium exchange in 2-carbomethoxybenzocyclobutenone.

(3) Synthesized by a modification of the procedure of H. Wasserman and J. Solodar, *J. Am. Chem. Soc.*, **87**, 4002 (1965).

(4) Compound **2a** is actually isolated primarily as a hydrate (**2c**) assigned the structure indicated on the basis of the nmr spectrum (τ 2.2–3.2 m, 6.25 s, 6.85, and 6.90, AB quartet, *J* = 16.5 cps; relative intensities 4:1:2), a strong OH band in the infrared, and a correct elemental analysis. Heating this hydrate above its melting point for a short period converts it to the ketone described in the text.



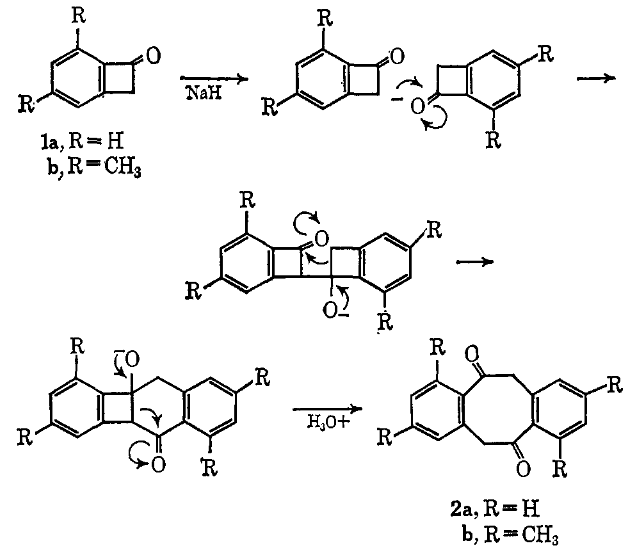
2c

(5) This compound gave a satisfactory elemental analysis.

(6) S. Wawzonek, *J. Am. Chem. Soc.*, **62**, 745 (1940); A. Cope and S. W. Fenton, *ibid.*, **73**, 1671 (1951).

(7) This scheme is not intended to represent a detailed mechanism, but rather a plausible reaction sequence.

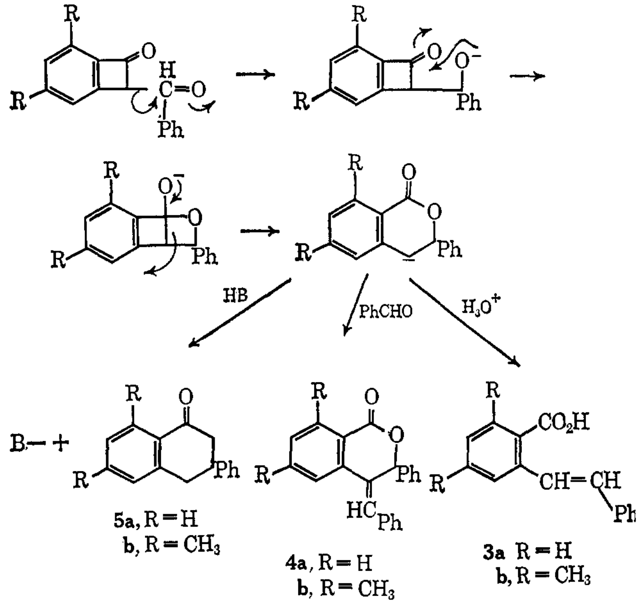
Scheme I



products (~50%) carboxylic acids **3a** and **3b**, along with trace amounts of four lactones, **4a**,**4b** and **5a**,**5b**. The mass spectral molecular weights of **3a** and **3b** (**3a**, m/e 224 ($C_{15}H_{12}O_2$); **3b**, m/e 252 ($C_{17}H_{16}O_2$)) and nmr spectra (**3a**, τ −2.3 broad s, 2.08 and 3.14, AB quartet, J = 16.5 cps, and 2.06–2.94 m; relative intensities 1:2:9; **3b**, τ 0.6 broad s, 2.90 doublet of an AB quartet, J = 16.5 cps, 2.4–3.06 m, 7.75 s, and 7.84 s; relative intensities 1:1:8:3:3) are consistent with the stilbene-2-carboxylic acid and 3,5-dimethylstilbene-2-carboxylic acid[5] structures indicated. Conclusive proof of structure **3a** could be obtained by comparison of the physical properties of this compound to those reported[8] for stilbene-2-carboxylic acid.

The mass spectral molecular weights of **4a**[5] and **4b**[5] (**4a**, m/e 312 ($C_{22}H_{16}O_2$); **4b**, m/e 340 ($C_{24}H_{20}O_2$)), infrared spectra (**4a**, ν 1726 (C=O), 1273 and 1225 (C—O) cm^{-1}; **4b**, ν 1720 (C=O), 1242 and 1236 (C—O), and nmr spectra (**4a**, τ 2.1–2.8 m and 3.37 s; relative intensities 15:1; **4b**, τ 2.3–2.8 m, 3.0 s, 3.4 s, 7.42 s, and 7.6 s; relative intensities 12:1:1:3:3) are consistent with the structures indicated. The two remaining lactones, **5a** and **5b**, were not isolated as crystalline compounds, but the infrared spectra (**5a**, ν 1726 (C=O), 1273, 1225 (C—O) cm^{-1}; **5b**, ν 1720 (C=O), 1242 and 1236 (C—O) cm^{-1}) and nmr spectra (**5a**, τ 1.8–3.0 m, 4.37 (X part of an ABX), and 6.75 (AB part; $\Delta\nu_{AB}$ = 24 cps, J_{AB} = 17 cps, J_{AX} = 12.5 cps, and J_{BX} = 2.5 cps); relative intensities 9:1:2; **5b**, τ 2.2–2.8 m, 4.64 (X part of an ABX), 6.97 (AB part; $\Delta\nu_{AB}$ = 24 cps, J_{AB} = 17 cps, J_{AX} = 12.5 cps, and J_{BX} = 2.5 cps), 7.35 s, and 7.73 s; relative intensities 7:1:2:3:3) are consistent with the structures assigned. The products arising from the reaction of benzocyclobutenone and benzaldehyde in the presence of NaH can be accounted for according to Scheme II.[7]

Scheme II



Addition of **2b** to a suspension of NaH in DMF containing either methyl iodide or methyl chloroformate yielded only alkylated or acylated dimer. Therefore the carbonyl of benzocyclobutenone is more reactive toward condensation than a typical ketone, but less reactive than an aldehyde. Although these data do not establish the enolate character of the anion of benzocyclobutenone, work presently in progress to obtain quantative data concerning the acidity of benzocyclobutenone as well as additional base-catalyzed reactions of this system may resolve this point.

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Domenick J. Bertelli, Phillip Crews
Department of Chemistry, University of California, Santa Barbara
Santa Barbara, California

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[8] D. F. DeTar and L. A. Carpino, *J. Am. Chem. Soc.*, **78**, 475 (1956).

Ylides from Salts of Sulfoximines[1,2]

Sir:

Sulfur ylides are now well established as reagents for organic synthesis. In large part the synthetic achievements with these reagents have originated from the work of Corey and coworkers.[3] This preliminary report describes a new series of oxosulfonium salts and some reactions of their derived ylides.

A series of N,N-dimethylaminoalkylaryloxosulfonium fluoroborates[4] has been prepared by the sequence shown in Scheme I. The oxosulfonium salts

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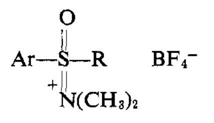
[1] (a) Part X in the series Chemistry of Sulfoxides and Related Compounds; (b) Part IX: C. R. Johnson, J. C. Sharp, and W. G. Phillips, *Tetrahedron Letters*, 5299 (1967).

[2] We gratefully acknowledge support by the National Science Foundation (Grant No. GP-5944).

[3] (a) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965); (b) E. J. Corey, M. Jautelat, and W. Oppolzer, *Tetrahedron Letters*, 2325 (1967); (c) E. J. Corey and M. Jautelat, *J. Am. Chem. Soc.*, **89**, 3912 (1967).

[4] Systematic nomenclature for the nitrogen analogs of sulfoxides and sulfones is not well established. The name sulfone imine has been proposed (R. G. Laughlin and W. Yellin, *ibid.*, **89**, 2435 (1967)) for compounds previously known as "sulfoximines"; accordingly, the final product shown in Scheme I would be termed N,N-dimethylamino alkyl aryl sulfone iminium fluoroborate. The origin of the latter name is more obvious from the resonance form.



$$\mathrm{Ar{-}\overset{\overset{\large O}{\|}}{\underset{\underset{+\,N(CH_3)_2}{\|}}{S}}{-}R}\quad BF_4^-$$

From the work in our laboratories on such salts it appears that the oxosulfonium nomenclature is more descriptive.