As previously shown,[2] mild aqueous alkaline treatment converts the non-basic antimycin to the antimycin lactone (II)[1,3] and—depending on conditions—either formic acid and antimycic acid,[1,4] or ar-N-formylantimycic acid (blastmycic acid) (III).[5] The infrared spectrum of antimycin A_1-

($C_{28}H_{40}N_2O_9$) or antimycin A_3 (blastmycin) ($C_{26}H_{36}$-N_2O_9)[6] in chloroform displays carbonyl absorption due to ester (5.73 μ), N-formyl (5.90 μ) and NH-acyl (6.09, 6.56 μ) functions, and reveals that a five-membered lactone ring is absent.[1-5] The ultraviolet spectra of antimycin A_1 (λ_{max} (alc.) 226, 320 mu log ϵ 4.54, 3.68) and III (λ_{max} (alc.) 223, 318 mu log ϵ 4.43, 3.76) are nearly identical, as are the spectra of antimycin A_3 (phenolic) methyl ether (Ic), m.p. 109–110° (C, 60.60; H, 7.03; OCH₃, 5.75) and the methyl ether methyl ester (non-crystalline) (IIIa) of III (both λ_{max} (alc.) 220, 294 mμ, shoulder at 215 mμ). Further, in the 5–7 u region of the infrared, IIIa (5.74, 5.89, 6.01, 6.23 (w), 6.31 and 6.60 μ) and Ic (5.73, 5.88, 6.00, 6.23 (w), 6.31 and 6.60 μ) are virtually superimposable. These comparisons demonstrate the presence in the antibiotic of the o-OH-m-NHCHO-C_6H_3-CONH-system, isolated from other chromophores.

Conversion of antimycin A_1 by ammonia to N-formylantimycyl amide, m.p. 189.5–191° (C, 51.55; H, 5.43; N, 15.07) shows that the antimycic acid carboxyl group is masked in the intact antibiotic. Hot alcoholic hydrochloric acid serves only to transform the antibiotic to deformylantimycin A_1 hydrochloride, m.p. 190–191° dec. (C, 58.10; H, 7.36; infrared peaks at 5.72, 6.02 and 6.57 μ), which regenerates the parent material on treatment with formic acid. Such behavior renders unlikely structures which bind the potential carboxyl groups of II and III in the form of (a) hemi-ketal esters, or O-acyl derivatives of (b) ketone enols, (c) 1,3-dicarbonyl enols or (d) ester enols. Type (c) esters also are excluded by the ultraviolet data listed above; and the absence of an infrared peak below 5.73 μ[7] supports the conclusion that type (b) and (d) esters do not form part of the antimycin system.

Attempts to detect either a ketonic or an alcoholic function in antimycin have been, without exception, unavailing. For example, antimycin O-methyl ether is unchanged on attempted acetylation or chromic acid oxidation. Antimycin itself is not convertible to carbonyl derivatives; is not

(2) G. M. Tener, F. M. Bumpus, B. R. Dunshee and F. M. Strong, This Journal, **75**, 1100 (1953).

(3) E. E. van Tamelen, F. M. Strong and U. C. Quarck, ibid., **81**, 750 (1959).

(4) G. M. Tener, E. E. van Tamelen and F. M. Strong, ibid., **75**, 3623 (1953).

(5) H. Yonehara and S. Takeuchi, J. Antibictics (Japan), Ser. A, **11**, 122, 254 (1958).

(6) W. Liu and F. M. Strong, This Journal, **81**, 4387 (1959).

(7) See H. H. Wasserman and P. S. Wharton, Tetrahedron, **3**, 321 (1958), and references cited therein.

hydrogenated over platinum in acetic acid in the presence of hydrochloric acid; and is only deformylated on attempted mercaptanolysis. Further, the infrared spectrum of deformyl antimycin hydrochloride (in chloroform) shows the absence of a ketone carbonyl group. We conclude that the antimycin system is dilactonic, and represented by structure I. This expression replaces earlier proposals,[5,8] and taken together with previous findings[1-5] requires the specific structure Ib for antimycin A_1, and Ia for antimycin A_3.

(8) Strong, "Topics in Microbial Chemistry," Squibb Lectures on Chemistry of Microbial Products (1956), John Wiley and Sons, Inc., New York, N. Y., 1958, Vol. I, p. 1.

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BICYCLO[2,2,2]-2,5,7-OCTATRIENE (BARRELENE), A UNIQUE CYCLIC SIX ELECTRON Pi SYSTEM

Sir:

Recently there has been considerable interest in bicyclo-[2,2,2]-2,5,7-octatriene (I) as a result of the possibility, first noted by Hine,[1] that this molecule might be aromatic. We now report the synthesis of this molecule using α-pyrone and methyl vinyl ketone as basic starting materials. We suggest the name barrelene because of the barrel shaped electron cloud.

I

II
a, R = COCH₃
b, R = C(NOH)CH₃
c, R = C(NOTs)CH₃

III
d, R = NHCOCH₃
e, R = NH₂
f, R = ⁺N(CH₃)₃ I⁻

α-Pyrone-5-carboxylic acid[2] was decarboxylated in 50–90% yield over copper at 650°, thus affording the critical and previously difficultly available[3] starting material α-pyrone in large quantity.[4]

A decarboxylative double diene synthesis was effected by heating α-pyrone with excess methyl vinyl ketone, affording both 5,7-diacetylbicyclo-[2,2,2]-2-octene (IIa) and 5,8-diacetylbicyclo[2,-2,2]-2-octene (IIIa). The solid isomer, m.p. 85–86°, tentatively assigned the more symmetrical

(1) J. Hine, et al., This Journal, **77**, 594 (1955).

(2) Org. Syn., **31**, 23 (1951).

(3) E.g., v. Pechmann, Ann., **264**, 272 (1891).

(4) The essentials of this procedure resulted from exploratory research of Mr. T. Beckmann with H. E. Z. We also are indebted to Mr. D. Paskovich for devoting two weeks of his research time to developing a scaled up procedure.

structure IIa, was utilized for further synthesis (*Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.95; H, 8.31). Bis-2,4-dinitrophenylhydrazide, m.p. 238–239° (*Anal.* Calcd for $C_{24}H_{28}N_4O_4$: C, 52.17; H, 4.35; N, 20.29. Found: C, 51.85; H, 4.38; N, 20.46). Dioxime (IIb), m.p. 228–229°. (*Anal.* Calcd for $C_{12}H_{18}N_2O_2$: C, 64.91; H, 8.10; N, 12.61. Found: C, 64.51; H, 8.29; N, 12.51). The dioxime (IIb) was converted to the di-*p*-toluenesulfonate (IIc), m.p. 141–142° (*Anal.* Calcd for $C_{26}H_{30}N_2O_6S_2$: C, 58.95; H, 5.64; N, 5.26. Found: C, 58.14; H, 5.62; N, 5.28). Solvolytic Beckmann rearrangement of IIc under alkaline conditions afforded 5,7-diacetamidobicyclo[2,2,2]-2-octene (IId), m.p. 260–261° (*Anal.* Calcd for $C_{12}H_{18}N_2O_2$: C, 64.91; H, 8.10; N, 12.61. Found: C, 64.20; H, 8.11; N, 12.62). Alkaline hydrolysis to the diamine (IIe) and quaternization with methyl iodide and sodium hydroxide afforded the dimethiodide (IIf) (*Anal.* Calcd. for $C_{14}H_{28}N_2I_2$: C, 35.18; H, 5.85; N, 5.85. Found: C, 34.53; H, 6.07; N, 5.26). Pyrolysis of the derived dimethohydroxide at 90–110° yielded an oil. Macro vapor phase chromatography of this (TCP, 1 inch × 6 ft., 300 cc. N_2/min., 15 mm. outlet press., 75° column) afforded as a minor product benzene (time 3.5 min.), identified by its infrared spectrum and as the major product barrelene (I) (37% based on dimethiodide; time 14 min.). Barrelene thus obtained melted at 15.0–16.0° (*Anal.* Calcd for C_8H_8: C, 92.30; H, 7.70. Found: C, 92.60; H, 7.73).

Infrared: ($CHCl_3$) strong peaks only at 3.29, 3.39, 6.34, 7.50, 9.80, 11.11, 12.35, 14.30 (broad and intense) microns; also 6.20 wk; in CS_2 also 8.20 microns. Ultraviolet: λ_{max} = 208.0 mμ (log ϵ 3.05), 239 mμ (2.48) in ethanol at 4.99 × 10^{-4} m./lit.

N.m.r.[5]: (*cf.* Table I) the vinyl hydrogen (at C-2) absorption was split (J_{12}) by spin coupling with the C-1 bridgehead hydrogen and split again (J_{13}) by weaker coupling with the C-4 hydrogen, thus giving the observed quartet. The bridgehead hydrogen absorption was split into a quartet by three adjacent (C-2, C-6, C-7) hydrogens and each component was split again into a quartet by coupling with the three equivalent hydrogens one carbon more removed. This sixteen component pattern is predicted nicely (Table I; values in

TABLE I[a]

NUCLEAR MAGNETIC RESONANCE DATA

Vinyl H Peaks: 134.0, 132.7, 132.1, 130.4 (all very strong). Bridgehead Peaks: 96.7, (96.5), 95.0 (95.0), 94.4 (94.4), 93.3 (93.5), 92.9 str. (92.9 str.), 92.4 (92.3), 92.0 (92.0), 91.3 str. (91.3 str.), 90.5 str. (90.9 str.) 90.2 (90.2), 89.8 (89.9), 89.2 str. (89.3 str.), 88.6 (88.7), 87.7 (87.8), 87.1 (87.2), 85.7 (85.7).

[a] C.p.s. downfield from tetramethylsilane; predicted values in parenthesis; run at 40 mc.

parentheses) by use of the equation $\bar{\nu}$ = 91.1 ± nJ_{12} ± mJ_{13} cps., where 91.1 cps. is the center of the sixteen component pattern, J_{12} = 2.10 cps. and J_{23} = 1.50 cps. are taken from the vinyl quartet, and where n and m are independently =

(5) We thank Mr. C. Creswell for running the n.m.r. spectra.

$^1/_2$ or $^3/_2$. The area under the peaks was in the ratio of 2.95:1 as expected.

Hydrogenation in ethanol with PtO_2 proceeded with constant uptake to 92% of the theoretical, giving bicyclo[2,2,2]octane, m.p. 171–172° after vapor phase chromatography (only one peak), identified also by infrared.

In contrast to bicyclo[2,2,2]-2,5-octadiene, reported by Grob[6] largely to decompose to benzene and ethylene, barrelene was recoverable (isolative vapor chromatography) to the extent of at least 71% after heating to 200° for 24 hr. At 250° it decomposed to benzene and acetylene.

Simple LCAO MO calculations show that were 2,6-overlap as effective as 2,3-overlap, barrelene would have the same delocalization energy (2β) as benzene. However, calculation suggests only 22.5% as much overlap, leading to the prediction that barrelene should have no delocalization energy, although the six pi electrons appear in three delocalized orbitals (deg. pair at 1.225β and one at 0.55β; note β is neg.) Thus barrelene is subject to electron delocalization without the usually attendant delocalization energy. The ultraviolet bands probably arise from electron excitation from the 0.55β orbital to two orbitals centering about a −0.775β degenerate pair predicted by the simple Hückel calculations.

This research together with the results of further investigations will be reported in more detail later.

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(6) C. A. Grob, H. Kny and A. Gagneux, *Helv. Chim. Acta,* **40**, 130 (1957).

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DITHIETENE AND BICYCLOÖCTATRIENE RING SYSTEMS FROM BIS-(FLUOROALKYL)-ACETYLENES

Sir:

Bis-(fluoroalkyl)-acetylenes have been found to undergo addition reactions with sulfur and phosphorus to form new types of cyclic compounds and with aromatic compounds to form bicycloöctatriene derivatives.

Thus, when hexafluoro-2-butyne[1] was passed through vapors of boiling sulfur under atmospheric pressure, bis-(trifluoromethyl)-1,2-dithietene (I) was obtained in 80% yield. The dithietene is a yellow liquid; b.p. 95–96°; $\lambda_{max}^{isooctane}$ 238 mμ (ϵ 7440), 340 mμ (ϵ 80). Strong infrared absorp-

(1) A. L. Henne and W. G. Finnegan, THIS JOURNAL, **71**, 298 (1949).