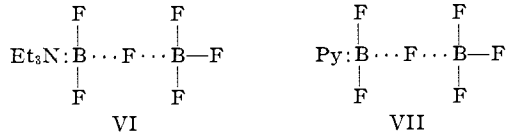
and 3-picoline in toluene solution absorb 2 molar equivalents of boron trifluoride. Consequently, in these cases the addition compounds exist in solution as well as in the pure phases. Although these compounds might be formulated as ion-pairs, $Et_3N{:}BF_2{}^+BF_4{}^-$ and $Py{:}BF_2{}^+BF_4{}^-$, their properties appear to be in better accord with the singly-bridged structures (VI, VII).



VI VII

An examination of the action of diborane on borane addition compounds at low temperatures has revealed similar higher order addition compounds. Thus, as shown by the vapor pressure data in Table I, pyridine–borane in diglyme solution absorbs a second molar equivalent of borane at 0° and a third at −64°: $Py{:}BH_3{\cdot}BH_3$ and $Py{:}BH_3{\cdot}B_2H_6$.

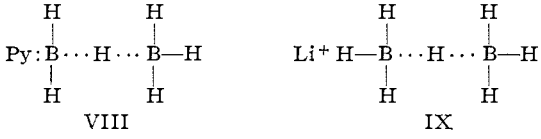
TABLE I

VAPOR PRESSURE–COMPOSITION DATA FOR DIBORANE AND PYRIDINE IN DIGLYME

0°		−64°	
Mole ratio B_2H_6/Py	Press., mm.	Mole ratio B_2H_6/Py	Press., mm.
0.51	2	1.15	2
.69	6	1.38	5
.79	8	1.51	7
.98	12	1.57	10
1.06	52	1.74	19
1.19	137	2.30	46
1.28	195	2.82	74

Similarly, triethylamine–borane adds a mole of borane at −64°, forming $Et_3N{:}BH_3{\cdot}BH_3$.

Finally, we have observed that both lithium and sodium borohydrides in diglyme solution absorb a molar equivalent of borane at 0°. Although the amine addition compounds might be formulated as borohydride ion-pairs $PyBH_2{}^+BH_4{}^-$, such a formulation is not possible for the corresponding derivatives of lithium and sodium borohydride. In view of the similarity of the phenomena under discussion, it appears preferable at this time to formulate these addition compounds in terms of single hydrogen bridges (VIII, IX).



VIII IX

The results suggest that numerous singly-bridged derivatives (without additional bonding) must exist in electron deficient systems and that electron valency theories proposed to account for the existence of doubly-bridged derivatives should, in all probability, also provide for the formation and existence of related singly-bridged structures.[5]

The assistance afforded by grants from the National Science Foundation and the Office of Ordnance Research is gratefully acknowledged.

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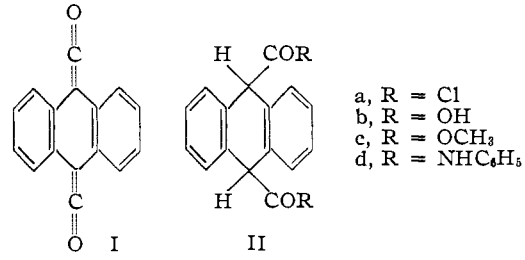
RECEIVED FEBRUARY 6, 1957

(5) It should be pointed out that the discussion by R. E. Rundle, *J. Chem. Phys.*, **17**, 671 (1949), strongly implies that singly-bridged derivatives of the type here reported should possess a measure of stability.

ANTHRAQUINOKETENE[1]

Sir:

Realization of an isolable, monomeric bisketene, anthraquinoketene (I), has been achieved by the dehydrochlorination of 9,10-dihydroanthracene-9,-10-dicarbonyl chloride (IIa) using triethylamine. Except for the unique case of carbon suboxide this represents the first successful preparation of a bisketene. Although a substantial part of the extensive studies of ketenes has been concerned with their synthesis[2] the previous attempts to obtain a bisketene seem to have failed either because of the low reactivity of the starting material used or because of the rapid spontaneous polymerization of the product formed.[3]



a, R = Cl
b, R = OH
c, R = OCH_3
d, R = NHC_6H_5

I II

With all operations performed under an atmosphere of dry nitrogen, a benzene solution of IIa was permitted to react with triethylamine at room temperature for several hours, the quantitative precipitate of triethylamine hydrochloride filtered, and the red benzene filtrate concentrated. The bisketene I separated as orange-red crystals (needles) in *ca.* 90% yield. *Anal.* Calcd. for $C_{16}H_8O_2$: C, 82.75; H, 3.47. Found: C, 82.94; H, 3.52. Upon heating, I slowly transformed into a dark colored substance which is possibly polymeric. The thermal transformation appeared to be instantaneous at 150° but no m.p. was observed below 300°. In the infrared I showed strong absorption at 4.80 μ but no appreciable absorption in the carbonyl region (see Fig. 1). The ultra-

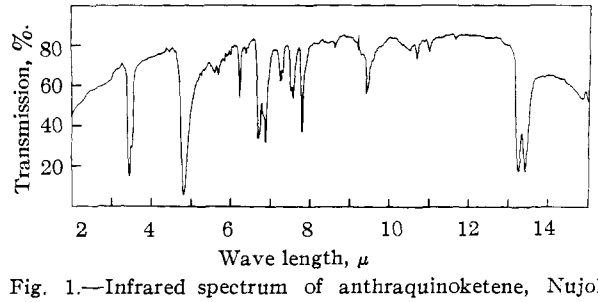


Fig. 1.—Infrared spectrum of anthraquinoketene, Nujol mull.

(1) The work reported here was done as part of a general research program in organic chemistry at Cornell University sponsored by the B. F. Goodrich Company.

(2) W. E. Hanford and J. C. Sauer, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 109–140.

(3) H. Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, pp. 7–31.

violet absorption spectrum of I in isoöctane showed the following maxima (log ϵ's in parentheses): 216 mμ (4.70); 256 mμ (4.36); 288 mμ (4.35); 395 mμ (2.77); with shoulders at 252 mμ (4.34) and 320 mμ (3.50).

The bisketene I in benzene solution reacted essentially instantaneously with oxygen, water, methanol and aniline. The bisketene–oxygen product was a yellow amorphous solid, m.p. 175–178° dec., insoluble in the common organic solvents. Its infrared spectrum showed absorption in the carbonyl region at 5.58 and 5.75 μ. The insoluble oxygen product (0.5 g.) upon prolonged boiling with dilute aqueous sodium hydroxide gave a solution from which, after acidification, crude 9,10-anthracenedicarboxylic acid (0.5 g.) separated, m.p. 328–332° dec. The infrared absorption spectrum of this acid was identical with that of pure 9,10-anthracenedicarboxylic acid, m.p. 341° dec. Part of the crude acid was converted to the dimethyl ester, m.p. 179–181° (lit.[4] value 180–181°).

With water I formed a mixture of *cis*- and *trans* - 9,10 - dihydroanthracene - 9,10 - dicarboxylic acid (IIb), m.p. 285° dec.,[5,6] identified by direct comparison with authentic IIb. Treatment of I with methanol gave a mixture of the *cis* and *trans* isomers of the dimethyl esters IIc, m.p. 137–155°.[5] *Anal.* Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 73.12; H. 5.49. This IIc was indistinguishable from IIc prepared by methanolysis of IIa. A mixture of dianilides (IId), m.p. 220–248° identical with that prepared directly from IIa was obtained on treatment of I with aniline. A sharp melting IId, m.p. 254–255°, was obtained after several recrystallizations from ethanol. *Anal.* Calcd. for $C_{28}H_{22}O_2N_2$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.10: H, 5.50; N, 6.51.

(4) H. Beyer and H. Fritsch, *Ber*, **74**, 494 (1941).

(5) J. Mathieu, *Ann. chim.*, **20**, 215 (1945); *Compt. rend.*, **219**, 555 (1944).

(6) A. H. Beckett, *J. Chem. Soc.*, 4159 (1955).

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RECEIVED MARCH 18, 1957

THE STRUCTURE OF THE ANTIBIOTIC NEOMETHYMYCIN

Sir:

We have recently[1] described experiments which demonstrate that the macrolide antibiotic methymycin[2] possesses structure Ia. From the fermentation mother liquors[3] it has been possible to isolate a second antibiotic ("neomethymycin")—isomeric with methymycin ($C_{25}H_{43}NO_7$)—for which the expression IIa has now been established.

Hydrochloric acid hydrolysis[4] of neomethymycin (IIa) (m.p. 156–158°, $[\alpha]D$ +93° (all rotations in $CHCl_3$), λ_{max}^{EtOH} 227.5 mμ, log ϵ 4.10, $\lambda_{max}^{CHCl_3}$ 2.93, 5.76, 5.90 and 6.10 μ; found for $C_{25}H_{43}NO_7$: C, 63.75; H, 9.04; N, 3.07; N-CH_3, 5.90; C-CH_3, 16.76; -OCH_3, 0.00; neut. equiv. (perchloric acid titration), 472), yielded desosamine hydrochloride,[4a] thus demonstrating that any structural difference between methymycin and neomethymycin must reside in the aglycone portion. Cleavage of neomethymycin with aqueous sulfuric acid[1] gave two products. The more polar one represented the authentic aglycone, neomethynolide (IIb) (m.p. 186–187°, $[\alpha]D$ +108°, λ_{max}^{EtOH} 227.5 mμ, log ϵ 4.10, $\lambda_{max}^{CHCl_3}$ 2.93, 5.75, 5.90 and 6.10 μ; found for $C_{17}H_{28}O_5$: 65.61; H, 9.02; C-CH_3, 21.74), as demonstrated by its analytical composition and retention of all pertinent ultraviolet and infrared bands associated with the lactone and unsaturated carbonyl chromophores of neomethymycin (IIa). Ozonolysis (decomposition with alkaline peroxide) of neomethynolide (IIb) afforded in good yield the lactonic acid III (m.p. 125–126°, $[\alpha]D$ +42°) already obtained earlier by permanganate oxidation of the antibiotics pikromycin,[5] narbomycin[5] and methymycin.[1] This establishes the carbon sequence from C-1 to C-7[6]; C-7 to C-9 can only be represented by $-\overset{9}{C}(=O)-\overset{8}{CH}=\overset{7}{CH}-$ or $-\overset{9}{CH}=\overset{8}{CH}-\overset{7}{C}(=O)-$ in order to explain the ready scission of the molecule at C-7 with formation of a carboxyl group.

In marked contrast to methynolide (Ib), neomethynolide (IIb) forms a diacetate (m.p. 199–201°, $[\alpha]D$ +84°; found for $C_{21}H_{32}O_7$: C, 63.90; H, 8.04; CH_3CO, 22.29), gives a positive iodoform test (as does dihydroneomethynolide[7]) and yields acetaldehyde (rather than propionaldehyde) upon successive treatment with lithium aluminum hydride and periodic acid.[8] These results require partial structures IV or V and together with the acid III account for four of the five C-methyl groups of neomethynolide (IIb). The remaining C-methyl group must be present as an additional $-\overset{CH_3}{\underset{|}{CH}}-$ grouping since location on the double bond is excluded by the ultraviolet absorption maximum.

The proper combination of these structural fragments follows from the structure of the second sulfuric acid cleavage product of neomethymycin (IIa) which has been named cycloneomethynolide (VIa). This substance (b.p. 140° (0.01 mm.), $[\alpha]D$ −39.5°, no high ultraviolet max., $\lambda_{max}^{CHCl_3}$

(1) C. Djerassi and J. A. Zderic, THIS JOURNAL, **78**, 2907, 6390 (1956).

(2) M. N. Donin, J. Pagano, J. D. Dutcher and C. M. McKee, "Antibiotics Annual 1953–1954," Medical Encyclopedia, Inc., New York, N. Y., p. 179.

(3) Kindly supplied by Dr. J. Vandeputte (Squibb Institute for Medical Research) who first encountered the chloroform solvate of neomethymycin.

(4) C. Djerassi, A. Bowers, R. Hodges and B. Riniker, THIS JOURNAL, **78**, 1733 (1956).

(4a) R. K. Clarke, *Antibiotics and Chemotherapy*, **3**, 663 (1953); E. H. Flynn, M. V. Sigal, P. F. Wiley and K. Gerzon, THIS JOURNAL, **76**, 3121 (1954); H. Brockmann, H. B. König and R. Oster, *Chem. Ber.*, **87**, 856 (1954).

(5) R. Anliker, D. Dvornik, K. Gubler, H. Heusser and V. Prelog, *Helv. Chim. Acta*, **39**, 1785 (1956).

(6) The numbering system employed for erythromycin (K. Gerzon, E. H. Flynn, M. V. Sigal, P. F. Wiley, R. Monahan and U. C. Quarck, THIS JOURNAL, **78**, 6396 (1956)) seems suitable for all macrolide antibiotics and has been adopted in this paper.

(7) Thus showing that this could not have been due to generation of a methyl ketone by reverse aldol condensation.

(8) Neomethynolide (IIb), like Ib, is not attacked by periodic acid showing that the lactone ring is involved with one of the two hydroxyl groups of the glycol moiety.