the known homocyclopropylcarbinyl rearrangement of 8-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonyl cations[15] in step VI → VII.

In contrast to many other α-bromo ketones[9] formation of XIII is not the favored process if XII is treated with base. The title compound XIV is a minor product and must be separated by vpc from XVI and several other by-products of unknown structure. This may reflect the high strain of II and its derivatives as well as the unfavorable stereoelectronic situation, the bromine, which has to be substituted, being bound to a cyclopropane ring.[16]

Assignment of structures XIV and XVI is based on mode of formation and on spectroscopic evidence: XIV, molecular ion at m/e 162.0680 (calcd for $C_{10}H_{10}O_2$: 162.0681), other strong peaks at m/e 77, 102, and 103 (base peak); also, m* 103 → 77 (calcd: 57.56; obsd: 57.5) indicates loss of acetylene;[19] nmr (τ, CCl$_4$) 3.98 (2 H, triplet, $|J| = 2$ cps, A$_2$ part of a degenerate A$_2$X$_2$ absorption pattern), 6.25 (2 H, multiplet), 6.40 (3 H, singlet, methoxyl), 7.23 (3 H, multiplet, $\Delta\nu_{1/2} = 5$ cps). Decoupling of the 7.23 signal causes the 6.25 signal to collapse into a triplet, which is the X$_2$ counterpart of the olefinic triplet. Decoupling of the 6.25 signal (H-1 and H-6) transforms both signals at 3.98 and 7.23 into singlets. This shows that XIV is a norbornene derivative with C$_s$ symmetry[20,21] and that the carbomethoxy group is attached to C-4:[23] ir (cm^{-1}, CCl$_4$) 3060, 1713, 1440, 1390, 1261, 1247, 1195, 1178, 1107, 1085. The absorption of the carbonyl group at relatively low wave number proves the cyclopropyl conjugation:[24] XVI, mp 107–108°; no molecular ion; strong peaks at m/e 183.9803 (C$_{10}$H$_{11}$BrO$_2$ − COOCH$_3$), 163.0752 (C$_{10}$H$_{11}$BrO$_2$ − Br), 131, 103 (base peak), 77; nmr (τ, CCl$_4$) 3.53 (2 H, triplet, $|J| = 1.8$ cps), 6.33 (3 H, singlet, methoxyl), 6.56 (2 H, broad singlet, H-1 and H-5), 6.64 (1 H, triplet, $|J_{23}| = 1.7$ cps, H-3), 8.10 (1 H, broad singlet, H-8), and 8.52 (2 H, doublet of doublets, $|J_{23}| = 1.7$ cps and $|J| = 1$

(14) K. W. Rosenmund and W. Kuhnhenn, *Ber.*, **56**, 1262 (1923), and earlier references cited by these authors.

(15) (a) P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967); (b) R. M. Coates and J. L. Kirkpatrick, *J. Amer. Chem. Soc.*, **90**, 4162 (1968).

(16) The Haller–Bauer type cleavage, which has also been observed on other attempted pseudo-Favorskii reactions,[17] prevails even more if XII is treated with KOH–THF at 0°. It is also predominating with dihydro-XII. One other reason for this preference may be that cyclopropyl anions are more stable than other cyclanyl anions.[18]

(17) K. V. Scherer, Jr., R. S. Lunt, III, and G. A. Ungefug, *Tetrahedron Lett.*, 1199 (1965).

(18) *Cf.* P. G. Gassman, J. T. Lumb, and F. V. Zalar, *J. Amer. Chem. Soc.*, **89**, 946 (1967).

(19) There is a close resemblance between the mass spectra of XIV and methyl cyclooctatetraenecarboxylate, even at low IP (9 eV). At 9 eV m/e 102 is the most intense peak besides the molecular ion.

(20) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964).

(21) Isomeric structures with C$_s$ symmetry, *i.e.*, those derived from i, are considered unlikely on the basis of published nmr data on bicyclo-[3.2.0]hept-6-enes[22] and because their formation is rather improbable mechanistically.
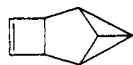
(22) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

(23) If the carbomethoxy group were located on C-5 one would expect the three cyclopropyl protons to give a broad absorption pattern, as is observed with I and appropriate derivatives of I.[3,10]

(24) Methyl tricyclo[2.2.0.0^{2,6}]hexane-1-carboxylate absorbs at 1706 cm^{-1} (J. Meinwald and J. K. Crandall, *J. Amer. Chem. Soc.*, **88**, 1292 (1966)), methyl 4-chlorobicyclo[2.2.0]hexane-1-carboxylate at 1735 cm^{-1} (W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *ibid.*, **90**, 1014 (1968)).

cps, H-2 and H-4). The configurations at C-3 and C-8 follow unequivocally from the coupling and shielding pattern:[25,26] ir (cm^{-1}, CCl$_4$) 3060, 1736, 1435, 1239, 1225, 1034, 725, 694.

Our work on the synthesis and chemistry of tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-enes is being continued.

(25) C. W. Jefford and W. Wojnarowski, *Tetrahedron*, **25**, 2089 (1969), report similar values of J_{23} in *anti*-3-halo-*exo*-tricyclo[3.2.1.0^{2,4}]- octanes.

(26) The exo–syn relation between cyclopropane ring and carbomethoxy group follows from the 1-cps splitting observed for H-2 and H-4 (probably long-range coupling with H-8) and from the strong shielding exerted by the cyclopropane ring on H-8.[27,28]

(27) H-7 of methyl bicyclo[2.2.1]hepta-2,5-diene-7-carboxylate[29] absorbs at τ 6.98. For examples and relevant literature on the use of long-range coupling and diamagnetic anisotropy as probes into tricyclo-[3.2.1.0^{2,4}]octane stereochemistry, *cf.* G. W. Klumpp, A. H. Veefkind, W. L. De Graaf, and F. Bickelhaupt, *Justus Liebigs Ann. Chem.*, **706**, 47 (1967).

(28) The relatively low-field resonance of H-3 may be a case of steric deshielding: M. A. Battiste and M. E. Brennan, *Tetrahedron Lett.*, 5857 (1966).

(29) G. W. Klumpp, and F. Bickelhaupt, *ibid.*, 865 (1966).

(30) To whom correspondence should be addressed.

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The Structure of Kromycin

Sir:

In a recent report[1] it was proposed that kromycin, the anhydro aglycone hydrolysis product of the macrolide antibiotic, pikromycin, has structure **1** and that pikromycin (**2**) is a hydroxylated narbomycin (**3**). Earlier views[2,3] had regarded pikromycin as a 12-membered

1   2, R = OH
           3, R = H
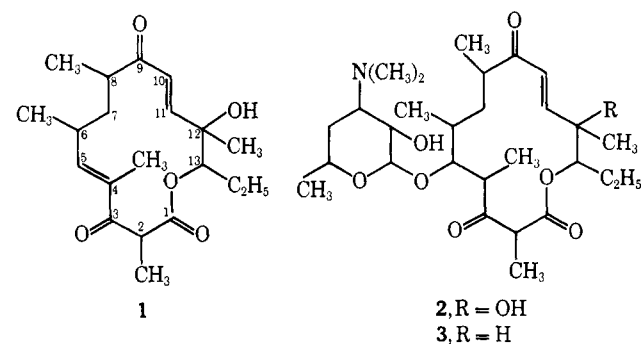
ring analog of methymycin[4] rather than the 14-membered ring structure (**2**). We now report an X-ray diffraction study of kromycin that fully corroborates structure **1** and provides a detailed configurational description of the molecule.

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(4) C. Djerassi and J. A. Ederick, *J. Amer. Chem. Soc.*, **78**, 2907, 6390 (1956).
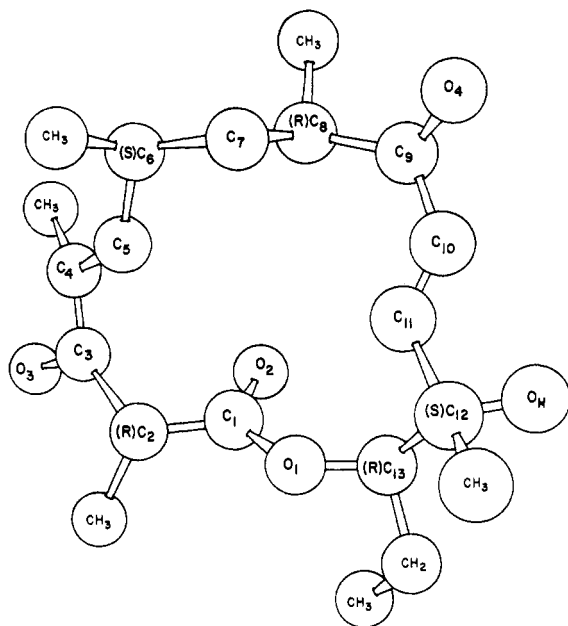
Figure 1. A perspective representation of the kromycin molecule.

A suitable crystal of kromycin, prepared by hydrolysis of pikromycin, was obtained by slow evaporation of an ether solution. Diffraction symmetry and extinctions corresponded to the orthorhombic space group $P2_12_12_1$ with $a = 8.218 \pm 0.007$, $b = 11.92 \pm 0.01$, $c = 21.93 \pm 0.02$ Å, and $Z = 4$. Intensities were measured in a θ–2θ scan mode with monochromated Mo Kα radiation on a Picker FACS-I diffractometer; of the 1737 independent reflections investigated (sin $\theta/\lambda \leq 0.58$), a total of 1539 were statistically observable. No corrections were made for extinction or absorption.

The structure was solved by direct methods[5,6] using a computerized multiple solution procedure[7] and tangent formula[8] phase refinement. Final full-matrix least-squares refinement of the structure, based upon 171 independent parameters, yielded a standard residual, $R = 0.088$, for the observed data; a weighted residual, $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ of 0.08, was obtained with $w = 1/\sigma_{F^2}$. Anisotropic thermal parameters were used for all oxygen atoms, all methyl and ethyl carbon atoms, and for atoms C_9 and C_{10} in the ring; all other atoms were included with isotropic thermal parameters. Difference Fourier syntheses established all hydrogen atoms, although some methyl hydrogens were poorly resolved.

The perspective view presented in Figure 1 displays all of the important conformational and configurational features of the molecule. The double bond at C_{10}–C_{11}, conjugated to the carbonyl at C_9, is in the trans configuration; analysis[1] of uv, ir, and nmr spectra indicates that the identical system occurs in pikromycin. The structure analysis further reveals that the double bond predicted[1] at C_4–C_5 is also trans.

Chemical evidence[9] has shown that pikromycin, and consequently kromycin, yield the same (+)-lactonic acid upon oxidation as do methymycin, neomethymycin,

and narbomycin. The absolute configuration of this lactonic acid has been determined[10] chemically and the appropriate chirality can be assigned to atoms C_6 and C_8 in the ring. The absolute chiralities of all asymmetrically substituted carbon atoms in kromycin are listed in Table I.

Table I. The Absolute Chirality of the Ring Atoms in Kromycin (K) and Erythromycin (E)

	2	3	4	5	6	8	10	11	12	13
K	R				S	R			S	R
E	R	S	S	R	R	R	R	R	S	R

A brief report[11] on the crystal structure of erythromycin provided the absolute configurations in a closely related 14-membered ring. It can be seen in Table I that carbon atoms C_2, C_8, C_{12}, and C_{13}, which have the same substituents in both molecules, display the same chiralities. The change in chirality at C_6 reflects the substitution of a hydroxyl group in erythromycin for a hydrogen atom in kromycin (and pikromycin). The carbonyl oxygen (at C_3) and the two double bonds in kromycin eliminate chirality at the remaining ring atoms. This striking equivalence and the presence of the desosamine side chain on C_5 in both erythromycin and pikromycin suggest that the latter also possesses a (R)-C_5 configuration; for similar reasons, it is probable that pikromycin also shares the (S)-C_4 configuration with erythromycin. Finally, the chemical equivalence and the structural rigidity[1,12] of the ring systems in narbomycin and kromycin indicate that they possess related configurations. Of course, the hydrogen atom at C_{12} in 3 would change the chirality to (R)-C_{12}.

Selected bond distances (esd < 0.01 Å) and bond angles (esd < 1°) are presented in Table II. The bond lengths are normal, but a slight ring strain is indicated

Table II. Selected Bond Distances (Å) and Bond Angles (Degrees)

C_1–C_2	1.497	O_1–C_1–O_2	123.5
C_1–O_1	1.321	O_2–C_1–C_2	124.6
C_1–O_2	1.207	O_1–C_1–O_2	111.9
C_2–C_3	1.536	C_1–C_2–C_3	107.2
C_3–O_3	1.222	C_2–C_3–C_4	119.1
C_3–C_4	1.470	C_2–C_3–O_3	119.3
C_4–C_5	1.335	O_3–C_3–C_4	121.5
C_5–C_6	1.508	C_3–C_4–C_5	122.2
C_6–C_7	1.522	C_4–C_5–C_6	129.7
C_7–C_3	1.491	C_5–C_6–C_7	110.3
C_8–C_9	1.468	C_6–C_7–C_8	114.9
C_9–C_{10}	1.447	C_7–C_8–C_9	111.2
C_9–O_4	1.224	C_8–C_9–C_{10}	122.3
C_{10}–C_{11}	1.273	C_8–C_9–O_4	123.0
C_{11}–C_{12}	1.507	O_4–C_9–C_{10}	114.7
C_{12}–C_{13}	1.545	C_9–C_{10}–C_{11}	127.7
C_{12}–O_H	1.432	C_{10}–C_{11}–C_{12}	127.7
C_{13}–O_1	1.443	C_{11}–C_{12}–C_{13}	110.0
		C_{12}–C_{13}–O_1	108.5
		C_{13}–O_1–C_1	117.9

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by the bond angles. Isotropic thermal parameters reveal that the atoms bonded to C_9 are relatively free to vibrate ($B \simeq 8$ Å^2) and that C_1 and C_2 are rigid ($B \simeq 3.5$ Å^2). This supports the proposal[1] that C_2 behaves like a bridgehead carbon atom in a rigid ring.

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Concerning the Phosphorescence of Phenyl Alkyl Ketones

Sir:

The spectroscopy[1–8] and photochemistry[8–15] of phenyl alkyl ketones are very interesting and have received much recent attention, primarily because the two lowest triplets of these compounds—one mostly n,π^* and one mostly π,π^*—lie very close together, their relative energy levels being quite substituent and solvent sensitive. Despite the fact that all workers acknowledge the energetic proximity of these two triplet levels, the possibility that they may attain thermal equilibrium before decaying has been almost totally ignored in published interpretations of the photobehavior of phenyl ketones.

In *nonpolar* media, the L_a π,π^* triplet of phenyl alkyl ketones presumably lies only a few hundred reciprocal centimeters above the lowest, n,π^* triplet.[3] Change to a polar medium[3,7,10] or the addition of electron-donating substituents[2,8] inverts the ordering. For ΔE of 250 cm^{-1} (700 cal), 1% of the triplets would exist in the upper state *at equilibrium*, even at 77°K. Such an equilibrium situation would not affect phosphorescence when the ^{3}n,π^* state is lower; but it would when the $^3\pi,\pi^*$ state is lower, because of the much faster emission rate of the ^{3}n,π^* state. We want to point out that some of our results as well as those of others are best interpreted as phosphorescence from an equilibrium mixture of both triplets.

Several authors have reported that in moderately polar solvents the overall phosphorescence decay of phenyl alkyl ketones is nonexponential, consisting of both a long-lived and a short-lived component.[1,3,7,10,14,16] These reports suggest that the short-lived component is the ^{3}n,π^* state, while the long-lived component is a state of mostly $^3\pi,\pi^*$ character. For such an interpretation to be correct, however, the two states could not be in equilibrium. But a nonequilibrium distribution would not be expected to occur unless internal conversion between the states were slower than phosphorescence, which seems highly improbable. Lim and coworkers have pointed out this problem and have offered a new interpretation.[17] They observe the same two-component phosphorescence from 1-indanone originally reported by Yang and Murov.[1] However, they find that 2,2-dimethyl-1-indanone, which possesses no protons α to the carbonyl, displays only short-lived emission and suggest that the long-lived emission from indanone arises from an excited enolate ion.

In agreement with previous reports, we find that all of a dozen various straight-chain phenyl alkyl ketones of the general formula PhCOCH$_2$R, as well as some ring-halogenated ketones, display both short- and long-lived phosphorescence in several solvents at 77°K.[18] The percentage of long-lived emission increases with the basicity of the solvent. However, both α,α-dimethylpropiophenone and α,α-dimethylvalerophenone display only short-lived emission through seven half-lives, even in a glass containing triethylamine. Their spectra resemble that of benzophenone closely, having classic n,π^* structure. The differences between the spectrum of valerophenone and that of its α-dimethyl derivative are very similar to those reported for the indanone system.[17] In particular, the slow emission seems to come from a state slightly *lower* in energy than the fast emitter. Table I contains those results of ours and others most pertinent to the problem.

We would make two points. First, we note that there is no significant polar solvent effect on the emission lifetime of benzophenone, whose lowest triplet is clearly n,π^*.[19] For the *p*-chloro ketone and for valerophenone, however, there is a substantial effect, such that the faster emitting component in ethanol is too slow to originate solely from an n,π^* state; such is also the case for the *p*-fluoro ketone in isopentane. Other workers have also reported intermediate phosphorescence lifetimes for *p*-chlorophenyl ketones,[6,13] which we suggest are due to the following equilibrium

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