

Figure 1. The conformational structure of leurocristine methiodide. Attached are $R_1 = \text{COOCH}_3$, $R_2 = \text{CHO}$, $R_3 = \text{OCH}_3$ and $R_4 = \text{COCH}_3$.

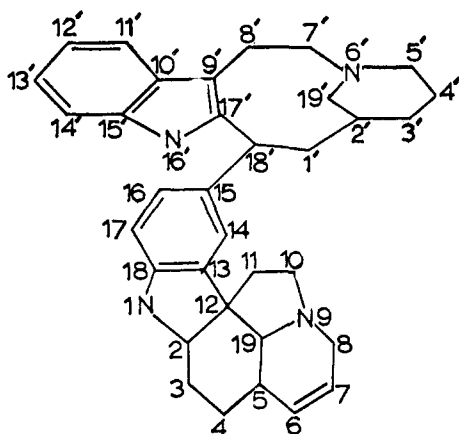


Fig. 2. The numbering system for the rings of leurocristine methiodide, LCR and VLB.

analysis, are indicated in Figure 1a. A reorientation by 180° about the bond between atoms 15 and 18' (Figure 2) has been made in order to facilitate comparison with the structure proposed in ref. 3. If the CH_3^+ on the nitrogen at position 6' is removed, then VLB has $R_1 = \text{COOCH}_3$, $R_2 = \text{CH}_3$, $R_3 = \text{OCH}_3$, and $R_4 = \text{COCH}_3$, while LCR has $R_1 = \text{COOCH}_3$, $R_2 = \text{CHO}$, $R_3 = \text{OCH}_3$, and $R_4 = \text{COCH}_3$.³ Of the ten asymmetric centers in the molecule, the five for which the assignment was made in ref. 3 are mirror images of those of the actual structure. The vindoline⁷ ring system of the molecule has asymmetric centers at 2, 3, 4, 5, 12, and 19, while the cleavamine-like ring region has centers at 2', 4', 6', and 18'. Our results for the absolute configuration of the centers 6' and 2' are in agreement with the absolute configuration assigned by Camerman and Trotter⁸ to cleavamine. In addition, leurocristine has asymmetric centers at 4' and 18', not present in cleavamine. Furthermore, the conformations of the nine-membered ring are considerably different in leurocristine and cleavamine owing to the strain imposed by the attachment at the bond (15–18') joining the two parts of the leurocristine molecule.

(7) (a) M. Gorman, N. Neuss, and K. Biemann, *J. Am. Chem. Soc.*, **84**, 1058 (1962); (b) W. W. Hargrove, *Lloydia*, **27**, 340 (1964).
 (8) N. Camerman and J. Trotter, *Acta Cryst.*, **17**, 384 (1964).

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Aryl Coupling by Irradiation of Lithium Aryls

Sir:

In connection with our studies of the photochemistry of ionic carbon species, we wish to report a novel, extremely specific photochemical reaction. On irradiation with a 450-w. Hanovia high-pressure mercury arc lamp, 0.04 *M* solutions of phenyllithium in ethyl ether¹ gave over 80% yield of biphenyl and metallic lithium. This coupling is specific, 2-naphthyllithium giving exclusively 2,2'-binaphthyl. Only small amounts of products resulting from radical attack on solvent were detected. In contrast, photochemical decompositions of organomercury,^{3,4} -bismuth,⁵ and -lead^{4,6} compounds lead to products derived from radical reactions with the solvent.

Addition of deuterium oxide in the workup of the reaction resulted in no incorporation of deuterium in the biphenyl. Thus biphenyl and not biphenyllithium is the product of the primary reaction. Phenyl radicals generated by the thermal decomposition of phenylazotriphenylmethane in ether produced only benzene and no biphenyl. Consequently the formation of biphenyl in the photolysis reaction is probably not a "simple" free radical coupling reaction. A possible pathway leading to biphenyl may be the reaction of a phenyl radical with phenyllithium. This need not be a typical radical reaction, however, since phenyllithium has been shown to be associated as dimers in ether,^{7,8} and production of a phenyl radical by homolysis of the carbon-lithium bond would probably occur in the immediate vicinity of another molecule of phenyllithium. The specificity of radical attack on the carbon-lithium bond is understandable in terms of the intermediate which would result from this reaction. Unlike the usual homolytic aromatic substitution intermediates, which are simply resonance-stabilized free radicals,⁹ this intermediate is, in effect, the considerably more stable biphenyl radical anion and lithium

(1) Phenyllithium was prepared in approximately 95% yield from bromobenzene and lithium metal,² and the solution was filtered before irradiation. All solutions were dry, oxygen free, and maintained under nitrogen.

(2) H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **54**, 1957 (1932).

(3) G. A. Razubaev, B. G. Zateev, and V. N. Myakov, *Proc. Acad. Sci. USSR*, **154**, 37 (1964), and earlier papers.

(4) J. M. Blair and D. Bryce-Smith, *J. Chem. Soc.*, 3174 (1959).

(5) D. H. Hey, D. A. Shingleton, and G. H. Williams, *ibid.*, 5612 (1963).

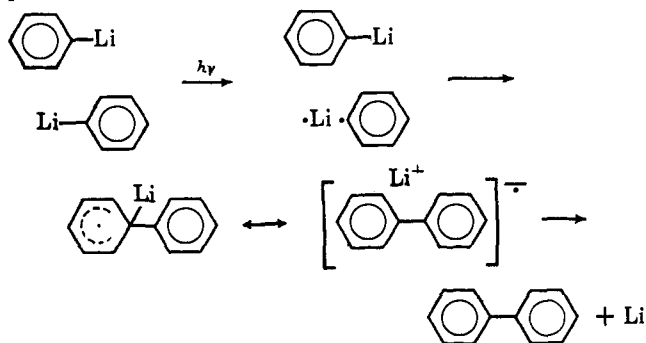
(6) P. A. Leighton and R. A. Mortensen, *J. Am. Chem. Soc.*, **58**, 448 (1936).

(7) G. Wittig, *Angew. Chem.*, **62**, 231 (1950); G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **571**, 167 (1951).

(8) T. V. Talalaeva, A. N. Rodionow, and K. A. Kocheskov, *Proc. Acad. Sci. USSR*, **154**, 47 (1964).

(9) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960.

cation. As the biphenyl radical anion is unstable in ether, lithium metal and biphenyl result.¹⁰ The postulated reaction sequence is



Alternatively, *direct* formation of biphenyl, or synchronous generation and coupling of two phenyl radicals, from the dimer would account for these results.

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(10) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

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Structure of the Complex $\text{CaBr}_2 \cdot 10\text{H}_2\text{O} \cdot 2(\text{CH}_2)_6\text{N}_4$

Sir:

A long time ago Barbieri and Calzolari¹ described a class of crystalline complexes having the general formula $\text{MeX}_2 \cdot n\text{H}_2\text{O} \cdot 2\text{HMT}$, where $\text{Me} = \text{Ca}^{2+}, \text{Ni}^{2+}, \text{Mg}^{2+}, \text{Co}^{2+}, \text{Ba}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}, \text{Cd}^{2+}, \text{Sr}^{2+}$; $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-, \text{NO}_2^-, \text{NO}_3^-, \text{ClO}_4^-, \text{S}_2\text{O}_3^{2-}, \text{SO}_4^{2-}, \text{S}_2\text{O}_6^{2-}, \text{Cr}_2\text{O}_7^{2-}$; HMT is hexamethylenetetramine. The most frequent value of n is 10 and a large group of complexes with ten water molecules appears to be isomorphous from a crystallographic examination. The formation of these complexes through crystallization from water solutions has been ascribed¹ to the tendency of HMT to stabilize high hydration forms of the inorganic salts.

In our laboratory a three-dimensional study of $\text{CaBr}_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{HMT}$ was carried out in order to establish the general features of the structure of this class of complexes. This compound was already investigated by a two-dimensional X-ray analysis by Bertinotti and Liquori,² but unfortunately the many superpositions of atoms in the projections did not allow a detailed solution of the crystal structure. The crystals were grown as platelets from a solution containing CaBr_2 and HMT in the proper stoichiometric ratio. The unit cell is triclinic and the parameters are: $a = 9.89$, $b = 9.75$, $c = 9.58$ Å.; $\alpha = 94^\circ 29'$, $\beta = 100^\circ 39'$, $\gamma = 119^\circ 20'$; $d_{\text{calcd}} = 1.41$ g./cm.³; $V = 776$ Å.³; $n = 1$.

Since the chemical formula of the complex is fully consistent with a centrosymmetric distribution of the

(1) G. A. Barbieri and F. Calzolari, *Atti Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat.*, [2] **19**, 584 (1910); [1] **20**, 119 (1911).
(2) F. Bertinotti and A. M. Liquori, *Ric. Sci.*, **23**, 1823 (1953).

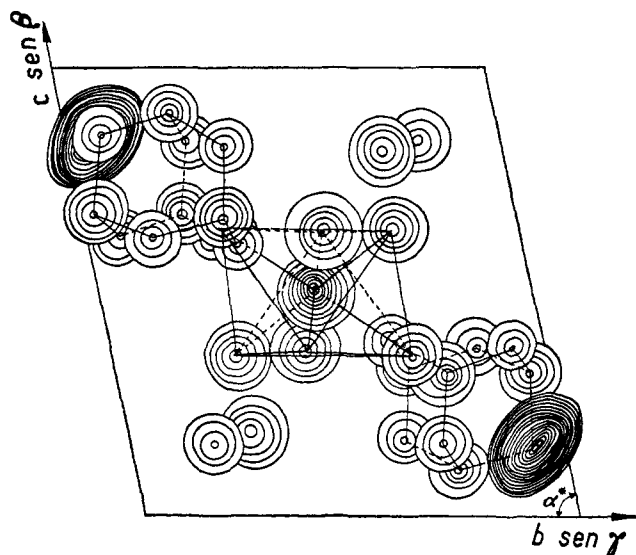


Figure 1. Composite projection of the three-dimensional electron density distribution on (100). Contours are at intervals of 4 electrons Å.⁻³ around the calcium and bromide ions and at intervals of 2 electrons Å.⁻³ around the other atoms, starting from 2 electrons Å.⁻³.

atoms in the unit cell, the space group $P\bar{1}$ was assumed. The density measured in a density gradient was found to be 1.44 g./cm.³, slightly higher than the calculated value, probably because of the tendency of the crystals to transform into the cubic modification investigated by Addamiano and Giacomello.³ Seventeen self-correlating levels were collected with the use of a Weissenberg camera and Cu K α radiation on a crystal mounted on the (100) and (010) axes. After the usual corrections, the intensities were scaled together using the method of Rollet and Sparks.⁴

The phase problem was solved taking advantage of the high scattering power of the Ca^{2+} and Br^- ions. The calcium was placed, from space group considerations, at the center of symmetry, and the coordinates of the bromine atom were derived from a three-dimensional Patterson function. After two cycles of three-dimensional Fourier and structure factor calculations, a value of $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.19$ was obtained. Isotropic thermal corrections for individual atoms were calculated from the electron density peaks of the three-dimensional Fourier synthesis.^{5,6} Further refinement is contemplated considering the anisotropic rigid body oscillations of the HMT molecules.

The three-dimensional electron density distribution shows up very clearly the structure of the complex as may be observed from the composite drawn in Figure 1 on (100). A schematic representation of the crystal structure is shown in Figure 2.

As was already foreseen from the study in projection,² the Ca^{2+} octahedrally coordinates six molecules of water at a distance of 2.3 Å. The threefold axis of the HMT is oriented approximately along the c axis. Three of the nitrogen atoms of each HMT molecule are linked by hydrogen bonds $\text{N} \cdots \text{H} \cdots \text{O}$ to the octahedrally coordinated water molecules surrounding three different calcium ions. This results in a two-

(3) A. Addamiano and G. Giacomello, *ibid.*, **21**, 2121 (1951).

(4) J. S. Rollet and R. A. Sparks, *Acta Cryst.*, **13**, 273 (1960).

(5) F. Bertinotti and A. M. Liquori, *Ric. Sci.*, **26**, 2118 (1956).

(6) A. Damiani, E. Giglio, and A. Ripamonti, *Ric. Sci., Rend. Sez. A.* [7] **3**, 757 (1963).