as b + H, b − H, and c which are indicative of a N-methyl-substituted aziridine ring were also observed.

Confirmatory evidence for the oxazinone ring was obtained from the uv and ir spectra. A uv stability study of I–V in aqueous 0.1 N HCl established that the chromophore of V is more stable by at least a factor of 50 than I–IV. This observation suggested that any proposed structure for mitiromycin must not have a function at position 9a which could be readily eliminated to give the mitosene ("apo") chromophore.[2,6] The proposed structure V is in accord with this requirement.

In the ir spectra of II and V, the carbonyl maximum from the carbamate in II and the oxazinone in V was found in the 5-8-μ region as expected. However, in the solid state the carbonyl maximum in II exhibited intermolecular hydrogen bonding characteristics whereas V did not. Additionally, in the 7.50-μ region the maximum assigned to the ester (ROC(=O)R) portion of the carbamate in the spectrum of II was essentially missing in the ir spectrum of V. This change is completely analogous to that obtained in the spectral changes that occur in going from an ester to a lactone. In the 9.20-μ region the maximum assigned to the alcohol function (Y in II) was missing in the ir spectrum of V as would be expected for the structural changes proposed.

Additional work including an X-ray structure determination of a suitable derivative of mitiromycin is planned.[7]

Acknowledgments. The authors are indebted to Dr. T. Mead, J. C. Cook, and K. Angyal for aid in determining the mass spectra. Acknowledgment is also due to Dr. J. E. Lancaster for the 100-MHz ^{1}H nmr spectra and to Dr. E. Patterson for a sample of mitiromycin.

(6) J. B. Patrick, R. P. Williams, W. E. Meyer, W. Fulmor, D. B. Cosulich, R. W. Broschard, and J. S. Webb, *J. Amer. Chem. Soc.*, **86**, 1889 (1964).

(7) NOTE ADDED IN PROOF. The reason for the structure determination of V was that although structurally very similar to the potent antibiotics I–IV, compound V has no antibiotic activity. Also, to our knowledge, this the first report of a naturally occurring oxazinone or six-membered cyclic carbamate ring.

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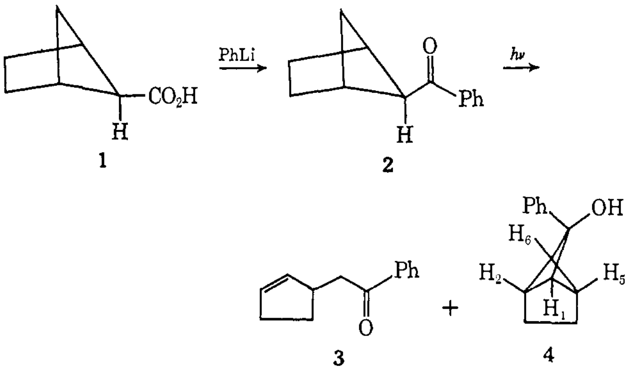
Photochemical Synthesis of the Tricyclo[3.2.0.0^{2,6}]heptane System[1]

Sir:

A recent report from this laboratory described a simple photochemical synthesis of phenylbicyclo[1.1.1]pentan-2-ol.[2] The formation of the bicyclopentanol was proposed to occur by a novel transannular hydrogen abstraction by the excited n-π^* triplet state of cyclobutyl phenyl ketone.[3,4] We now wish to report an extension of the transannular hydrogen abstraction route which provides a convenient synthesis of the heretofore unknown tricyclo[3.2.0.0^{2,6}]heptane ring system.

exo-5-Benzoylbicyclo[2.1.1]hexane (**2**) was readily prepared by the reaction of bicyclo[2.1.1]hexane-*exo*-5-carboxylic acid[5] (**1**) with phenyllithium.[6] Its stereochemistry is clear from its nmr spectrum, which shows a 7.0-Hz long-range coupling constant between the distant *endo* C-5 and C-6 protons.[7] Irradiation of a 1% solution of **2** in benzene using a 450-W Hanovia lamp through a Pyrex filter for 8 hr led to the formation of two new photoisomers, shown to be Δ^2-cyclopentenylacetophenone (**3**, 66%) and 7-phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol (**4**, 30%).[8]



The structure of the major product (**3**), analogous to the ketoolefin produced photochemically from cyclobutyl phenyl ketone,[2] is apparent from its spectral characteristics: uv $\lambda\lambda_{max}$ (95% ethanol) 238, 270, and 305 mμ (ϵ 11,700, 6000, 75); ir λ_{max} (CCl$_4$) 5.92, 6.02 μ; 60-MHz nmr (deuteriochloroform) multiplets at τ 2.18, 2.65, 6.90, and 8.75, singlet at τ 4.35, triplet at τ 7.73. The peak areas are in the ratio of 2:3:3:2:2:2. The mass spectrum of **3** included peaks with m/e 186 (M$^+$) and 105 (base peak). This product also has a prominent peak at m/e 120 corresponding to loss of cyclopentadiene in a McLafferty rearrangement. Structure **3** was further confirmed by an independent synthesis from Δ^2-cyclopentenylacetic acid and phenyllithium.

The structure of **4** (p-bromophenylurethan derivative, mp 137–138°) was elucidated on the basis of the physical and chemical data cited. The infrared spectrum shows hydroxyl bands at 2.86 and 3.04 μ and a carbon–oxygen stretching band at 8.32 μ. Its ultraviolet spectrum exhibited an absorption characteristic of an isolated benzene ring. The mass spectrum of **4** included peaks with m/e 186, 168, 120, 105, 91, and 77 and is very similar to that of **3**. Confirmation of the structure of **4** was available from its unique nmr spectrum. The 100-MHz nmr spectrum showed the aromatic hydrogens as a singlet at τ 2.75, the two bridgehead hydrogens (H$_1$ and H$_6$) as a singlet at τ 7.34, H$_5$ as a doublet at τ 6.45 (J = 7.0 Hz), H$_2$ as a doublet at τ 7.88 (J = 7.0 Hz), the hydroxyl proton as a broad singlet at τ 7.09, and the four methylenic hydrogens as

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(1) Photochemical Transformations of Small Ring Carbonyl Compounds. XXV. For part XXIV, see A. Padwa, S. Clough, and E. Glazer, *J. Amer. Chem. Soc.*, **92**, 1778 (1970).

(2) A. Padwa and E. Alexander, *ibid.*, **89**, 6376 (1967).

(3) A. Padwa, E. Alexander, and M. Niemcyzk, *ibid.*, **91**, 456 (1969).

(4) A. Padwa and D. Eastman, *ibid.*, **91**, 462 (1969).

(5) J. Meinwald, C. B. Jensen, A. Lewis, and C. Swithenbank, *J. Org. Chem.*, **29**, 3469 (1964).

(6) Each new compound described gave satisfactory elemental analysis, as well as ir and nmr spectra compatible with the assigned structures.

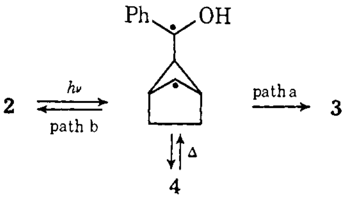
(7) J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, **83**, 2769 (1961).

(8) The reported yields were determined by vpc and have not been corrected for the small amount of thermal decomposition of **4** (~10%) on the vpc column.

an AB quartet (J = 10.0 Hz) centered at τ 8.31. The strong upfield shift of H_2 (relative to H_5) can be attributed to long-range shielding by the π electrons of the phenyl ring.[9] The H_1–H_6 bridgehead–bridgehead long-range coupling in **4** was determined by the preparation of 7-phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol-1-d_1 (**5**) *via* the irradiation of *exo*-5-benzoylbicyclo[2.1.1]hexane-5-*endo*-d_1 (**6**).[10]

The nmr spectrum of the monodeuterated compound (**5**) showed a coupling constant of 2.70 Hz between the deuterium and the bridgehead hydrogen. Since hydrogen–hydrogen coupling is as great by a factor of 6.55 as deuterium–hydrogen coupling,[11] the value obtained is essentially identical with that encountered in the bicyclo[1.1.1]pentane system (*i.e.*, J = 18.0 Hz)[12,13] indicating that the geometries of both ring systems are essentially the same.

Thermal decomposition of **4** at 150° afforded a mixture of **2** (33%) and **3** (67%). The formation of these products can best be accounted for by a thermal cleavage of the bridgehead C–C bond followed by ring opening of the diradical (path a) or by a 1,5-H transfer step (path b). The formation of **3** and **4** from the irradiation of **2** may be considered to be analogous to the Norrish type II cleavage and cyclobutanol formation observed with the irradiation of aliphatic ketones containing γ-hydrogens.[14] The behavior of the diradical generated by thermolysis of **4** is essentially the same as that encountered in the Norrish type II process and once again illustrates the reverse hydrogen transfer step of 1,4 diradicals.[15–17]



The quantum yield for disappearance of ketone (Φ = 0.06) is considerably lower than that of related acyclic phenyl ketones[18] and its value is not significantly enhanced with added *t*-butyl alcohol. The photolysis is readily quenched by the addition of piperylene, in agreement with a n–π^* triplet as the reactive excited state. Since the quantum yield is independent of solvent, the low efficiency cannot be attributed to disproportionation of the 1,4 diradical.[18] The low efficiency must be related instead to some molecular feature of **2** which retards formation of the biradical and allows direct radiationless decay to compete with chemical reaction of the triplet. We suspect that the inefficiency of the photoprocess is due to the unfavorable geometry required for internal hydrogen abstraction. The preferred transition state for internal hydrogen transfer is one in which carbon, hydrogen, and the nonbonding electron on oxygen can approximate a linear configuration.[19] These stereoelectronic requirements cannot be readily met with the above ketone.

It is interesting, at this point, to compare the photoefficiency of **2** with that of cyclobutyl phenyl ketone (**7**) (Φ = 0.03). The cyclobutane ring is quite flexible and exhibits a dynamic ring-bending equilibrium which allows for conformation equilibration of monosubstituted cyclobutanes.[20] It was previously argued that one possible source of inefficiency in the cyclobutyl phenyl ketone system was the low concentration of the conformer having the benzoyl group in the pseudoaxial position.[2] Bicyclo ketone **2** is an appropriate model for the reactive conformer of **7**, since the benzoyl group is now locked into the axial position. If the inefficiency of **7** was totally due to the low population of the reactive conformer, then we would expect that **2** would be similar to valerophenone in terms of photoefficiency.[21] This is certainly not the case and suggests that the inefficiency of both **2** and **7** are related to the poor stereoelectronic features of these ketones.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant No. GP-9385).

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[9] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 125.

[10] The monodeuterated bicyclo ketone **6** was prepared from the photolysis of *syn*-7-chlorodiazonorcamphor in D_2O followed by removal of the 7-chloro substituent with lithium metal and conversion of the acid to the ketone with phenyllithium.

[11] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 188.

[12] K. B. Wiberg and D. S. Connor, *J. Amer. Chem. Soc.*, **88**, 4437 (1966).

[13] A. Padwa, E. Shefter, and E. Alexander, *ibid.*, **90**, 3717 (1968).

[14] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 154.

[15] P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967); *Tetrahedron Lett.*, 1753 (1967).

[16] A. Padwa and E. Alexander, *J. Amer. Chem. Soc.*, **90**, 6871 (1968).

[17] N. C. Yang, S. P. Elliott, and B. Kim, *ibid.*, **91**, 7551 (1969).

[18] P. J. Wagner and H. N. Schott, *ibid.*, **91**, 5383 (1969).

[19] N. J. Turro and D. W. Weiss, *ibid.*, **90**, 2185 (1968).

[20] J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *ibid.*, **69**, 2483 (1947).

[21] It has been pointed out that the quantum efficiency of type II photoelimination is not directly related to triplet-state reactivity for phenyl ketones that undergo significant disproportionation from the 1,4 diradical.[22] However, ketones **2** and **7** show no significant solvent effects and consequently it is assumed that quantum efficiency and triplet reactivity of these ketones are closely related.

[22] P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5896 (1968).

[23] Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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Dibenzopentalenyl Dianion. A Perturbed [12]Annulene Dianion

Sir:

Perturbation theory predicts that dibenzo[*cd,gh*]pentalene (I) should be an unusually good example of the periphery electronic model which describes this system as a perturbed [12]annulene.[1a,b] SCF calculations[2] confirm this prediction; these calculations suggest that the first excited triplet state lies only 0.3 eV above the ground state! In this communication we wish to report the synthesis of the first derivative of this molecule, dilithium dibenzo[*cd,gh*]pentalenide (II). The properties of this derivative clearly support the periphery model as

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[1] (a) B. M. Trost and G. M. Bright, *J. Amer. Chem. Soc.*, **89**, 4244 (1967), and references therein; (b) P. Kinson and B. M. Trost, *Tetrahedron Lett.*, 1075 (1969).

[2] We express our gratitude to Dr. Howard E. Simmons for carrying out a SCF–PPP calculation on this system.