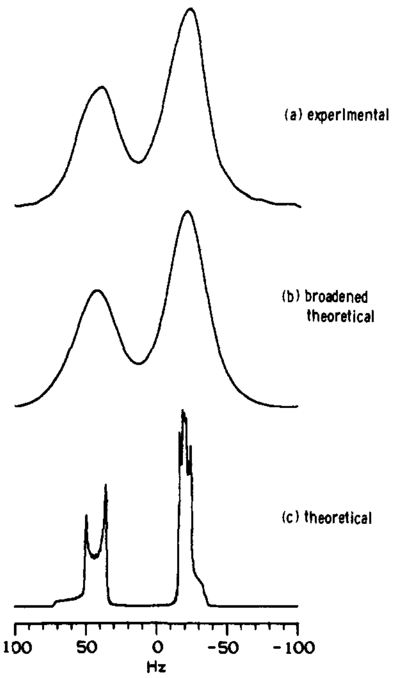

Figure 2. α-Carbon resonance of glycine. (a) Expansion of experimental spectrum where the zero frequency is the chemical shift of ^{15}N labeled glycine; (b) theoretical spectrum c with approximately 20 Hz of line broadening added; (c) theoretical spectrum calculated for a C–N bond length of 1.49 Å in a magnetic field of 3.5338 T with $e^2Qq/h = 1.18$ MHz and $\eta = 0.54$. The dipolar shifts were calculated to ±0.1 Hz for 1000 data points.

expectation value of the Z spin component. The upfield two powder patterns are nearly superimposed and correspond to the shifts caused by the highest and lowest energy states of ^{14}N ($n = 1$ and $n = 3$). The shift due to the $n = 2$ spin state of ^{14}N is twice as large and occurs in the opposite direction; thus the downfield pattern is twice as broad with the shift for any crystal orientation twice the magnitude of the upfield patterns. There is a 2:1 ratio of areas between the two regions.

When the theoretical α-carbon spectrum is broadened by convolution with a function corresponding to about 20 Hz of line broadening at half-height, the spectrum in Figure 2b results, which closely matches the appearance of the experimental spectrum in Figure 2a. In particular, the peak to peak separation is 61 Hz in both the theoretical and experimental spectra. The observed splitting would increase with an increase in the ^{14}N quadrupole coupling constant, a decrease in the ^{13}C–^{14}N bond length, or a decrease in the strength of the applied magnetic field.

Several types of molecular information can be derived from ^{13}C NMR spectra where the resonance line shapes are determined by ^{14}N properties. For molecules where the C–N bond length is known, the magnitude of the split of the peaks can be used to determine the quadrupole coupling constant. Conversely, for those molecules where a quadrupole coupling constant has been measured independently, structural parameters can be obtained. An accurate measurement of the C–N bond length is possible. The ^{13}C spectrum depends on the relative orientation of the quadrupolar and dipolar principal axis systems which is fixed in the molecular frame; therefore geometrical information is potentially available. This may prove useful in determining peptide group conformations of polycrystalline proteins, since splits of both carbonyl and α-carbon resonances are induced by the ^{14}N of the peptide bonds.[5,6]

Acknowledgment. We thank J. S. Waugh for helpful discussions, R. G. Griffin for sending us the [^{14}N]glycine data prior to publication, and N. Zumbulyadis and M. Heinrichs for keeping us informed of their work on the same problem. This research is being supported by grants from the National Institutes of Health (GM-24266), National Science Foundation (PCM-05598), and the American Cancer Society (NP-225A). S.J.O. is a fellow of the A. P. Sloan Foundation (1980–1982).

Unusual Photoisomerization of an "Encased" α-Diketone

Douglas W. Balogh† and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University
Columbus, Ohio 43210

Peter Engel

Abteilung fur Kristallographie und Strukturlehre
Universität Bern, CH-3012 Bern, Switzerland

John F. Blount

Research Division, Hoffmann-La Roche Inc.
Nutley, New Jersey 07110

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Unstrained aliphatic and alicyclic α-diketones possessing γ-hydrogens characteristically undergo photoinduced 1,5-hydrogen transfer to yield exclusively 2-hydroxycyclobutanones.[1-3] The normal absence of competing δ-hydrogen abstraction suggests an overwhelming kinetic preference for passage through a strain-free pseudo-six-membered ring which incorporates an sp^2-hybridized carbon. In this communication, we wish to describe the unprecedented photochemical behavior of **4**, an α-diketone which cannot undergo 1,5-hydrogen transfer. Our expectation was that **4**, for reasons of exceptionally favorable spatial proximity, would undergo twofold δ-hydrogen abstraction and deliver **5**. The subsequent cleavage of this *gem*-diol with lead tetraacetate was to serve as the basis of an expedient route to a suitably functionalized trisecododecahedrane (**7**). Actually, there can be found numerous examples of monocarbonyl compounds which yield cyclopentanols by 1,6-hydrogen transfer upon irradiation.[4] Such departures from normal type II behavior are particularly common when γ C–H bonds are lacking and the δ C–H bonds are inductively activated.[5-7] Although the latter of these conditions is not met in **4**, steric congestion was expected to facilitate δ-hydrogen abstraction.[8]

The topologically attractive diketone was conveniently prepared in five steps from the previously described dilactone **1**.[9] When heated with trimethyloxonium fluoroborate in 1,1-dichloroethane, **1** experienced cleavage of both lactone rings to give a mixture of diene diesters, the catalytic hydrogenation of which over Pd–C produced **2** (70% overall).[10] Reduction of **2** with sodium in liquid ammonia resulted in fission of the central bond and generation of a dianion whose methylation can only proceed from the exo surface. This transformation afforded the axially symmetric **3**

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† Presidential Fellow, The Ohio State University, 1979–1980.

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[10] This route is more efficient than that previously described by us.

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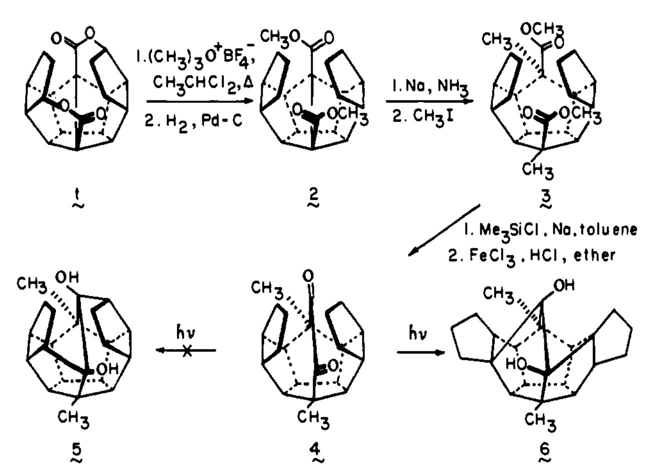


(60%) in which the carbomethoxy groups are oriented endo on the polyquinane[11] framework. The acyloin cyclization of **3** was effected with sodium and chlorotrimethylsilane in toluene.[9,12] When the resulting product was treated with anhydrous ferric chloride in ether containing a few drops of concentrated HCl[13] smooth oxidation resulted to give **4**: mp 182–183 °C[14] (65%); IR (KBr) 1690 cm^{-1}; UV (isooctane) 260 (ϵ 165), 310 (55), and 430 nm (47); ^{13}C NMR (CDCl$_3$) 201.96, 61.29, 60.08, 57.23, 48.91, 32.41, 26.03, and 24.88 ppm. The three-dimensional features of this yellow solid, which was isolated as parallel plates (010), were elucidated by *X*-ray analysis: space group $P2_1/c$ with $a = 7.326$ (4), $b = 32.29$ (1), $c = 7.468$ (4) Å; $\beta = 108.07$ (4)°; $d_{\text{calcd}} = 1.28$ g cm^{-3} for $Z = 4$ (M_r 324.47).[15] The shape of the molecule, which is clearly C_2 symmetric and projects an O=C—C=O dihedral angle of 19.7°, is given in Figure 1. On this basis, **4** was expected to be highly responsive to photoexcitation.[16]

Irradiation of **4** with a 450-W Hanovia lamp through Pyrex in a variety of solvents and solvent systems (C$_6$D$_6$, CDCl$_3$, benzene–*tert*-butyl alcohol (4:1), benzene–acetone–*tert*-butyl alcohol (3:1:1), etc.; the diketone is insoluble in hexane) for 8–16 h afforded a highly crystalline diol, mp 142–143 °C, in 15% yield after isolation by preparative layer chromatography on silica gel (elution with 15% ether in hexane). From the simplified nature of its ^{13}C NMR spectrum (11 lines) and the chemical shifts of key proton and carbon resonances, it was clear that twofold axial symmetry had been maintained. The vicinal nature of the hydroxyl groups in this photoproduct was ascertained by cleavage to an equally symmetric diketone, mp 176–177.5 °C, upon reaction with lead tetraacetate in pyridine (91%). Suspicion that this substance was not **7** arose when H/D exchange could not be effected at either of its α-carbonyl positions despite the ultimate deployment of forcing conditions. Furthermore, an extraordinarily facile reconversion of the diketone to the diol (97% yield) was observed in the presence of a slight excess of lithium diisopropylamide (LDA) in tetrahydrofuran solution (25 °C, 6 h). While the ability of LDA to reduce certain types of carbonyl groups has been previously noted,[17] no examples of intramolecular pinacolization have been reported. The examination of various molecular models of **7** suggested that its lowest energy conformation is attained when sphericality is approached. In this structural arrangement, the pair of carbonyl groups are not in close proximity and consequently do not appear predisposed for reductive coupling under unusually mild conditions.

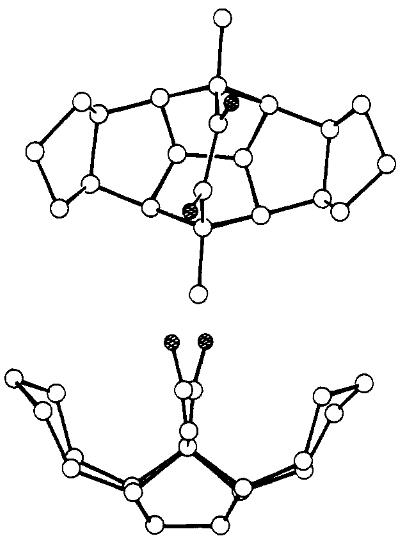


Figure 1. Three-dimensional view of **4** as determined by X-ray analysis.

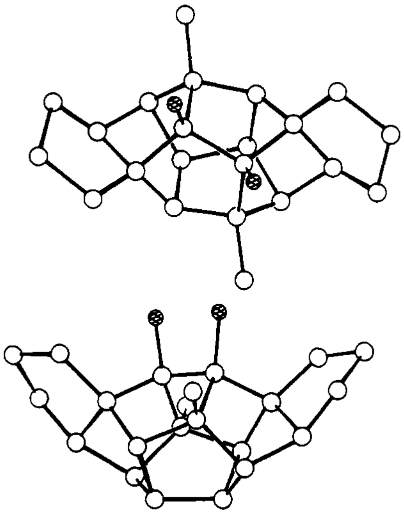
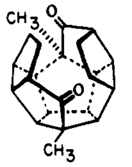


Figure 2. Three-dimensional view of **6** as determined by X-ray analysis.



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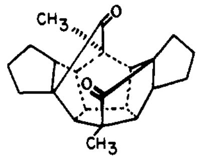

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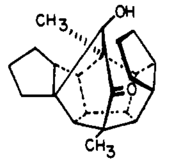

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Due consideration of these observations led us to propose **6** as the diol photoproduct and **8** as its diketone counterpart. These structural assignments were subsequently confirmed by X-ray analysis of **6**: space group $P\bar{1}$ with $a = 9.778$ (5), $b = 9.882$ (5), $c = 10.096$ (5) Å; $\alpha = 75.4$ (1)°, $\beta = 68.0$ (1)°, $\gamma = 71.1$ (1)°; $d_{\text{calcd}} = 1.27$ g cm^{-3} for $Z = 2$ (M_r 322.19).[18] The twisted shape

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(15) Extinction $h0l$ with $l = 2n + 1$ and $0k0$ with $k = 2n + 1$; R factor = 0.059 for 2121 observed reflections ($I > 3\sigma(I)$). $R = [\sum(k|F_o| - |F_c|)/\sum k|F_o|] = 0.072$ for 2698 measured reflections. Function minimized in block diagonal least squares: $M = \sum_{hkl} w[|F_o(hkl)| - (1/k)|F_c(hkl)|]^2$, $w = 1/[6 + F_o(hkl) + 0.04|F_o(hkl)|^2]$. The method of structure solution was by a symbolic addition procedure.

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(18) R factor = 0.065 for 2464 observed reflections ($I > 3\sigma(I)$). $R = [\sum(k|F_o| - |F_c|)/\sum k|F_o|] = 0.069$ for 2764 measured reflections. Other data as in footnote 15.

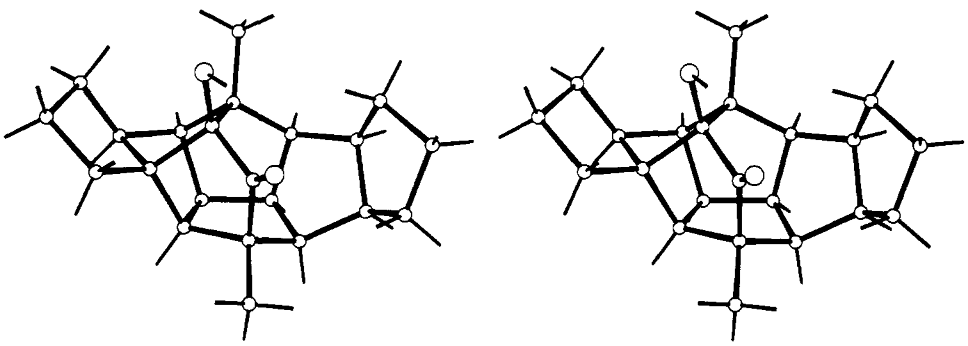
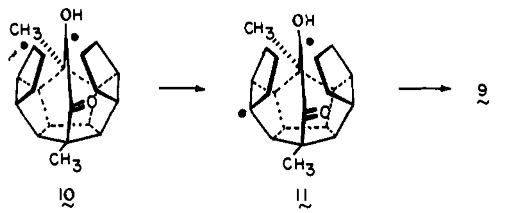


Figure 3. Three-dimensional view of **9** as determined by X-ray analysis.

of this decaquinane is shown in Figure 2.

A novel aspect of the formation of **6** is that precedence would suggest that all of the reactions necessary to go from starting material to product are unlikely, with the exception of the initial hydrogen atom abstraction. The possibility that **6** may have resulted from acid-catalyzed rearrangement of a primary photoproduct was considered, since trace amounts of acids are known to be produced during photochemical reactions in alcoholic solvents. However, irradiations conducted in the presence of either triethylamine or potassium carbonate gave entirely comparable results. Nor was the silica gel employed during purification responsible for promoting secondary chemical changes.

Although the photocyclization of **4** to **6** could involve δ-hydrogen abstraction to give **10**, hydrogen-atom transfer from the ε position (central CH$_2$ group) cannot be discounted. In either event, subsequent rearrangement to biradical **11** appears to be kinetically favored. This conversion could be the result of two sequential 1,2-hydrogen shifts (little precedented[19]) or more direct 1,3 migration (limited analogy[20]). Such unusual hydrogen shifts may be facilitated by partial relief of the extreme steric congestion in **10** (and **4**). While it is most unusual that biradical cyclization does not occur until hypothetical intermediate **11** is reached, closure at this stage is seen to lead to **9**. In fact, a colorless crystalline solid, mp 132.5–134 °C,[14] identified as **9** could be isolated at shorter reaction times. The structure of this product which exhibits intense infrared peaks (KBr) at 3450, 2940, 1710, and 1062 cm^{-1} and compatible NMR data (^{1}H, ^{13}C)[21] was established by X-ray analysis (Figure 3).[22] Further irradiation of **9** in mixed solvent systems (e.g., benzene-*tert*-butyl alcohol-acetone, 8:2:1) gave **6**. The presence of acetone was mandatory for the success of this conversion. Since the **9** → **6** process may differ substantively from the **4** → **9** reaction, the assumption of similar mechanisms for these photocyclizations is not warranted.



10 11

The present findings provide groundwork for the belief that α-diketone photochemistry may, under appropriate circumstances, be accompanied by radical rearrangements involving saturated carbon centers.[23]

Supplementary Material Available: Tables of atomic coordinates for compounds **4** and **6** with standard deviations and interatomic distances and angles together with their associated standard deviations for **9** (52 pages). Ordering information is given on any current masthead page.

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(21) ^{1}H NMR (δ, CDCl$_3$) 3.50 (s, 1 H), 3.5–0.8 (series of m, 21 H), 1.22 (s, 3 H), and 1.13 (s, 3 H); ^{13}C NMR (ppm, CDCl$_3$) 221.56, 89.63, 64.75, 62.63, 61.29, 60.75, 59.72, 59.59, 58.87, 58.68, 58.50, 51.22, 49.82, 46.85, 32.04, 31.31, 27.37, 23.91, 23.24 (2 C), 23.06, 22.94, and 22.39 (one C signal not evident). *m/e* calcd: 324.2089; found: 324.2096.

(22) The crystals of **9** were orthorhombic, space group $P2_12_12_1$, with a = 8.581 (2), b = 10.963 (3), c = 17.619 (5) Å; d_{calcd} = 1.300 g cm^{-3} for Z = 4 ($C_{22}H_{28}O_2$, M_r 324.46). A total of 1312 reflections were measured for $\theta < 57°$, of which 1247 were considered to be observed. The final discrepancy indexes are R = 0.035 and wR = 0.042 for the remaining 1245 observed reflections. The final difference map has no peaks greater than ±0.2 e Å^{-3}.

(23) The financial support of this work by a grant by the National Institutes of Health (AI-11490) is gratefully acknowledged.

Model Approach to the Pentagonal Dodecahedrane. Synthesis and Properties of a Monoseco Derivative

Leo A. Paquette[*] and Douglas W. Balogh[†]

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

John F. Blount

Research Department, Hoffmann-La Roche, Inc.
Nutley, New Jersey 07110

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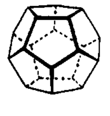
Any stepwise synthetic elaboration of the magnificently symmetric dodecahedrane molecule **1** must overcome the strong penchant shown by its partially constructed precursors for transannular bonding, framework isomerization, and noncyclopentanoid cyclization.[1] Generally, these undesirable processes gain their kinetic prominence from (a) the need to enclose a solvent-free cavity, (b) the onset of large allosteric effects[2] which force the partially constructed systems to become markedly nonspherical, and (c) the topological requirement that nearest-neighbor peripheral hydrogens ultimately become perfectly eclipsed. It is the sum total of these and other factors which have caused several groups to attempt convergent approaches to **1**,[3] but



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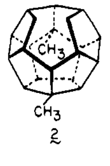

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