done derivative) in the experiment where the $[\alpha,\beta,\gamma,\delta\text{-}^{14}C_4]$uro'gen mixture was used.

(17) Prolonged incubation or heat treatment of any of the $^{14}C$-meso labeled uro'gen species described in this communication led to extensive decomposition to $^{14}CH_2O$ as determined by dimedone trapping and crystallization of the adduct to constant activity.

(18) In one experiment, the uro'gen mixture was isolated from the $[^{14}CH_2O\text{-}^3H]$porphobilinogen condensation without acid-catalyzed equilibration. When this sample ($^3H/^{14}C$, 15.2) was incubated with the complete enzyme system as before, the resultant cobester showed little change in $^3H/^{14}C$ ratio (16.0) indicating that the $\delta$ position has been exchanged with $^{14}CH_2O$ to a minor extent compared with the other ($\alpha,\beta,\gamma$) positions, and also that the mechanism of in vitro synthesis of uro'gens[13] is worthy of reexamination.

(19) A. R. Battersby, E. Hunt, M. Ihara, E. McDonald, J. B. Paine, III, F. Satch, and J. Saunders, *J. Chem. Soc., Chem. Commun.*, 994 (1974). We thank Professor Battersby (Cambridge) for exchanging samples of synthetic **10** and for confirming their identity.

(20) Administration of $[\alpha,\gamma\text{-}^{14}C_2]$-(**9**) to whole cells of *P. shermanii* afforded cyanocobalamin (**2**) with a specific incorporation of 1.0% after crystallization to constant activity.

(21) The role of intact, unsymmetrically labeled uro'gen III as a specific precursor for the corrin nucleus has recently been confirmed at Cambridge by Professor A. R. Battersby and coworkers (private communication, Mar 10, 1975).

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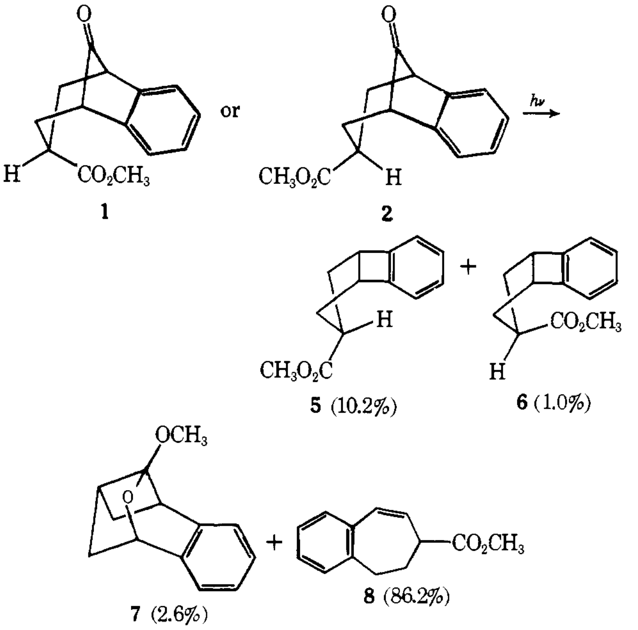
## Photodecarbonylation of Methyl Benzobicyclo[3.2.1]octen-8-one-3-*exo*- and -*endo*-carboxylate. Orbital Symmetry Control in the Chemistry of a Twisted *o*-Quinodimethane

*Sir:*

Photochemical elimination of carbon monoxide or carbon dioxide from appropriate precursors has been successfully used to produce *o*-quinodimethanes.[1] Photodecarbonylations of 2-indanones have been studied by Quinkert and coworkers.[1a] Their work focused mainly on phenyl substituted 2-indanones where for example it was elegantly shown that *cis*- and *trans*-1,3-diphenyl-2-indanone afforded diphenyl substituted *o*-quinodimethanes in a two step nonstereospecific decarbonylation from the singlet state. These underwent subsequent thermal and photochemical reactions but could be observed by low temperature ultraviolet spectroscopy and trapped with dienophiles. Jones and coworkers have examined the photochemical production of relatively strain-free *o*-quinodimethanes related to 2,3-dihydronaphthalene.[1b] These molecules were found to be detectable by ultraviolet spectroscopy if the facile 1,5-suprafacial hydrogen shift was prevented by appropriate substitution and isolable if in addition 1,4-diphenyl substitution was present.

We have examined the photochemistry of methyl benzobicyclo[3.2.1]octen-8-one-3-*endo*- and -*exo*-carboxylate, **1** and **2**.[2] Our principal goal was to determine the effects of phenyl substitution absence coupled with structural constraints on the propensity for formation and subsequent reactions of the expected *o*-quinodimethane, **4**. Due to the constraining influence of the three-carbon bridging group **4** must exist in the *Z,Z* configuration and must be substantially twisted. We anticipated that this effect coupled with the absence of phenyl substitution would destabilize **4** relative to the strain-free biradical **3** and a one- or two-step photodecarbonylation would perhaps lead to products derived from the biradical. These reactions might show stereospecificity since inversion of the benzylic radical requires transient formation of **4** and the pendant carbomethoxy group would serve as a nonparticipating stereochemical probe.



Irradiation[3] of **1** or **2** gave rise to several products:[4] methyl benzobicyclo[3.2.0]hepten-3-*exo*- and -*endo*-carboxylate, **5** and **6**, 7-methoxy-2,3-benzo-8-oxatricyclo-$[4.2.1.0^{4,7}]$nonene, **7**, and methyl 1,2-benzo-1,3-cycloheptadiene-5-carboxylate, **8**, in a nonstereospecific reaction; see equation.[5] The reaction is moderately efficient,[6] not sensitized by acetone, and only slightly quenched by *trans*-1,3-pentadiene.[7] These facts indicate that the reaction may occur from the excited singlet state.

Product formation can be rationalized in terms of an intermediate biradical, **3**, or *o*-quinodimethane, **4**, undergoing closure to epimeric bicyclic benzocyclobutenes, **5** and **6**;[1] 1,5-hydrogen shift to **8**,[1,8] or an intramolecular Diels–Alder reaction to **7**.[9]

Experiments in which temperature and excitation wavelength were varied (Tables I and II) showed that **5**, **6**, and **7** are produced in a common reaction independent of formation of **8**. Thus the ratio of **5**:**6**:**7** remains essentially constant and irradiation at low temperatures (Table I) or simultaneous irradiation with 366 and 313 nm light (Table II) results in striking decreases in the relative amount of **8**.

Table I. Effect of Temperature on Photochemistry of 1 and 2[a]

| Compound | Temp, °C | Solvent | % 8 in product mixture | 5:6:7 |
|---|---|---|---|---|
| 1 or 2 | 35 | Cyclohexane | 86.2 | 1.00:0.07:0.19 |
| 1 | 0 | Cyclohexane–Benzene (1:1) | 48[b] | 1.00:0.05:0.26 |
| 2 | 0 | Cyclohexane–Benzene (1:1) | 47[b] | 1.00:0.05:0.23 |
| 1 | –40 | Dichloromethane | 0 | 1.00:0.06:0.13 |
| 2 | –40 | Dichloromethene | 0 | 1.00:0.08:0.15 |

[a] Rayonet reactor 3000 Å lamps. [b] Cyclohexane–benzene (2:1) is the solvent in these experiments.

Table II. Effect of Excitation Wavelength on the Photochemistry of 2 in Cyclohexane at Room Temperature

| Excitation wavelength (nm) | % of 8 in ·product mixture | 5:6:7 |
|---|---|---|
| 254[a] | 76.2 | 1.00:0.06:0.17 |
| 280–330[b] | 89.6 | 1.00:0.06:0.28 |
| 325–385[c] | 41.2 | 1.00:0.07:0.28 |
| >285[d] | 12.3 | 1.00:0.08:0.32 |
| 313[e] | 99.4 | |
| 313[e] plus 366[f] | 29.6 | 1.00:0.06:0.29 |

[a] Rayonet reactor, RPR-2537 Å lamps, vycor vessel. [b] Rayonet reactor, RPR-3000 Å lamps (broad emmission maximum at 300 nm) Pyrex vessel. [c] Rayonet reactor, RPR-3500 Å lamps (broad emission maximum at 350 nm) Pyrex vessel. [d] Hanovia 450 W mercury lamp, Pyrex vessel. [e] As in footnote *d* but with a filter solution of basic potassium chromate. [f] Osram super pressure mercury lamp with a Bausch and Lomb high intensity monochromator.

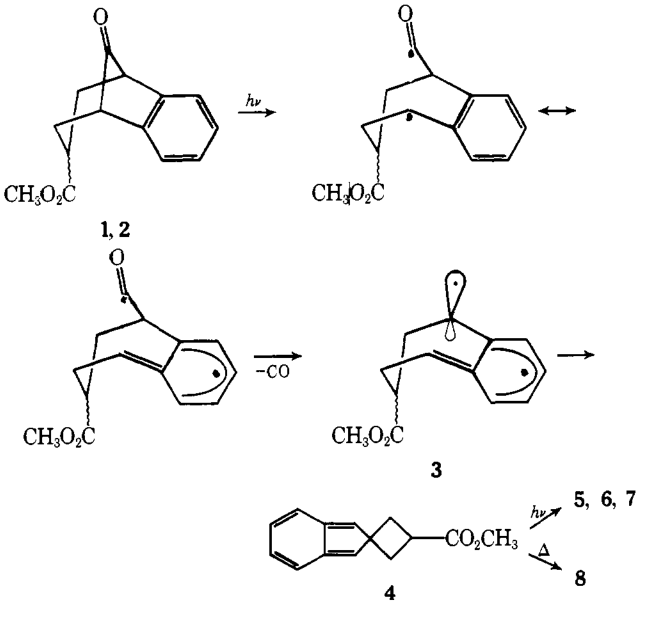
This effect could be duplicated by using a Rayonet reactor with one or two 3000 Å lamps, the rest being 3500 Å.

The simultaneous dual excitation experiments require the presence of an intermediate capable of absorbing light of wavelengths greater than 350 nm since this is not absorbed by **1** or **2**. We believe this intermediate to be the strained *o*-quinodimethane, **4**. Independent evidence for **4** comes from the formation of a one to one Diels–Alder adduct on irradiation of **2** in the presence of maleic anhydride.[10,11]

In view of these results we propose the mechanism shown in Scheme I[5] to explain the photochemistry of **1** and **2**. The most likely primary photochemical process is a singlet state (vide supra) $\alpha$-cleavage producing the acyl–alkyl radical pair shown, followed by loss of carbon monoxide to biradical **3** which relaxes to the *o*-quinodimethane, **4**. The observed wavelength dependence (Table II) indicates that **5**, **6**, and **7** are produced in a secondary photochemical reaction of **4** by absorption of light (longer wavelengths) not absorbed by **1** or **2**. At low conversions it is unlikely that **4** will be able to compete successfully with the starting ketone for short wavelength light. The decreases observed in the relative yield of **8** with lowered reaction temperature (Table I) indicate that it is probably derived from **4** in a thermal reaction.

The unexpected stability as well as subsequent thermal and photochemical reactions of **4** are explicable in terms of orbital symmetry requirements[12] in product formation. Thermally allowed conrotatory closure of **4** cannot occur as this would lead to a very strained trans-fused bicyclic benzocyclobutene. Instead an allowed 1,5-suprafacial hydrogen shift takes place yielding **8**. With simultaneous irradiation at long wavelengths or photolysis at low temperatures where the 1,5-hydrogen shift is slowed down or stopped, **4**, absorbs light giving rise to the allowed disrotatory cyclization to the cis-fused bicyclic benzocyclobutenes, **5** and **6**, as well as a photochemical Diels–Alder reaction to **7**.

**Scheme I**



We have shown that the twisted and strained *o*-quinodimethane, **4**, is the only primary photoproduct formed on irradiation of the 2-indanones, **1** and **2**; however it undergoes competing thermal and photochemical reactions to produce the isolated products **5**–**8**. The surprising stability of **4**, even at room temperature, is no doubt due to a structural prohibition for the orbital symmetry allowed conrotatory ring closure, and the observed thermal and photochemical reactions of **4** apparently do not proceed via biradical intermediates but are instead concerted reactions governed by orbital symmetry.

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## References and Notes

(1) (a) G. Quinkert, J. Palmowski, H.-P. Lorenz, W.-W. Wiersdorff, and M. Finke, *Angew. Chem., Int. Ed. Engl.*, **10**, 198 (1971), and references therein; (b) D. W. Jones and G. Kneen, *Chem. Commun.*, 1356 (1971); *J. Chem. Soc., Chem. Commun.*, 1038 (1972), and references therein.

(2) The synthesis of these compounds was carried out by R. G. Lawton and coworkers using a method developed previously. *J. Org. Chem.*, **35**, 690 (1970). A description of the synthesis will be provided in a future publication by these workers.

(3) In cyclohexane with nitrogen bubbling using a Rayonet reactor and RPR-3000 Å lamps.

(4) Assigned structures are consistent with observed spectroscopic and chemical properties. Products were shown to be isomeric by chemical studies as well as a combination of elemental analysis and high resolution mass spectroscopy, the details of which will be given in a future publication.

(5) Molecular conformations have been idealized.

(6) Quantum yield of product formation from **1** is 0.39 ± 0.05 in degassed (four freeze-pump-thaw cycles) benzene. Hanovia 450-W mercury lamp, with a basic potassium chromate filter solution (transmission maximum about 313 nm) was used for excitation.

(7) Stern-Volmer slopes 0.4 in benzene and 0.5 in cyclohexane. Product ratios were unchanged in the presence of *trans*-1,3-pentadiene.

(8) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

(9) W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, **11**, 1031 (1972).

(10) The structure of this adduct (stereochemistry unknown) is based upon ir (KBr), 1856, 1781, and 1726 $\text{cm}^{-1}$, and mass spectral (parent at *m/e* 300) data. The Diels–Alder assignment is consistent with the known behavior of o-quinodimethanes with dienophiles.[11]

(11) B. J. Arnold, S. M. Mellows P. G. Sammes, and T. W. Wallace, *J. Chem. Soc., Perkin Trans. 1*, 401 (1974); G. Quinkert, K. Opitz, W-W. Wiersdorff, and M. Finke, *Justus Liebigs Ann. Chem.*, **693**, 44 (1966), and references therein.

(12) R. Hoffmann and R. B. Woodward, *Acc. Chem. Res.*, **1**, 17 (1968).

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## Dicarbonyltetraiodorhodate(III). An Example of a Thermodynamically Stable Trans Dicarbonyl Species

*Sir:*

The rationalization of the structures adopted by metal complexes containing two or more different types of ligand is a fundamental goal in inorganic chemistry. Some years