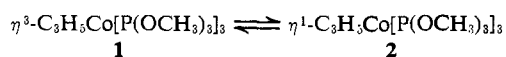


hexane, and ethyl benzoate to ethyl cyclohexenylcarboxylate. Selectivity in the last case seems to be a steric or a kinetic effect due to conjugative stabilization<sup>6</sup> in the unsaturated ester. Hydrogen exchange through CoH-CH reactions is not significant in the catalytic sequence because perdeuteriobenzene yielded only C<sub>6</sub>H<sub>6</sub>D<sub>6</sub>.<sup>7</sup> There is stereoselectivity in this catalytic reaction since *m*-xylene was converted to *cis*-1,3-dimethylcyclohexane and *o*-xylene to *cis*-1,2-dimethylcyclohexane. A clear indication of steric encumbrances in the hydrogenation reaction was the very low rate of reaction with mesitylene at 25° to give *cis,cis*-1,3,5-trimethylcyclohexane. The aromatic ring in furan is also reduced to yield tetrahydrofuran.

We confidently presume that the first step in the catalytic hydrogenation is an  $\eta^3 \rightleftharpoons \eta^1$  conversion<sup>8</sup> to yield a coordinately unsaturated complex **2**



Confirmatively, we found that **1** reacts far faster with CO to give carbonyl derivatives than do HCo[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>4</sub> and CH<sub>3</sub>Co[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>4</sub> which ostensibly must dissociatively lose a phosphite ligand before CO reaction may occur.<sup>9</sup> Subsequent to the  $\eta^3 \rightleftharpoons \eta^1$  reaction would be oxidative addition of hydrogen<sup>10</sup> to **2** to give  $\eta^1\text{-C}_6\text{H}_5\text{CoH}_2\text{[P(OCH}_3)_3]_3$  (**3**). This addition of hydrogen was tentatively indicated in reaction of **1** with hydrogen in a pyridine and in an acetonitrile solution; neither solvent was hydrogenated. Nmr spectroscopic studies of **1** in nonpolar and polar solvents under hydrogen pressure, in fact, showed an allyl proton nmr resonance that can be interpreted in terms of a  $\eta^1$  allyl ligand, as in **3**, but a metal hydride resonance for the putative hydride has not yet been detected. We fully expected to see rapid elision of the allyl group in **3** by proton transfer to give propylene and a coordinately unsaturated HCo[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub> (**4**) and further expected **4** to be the active catalyst. Actually, we found no evidence of **4** although this species may be present in very low concentrations. Essentially complete recovery of **1** from hydrogenation reactions was realized when the reaction time did not exceed ~24 hr. After reaction times of several days, the hydrogenation rate fell sharply due to catalyst destruction; and, in these instances, **1**, HCo[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>, and free phosphite<sup>11</sup> were detected in addition to a small amount of paramagnetic solid.

The geometric mode of initial arene attachment to the cobalt center is probably "over an edge."<sup>12</sup> This in-

(6) No ethyl cyclohexylcarboxylate was detected. Some cyclohexane is formed which suggests that the rate of hydrogenation of the cyclohexenylcarboxylate is substantially lower than reductive cleavage of the carboxylate in the cyclohexyl derivative.

(7) This was the only species detected within the limits of the gas chromatographic and mass spectrometric analysis procedure. The stereochemistry has not as yet been unequivocally established.

(8) The rate of this process is low with respect to the nmr time scale.<sup>2</sup>

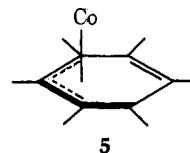
(9) E. L. Muetterties and F. J. Hirsekorn, to be submitted for publication.

(10) Oxidative addition of hydrogen to coordinated unsaturated complexes is a well-established reaction and, in fact, has been reported for cobalt(I) complexes. For general and specific references, cf. E. L. Muetterties, "Transition Metal Hydrides," Marcel Dekker, New York, N. Y., 1971, Chapters 5 (pp 210 and 211) and 6.

(11) Free phosphite ligand is an expected hydrogenation reaction inhibitor.

(12) This would be analogous to a quasi olefin complex. Certainly intermediates of this general form must be involved in the sequential reaction steps of metal hexacarbonyls with aromatic hydrocarbons, where  $\eta^6$ -arene complexes are the ultimate products.

teraction would be followed by hydrogen migration to give a cyclohexadienylcobalt complex. Further hydrogen transfer would then yield cyclohexadiene by reductive elimination. Cyclohexadiene, and the next intermediate cyclohexene, *might* then compete more effectively than the arene in further sequences to preferentially give, as observed, cyclohexane. Alternatively an  $\eta^3$ -cyclohexadienyl complex, **5**, might be an



intermediate. In any case, the stereochemical character of an  $\eta^2$ -olefin or  $\eta^3$ -cyclohexadienyl complex must be such that methyl substituents are always preferentially directed away from the cobalt center to account for the stereoselective formation of *cis*-polyalkylcyclohexanes from *o*- and *m*-xylene and mesitylene.

All plausible mechanistic schemes would seem to require phosphite ligand dissociation. We find that polar media like alcohols and nitriles raise the rate of phosphite ligand dissociation<sup>13</sup> and the rate of the hydrogenation reaction. This ligand dissociation step might be rate determining in the hydrogenation reaction. However, the  $\eta^3 \rightleftharpoons \eta^1$  interconversion may also be a significant rate limiting step. Donor molecules or ligands are known to promote  $\eta^3 \rightleftharpoons \eta^1$  processes in allylmetal complexes.<sup>14</sup>

We are presently attempting synthesis of model structures, like HCo[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>,  $\eta^3$ - or  $\eta^1$ -C<sub>6</sub>H<sub>7</sub>Co[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>x</sub> (*x* = 3 or 4), and RCoH<sub>2</sub>[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>, that are or that emulate the possible intermediates in this catalytic hydrogenation in order that the hydrogenation reaction might be logically extended to other classes of aromatic hydrocarbon reactions. We consider these findings as an important first step in the generation of a broad range of homogeneous catalytic reactions of aromatic and aliphatic hydrocarbons; hydrocyanation and hydroformylation of arenes are realistic extensions.

**Acknowledgments.** Support of our work by the National Science Foundation, Grant No. GP-39306X, and by the Materials Science Center, Cornell University, is gratefully acknowledged.

(13) This phenomenon has been observed for HCo[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>4</sub> and for the allyl complex.<sup>3</sup>

(14) K. Vrieze, C. MacLean, P. Cossee, and C. W. Hilbers, *Recl. Trav. Chim. Pays-Bas*, **85**, 1077 (1966); *J. Organometal. Chem.*, **6**, 672 (1966).

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### Photochemical Synthesis of a 1,8-Naphthoquinodimethane, Generation of a Thermally Accessible Triplet

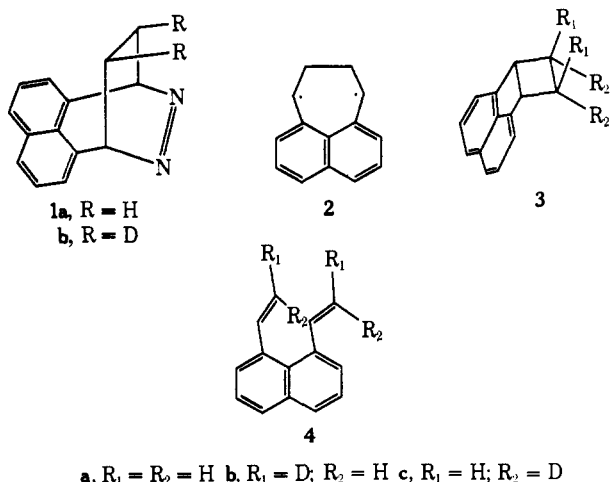
Sir:

In a previous communication,<sup>1</sup> the thermolysis of **1a** was described. By studying the decomposition of **1a** and **1b** under a wide variety of conditions, it was con-

(1) R. M. Pagni and C. R. Watson, Jr., *J. Amer. Chem. Soc.*, **96**, 2291 (1974).

cluded that the 1,8-naphthoquinodimethane, **2**, was an intermediate in the reaction, it behaved as if it were planar, and it underwent subsequent reaction to **3** and **4** from either a singlet ground state or an unquenchable triplet excited state.

In the present communication, we wish to report on the photochemical generation of **2** and an esr study of **2** in conjunction with a theoretical investigation on several conformations of **2**, all of which help to further elaborate the nature of this quinodimethane.



Photolysis of **1a** at room temperature in numerous solvents afforded the same products, **3a** and **4a**, in approximately the same ratio as was observed in the thermal decomposition.<sup>2</sup> Some representative thermal and photochemical data are shown in Table I. As was

**Table I.** Product and Deuterium Distribution<sup>a, b</sup>

Reactant	Solvent <sup>c</sup>	Reaction conditions	(4/3) <sup>d</sup>	(3b/3c) <sup>e</sup>	(4b/4c) <sup>e</sup>
<b>1a</b>	CH <sub>3</sub> OH	Δ, <sup>f</sup> 134°	0.12		
<b>1a</b>	CH <sub>3</sub> OH	hν, <sup>g</sup> 20°	0.15		
<b>1b</b>	CCl <sub>4</sub>	Δ, <sup>f</sup> 134°	0.15	1.2 <sup>j</sup>	1.0
<b>1b</b>	CCl <sub>4</sub>	hν, <sup>g</sup> 20°	0.18	0.9 <sup>i</sup>	0.8 <sup>i</sup>
<b>1a</b>	CH <sub>2</sub> Cl <sub>2</sub>	hν, <sup>g</sup> -77°	<0.02 <sup>h</sup>		
<b>1b</b>	Ethanol glass	hν, <sup>g, i</sup>	2.5	1.1 <sup>j</sup>	1.0

<sup>a</sup> All product and deuterium ratios were determined by pmr. <sup>b</sup> See ref 2 and 3. <sup>c</sup> All reactions were prepared *in vacuo* by the freeze-pump-thaw procedure except the ones in CH<sub>2</sub>Cl<sub>2</sub> and ethanol glass which were run under nitrogen. <sup>d</sup> Product ratio from the decomposition of **1a** or **1b**. <sup>e</sup> Deuterium ratio from the decomposition of **1b**. <sup>f</sup> Δ, thermal decomposition. <sup>g</sup> hν, photochemical decomposition. <sup>h</sup> **4** was barely detectable. <sup>i</sup> Liquid nitrogen temperatures. <sup>j</sup> The ratio was unity within the accuracy of the measurement.

the case in thermal reaction, no dimers, adducts, or products derived from hydrogen or chlorine abstraction were formed in any of the solvents or in the presence of dienophiles.

Irradiation of the deuterated azo compound **1b** gave identical results<sup>2</sup> with those observed in the thermal decomposition, *i.e.*, the deuterated naphthocyclobutane **3** had half its label anti,cis and half syn,cis (50% **3b** and 50% **3c**) while the divinyl naphthalene had half its label cis and half trans (50% **4b** and 50% **4c**).<sup>2, 3</sup>

(2) All the necessary controls were run to demonstrate that the observed product ratios were the initial ones.

(3) For the divinyl naphthalenes, one does not really know that there

Therefore, the thermal and photochemical decompositions must proceed largely along the same energy surface and produce the same 1,8-naphthoquinodimethane.

Is a triplet state of **2** an intermediate in the above reactions? To answer this question, the following esr experiments were performed.

A 0.15 M solution of the azo compound **1a** in hexafluorobenzene was rapidly frozen in liquid nitrogen and irradiated at -160° inside an optical transmission esr cavity with an Oriel 200-W mercury lamp. After several minutes of irradiation, an esr spectrum was obtained which exhibits resonance lines characteristic<sup>4</sup> of a randomly oriented triplet species and, in addition, a stronger resonance near *g* = 2 which is attributable to a radical species. With 9.221-GHz microwave radiation, resonance lines were observed at 3088 and 3480 G and at 3192 and 3375 G and can be assigned, respectively, to the signals of a randomly oriented triplet state of **2** oriented perpendicular and parallel to the magnetic field and having an axially symmetric or nearly axially symmetric spin distribution. The Δ*M<sub>S</sub>* = ±2 transition for the triplet was very weak but could be observed under high gain and modulation at 1640 G.<sup>5</sup> The zero field splitting parameters for **2** are |*D*| = 0.018 cm<sup>-1</sup> and |*E*| < 0.003 cm<sup>-1</sup>.<sup>6</sup> In case of the latter, the fact that only four triplet resonances appear in the high field portion of the triplet spectrum indicates that |*E*| is nearly zero, and one can take the line width of the inner pair of triplet resonance as an upper limit for |*E*| in this case.

The intensity of the triplet esr absorption was studied as a function of temperature in order to determine if the observed species is a ground state triplet or a thermally accessible triplet state.<sup>7</sup> From this study it

is 50% **4b** and 50% **4c**. One only knows that half the deuterium label is *cis* and half *trans*.

(4) Cf. J. E. Wertz and J. R. Bolton, "Electron Spin Resonance, Elementary Theory and Practical Applications," McGraw-Hill, New York, N. Y., 1972, Chapter 10.

(5) The Δ*M* = ±2 transition typically has a greatly reduced probability in comparison to the upfield transitions (Δ*M* = ±1). For a triplet randomly oriented in a matrix, however, the intensity of the former transition is often comparable to or greater than those of the Δ*M* = ±1 transitions, because the anisotropy associated with the former resonance is usually much less than that of the latter. In the case of **2**, the weak intensity of the low field transition probably results from an abnormally low transition probability for this transition. Other reports of triplets having weak low field intensities have appeared in the recent literature. See (a) J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Amer. Chem. Soc.*, **93**, 1544 (1971); (b) W. R. Roth and G. Erker, *Angew. Chem., Int. Ed. Engl.*, **12**, 503 (1973).

(6) Examples of triplets lacking a three-fold or greater axis of symmetry yet having a zero or negligible |*E*| value are known. For example, see D. R. Arnold, A. B. Evinin, and P. H. Kasai, *J. Amer. Chem. Soc.*, **91**, 784 (1969).

(7) As expected, the radical species obeyed Curie's law, *i.e.*, a plot of intensity (*I*) vs. 1/*T* was linear. A similar plot for the triplet species deviated markedly from linearity.<sup>8</sup> A thermally accessible triplet should obey the expression *IT* = (e<sup>-Δ*E*/RT</sup>)/(1 + 3e<sup>-Δ*E*/RT</sup>).<sup>10</sup> This expression was indeed obeyed when Δ*E* = 200 cal/mol. Details of how this calculation was performed will be given in our full paper.

(8) The triplet signal underwent an irreversible, non-first-order decay around -130°. Most irradiations were run, though, at around -160° where the irreversible decay was exceedingly slow. In any event, corrections could be made by reference to -177° where the irreversible decay did not occur. It should also be noted that the triplet intensity was perfectly reversible if the temperature changes occurred over a short period of time. Measurements for the *IT* plots were measured in the -140 to -177° range.

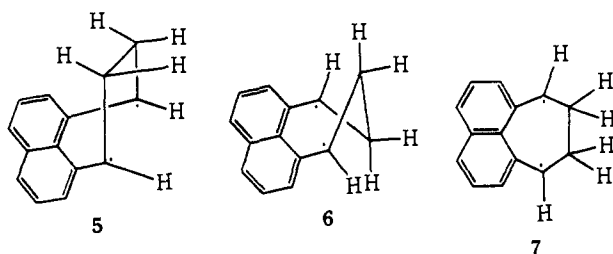
(9) The nonlinear decay of the triplet could be attributed, in part, to a relatively fast formation of the radical species. At -130°, the decrease of the triplet signal could be correlated with the increase in intensity of the radical. The remainder and slower part of the decay could be attributed to the formation of **3** and/or **4**.

(10) R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *J. Amer. Chem. Soc.*, **89**, 1112 (1967).

was determined that the detectable triplet was the excited state lying about 200 cal/mol above the singlet.

The same esr spectrum was observed when **1a** was irradiated in an ethanol glass at  $-160^\circ$ . This is particularly exciting because, as seen in Table I, irradiation of **1b** in an ethanol glass at liquid nitrogen temperatures afforded the same products, **3** and **4**, and the same distribution of deuterium in **3** and **4**, as was observed in the thermal and photochemical decomposition in fluid solution. Thus, one can implicate a triplet state of the quinodimethane in the reaction sequence, at least in part.<sup>11</sup>

**2** is a highly flexible biradical. As a result of this inherent flexibility, it is not at all clear which conformation is responsible for the triplet signal and which conformation is responsible for the formation of products. Molecular models suggest that there are two stable conformations of **2**, one which is bent, **5** ( $C_s$  symmetry), and one which is twisted, **6** ( $C_i$ ). To look into the questions raised above, we have carried out open shell INDO calculations<sup>12-14</sup> on **5** and **6** as well as planar



**7** ( $C_{2v}$ ). The results of these calculations are shown in Table II.

As expected, the singlet (S) and triplet (T) electronic configurations of **7** are much less stable than the ground state configurations of **5** and **6**. This is what one would

(11) One cannot correlate the intensity of the triplet esr signal with the concentration of the biradical responsible for the signal. Consequently, it is conceivable that only a very small fraction of the reaction involves the triplet quinodimethane.

(12) Quantum Chemistry Exchange Program (Bloomington, Indiana), Program No. 141 by P. A. Dobosh described in detail in J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970. Known bond lengths of naphthalene and standard bond lengths of the remaining bonds were used.

(13) INDO calculations have previously been carried out on small open shell molecules. In these cases, the ordering of the singlet and triplet states is correctly predicted. In some instances the energy gap is somewhat large, though. See (a) R. N. Dixon, *Mol. Phys.*, **12**, 83 (1967); (b) J. A. Pople, D. C. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); (c) the book cited in ref 12.

(14) INDO calculations of a similar vein have been carried out on the "parent" of **2**, i.e., tetramethylene. See L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, **94**, 4599 (1972).

Table II. Calculated Binding Energies (au)

	5	6	7
Singlet	-14.246	-14.379	-14.146
Triplet	-14.323	-14.314	-14.246

expect intuitively due to the anticipated large angle strain of this molecule. It seems clear that **7** is not involved in the thermal or photochemical decomposition of **1**.

**S-6** is seen to be lower in energy than **T-6** and all other calculated geometries and multiplicities. Recall that the conclusion reached from the thermal and photochemical work was that the reactive intermediate was a ground state singlet or unquenchable triplet excited state. Thus, these calculations suggest that **3** and **4** are formed from the singlet twist conformation.

If **3** and **4** arise from a singlet twist conformation of **2**, what conformation of **2** yields the triplet esr? One cannot make any predictions from the calculations; in fact, a conformation other than those shown may be responsible for the esr.<sup>15</sup> Perhaps the most interesting possibility is that one conformation is observed by esr while another goes directly to product, i.e., there may be more than one conformation of **2** on the reaction surface between the reactant and products.

In conclusion, it has been demonstrated that the same naphthoquinodimethane is generated thermally and photochemically, that a thermally accessible triplet also is an intermediate in the reaction, and, as inferred from the INDO calculations, the direct precursor to the products likely has a twist conformation and singlet multiplicity. Further efforts to define the nature of the 1,8-naphthoquinodimethane are in progress.

**Acknowledgment.** Appreciation is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Research Corporation for the generous support of this research.

(15) A referee has suggested that because the radical centers in the bent conformation (**5**) overlap so strongly, the species which gives the esr signal resembles closely the naphthocyclobutane (**3**) in structure.

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## Additions and Corrections

**Stereochemistry and Mechanism of Acetolysis of 4,4-Dimethylcyclohexyl Tosylate** [*J. Amer. Chem. Soc.*, **94**, 5133 (1972)]. By J. ERIC NORDLANDER\* and THOMAS J. MCCRARY, JR., Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

The *E* configuration assigned to the minor solvolysis product, 3-methylcyclohexyl-3-methyl-*d*<sub>3</sub> acetate, **5**, is

incorrect; the proper assignment is *Z*. It was inferred correctly that the undeuterated methyl is that closer to the acetoxy group, but this position was mistakenly identified as *cis*. The substitution with hydride shift thus proceeds with *inversion* of configuration at the migration origin (and conforms with the results of ref li, j). The paper's principal conclusions, from the un-rearranged acetate, are not affected.