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SYNTHESIS OF THE COVALENT BENZENE–CARBON MONOXIDE CYCLOADDUCT, NORBORNA-2,5-DIEN-7-ONE

CORRELATION OF KINETIC AND THERMODYNAMIC STABILITIES IN CYCLOREVERSION REACTIONS

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Abstract—*endo*-Tricyclo[4.2.1.0^{2,5}]non-7-ene-3,4,9-trione (**14**) is prepared from the 5,5-diethoxycyclopentadiene–diethyl maleate Diels–Alder adduct. Photolysis of the trione in CD_2Cl_2 solution at 192 K forms norborna-2,5-dien-7-one (**2**). The latter substance is thermally unstable and decomposes to benzene and CO with $\Delta G^{\ddagger} = 15$ kcal mol^{-1}. This appears to be the lowest activation energy for a cycloreversion yet measured. A correlation is found for the kinetic and thermodynamic stabilities in a series of 18 orbital symmetry allowed cycloreversions by plotting $\Delta G^{\ddagger}$ vs ΔH_r.

A corollary of the Hammond postulate[1] suggests that the exothermicities and rates of thermal cycloreversions should be correlated. A few experimental examples in the literature[2,3] have stimulated the broader examination in the present paper,[4] which has the aim of developing and testing a method for prediction of the kinetic stability of a cycloadduct from thermodynamic data. If a correlation can be found, we propose also to explore its implications in the region of very high exothermicities, where very fast cycloreversion rates (low $\Delta G^{\ddagger}$ values) would be expected. In fact, such a correlation would raise the question of whether any hypothetical full-valence molecule can fail to exist because the activation energy for its thermal cycloreversion to stable fragments is zero. In other words, are there possible ground state molecular energy surfaces for cycloreversion that are everywhere dissociative?

Epistemologically, of course, the question in this form may be considered objectionable, since it seems to ask: can non-existent compounds exist? It is difficult to imagine how such an unfalsifiable proposition could be tested experimentally. However, as a practical matter, the synthesis of molecules of very low kinetic stability would permit an exploration of the lower reaches of the correlation and would provide an experimental framework for tests of theoretical models.[5]

Correlation of $\Delta G^{\ddagger}$ and ΔH_r for thermal cycloreversions

Experimental values for the reaction enthalpies (ΔH_r) of cycloreversion are not available for most of the cases studied and therefore were estimated from Benson's additivity tables.[6g] Strain energy corrections were applied, when these were not available in the tables, by analogy to model compounds. Where available, experimentally measured $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were used to extrapolate an observed $\Delta G^{\ddagger}$ to 300 K. Most of the $\Delta S^{\ddagger}$ values in the literature for thermal cycloreversions are near +5 e.u., and this was used when an experimental value was not available. The error in ΔH_r is estimated to be ± 5 kcal mol^{-1} and is mostly ascribable to uncertainties in the strain energies, whereas the error in $\Delta G^{\ddagger}$ is estimated to be ± 1 kcal mol^{-1}.

A correlation of $\Delta G^{\ddagger}$ vs ΔH_r might be expected for concerted cycloreversions, since the heats of formation of the reactant and products both influence the energy of the transition state. Although a correlation might also prevail for a series of step-wise cycloreversions, there is no obvious reason to expect these points to fall on the same curve as the data from the concerted reactions. Accordingly, we have plotted $\Delta G^{\ddagger}$ vs ΔH_r for 18 orbital symmetry allowed[22] cycloreversions (Table 1, Fig. 1) and observe a smooth monotonic correlation (open ovals). An additional group of eight orbital symmetry forbidden reactions (filled ovals) falls uniformly above the correlation curve. The substantial uncertainty in the ΔH_r estimates and hence in the exact location of the curve suggests that caution is advisable in the use of the correlation to assign any specific new reaction to a concerted or non-concerted category. Nevertheless, it seems probable that most of the reactions represented by the open ovals of Fig. 1 belong to the concerted class.

The data correspond to rate and equilibrium constant ranges of 10^{27} and 10^{70}, respectively, and therefore represent an extensive test of the Hammond postulate. It is noteworthy that in the region of large endothermicities, the slope of Fig. 1 approaches unity, as would be expected of a reaction series conforming to the Postulate.

Rationale for the synthesis of norbornadienone and ethylenedione

The lowest activation energy for cycloreversion ($\Delta G^{\ddagger} = 17$ kcal mol^{-1}) in the correlation (open ovals) of Fig. 1 is that for the tricyclic diazene **1**[19]. With present-day cryogenic techniques, substances of much lower kinetic stability can be studied. For example, at 10 K, a now routinely accessible temperature, a reaction with $\Delta G^{\ddagger}$ as low as 1 kcal mol^{-1} will have a half-life greater than 500 years. This circumstance encourages an attempt to explore the unknown region below the present terminus of the curve. Among the purposes of such a study would be an attempt to find the functional form[5a–d] of the structure–reactivity correlation and to determine whether the curve continues monotonically toward zero $\Delta G^{\ddagger}$, recedes asymptotically to some finite

Table 1. $\Delta G^{\ddagger}$ and ΔH_r values (kcal mol^{-1}) for thermal cycloreversions

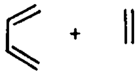
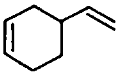
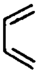
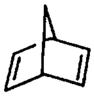
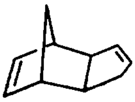
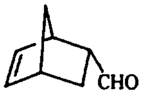
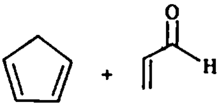
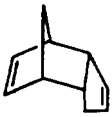
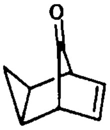
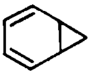
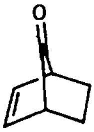
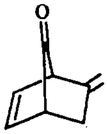
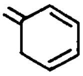
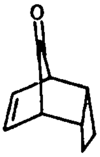
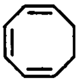
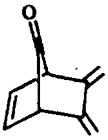
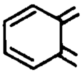
Reactant	Products	$\Delta G^{\ddagger}$	ΔH_r	Refs
	Allowed reactions			
		64.5	40.5	6*a*
	2 	59	37	6*b*
		49.3	30	6*c*
	2 	38.5	20	6*d*
		34.1	15	6*f*
	2 	34.0	16	6*e*, 7
	CO + 	32.9	0.5	8, 9
	CO + 	32	1	9, 10*b*
	CO + 	28.7	−1	9, 10*a*
	CO + 	28.0	−3	9, 11
	CO + 	24.5	−7.7	9, 18

Table 1.—*continued*

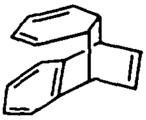
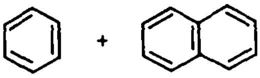
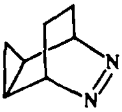
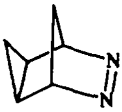
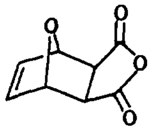
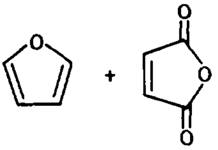
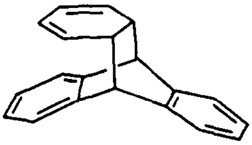
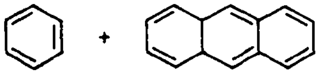
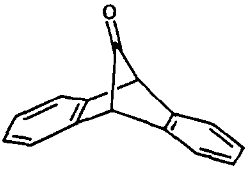
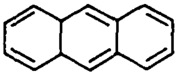
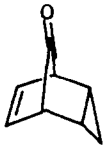
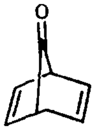
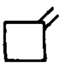
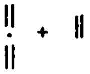
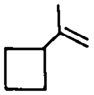
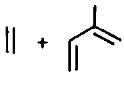
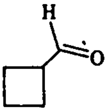
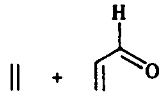
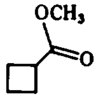
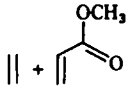
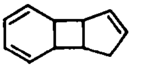
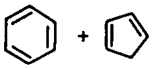
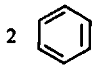
Reactant	Products	$\Delta G^{\ddagger}$	ΔH_r	Refs
		20	−33.5	14, 15
	N_2 + 	20	−50.5	20, 21
	N_2 + 	17	−57	19, 20
		26.0	−17	13
		24.5	−21	14, 15
	CO + 	24.0	−20	16, 17
	CO + 	23.5	−18	8, 9
	CO + 	15	−51	17
	Forbidden reactions			
	2 ||	61	19	23*a*
		61	29	23*b*

Table 1.—*continued*

Reactant	Products	$\Delta G^{\ddagger}$	ΔH_r	Refs
	Forbidden reactions			
		49	14	23*c*
		52	14	23*d*
		55	16	23*e*
		30	−20	24
		25	−41	25

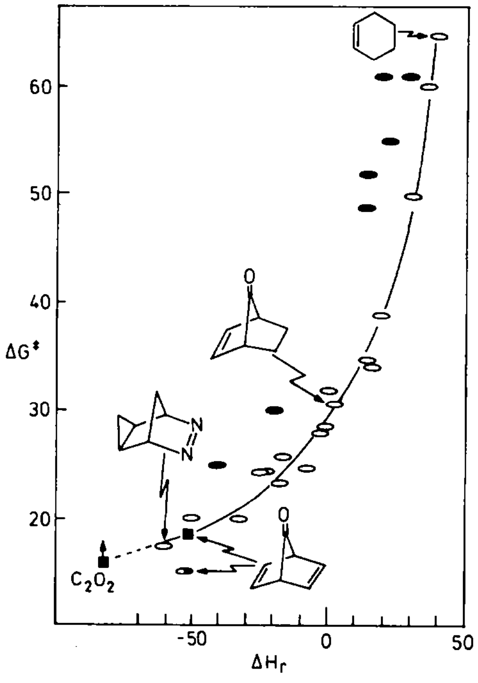
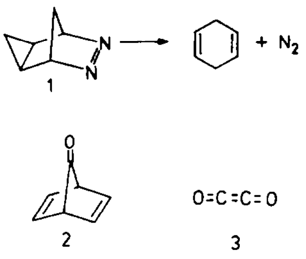


Fig. 1. Relationship of observed free energy of activation ($\Delta G^{\ddagger}$ kcal mol^{-1}) for cycloreversion and enthalpy of reaction (ΔH_r) calculated as described in the text. The open and filled ovals represent orbital symmetry allowed and forbidden reactions, respectively. The half-filled oval represents the observed $\Delta G^{\ddagger}$ value for norbornadienone (**2**); the filled squares represent the predicted $\Delta G^{\ddagger}$ values for **2** and ethylenedione (**3**).

value, or conceivably, passes through a minimum and turns upward.[5e]

As the first goals in this study, we have chosen two molecules of current theoretical and preparative interest, norborna-2,5-dien-7-one (**2**)[26] and ethylenedione (**3**).[27]



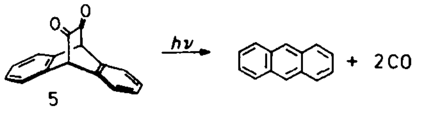
Norbornadienone **2** is the formal 1,4-cheletropic adduct of benzene and carbon monoxide, whereas ethylenedione **3** is a formal dimer of carbon monoxide. Ethylenedione **3**, the simplest even cumulog of dioxygen, has additional significance as a substance whose ground electronic state has a degenerate pair of singly occupied molecular orbitals (MOs) and should be triplet.[28] An approximate lifetime for **2** may be predicted from Fig. 1 and the molecule's calculated ΔH_r, −51 kcal mol^{-1} for cycloreversion to benzene and CO: $\Delta G^{\ddagger}$ should be ~18 kcal mol^{-1}, which corresponds to a half-life of several months at −78°.

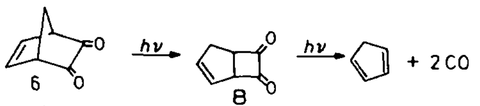
A corresponding prediction for **3** is not so straightforward. The correlation of Fig. 1 refers to reactions in which two conventional σ-bonds are being cleaved in the transition state. However, in **3**, one of the two formal C—C "bonds" being broken is of a different nature, and in the open-shell singlet and triplet states of this molecule, the utility of the whole concept of two two-electron "bonds" between the carbons is debatable. For the sake of argument, we disregard this difficulty. To the value derived from *ab initio* quantum calculations for dissociation of triplet **3** to two ground state singlet CO molecules,[27b] 65 kcal mol^{-1}, we add a calculated[27a] singlet–triplet energy separation for **3** of 19 kcal mol^{-1}, obtaining thereby $\Delta H_r = -84$ kcal mol^{-1} as the singlet–singlet dissociation energy. This ΔH_r value applied to an extrapolation of the plot of Fig. 1, would predict $\Delta G^{\ddagger} \cong 16$ kcal mol^{-1}. The $\Delta G^{\ddagger}$ value for the triplet to singlet dissociation could be higher because of its spin-forbidden nature.

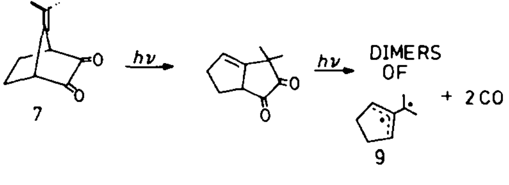
Since the curvature in this region appears to be rather shallow, the predicted $\Delta G^{\ddagger}$ is not very sensitive to the uncertainties in ΔH_r. However, it must be emphasized that this analysis may well be misleading because of the dubious assumptions already mentioned. Moreover, further doubt is cast on the prediction by quantum mechanical calculations[27a] of the reaction pathways for dissociation of C_2O_2 to 2CO, which suggest that the singlet should decompose *via* a *trans*-bent transition state with little or no activation energy.

Choice of the triketone 4 *as a potential precursor of* 2 *and* 3

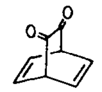
Among the previous approaches to ethylenedione **3**, we note especially three attempts using α-diketone precursors: **5**[29], **6**[30], and **7**[31]. Photolyses of **5** and **6** at room temperature ultimately caused decarbonylation to the corresponding hydrocarbons. In the latter case, decarbonylation was shown to be preceded by an acyl shift to the rearranged α-diketone **8**.[30] Compound **7** was of interest as a candidate for a hypothetical spin-allowed (singlet → 2 triplets) reaction proceeding directly from the singlet excited state to triplet ethylenedione and triplet biradical **9**.



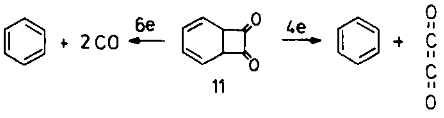


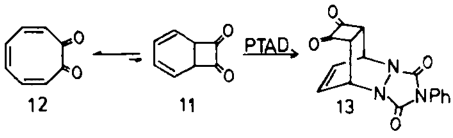


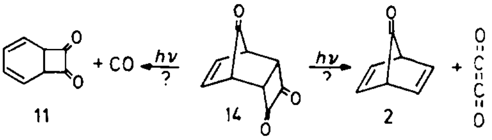
None of these photolyses had been carried out at temperatures low enough to ensure the survival of ethylenedione had it been formed. Accordingly, we photolyzed the α-diketone precursor **10** at greater than 280 nm in an argon matrix at 12 K. Scrutiny by FT-IR spectroscopy of the cryogenic matrix after photolysis again revealed benzene. New absorptions near 2140 cm^{-1} were ascribable to CO. Other bands in the "carbonyl" region appeared, but so far we have been unable to assign them. In particular, they do not appear to be bands of norbornadienone **2** (see below).



10







Although we intend to study the photochemistry of **10** further, we conjecture that the expulsion of ethylenedione from **10**, a six-electron (retro-Diels–Alder) process, might be orbital symmetry forbidden in the excited state, whereas the eight-electron process leading directly to CO might be allowed. This led to the thought that a better precursor might be the isomeric bicyclic ketone **11**, in which the desired reaction would be a four-electron process, while the fragmentation to CO would involve six.

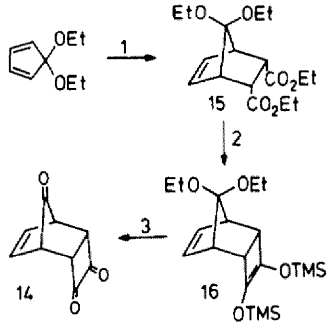
Ketone **11** has not been observed directly, but it seems likely that it is present to a very small extent in equilibrium with its valency tautomer, cyclooctatriene-1,2-dione, **12**, which gives the Diels–Alder adduct **13** when treated with N-phenyltriazolinedione (PTAD).[32]

If this assumption is correct, the desired precursor **11** for the ethylenedione synthesis would have to be generated and photolyzed at a temperature below the threshold for its thermal electrodecyclization to the monocyclic triene **12**. Hence, it is natural to think of a photochemical precursor to **11**, and the triketone **14** quickly suggests itself.

At least two likely photochemical pathways may be anticipated for **14**: elimination of the bridge carbonyl group as CO to give diketone **11**, or elimination of the α-diketone moiety to give ethylenedione **3** and norbornadienone **2** in a single reaction. These possibilities attracted us to the study of triketone **14**.

Synthesis of triketone 14

Scheme 1 outlines the synthesis of *endo*-tricyclo$[4.2.1.0^{2,5}]$non-7-ene-3,4,9-trione, **14**, by a short sequence from 5,5-diethoxycyclopentadiene[33] and diethyl maleate. The Diels–Alder adduct **15** contains all the carbon atoms of **14**. Closure of the four-membered ring by a modified acyloin condensation[34]



Scheme 1. Methods: (1) diethyl maleate, pentane; (2) Na, Me_3SiCl, toluene; (3) Br_2, pentane, −78°.

gave the enediol *bis*-trimethylsilyl ether **16**, which upon bromination gave trione **14**. The latter reaction seems to occur in two stages, the first of which generates the α-diketone system and Me_3SiBr. The latter reagent is known[35] to cleave ketals to ketones, and this reaction converts the intermediate ketal dione to trione **14**. The trione was obtained as an orange (pink in solution), volatile crystalline solid, m.p. 123–124° (dec).

Photochemistry of trione 14

Photolysis of CD_2Cl_2 solutions of **14** at 25° gave benzene as the only identified product. Photolyses in low-temperature matrices were followed by FT-IR spectroscopy, which provided sensitive detection of changes by difference display.

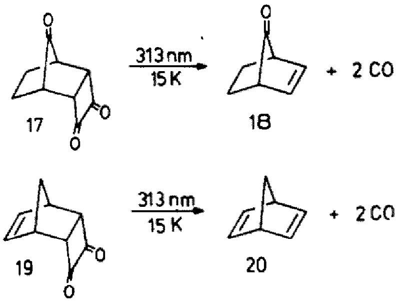
Photolysis of an argon matrix of **14** at 15 K with light of wavelength 313 nm led to the disappearance of the bands of **14** (notably those at 1820 and 1772 cm^{-1}) and to the appearance of bands of CO[36a] at 2136 and 2121 cm^{-1}. Prominent bands of an intermediate grew at 1846 (s), 1801 (m), 1795 (s), 1327, 1317, 1206, 1112 (weak), 809 and 716 cm^{-1}. The latter band is tentatively assigned to an olefinic C—H out-of-plane deformation mode. Warming the sample or prolonged irradiation caused these bands to disappear. Benzene[36b] and CO were the only identified products.

The two strong "carbonyl" bands at 1846 and 1795 cm^{-1} in the photolysate at first aroused our hopes that both norbornadienone **2** and ethylenedione **3** had indeed been generated. In particular, the higher frequency band seemed to be in an appropriate position for a strained cyclopentanone, and the lower frequency band position agreed approximately with that predicted[27b] for **3**, 1745 cm^{-1}. However, these hopes were dashed by observations in the photolysis of **14**-d_6.

A synthesis of perdeuterated trione, **14**-d_6 was accomplished via *endo,endo*-3,4,5,6-tetrachloro-7,7-dimethoxynorborn-5-ene-1,2-dicarboxylic acid, the hydrolysis product of the adduct of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and maleic anhydride. Reductive dehalogenation (Na–EtOD) led to exchange of the α-CO_2^- protons as well, giving the hexadeuterio diacid, which was esterified (CH_2N_2) and carried on to **14**-d_6, by the procedures outlined in Scheme 1.

Photolysis of **14**-d_6 under the same matrix-isolated conditions used for **14** gave rise to an intermediate with a strong IR absorption at 1808 cm^{-1} and a weak one at 1861 cm^{-1}. Clearly, deuteration has perturbed the spectrum previously observed in the carbonyl region of the undeuterated photolysate. This is difficult to reconcile with assignment of either band to ethylenedione, a molecule that contains no hydrogen. A more plausible interpretation would ascribe the two bands originally observed to a Fermi resonance[27d,e] which couples the carbonyl stretching frequency of norbornadienone **2** with another vibration. Although we have not established which vibrations are involved, a possible candidate is the out-of-plane deformation of the olefinic hydrogens of **2**. This mode is of the proper symmetry to couple with the C═O stretch. If the assignment of the 716 cm^{-1} band to the C—H out-of-plane mode is correct, one could imagine that combination with the weak band observed at 1112 cm^{-1} would give a frequency (1828 cm^{-1}) close to that of the C═O fundamental of **2** at 1808 cm^{-1}. Symmetrical splitting would then lead to bands at 1846 and 1794 cm^{-1}, very close to those observed in the undeuterated photolysate.

Corresponding results were observed in the 313 nm photolysis of the dihydro trione analog **17**, which gave CO and norbornenone **18** as the only observed products in an argon matrix at 15 K. Ketone **18** also showed a complex pattern in the carbonyl region, with bands at 1865, 1856, 1795, and 1783 cm^{-1}. These band positions as well as others in the spectrum exactly matched those of a matrix-isolated sample of norbornenone. Similarly, photolysis of the diketone **19** gave CO and norbornadiene **20**.



Characterization and properties of norbornadienone

At this point, the assignment of the 7-norbornadienone structure **2** to the carrier of the IR bands at 1846 and 1795 cm^{-1} was tentative, since the data did not rule out other imaginable species. A more definitive assignment was based upon NMR spectroscopy of samples of **2** in fluid medium.

We first investigated the thermal stability of **2** up to the softening points, 30 and 100 K, respectively, of argon and 3-methylpentane matrices. No decomposition was observed. In a polyethylene matrix, diminution of the IR bands attributed to **2** occurred only when the temperature reached 200 K, at which point the formation of benzene was also observed.

These findings encouraged us to carry out the 313 nm photolysis of trione **14** in CD_2Cl_2 solution at −81° (192 K). The ^1H-NMR spectrum (250 MHz) of the trione, observed at −90° (183 K), gradually diminished in intensity and was replaced by a new spectrum (Fig. 2) consisting of only two absorptions: δ 6.72 (pseudo-t, 4H, J = 2 Hz) and 4.08 (quintet, 2H, J = 2 Hz). The ^{13}C spectrum shows three absorptions: δ 194.9 (s), 132.3 (d), and 55.4 (d). These data leave little doubt that 313 nm photolysis of **14** efficiently generates norbornadienone **2**.[37]

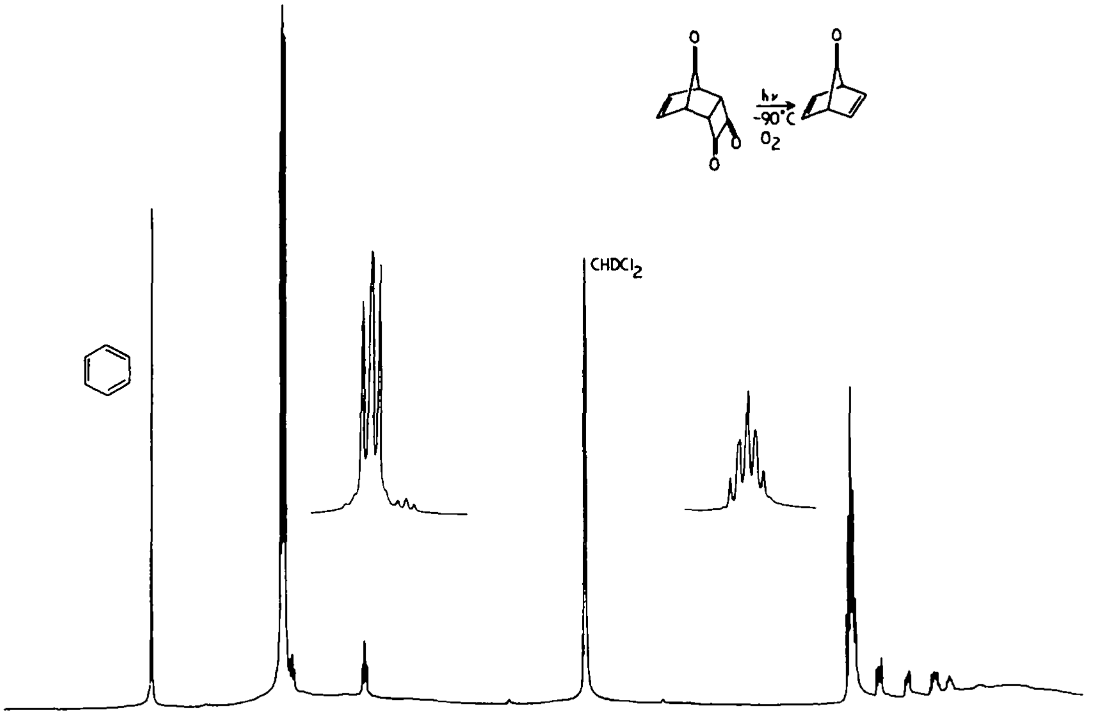
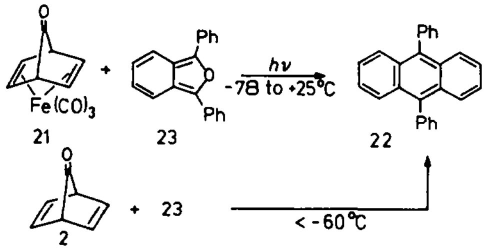


Fig. 2. ^{1}H-NMR spectrum (183 K, 250 MHz) obtained by irradiation (192 K) of a CD_2Cl_2 solution of trione **3**. The major resonances are due to **1**. Small peaks near δ 6.3, 3.9 and 3.7 are due to unreacted **3** (~5–10%). The small peaks near δ 3.8 and 3.6 are associated with an impurity whose formation can be suppressed by degassing the sample before irradiation.

We are still uncertain of whether ethylenedione is also formed in the photolysis. Theory predicts it to be a ground state triplet, and hence one might expect to observe an EPR signal. However, irradiation with light of 313 nm, of a 3-methylpentane glass containing **14** at 4 K in the cavity of an EPR spectrometer gave no EPR signal. Since both carbons of ethylenedione bear no hydrogen, nuclear Overhauser enhancement of the ^{13}C-NMR signals is absent, and the ^{13}C spectrum would be expected to be weak. In some of the matrix-isolated preparations, a weak IR band at 1651 cm^{-1} is observed which is not associated with norbornadienone. The origin of this band and of the polymeric material sometimes observed in the solution phase photolysis of **14** (Fig. 2) are under investigation.

Norbornadienone decomposes thermally to benzene and CO at higher temperatures. The rate of this reaction was readily followed by ^{1}H-NMR spectroscopy. The half-life at 213 K is 25 min. $\Delta G^‡$ (300 K) and E_a, respectively, are 15 and 16 ± 2.5 kcal mol^{-1}, and $\log A = 13.0 \pm 1.8$ (A in s^{-1}). The $\Delta G^‡$ value is lower than that predicted by the extrapolation of Fig. 1 and seems to be the lowest yet measured for a cycloreversion. The observed $\Delta G^‡$ value now may be compared to the theoretical predictions of 21.5 and 25.7 kcal mol^{-1} derived,[26a] respectively, from MINDO/3 and MNDO calculations and to the value 18 kcal mol^{-1} obtained by extrapolation from Fig. 1.

Free norbornadienone behaves similarly to the transient species implicated[26c] in the photochemistry of its $Fe(CO)_3$ complex **21**, which forms 9,10-diphenylanthracene **22** when generated in the presence of diphenylisobenzofuran **23**. Product **22** now is also observed when a cold solution of **2** is treated with **23** and kept below −60°. Although the observation of **22** from the metal complex **21** does not strictly require the intermediacy of norbornadienone, the properties of the latter ketone found in the present work make it a permissible (and likely) intermediate in the photochemistry of the organometallic system.



CONCLUSIONS

The correlation of $\Delta G^‡$ and enthalpy of reaction for orbital symmetry allowed cycloreversions (Fig. 1) has stimulated the synthesis of 7-norbornadienone, which extends the curve to the lowest $\Delta G^‡$ value yet measured. The correlation, slightly modified to incorporate the new point, would seem to offer predictive utility in the region covered by experiment to date. The shape of the curve at still lower $\Delta G^‡$ values remains to be explored.

EXPERIMENTAL

M.ps were obtained on a Hoover m.p. apparatus and are uncorrected. NMR spectra were obtained on a Bruker WM250 (250 mHz) or a Jeol FX-90Q (90 mHz) instrument. High resolution mass spectra were obtained at the Mass Spectrum Facility, Cornell University. Low resolution mass spectra were obtained on a Hewlett Packard 5985-GC-MS instrument. UV spectra were obtained on Cary 219 spectrophotometer. A Varian E-9 EPR spectrometer was used for the EPR experiment. Room temp IR spectra were obtained on a Nicolet 5SX Fourier Transform spectrometer (2 cm^{-1} resolution). IR spectra of matrices were obtained on a Nicolet 7002 Fourier Transform spectrometer (0.5 or 0.25 cm^{-1} resolution). All reactions were run under dry N_2, unless otherwise specified. Dimethyl sulfoxide (DMSO) and CH_2Cl_2 were distilled from CaH_2. Toluene, pentane, and 3-methylpentane were stirred with conc H_2SO_4, washed, dried, and distilled from Na or CaH_2. 2-Methyltetrahydrofuran (2-MTHF) was distilled from $LiAlH_4$ and stored under argon, in the dark.

endo,endo - 2,3 - *Dicarboethoxy* - 7,7 - *diethoxybicyclo* - [2.2.1]*hept* - 7 - *ene* (**15**). A soln of 2,5 - dibromo - 1,1 - diethoxycyclopentane[38] (75.8 g, 0.24 mol) in 50 ml DMSO was slowly added to a mechanically stirred, freezing soln of t-BuOK (101 g, 0.9 mol) in 100 ml DMSO. After 5 min the mixture was quenched by pouring it onto an ice–salt mixture and extracting it with 5 × 200 ml pentane. The pentane extracts were stored in dry ice until they could be added, over several hours, to 350 ml diethyl maleate (2.16 mol) at 40°. The pentane was distilled off, and the excess diethyl maleate was removed by distillation (60°, 0.2 Torr). The desired adduct **15** was contaminated with the dimer of diethoxycyclopentadiene. It was most conveniently purified on a large scale by hydrolysis of the dimer's enone ketal function with *p*-TsOH in wet acetone, followed by formation of the enone semicarbazone and extraction of **15** with ether. Distillation gave 19.2 g (20% from dibromodiethoxycyclopentane) of **15**, as a light yellow oil, b.p. 140–150°, 0.4 Torr. The analytical sample was purified by preparative GC on 2% OV-101, 5 ft at 170°. IR (CCl_4) 2980 (st), 2930, 1745 (v. st.), 1444, 1368, 1320, 1277, 1196 (st.), 908 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 250 mHz) δ 6.23 (t, J = 2 Hz, 2H), 4.04 (AA'X, J = 7 Hz, 4H [at 90 mHz, this is a simple quartet]), 3.47 (brs, 2H), 3.46 (q, J = 7 Hz, 2H), 3.36 (q, J = 7 Hz, 2H), 3.11 (brs, 2H), 1.19 (t, J = 7 Hz, 6H), 1.17 (t, J = 7 Hz, 3H), 1.11 (t, J = 7 Hz, 3H). Detailed comparison of the 3.47 and 3.11 resonances (associated with H_2—H_3 and H_1—H_4, respectively) with those of model compounds, the *endo,endo*- and *exo,exo* - 2,3 - dicarboethoxybicyclo[2.2.1]hept - 5 - enes,[34b] supports the assignment of the *endo,endo* stereochemistry to **15**. ^{13}C-NMR ($CDCl_3$, ppm) 171.6 (s), 131.8 (d), 116.4 (s), 60.0 (t), 57.7 (t), 49.0 (d), 46.2 (two coincident peaks, t and d), 15.1 (q), 14.8 (q), 13.8 (q). *m/e*, 326.1731; calc for $C_{17}H_{26}O_6$, 326.1729.

endo - 3,4 - *Bis*(*trimethylsiloxy*) - 9,9 - *diethoxytricyclo*[4.2.1.0^{2,5}]*nona* - 3,7 - *diene* (**16**). To a mechanically stirred Na sand (5.0 g, 0.22 mol) in 200 ml toluene, was added 27 ml trimethylsilyl chloride (23 g, 0.21 mol), followed by 5.2 g **15** (16 mmol) in 5 ml toluene. The mixture was heated at reflux overnight. The resulting purple mixture was filtered through celite, and the toluene was carefully removed on the rotovap to avoid foaming. The resulting dark oil was distilled, giving 3.7 g of **16** (b.p. 100–104°, 0.15 Torr) as a light yellow oil. When stored under N_2 in the freezer it solidified but could not be easily recrystallized. IR (CCl_4) 2976, 1709, 1304, 1253, 1092, 908 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 5.87 (brs, 2H), 3.4 (2 overlapping quartets, J = 7 Hz, 4H), 2.74 (brs, 4H), 1.2 (2 overlapping triplets, J = 7 Hz, 6H), 0.16 (s, 18H). ^{13}C-NMR ($CDCl_3$, ppm) 129.25 (d), 123.27 (s), 122.79 (s), 59.04 (t), 57.43 (t), 45.51 (d), 38.29 (d), 15.39 (q), 15.26 (q), 0.39 (q). *m/e*, 382.2005; calc for $C_{19}H_{34}O_4Si_2$, 382.1996.

endo - *Tricyclo*[4.2.1.0^{2,5}]*non* - 7 - *ene* - 3,4,9 - *trione* (**14**). Compound **16** (1.23 g, 3.2 mmol) was dissolved in 75 ml pentane, with 1 ml trimethylsilyl chloride, at −78° under argon Br_2 (150 μl, 2.9 mmol) in 2 ml pentane was added dropwise, and then 100 ml CH_2Cl_2 was added. The mixture was warmed to 25°, stirred overnight, and chromatographed on silica gel (CH_2Cl_2), and the orange band was collected and concentrated by evaporation. Trituration of the residue with pentane gave **14** as an orange–pink crystalline solid (0.22 g, 41%), m.p. 123–124° (dec), which readily sublimes, 40–50°, 10^{-2} Torr. IR (CCl_4) 1817, 1783, 1770 cm^{-1}. IR (Ar matrix 12 K) 1820 (vs), 1805, 1780, 1772 (vs), 1280, 1153, 1090, 1075, 1040, 975 (vw), 964 (vw), 884 (w), 850, 810, 791, 730, 713, 599, 420 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 250 mHz) δ 6.39 (pseudo triplet, J = 2.3 Hz, 2H), 3.89 (d of d, J = 2.3, 3.6 Hz, 2H), 3.71 (m, upon irradiation at δ 6.39 simplifies to d of d, J = 2.3, 3.6 Hz, 2H). ^{13}C-NMR (CD_2Cl_2, ppm, 298 K) 206.4 (s), 193.2 (s), 130.0 (d), 50.4 (d), 47.9 (d). *m/e*, 162.0316; calc for $C_9H_6O_3$, 162.0317. UV (λ_{max} (nm), (ε)) 525 (79), 485 (28), 298 (137).

Under some circumstances, the intermediate ketal dione, *endo* - 9,9 - diethoxytricyclo[4.2.1.0^{2,5}]non - 7 - ene - 3,4 - dione, could be isolated in up to 70% yield as a pink solid. Treatment with Me_3SiBr in CH_2Cl_2 gave **14**. IR (CCl_4) 1794, 1769 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 6.0 (pseudo t, 2H), 3.7 (m, 2H), 3.4 (2 q and m, 6H), 1.13 (2t, 6H). ^{13}C-NMR ($CDCl_3$, ppm) 209.9 (s). 132.1 (d), 124.3 (s), 62.4 (t), 59.9 (t), 56.3 (d), 49.9 (d), 16.8 (q), 16.3 (q). *m/e*, 236.1044; calc for $C_{13}H_{16}O_4$, 236.1049.

endo - *Tricyclo*[4.2.1.0^{2,5}]*non* - 7 - *ene* - 3,4 - *dione* (**19**)[34b] *and bicyclo*[2.2.2]*octa* - 5,7 - *diene* - 2,3 - *dione* (**10**)[39] were prepared according to literature methods and sublimed from a sidearm onto the cold window for matrix isolation studies. *Bicyclo*[2.2.1]*hept* - 2 - *ene* - 7 - *one* (**18**)[40] and argon were mixed in the gas phase and codeposited on the cold window.

endo,endo - 2,3 - *Dicarboethoxy* - 7,7 - *diethoxybicyclo*[2.2.1]*heptane*. To an ice cold soln of hydrazine (2.25 ml, 71 mmol), **15** (232 mg, 0.7 mmol), and $Cu(OAc)_2$ (about 1 mg) in 40 ml EtOH was added H_2O_2 (2.9 ml, 30% soln, 28 mmol) over 1 hr. The mixture was then stirred at room temp for a further 2 hr. Excess hydrazine was destroyed with H_2O_2, then H_2O was added, and the product was extracted into CH_2Cl_2, dried, and the solvent removed giving an oil (187 mg, 80% yield). ^{1}H-NMR ($CDCl_3$) δ 4.05 (q, J = 7 Hz, 4H), 3.45 (q, J = 7 Hz, 4H), 3.20 (brs, 2H), 2.27 (brs, 2H), 1.71 (brm, 4H), 1.14 (2 overlapping triplets, J = 7 Hz, 12H).

endo - 3,4 - *Bis*(*trimethylsiloxy*) - 9,9 - *diethoxytricyclo*[4.2.1.0^{2,5}]*non* - 3 - *ene* was prepared in analogy to **16**. ^{1}H-NMR ($CDCl_3$) δ 3.42 (q, J = 7 Hz, 4H), 2.77 (brd, 2H), 2.06 (brd, 2H), 1.58 (brs, 2H), 1.36 (brd, 2H), 1.17 (t, J = 7 Hz, 6H), 0.1 (m, 18H).

endo - 9,9 - *Diethoxytricyclo*[4.2.1.0^{2,5}]*nona* - 3,4 - *dione* was formed by treatment of the above ketal bis-TMS ether with Br_2. ^{1}H-NMR ($CDCl_3$) δ 3.7 (m, 2H), 3.5 (q, J = 7 Hz, 4H), 2.6 (m, 2H), 1.8 (m, 2H), 1.4 (m, 2H), 1.19 (t, J = 7 Hz, 6H).

endo - *Tricyclo*[4.2.1.0^{2,5}]*nona* - 3,4,9 - *trione* (**17**) was prepared in analogy to **14**. IR 1792, 1766 cm^{-1}. ^{1}H-NMR ($CDCl_3$) 3.64 (m, 2H), 2.60 (m, 2H), 1.9 (m, 2H), 1.4 (m, 2H).

endo,endo - 1,2,3,4 - *Tetrachloro* - 7,7 - *dimethoxybicyclo*[2.2.1]*hept* - 2 - *ene* - 5,6 - *dicarboxylic acid*. 1,2,3,4 - Tetrachloro - 7,7 - dimethoxybicyclo[2.2.1]hept - 2 - ene - 5,6 - dicarboxylic anhydride, m.p. 194–195°, was prepared according to Salakhov *et al.*[41] ^{1}H-NMR ($CDCl_3$) δ 3.89 (s, 2H), 3.62 (s, 3H), 3.57 (s, 3H). The anhydride (9.3 g, 35 mmol) was hydrolyzed in hot H_2O–THF, extracted into CH_2Cl_2, dried and the CH_2Cl_2 removed, giving 8.6 g of white powder, m.p. 190–210° (dec). ^{1}H-NMR ($CDCl_3$) δ 3.86 (s, 2H), 3.62 (s, 3H), 3.55 (s, 3H). The position of the acid protons was variable.

endo,endo - 1,2,3,4,5,6 - *Hexadeuterio* - 7,7 - *dimethoxybicyclo*[2.2.1]*hept* - 5 - *ene* - 2,3 - *dicarboxylic acid*. Na (3.37 g, 147 mmol) was added slowly to a refluxing soln of the above tetrachlorodiacid (1.02 g, 268 mmol) in EtOH-0-d (16 ml, 270 mmol) with stirring. The resulting pale purple slurry was heated at reflux for 4 hr, quenched with ice, and extracted with ether. The aqueous layer was acidified and continuously extracted with ether again. The ether extracts gave 0.501 g (69%) of a white powder, m.p. >140° (dec). ^{1}H-NMR ($CDCl_3$) δ 3.19 (s, 2H), 3.13 (s, 3H), 3.11 (s, 3H).

endo,endo - 1,2,3,4,5,6 - *Hexadeuterio* - 2,3 - *dicarbomethoxy* - 7,7 - *dimethoxybicyclo*[2.2.1]*hept* - 5 - *ene*. A sample of the d_6-diacid (0.52 g, 2.1 mmol) was dissolved in 20 ml ether, and 1.8 mmol CH_2N_2 in ether was added. Excess CH_2N_2 was quenched with HOAc, the soln was dried, and the ether was removed under vacuum. Chromatography (neutral alumina, pentane–ether 1 : 1) gave d_6-diester (0.4 g, 70%), m.p. 57–58°. ^{1}H-NMR ($CDCl_3$, 250 mHz) 6.28 (s, 0.05H, 98% D), 3.62 (s, 6H), 3.49 (s, 0.4H, 80% D), 3.22 (s, 3H), 3.15 (s, 3.1H, 95% D and H_3 methyl group). GC–MS indicates 75% $C_{13}H_{12}D_6O_6$, 14% $C_{13}H_{13}D_5O_6$, 10% $C_{13}H_{14}D_4O_6$. ^{13}C-NMR ($CDCl_3$, broad band ^{1}H decoupled) 173 (s), 132 (t), 118 (s), 52.5 (s), 52.1 (s), 50 (s), 47.8 (t), 45.5 (t).

endo - 1,2,5,6,7,8 - *Hexadeuterio* - 2,3 - *bis(trimethylsiloxy)* - 9,9 - *dimethoxytricyclo*[4.2.1.0^{2,5}]*nona* - 3,7 *diene* was prepared in analogy to **16**. ^{1}H-NMR ($CDCl_3$) δ 3.17 (s, 3H), 3.14 (s, 3H), 0.17 (m, 18H). ^{13}C-NMR ($CDCl_3$, broad band ^{1}H decoupled) 129 (t), 124 (s), 123 (s), 51 (s), 49 (s), 45 (t), 38.7 (t), 0.3 (s).

endo - 1,2,5,6,7,8 - *Hexadeuteriotricyclo*[4.2.1.0^{2,5}]*non* - 7 - *ene* - 3,4,9 - *trione* (**14**-d_6). Treatment of the d_6-bis-TMS ether dimethylketal with Br_2 in analogy to formation of **14**, gave, after chromatography, a pink solid. IR 1803, 1789 cm^{-1}. ^{1}H-NMR ($CDCl_3$) residual H at δ 6.33. DIP-MS many bands, including 168 ($C_9D_6O_3$) and 140 ($C_8D_6O_2-CO$).

EPR spectroscopy on photolysate of **14**. A sample of **14** was dissolved in 2-methyltetrahydrofuran, freeze-pump-thawed, and sealed in a quartz EPR tube. In the EPR cavity, it was cooled to 8 K, using an Air Products Helitran liquid helium transfer line, and photolyzed through an Oriel 5180 band pass filter using a Hg high pressure lamp (primarily 313 nm light). No triplet EPR signal was observed at various irradiation times. These conditions were similar to those used for photolysis in the IR experiments (see below), but no direct evidence is available that photolysis actually occurred in the EPR microwave cavity.

Trapping of norbornadienone with 1,3-*diphenylisobenzofuran*. A soln of **14** (2 mg) in freshly distilled ether (9.5 ml) was photolyzed for 80 min at about −90° through an Oriel 5180 band pass filter, with a Hanovia high pressure lamp (313 nm light), while O_2 was bubbled through. Diphenylisobenzofuran **23** (2 mg) in ether (0.5 ml) was added. After 30 min, it was warmed, the ether was removed, and the residue was chromatographed (basic alumina, CCl_4), giving **22**, as determined by NMR, compared to authentic material.

Matrix isolation photochemistry and spectroscopy. Argon and 3-methylpentane matrices were prepared on KBr windows attached to the cold end of an Air Products model CSW-202E Displex closed-cycle helium cryostat. Argon, 99.998%, was supplied by Linde. Argon was deposited at about 6 mmol h^{-1}, with the window at 21 K. Sublimation of **14** at a desirable rate was controlled by cooling or gently warming the sample on a thermoelectric module. Proper matrix isolation was judged by the sharpness of the IR absorptions.

IR spectra were obtained on a Nicolet 7002 Fourier Transform spectrometer at 0.5 or 0.25 cm^{-1} resolution. Irradiations were carried out using a 200 W high-pressure Hg lamp, filtered through Pyrex or an Oriel 5180 band pass filter (260–410 nm). The matrix was at 12–13 K during the irradiation. Pyrex filtered light and Oriel 5180 filtered light gave the same photochemistry in the matrix. Using light of wavelength greater than 425 nm gave much slower photochemistry, but the same products by IR.

By photolyzing through a fiber optics light pipe, sample positioning was preserved, and it was possible to monitor very small changes in the matrix. Short or long irradiation gave the same products. Upon prolonged irradiation, the intermediate(s) is photolyzed, and benzene and CO are produced.

Low temperature solution-phase photochemistry. For ^{1}H and ^{13}C spectra, respectively, about 1 or 10 mg of **14** was dissolved in 0.5 ml CD_2Cl_2. The samples were irradiated with a Hanovia high-pressure Hg lamp and Oriel 5180 band-pass filter. Reactions were carried out in an unsilvered Pyrex Dewar flask cooled with a stream of cold N_2. Some reactions were also carried out using 300 nm bulbs in a Rayonet reactor; these samples were cooled to −91° with a heptane slush. The samples were stored in liquid N_2 and then the tubes were partly thawed and placed in the precooled NMR probe. It seems that bubbling O_2 through the tube increases the rate of overall photolysis, with concomitant formation of a new, minor component (probably the ketoanhydride[42]) in addition to norbornadienone. Warming to room temp gave benzene.

Kinetic measurements were carried out either by holding a sample in the NMR probe at a constant temp (±0.5°) or by photolyzing several tubes of equal concentration, in a merry-go-round apparatus in a heptane slush (−90°) in the Rayonet and then warming them in a thermostatted cold bath (±0.5°) for various lengths of time. Rate constants obtained by monitoring either the disappearance of the olefinic band of **2** or the appearance of the benzene resonance were identical within experimental error.

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