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$(CH)_{10}$ Transformations. Evidence for Competing Concerted and Stepwise Mechanistic Processes in the Photochemical Reactions of *syn*-Tricyclo[4.4.0.$0^{2,5}$]deca-3,7,9-triene

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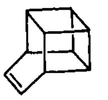
Abstract: The photochemical behavior of *syn*-tricyclo[4.4.0.$0^{2,5}$]deca-3,7,9-triene (**3**) in Pyrex with 3000-Å light has been examined. Nenitzescu's hydrocarbon (**2**), tetracyclo[5.3.0.$0^{2,10}$.$0^{3,6}$]deca-4,8-diene (**5**), benzene (**7**), cyclooctatetraene (**8**), and tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene (**9**) were observed as products. This result and investigation with two different specifically deuterium labeled reactants, **3a**-d_2 and **3b**-d_2, show that the photochemical reaction and rearrangement involves a remarkable variety of closely competing mechanistic processes. Analysis of deuterium scrambling indicates that the minimum set of reaction pathways for the **3** → **2** rearrangement consists of a discrete concerted [1,3] sigmatropic shift and the separate formation of a stabilized bis-allylic diradical intermediate **10** which closes to product and also gives degenerate rearrangement (**3** → **3**). Plausible mechanistic paths for formation of **7** and **9** are dissociation of diradical **10** or a concerted [2 + 2] cycloreversion of **3** to **7** and cyclobutadiene.

For over a decade the $(CH)_{10}$ family of compounds with their remarkable propensity for thermal and photochemical transformation has surprised and fascinated chemists.[1] Because the variety of $(CH)_{10}$ structures[2] and the range of accessible reaction pathways are so great,[1] this research field has become important for increasing our understanding of mechanistic processes and for the discovery of new theoretical concepts. For these reasons, interest in the $(CH)_{10}$ hydrocarbons has continued to be high.[3-8]

An ongoing interest in better understanding the roles of structure, bonding, and reactivity and energy in chemical transformations has attracted us to this area. We now have undertaken work aimed at investigating the $(CH)_{10}$ thermal and photochemical energy surfaces. Our initial effort[4b] arose from an interest in seeing if concurrent thermolysis and photolysis of $(CH)_{10}$ compounds would produce new isomers and lead to discovery of novel reaction pathways. In this connection, basketene (**1**) appeared to be a system of choice for study. Other work[8] had recently indicated that thermolysis of **1** produced **2** via the intermediacy of **3**. We found[4b] that modification of the conditions to include heating of **1** with accompanying irradiation through Vycor gave a significant amount of hexacyclic compound **4** along with **2**. Isomer **4**, which was previously unknown, represents a new facet of $(CH)_{10}$ chemistry.

The question of the nature of the reaction process(es) which leads from **1** to **4** is of particular interest since there is an obvious intrinsic need for other $(CH)_{10}$ intermediates in effecting the transformation. Using orbital symmetry rules and the principle of "precedent" it is possible to formulate a simple, straightforward mechanistic scheme which relates **1** and **4** as shown in eq 1. The considerations pertaining to this were outlined in the preliminary report.[4b] More recently, we discovered that heating and irradiating **1** in Pyrex stopped formation of **4** but produced the proposed intermediate **5** (eq 1) and also gave **2**.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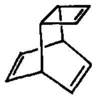
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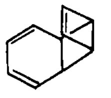
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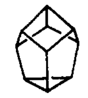
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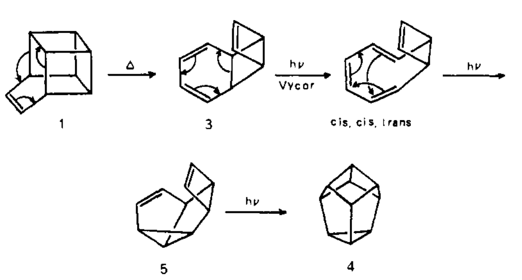
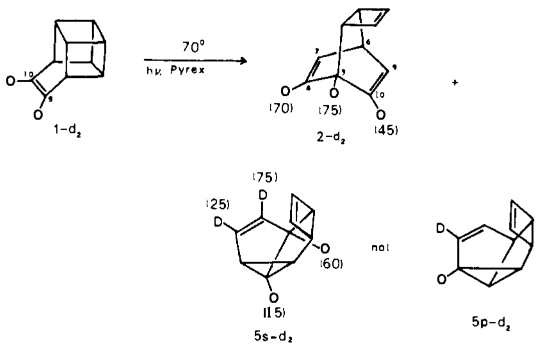


(1)

As a test of the adequacy of the mechanistic description in eq 1, we carried out scouting experiments with deuterium labeled basketene (**1**-d_2). Simultaneous heating and irradiation of **1**-d_2 in Pyrex did not afford **5p**-d_2 with the specific deuterium distribution predicted by eq 1, but yielded instead uniquely deuterium scrambled **5s**-d_2 (eq 2).[9] Also, product **2**-d_2 had deuterium at the C(1)C(6), C(7)C(8), and C(9)C(10) positions. This latter result contrasts with the thermal rearrangement of **1**-d_2 where all of the deuterium ends up equally at C(1)C(6) and C(7)C(8) of **2**-d_2.[8a]

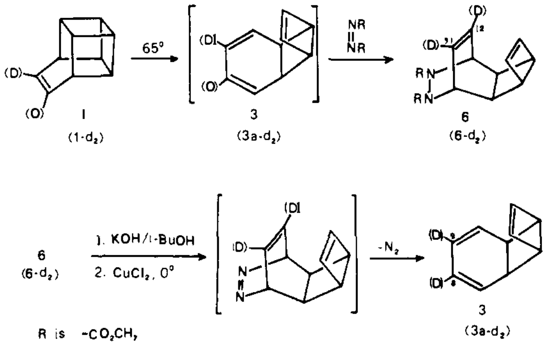


(2)[9]

The finding of **5s**-d_2 (eq 2) clearly indicates that the initial mechanistic hypothesis portrayed by eq 1 is incomplete. It is evident that a study seeking to fill in the missing details of the **1** → **4** conversion mechanism is needed; such inquiry can be expected to provide valuable, new mechanistic insight. We began investigation of the problem by examining the photochemical behavior of **3** since all considerations pointed to **3** as an early key intermediate in the reorganization reaction. This paper identifies the major photolysis products of **3** and reports advances toward elucidation of the mechanisms involved.

Results

Synthesis. A preliminary survey of possible experimental approaches to the problem suggested that study of specifically deuterium labeled **3** could be expected to provide considerable mechanistic information. Consideration of the labeling alternatives indicated that a system such as **3a**-d_2 would be the most instructive. Synthesis of **3a**-d_2 was accomplished using **1**-d_2 as the starting material in the reaction sequence outlined in eq 3. When unlabeled **1** was used as the starting reactant, the method yielded product with properties identical with those reported[8b] for **3**. Use of **1**-d_2 afforded **3a**-d_2 which NMR analysis showed to have deuterium content of 96% at C(8) and C(9).

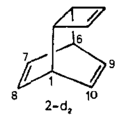


(3)

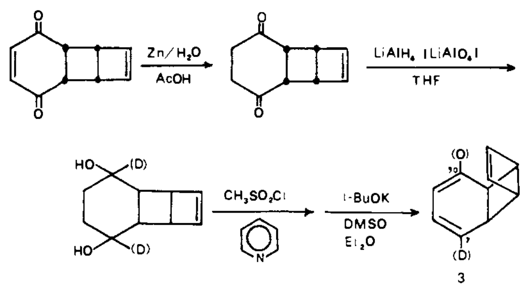
As a check on the mechanistic diagnosis, we prepared a second labeled isomer **3b**-d_2. This isomer was prepared by a modification of the published synthesis.[8b] The series of steps is presented in eq 4. The product obtained from reactants without deuterium had spectral properties identical with those reported[8b] for **3**. NMR analysis of **3b**-d_2 showed the deuterium content at C(7) and C(10) to be 99%.

Thermolysis of 3a-d_2 and 3b-d_2. With **3a**-d_2 and **3b**-d_2 available, it was possible to directly experimentally test the Cope rearrangement mechanism proposed[8] for the thermal conversion of **3** → **2**. Thermolysis of **3a**-d_2 at 94 °C gave **2**-d_2 as the only detectable product. NMR analysis of this sample of **2**-d_2 showed all deuterium essentially equally distributed at the C(1)C(6) and C(7)C(8) positions. Thermolysis of **3b**-d_2 at 94 °C yielded only **2**-d_2 with the deuteriums almost equally located at C(7)C(8) and C(9)C(10). The results are listed in Table I. This data is also valuable in that it is an indicator of the accuracy of the NMR analysis. We estimate the experimental error to be <±0.05 deuterium (footnotes *a* and *b*, Table I).

Table I. Observed and Predicted Analyses of Product **2**-d_2 from the Rearrangements of 3a-d_2 and 3b-d_2

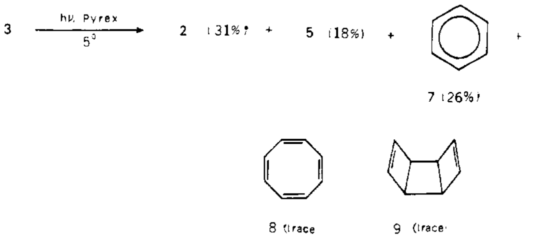
	Deuterium contents for **2**-d_2 products at positions[a]		
	C(7)C(8)	C(1)C(6)	C(9)C(10)
Observed values from 3a-d_2[b]			
Thermolysis[c]	0.98	0.91	0.00
Photolysis[d]	0.36	0.84	0.68
Predicted values from 3a-d_2[e]			
Concerted Cope path i	0.96	0.96	0.00
Concerted [1,3] sigmatropic path ii	0.00	0.96	0.96
Diradical path iii[f]	0.48	0.96	0.48
Diradical path iii + reclosure path v[g]	0.64	0.64	0.64
Concerted path vi[h]	0.64	0.64	0.64
Observed values from 3b-d_2[b]			
Thermolysis[c]	1.05	0.00	0.97
Photolysis[d]	0.91	0.15	0.91
Predicted values from 3b-d_2[e]			
Paths i, ii, or iii[f]	0.99	0.00	0.99
Diradical path iii + reclosure path v[g]	0.66	0.66	0.66
Concerted path vi[h]	0.66	0.66	0.66

[a] Obtained by difference from NMR integration values based on 8.08 hydrogens (0.08 H at C(8)C(9)) for 3a-d_2 and 8.02 hydrogens (0.02 H at C(7)C(10)) for **3b**-d_2. [b] Duplicate experiments gave the same results. The reported values are the average of three–four measurements with a precision better than ±0.05. [c] Sealed tube at 94 °C for 90 min. [d] In *n*-pentane with 3000-Å light (Pyrex) at 5 °C. [e] Predicted values are corrected to 1.92 deuteriums for 3a-d_2 and 1.98 deuteriums for 3b-d_2. [f] No reclosure by way of path v or no path vi. [g] Reclosure of diradical by path v sufficient for complete deuterium scrambling over C(7)C(8), C(1)C(6), and C(9)C(10) (v >> iii). [h] Path vi occurring much faster than product formation (vi >> i, ii, or iii).



(4)

Products from the Photolysis of 3. Irradiation of a 0.1% solution of **3** in *n*-pentane (Pyrex tube) with 3000-Å light for 20 min at 5 °C produced **2**, **5**, **7**, **8**, and **9** as the only volatile materials.[10] The major products were isolated by GLC and identified by NMR spectral comparison with authentic samples of **2**,[8a] **5**,[11] and **7**. Identities of the very low yield products were determined by GLC retention time comparisons (three different columns) with authentic **8** and **9**. The results are summarized in eq 5. Photolysis at 25 and −78 °C yielded the same products. Control experiments showed that the products do not interconvert and that they are stable to photolysis conditions.



(5)

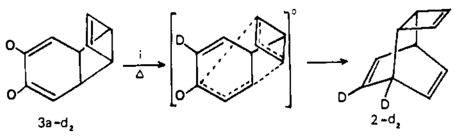
Deuterium Distributions Resulting from Photolysis of Labeled 3. Irradiation of a 0.1% solution of **3a**-d_2 in *n*-pentane through Pyrex with 3000-Å light at 5 °C gave the products shown in eq 5. NMR analysis of the **2**-d_2 sample which had been isolated by GLC showed significant but unequal amounts of deuterium at C(7)C(8), C(1)C(6), and C(9)C(10). Photolysis of **3b**-d_2 under the same conditions yielded a **2**-d_2 sample which had most of the deuterium in equal amounts at C(7)C(8) and C(9)C(10). A considerably smaller amount of deuterium appeared at C(1)C(6). The numerical values are given in Table I. Extended irradiation of product samples of different deuterium distributions did not cause any change in **2**-d_2 composition or show any after-the-fact deuterium scrambling.

Product **7**, from photolysis of **3a**-d_2, was shown by mass spectral analysis to contain two deuteriums. NMR analyses of **5**-d_2 samples from photolysis of **3a**-d_2 and **3b**-d_2 showed different unique deuterium distributions which were consistent with the **5s**-d_2 observation cited above. The details of the latter results will be reported and discussed in a later paper.

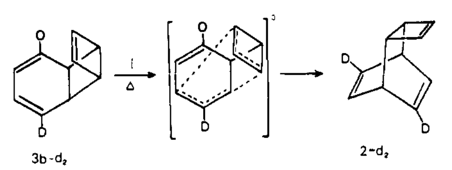
In order to see if **3** undergoes degenerate self-rearrangement during photolysis, **3a**-d_2 was irradiated through Pyrex until conversion to product was ca. 50% complete. At this point the remaining starting material was trapped as Diels-Alder adduct **6**-d_2 with dimethyl azodicarboxylate (eq 3). This recovered **6**-d_2 now showed some 30% hydrogen at C(11) and C(12).

Discussion

Thermolysis. Earlier observations[8] pointed to an allowed concerted Cope rearrangement as the only mechanism occurring in the thermal conversion of **3** → **2**. The uniquely definitive deuterium distributions observed in the thermal products from **3a**-d_2 and **3b**-d_2 are in full accord with this. As shown by the mechanistic predictions in Table I, there are no detectable contributions from diradical processes[3,5a] or from other concerted sigmatropic pathways at temperatures near 100 °C. Equations 6a and 6b illustrate the specific deuterium patterns arising from Cope rearrangement.[12]

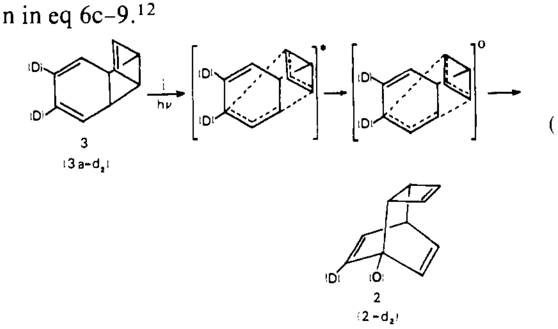


(6a)

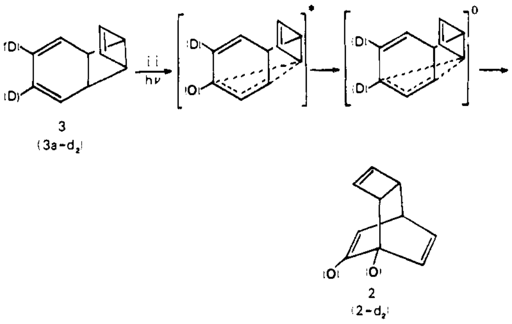


(6b)

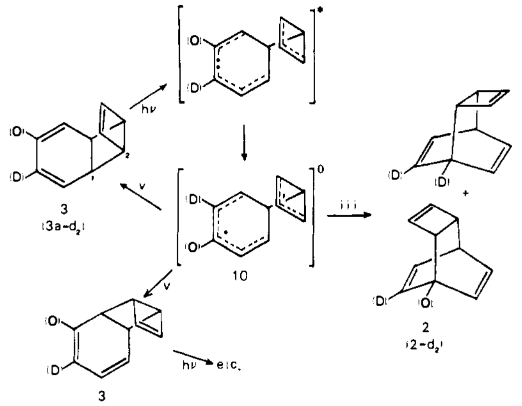
Photolysis. Any mechanistic interpretation of the **3** → **2** photoconversion requires consideration of a variety of different reaction processes. This includes: (i) a concerted [3,3] sigmatropic (Cope) rearrangement, (ii) a concerted [1,3] sigmatropic rearrangement, (iii) a stepwise pathway involving formation of diradical **10** as an intermediate, and (iv) various blends of i, ii, and/or iii operating simultaneously. In addition, there are two possible pathways for degenerate rearrangement of **3**. They are, (v) formation of **10** with reclosure to **3** and (vi) a concerted [3,5] sigmatropic shift. These possibilities are shown in eq 6c-9.[12]



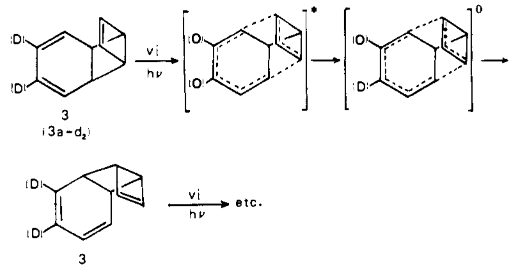
(6c)



(7)



(8)



(9)

It is instructive to compare the observed deuterium scrambling results for **3a**-d_2 and **3b**-d_2 with the respective predictions for the various mechanistic pathways i, ii, iii, v, and vi. These comparisons are summarized in Table I.

In the case of the **3a**-d_2 system which forms **2**-d_2 with significantly different amounts of deuterium at the C(7)C(8), C(1)C(6), and C(9)C(10) positions, it is readily apparent that more than one reaction process is operative. The appearance of deuterium at all three positions is indicative of degenerate self-rearrangement. Substantiation of this is found in the observation that **3a**-d_2 shows scrambling of deuterium around the cyclohexadiene moiety concurrent with conversion to products. The most singular feature of the comparison is that appreciably more deuterium appears at C(9)C(10) than at C(7)C(8). This is unambiguous evidence for the occurrence of [1,3] sigmatropic rearrangement ii (eq 7).

Table II. Comparisons of Photoproduct 2-d_2 Observed Deuterium Contents with Values Calculated[a] for Various Mechanism Combinations[b]

Entry	Reactant	% Mechanism composition[c]	% conversion	2-d_2 deuterium contents		
				C(7)C(8)	C(1)C(6)	C(9)C(10)
1	3a-d_2	Observed	100	0.36	0.84	0.68
2	3a-d_2	80 (ii) + 20 (vi)	96	0.08	0.88	0.99
3		50 (ii) + 50 (vi)	94	0.24	0.79	0.89
4		10 (ii) + 90 (vi)	93	0.54	0.66	0.72
5	3a-d_2	80 (ii) + 20 (iii)	100	0.10	0.96	0.86
6		50 (ii) + 50 (iii)	100	0.24	0.96	0.72
7		20 (ii) + 80 (iii)	100	0.38	0.96	0.58
8	3a-d_2	80 (ii) + 20 (i)	100	0.19	0.96	0.77
9		50 (ii) + 50 (i)	100	0.48	0.96	0.48
10		20 (ii) + 80 (i)	100	0.77	0.96	0.20
11	3a-d_2	50 (ii) + 50 (iii + v[d])	97	0.20	0.90	0.81
12		30 (ii) + 70 (iii + v[d])	97	0.29	0.87	0.72
13		20 (ii) + 80 (iii + v[d])	97	0.38	0.86	0.67
14		10 (ii) + 90 (iii + v[d])	93	0.46	0.84	0.61
15	3a-d_2	47 (ii) + 23 (i) + 30 (vi)	98	0.40	0.84	0.68
16		47 (ii) + 35 (i) + 18 (vi)	99	0.46	0.88	0.58
17	3a-d_2	25 (ii) + 45 (iii[e]) + 30 (vi)	98	0.39	0.84	0.68
18	3b-d_2	Observed	100	0.91	0.15	0.91
19	3b-d_2	20 (ii) + 80 (iii + v[d])	97	0.89	0.21	0.89
20	3b-d_2	50 (ii) + 50 (iii + v[f])	98	0.94	0.11	0.94
21		30 (ii) + 70 (iii + v[f])	96	0.92	0.15	0.92
22		20 (ii) + 80 (iii + v[f])	95	0.91	0.16	0.91
23		10 (ii) + 90 (iii + v[f])	95	0.90	0.17	0.90
24	3b-d_2	47 (ii) + 35 (i) + 18 (vi)	100	0.91	0.16	0.91
25	3b-d_2	37 (ii) + 45 (iii[e]) + 18 (vi)	100	0.91	0.16	0.91
26		25 (ii) + 45 (iii[e]) + 30 (vi)	99	0.86	0.25	0.86

[a] Calculated values are corrected to the experimental observations of 1.92 deuteriums for **3a**-d_2 and 1.98 deuteriums for **3b**-d_2. [b] See reference note 16 for the description of the method of calculation. [c] See eq 6c-9 for the mechanism designation and description. [d] 50% reclosure of diradical **10** to reactant **3**. [e] No reclosure from diradical **10**. [f] 45% reclosure of diradical **10** to reactant **3**.

Structure **3b**-d_2 is less informative since the predicted deuterium distributions for **2**-d_2 are the same for pathways i, ii, and iii. However, one important observation is that a perceptible amount of deuterium shows up at C(1)C(6) of this **2**-d_2 sample. This is additional verification of a degenerate rearrangement. It also provides another measure of the magnitude of the effect.

The net [1,3] sigmatropic rearrangement observed with **3a**-d_2 is an important piece of mechanistic information. This result indicates that part of the migration is a concerted process in which bonding between the reacting sites is maintained throughout (path ii, eq 7).[12] Stepwise reaction would involve a diradical intermediate which of necessity would give equal amounts of deuterium at C(7)C(8) and C(9)C(10) (path iii, eq 8).[12,13]

Further insight into the nature of the mechanism comes from consideration of orbital symmetry and related factors. The structural constraint imposed by the tricyclic nature of **3** limits rearrangement to suprafacial migration. This condition makes the concerted [3,3] sigmatropic shift (Cope rearrangement) symmetry-forbidden and the concerted [1,3] and [3,5] shifts symmetry-allowed.[14] Stepwise rearrangement by way of diradical **10** (eq 8)[12] can be expected to provide strong allylic stabilization at each end of the breaking C(1)–C(2) bond. It is quite possible that this might cause the diradical transition-state energy to be comparable with that of any concerted process.[14,15]

Additional mechanistic information concerning the **3** → **2** phototransformation can be obtained by comparing the **2**-d_2 experimental C(7)C(8):C(1)C(6):C(9)C(10) deuterium content ratio of 0.36:0.84:0.68 (Tables I and II) with values calculated for various blends of path ii and other paths i, iii, v, and vi.[16] Calculation results for the symmetry-allowed combination of competing processes ii and vi[13] show that no combination will fit the observed ratio.[16] In this case, increasing the contribution of vi simply increases deuterium scrambling and tends toward the equilibrium value of 0.64:0.64:0.64 given in Table I. This trend is indicated by entries 2-4 in Table II. Similar analyses also show that the other dual pathway possibilities cannot produce the observed ratio. These trends are illustrated by listings 5-7 and 8-10 in Table II. It is clear that the mechanism must be expanded to include more than two competing processes.

First, let us consider the case of **3a**-d_2 with ii + iii and added step v giving reclosure from the intermediate diradical **10** (eq 7 and 8). Calculation of **2**-d_2 deuterium ratios for various compositions of ii and (iii + v) reveals that appropriate ordering of the deuterium content values can be obtained.[16] By successive approximation it is possible to reproduce the observed ratio within the experimental error limit with compositions in the vicinity of 20% (ii), 80% (iii + v), and 50% (v). A summary of this is shown by entries 1 and 11-14 in Table II.

It is of interest to see if the best ii + (iii + v) mechanistic mixture for **3a**-d_2 also reproduces the C(7)C(8):C(1)C(6):C(9)C(10) **2**-d_2 deuterium content ratio from **3b**-d_2. As shown by comparing items 18 and 19 in Table II, calculation with this composition does yield a ratio in satisfactory agreement with the experimental value. A small improvement in fit is achieved by adjusting the contribution of v to ca. 45% reclosure. This is illustrated by entry 22.

Some comments regarding the computational results are now in order. In making the calculations we have assumed that isotope effects are negligible since literature experimental data needed for evaluation of the **3** → **2** photoreaction is lacking at present. The fact that the same ii + (iii + v) blend generates the appropriate ratios from two differently deuterium substituted species **3a**-d_2 and **3b**-d_2 is evidence of the suitability of the assumption. In this connection, there is nothing about the calculations which predestines such congruity.

Two other mechanistic formulations with three competing pathways require examination. As shown by entries 1,15 and 18,24 in Table II, the ii + i + vi combination can produce satisfactory agreement between computed and observed **2**-d_2 deuterium ratios from both **3a**-d_2 and **3b**-d_2. For the other set consisting of ii + iii + vi, entries 1,17, and 18,25 also show similar agreement.

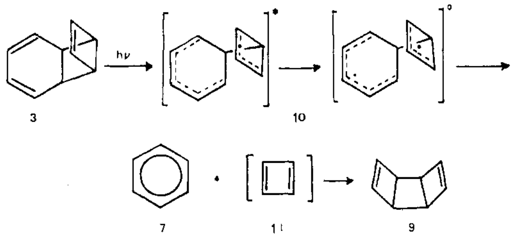
Although the combination of ii + i + vi gives acceptable fit of the data, there are grounds for discarding it. First of all, path i as a concerted reaction[13] is symmetry-forbidden in the excited state and thus is predicted to be of least importance.[14] A second reason comes from comparison of items 15, 16, and 24 in Table II. This shows that the **3a**-d_2 and **3b**-d_2 transformations require significantly different contributions from i and vi to match calculation with observation. Such a result is mechanistically incongruous. However, the result is consistent with the finding that the same mixture of ii + (iii + v) computes the correct deuterium ratio from both **3a**-d_2 and **3b**-d_2 (vide supra).

For the case of ii + iii + vi both concerted paths ii and vi[13] are symmetry-allowed in the excited state.[14] On this basis the combination is a favorable one. However, as shown by items 17, 25, and 26 in Table II, the **3a**-d_2 and **3b**-d_2 conversions require different contributions from ii and vi to attain agreement between calculation and observation. This behavior is entirely analogous to that found with ii + i + vi. Again, it is not a compatible result from a mechanistic standpoint.

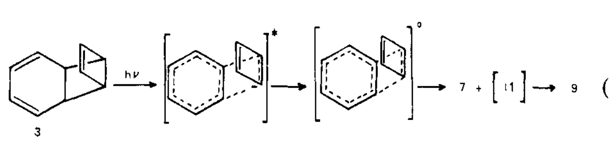
Inspection of cases with more than three competing processes shows that more complicated mechanistic formulations will produce satisfactory fits. However, we have not pursued this since there is nothing in our experimental data which indicates the need for more complexity.

The best working hypothesis for the mechanism of the **3** → **2** photochemical rearrangement at this time is the simplest combination of reaction features which will fit the facts we know.[17] All of the evidence taken together indicates a minimum set of separate contending processes. They are (a) a discrete concerted [1,3] sigmatropic shift (path ii, eq 7) and (b) formation of a discrete stabilized diradical intermediate **10** which closes to product and gives degenerate rearrangement (paths iii + v, eq 8). It remains to be seen if further study will make it necessary to increase the complexity of this mechanistic scheme.

The question of the mechanistic origin of product **7** needs to be examined. Inspection of the foregoing considerations suggests diradical **10** as a likely precursor of **7**. A strong driving force for this is formation of the very stable benzene ring. The accompanying formation of cyclobutadiene also serves to account for product **9**. This sequence of events is shown in eq 10.[12]



(10)



(11)

A plausible alternative source of **7** (and **9**) is a concerted [2 + 2] cycloreversion reaction. Such processes are symmetry-allowed in the excited state and are among the most widely observed photochemical processes.[18] This pathway is illustrated with eq 11.[12] The information now available does not provide a basis for choosing between eq 10 and 11.

The question of the mechanistic process(es) which convert(s) **3** → **5** remains to be considered. However, the details of this are still being worked out and discussion will be delayed to a later report.

In contrast with the thermal chemistry the photochemistry of **3** shows a remarkable variety of concurrently operating mechanistic pathways. It is interesting that the contributions of the photochemical processes are so closely balanced in competition.

Epilogue

The findings reported here are of considerable fundamental interest. With the advent of "conservation of orbital symmetry" ideas, there has been increased discussion about the question of the nature of concerted and nonconcerted reactions and the proper description of the mechanisms involved.[14,15,19] This has caused much experimental and theoretical investigation of organic transition states.[20-22] A related facet of this is concerned with the ongoing development of the theory of photochemical reactions.[12,23] In these regards, the observations with system **3** provide one important calibration point for guiding the development of ideas about bond breaking and making. They also suggest some future lines of inquiry.

Experimental Section

Melting points are uncorrected. Infrared and ultraviolet spectra were obtained with Beckman IR-5A and Cary 14 spectrophotometers, respectively. Proton NMR spectra were recorded with either a Varian A-60 or XL-100-15 spectrometer using tetramethylsilane as an internal standard. Analytical GLC measurements were made with a Varian Hy-Fl III Model 1200 chromatograph equipped with a flame ionization detector and an Autolab Model 6300 digital integrator. Preparative separations were carried out with an Aerograph Autoprep Model A-700 instrument. Mass spectra were obtained with an Associated Electrical Industries, Ltd. MS 30 double beam combination GLC-mass spectrometer. Elemental analyses were obtained from M-H-W Laboratories, Garden City, Mich. Irradiations were performed with a Rayonet Photochemical Reactor Model RPR-100 equipped with RPR-3000 Å lamps or with a 450-W Hanovia 679 A36 medium-pressure mercury lamp fitted with appropriate filters.

Basketene (1). This compound was prepared from cyclooctatetraene by a published procedure.[24] It was purified by GLC: mp 60-61 °C (lit.[24] mp 61-62 °C).

Basketene-d_2 (1-d_2) was prepared by following the published procedure:[8a] mp 59-60 °C; NMR ($CDCl_3$) δ 6.48 (<0.08 H), 3.7 (2 H, multiplet), 3.29 (2 H, quintet), 2.68 (4 H, multiplet). Deuterium incorporation was 96% at C(9) and C(10).

***syn*-Tricyclo[4.4.0.0^{2,5}]deca-3,7,9-triene (3), eq 3.** A solution of 3.76 g (0.029 mol) of **1** and 16.61 g (0.114 mol) of dimethyl azodicarboxylate in 50 mL of carbon tetrachloride was stirred at 65 °C for 20 h. At this point, the carbon tetrachloride and unreacted **1** and dimethyl azodicarboxylate were removed under reduced pressure (0.05 mm, <65 °C). The recovered solvent and reactants were heated together at 65 °C for 20 h; again the volatiles were removed under vacuum. The combined crude adduct mixture from nine such cycles amounted to 13.2 g. Separation of a 9.9-g sample of this mixture was effected by dry column chromatography[25] using silica gel (Woelm, dry column grade which contained 0.05% inorganic fluorescent indicator) with ether as eluent. The 1:1 adduct 9,10-dicarbomethoxy-9,10-diazatetracyclo[6.2.2.0^{2,7}.0^{3,6}]dodeca-4,11-diene (**6**) had an R_f value of ca. 0.6 and was easily detected with a short wavelength (254 nm) lamp. The dry column (Nylon) was cut and the segment containing **6** was extracted with ether. This produced 1.51 g of **6** (25% overall yield from **1**): colorless glass; IR (Nujol) 5.9 μ (>C=O); NMR ($CDCl_3$) δ 6.30 (2 H, multiplet), 5.66 (2 H, broad singlet), 4.88 (2 H, multiplet), 3.73 (6 H, singlet), 3.48 (2 H, multiplet), 2.99 (2 H, multiplet). As reported earlier,[4a] one structure proof of **6** was accomplished by converting it to 10,11-diazahexacyclo[6.4.0.0^{2,7}.0^{3,6}.0^{4,12}.0^{5,9}]dodec-10-ene.

Intermediate compound **6** was converted directly to **3** by the following method. A solution consisting of 40 mg (0.36 mmol) of potassium *tert*-butoxide, 3 mL of *tert*-butyl alcohol, and 10 mg (0.036 mmol) of **6** was stirred under air at 23 °C for 136 h. The reaction mixture was worked up by adding 5 mL of water and then extracting with 3-mL and 1-mL portions of pentane. The combined extracts which were washed with 2 mL of water and dried ($MgSO_4$) gave a pentane solution containing 1.5 mg (0.12 mmol) of **3** (ca. 30% yield, estimated by GLC analysis of a small portion of solution which had been thermally converted to **2**). The product had properties in agreement with those reported for **3**.[8b]

***syn*-8,9-Dideuteriotricyclo[4.4.0.0^{2,5}]deca-3,7,9-triene (3a-d_2).** A sample of 11,12-dideuterio-9,10-dicarbomethoxy-9,10-diazatetracyclo[6.2.2.0^{2,7}.0^{3,6}]dodeca-4,11-diene (**6**-d_2) was prepared by the sequence given above for **6** using **1**-d_2 as the starting material: NMR ($CDCl_3$) δ 5.66 (2 H, broad singlet), 4.88 (2 H, broad singlet), 3.73 (6 H, singlet), 3.48 (2 H, multiplet), 2.99 (2 H, multiplet). No NMR signal was detectable at δ 6.30, the signal region for the C(11) and C(12) hydrogens.

The conversion of **6**-d_2 to **3a**-d_2 was modified from that given above for **6** → **3**. A 0.91-g (3.3 mmol) sample of **6**-d_2 in 5 mL of *tert*-butyl alcohol was added to a solution of 3.0 g (27 mmol) of potassium *tert*-butoxide in 40 mL of *tert*-butyl alcohol. After oxygen had been carefully displaced with nitrogen, the reaction mixture was stirred and heated at 46 °C for 18 h and then poured into 350 mL of ice water and 50 mL of cold pentane. A total of 3 g (18 mmol) of cupric chloride dihydrate was added in small portions to this mixture; nitrogen evolution was observed. The cold pentane layer was removed, and the aqueous phase was extracted with three 25-mL portions of pentane. The pentane extracts were washed twice with cold water and the combined extract was dried ($MgSO_4$). Direct GLC analysis of the pentane solution (10 ft × 0.125 in. column at 90 °C, 20% SE-30 on Chromosorb W 60–80 mesh) showed a 56% recovery of product (measured as **2**-d_2 arising from the **3** → **2** thermal rearrangement on the injection port and column) corresponding to ca. 240 mg of **3a**-d_2. A portion of solution was worked up for NMR examination: (pentane) δ 6.31 (2 H, broad singlet), 5.49 (2.08 H, broad singlet), 3.58 (2 H, broad multiplet), 3.31 (2 H, broad multiplet). A part of the signal near δ 5.5 and corresponding to the C(8)C(9) hydrogens[8b] was missing. Deuterium incorporation in **3a**-d_2 was found to be 96%.

***syn*-Tricyclo[4.4.0.0^{2,5}]deca-3,7,9-triene (3), eq 4.** *syn*-Tricyclo[4.4.0.0^{2,5}]deca-3,8-diene-7,10-dione was prepared by the method described in the literature,[7] mp 77–77.5 °C (lit.[7] mp 77–77.5 °C). A 2.25-g (14.1 mmol) sample of this dione in 15 mL of glacial acetic acid was added to a vigorously stirred slurry of 10 g of activated zinc dust[26] in 10 mL of water which was cooled with ice water. After stirring for 10 min, the mixture was filtered through a pad of Celite and the filter cake was washed with dichloromethane. The filtrate was extracted with dichloromethane and combined extract washed with 5% $NaHCO_3$ solution. After drying the extract ($MgSO_4$), the solvent was evaporated leaving 2.15 g (95% of theory) of *syn*-tricyclo[4.4.0.0^{2,5}]deca-3-ene-7,10-dione, mp 49–50 °C. Two successive sublimations of this crude product gave an analytical sample: mp 53–54.5 °C; NMR ($CDCl_3$) δ 6.33 (2 H, singlet), 3.65 (4 H, multiplet), 2.64 (4 H, 14 line multiplet); IR (neat melt) 5.92 μ (C=O).

Anal. ($C_{10}H_{10}O_2$) C, H.

This dione was reduced with lithium aluminum hydride in dry tetrahydrofuran to give crude *syn*-tricyclo[4.4.0.0^{2,5}]deca-3-ene-7,10-diol: IR 3.3–3.7 μ (—OH) and no C=O. A solution of 1.15 g (7.1 mmol) of the crude diol in 30 mL of dry pyridine was cooled in an ice bath and 2.6 g (23 mmol) of freshly distilled methanesulfonyl chloride was added. After 18 h at −5 °C, the reaction mixture was filtered and most of the pyridine was removed by vacuum distillation at or below room temperature. The crude, brown oily product showed no IR O-H absorption. The crude bis-mesylate sample was dissolved in 10 mL of dimethyl sulfoxide, and this solution was added to a stirred and cooled (0 °C) mixture of 5 g of potassium *tert*-butoxide, 30 mL of dimethyl sulfoxide, and 60 mL of dry ether (two phases). After stirring for 1 h, the reaction mixture was cooled to −20 °C and the ether layer was removed by decantation. The remaining residue was allowed to melt, then shaken with pentane, cooled to −20 °C, and the pentane removed by decantation. After three such treatments, the ether and pentane extracts were combined, washed twice with water, and dried ($MgSO_4$). The desired compound **3** was isolated from the other products by dry column chromatography[25] (36 in. × 1 in. column packed with dry column grade silica gel and pentane eluent). Short wavelength UV light showed **3** $R_f \sim 0.7$, 1,2-dihydronaphthalene $R_f \sim 0.5$, and naphthalene. A pentane solution containing ca. 100 mg of **3** was obtained from the separation: NMR (pentane) δ 6.26 (2 H, singlet), 5.52 (4 H, broad singlet), 3.51 (2 H, broad multiplet), 3.27 (2 H, broad multiplet); UV max 278 nm and a min 240 nm. The observations were identical with those cited in the literature.[8b]

***syn*-7,10-Dideuteriotricyclo[4.4.0.0^{2,5}]deca-3,7,9-triene (3b-d_2).** A sample of *syn*-7,10-dideuteriotricyclo[4.4.0.0^{2,5}]deca-3-ene-7,10-diol was prepared by reducing *syn*-tricyclo[4.4.0.0^{2,5}]deca-3-ene-7,10-dione with lithium aluminum deuteride (99% D). The deuterium labeled diol was converted to **3b**-d_2 by the eq 4 sequence given above: NMR (CCl_4) δ 6.26 (2 H, singlet), 5.47 (2 H, broad singlet), 3.43–3.21 (4 H, multiplet). The part of signal missing near δ 5.5 corresponds to the C(7)C(10) hydrogens.[8b] NMR analysis showed the deuterium content to be 99%.

Concurrent Thermolysis and Photolysis of Basketene (1-d_2). A solution of 430.9 mg (3.31 mmol) of **1**-d_2 and 37.8 mg of adamantane (internal standard) in 50 mL of freshly distilled cyclohexane was placed in three 10 mm × 30 cm Pyrex tubes. These tubes were degassed by five freeze-pump-thaw cycles, sealed under 0.2 mm pure nitrogen, and then irradiated at 70 °C for 10 days. The contents of the tubes were combined and analyzed by GLC (10 ft × 0.125 in. column at 100 °C, 20% SE-30 on Chromosorb W 60–80 mesh). Two $C_{10}H_8D_2$ products were observed in 58 and 22% yields. These products were isolated by preparative GLC (10 ft × 0.375 in. column at 100 °C, 20% SE-30 on Chromosorb W 60–80 mesh). The 58% product was a **2**-d_2 compound: mass spectrum *m/e* 132; NMR (CCl_4) δ 6.4 (1.25 H, broadened doublet), 6.08 (2 H, singlet), 6.02 (1.55 H, apparent doublet), 3.27 (1.35 H, broad multiplet), 2.49 (2 H, multiplet). The positions of the NMR signals were in agreement with those reported for **2**.[8a] The reduced hydrogen integration values occur at the C(7)C(8), C(9)C(10), and C(1)C(6) positions, respectively. The 22% product was **5s**-d_2: mass spectrum *m/e* 132; NMR (C_6D_6) δ 6.18 (1 H, multiplet), 5.62 (0.75 H, apparent doublet), 5.50 (1 H, apparent doublet), 5.00 (0.25 H, broadened doublet), 3.86 (1 H, multiplet), 3.70 (1 H, multiplet), 3.18 (0.40 H, apparent triplet), 2.96 (0.85 H, multiplet), 1.66 (1 H, apparent doublet of triplets), 0.94 (1 H, apparent quartet). The positions of the NMR signals agreed with those reported for **5**.[11] The reduced hydrogen integrations correspond to the deuterium containing positions shown on **5s**-d_2 (vide supra). (More details will be reported in a later paper.)

Thermolysis of 3a-d_2 and 3b-d_2. A solution of 20 mg of **3a**-d_2 in 16 mL of pentane in a Pyrex tube was degassed by two freeze-pump-thaw cycles, sealed under vacuum, and then placed in bath at 94 °C. After 90 min the tube was cooled with ice, opened, and the contents concentrated to ca. one-half the volume by careful distillation. GLC analysis (10 ft × 0.25 in. column, 15% FFAP on Chromosorb W 60–80 mesh) showed **2**-d_2 to be the only detectable product. Separation by preparative GLC gave pure **2**-d_2. The deuterium content values (see footnote *a*, Table I) are reported in Table I.

Thermolysis of **3b**-d_2 was carried out in an identical manner. The deuterium distributions for the corresponding **2**-d_2 appear in Table I.

Products from the Photolysis of 3. Samples of a 0.1% solution of **3** in *n*-pentane with either 0.1% adamantane or 0.1% *n*-octane (internal standards) were placed in 4-mm o.d. Pyrex tubes, degassed by the freeze-pump-thaw method, and sealed. Irradiation of the samples at 5 °C with 3000-Å lamps was followed by GLC until there was no change in the product ratios (ca. 20 min). Control experiments for up to 2 h showed that the products were stable to photolysis conditions. GLC analysis of the photolyzed solution with three different columns (10 ft × 0.125 in. column, 20% SE-30 on Chromosorb W 60–80 mesh; 10 ft × 0.125 in. column, 20% QF-1 on Chromosorb W 45–60 mesh; and 8 ft × 0.125 in. column, 15% FFAP on Chromosorb W 60–80 mesh) identified **2**, **5**, **7**, **8**, and **9** as products by retention time comparisons with authentic samples of each. Products **2**, **5**, and **7** were isolated by GLC and also identified by NMR spectral comparisons with authentic samples. The product yields are listed in eq 5. Similar experiments at 25 and −78 °C showed that the same products were formed.

Deuterium Distributions Resulting from Photolysis of 3a-d_2 and 3b-d_2. A sample of a 0.1% solution of **3a**-d_2 in *n*-pentane in a 12 in. × 8 mm o.d. Pyrex tube was irradiated at 5 °C with 3000-Å lamps by the above described method. After photolysis, the contents of the tube was filtered through a Celite pad and the filtrate was concentrated by careful distillation. The three major components were separated and isolated by preparative GLC (10 ft × 0.25 in. column at 90 °C, 15% FFAP on Chromosorb W 60-80 mesh). Benzene (**7**): mass spectrum showed two deuteriums. The deuterium content values (see footnote *a*, Table I) for the **2**-d_2 product are listed in Table I. Compound **5a**-d_2 results will be reported later.

A sample of **3a**-d_2 pentane solution which had been irradiated until the conversion to products was ca. 50% complete (GLC) was treated with dimethyl azodicarboxylate. The Diels-Alder adduct **6** was isolated by dry column chromatography as described earlier. The NMR spectrum of this **6**-d_2 sample showed a significant signal at δ 6.30 (ca. 0.6 H) corresponding to hydrogen at C(11)C(12) (vide supra).

Photolysis of **3b**-d_2 was carried out by the above procedure. The pertinent deuterium distributions for the **2**-d_2 product are given in Table I. Compound **5b**-d_2 results will be reported later.

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Fragmentation Pathways in the Photolysis of Phenylacetic Acid

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Abstract: The pathways leading to formation of toluene from the photodecarboxylation of phenylacetic acid have been delineated by performing photolyses in solvents bearing appropriate deuterium labels. The photolysis of the acid produces toluene and bibenzyl from an intermediate benzyl radical, and the photolysis of the sodium salt produces toluene through the intermediacy of the benzyl anion. The results are remarkably independent of the solvent employed. A concerted photodecarboxylation is inconsistent with the results obtained.

Numerous reports of photochemical decarboxylation of carboxylic acids or esters have established the generality, but modest quantum efficiency of their reaction.[1-8] Although the gross molecular changes are deceivingly simple, Miller[2] has cataloged 25 distinct primary cleavage modes of the carboxyl function which must be considered in pinpointing the mechanism. Previously, flash photolysis,[2,3,9] CIDNP,[10] kinetic measurements,[11] and product analysis have been used as tools to probe this reaction. These studies have led to the conclusion that a variety of mechanisms are operable, depending on the substrate and conditions employed. We have investigated the mechanism using isotopic labeling, which allows a more definitive quantitative interpretation.

We have initially focused attention on the decarboxylation of phenylacetic acid (**1**) and its sodium salt, since they have been reported to react via two different pathways.[2,3,9] The major monomeric product of decarboxylation, toluene, can potentially arise from either of two penultimate species, a radical or carbanion. These pathways can be shown schematically (eq 1 and 2). Additionally, one might envisage a concerted mechanism for toluene formation (eq 3).

Previously, the occurrence of a spectral absorption from the