mations in which they are most stable in solution, we have suggested[1] that the formation of **3** and **5** upon irradiation in solution also occurs through conformation **1**.

(15) Adduct **6**, mp 163 °C, was prepared according to the procedure of C. F. H. Allen, C. G. Eliot, and A. Bell, *Can. J. Res.*, **17**, 75–88 (1939). The characterization of **7** and **8** will be discussed in our full paper.

(16) Invariably, cyclobutanone-containing products (e.g., **5**) are not formed from the irradiation, either in solution or in the solid state, of Diels–Alder adducts which lack C_2 and C_3 methyl substitution.[1,10] The source of this effect is not clear at the present time, but is likely[1] related to the requirement for a low-lying $(\pi,\pi^*)^3$ state (favored by ene–dione methyl substitution) in process γ which leads to **5**.

(17) The Diels–Alder adducts formed between *p*-benzoquinone and butadiene and 2,3-dimethylbutadiene also undergo solid state photodimerization in preference to the intramolecular processes (hydrogen abstraction[10]) observed in solution. Preliminary results indicate topochemical control in these cases as well. The competing effects of an intramolecular and intermolecular solid state reaction, albeit of the same type (photodimerization), have been described by J. K. Frank and I. C. Paul, *J. Am. Chem. Soc.*, **95**, 2324 (1973).

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Thermally Induced Decarbonylation of Cage Ketones[1]

Sir:

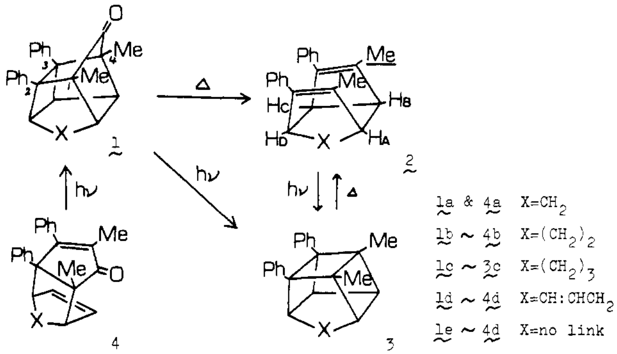
Recently much attention has been focused on edge participation of the cyclobutane vs. cyclopropane ring in thermally induced extrusion reactions.[2] In the decarbonylation of bridged ketones, the contribution of a cyclopropyl σ-bond has been well documented,[3] but as to cyclobutyl edge participation the situation is not well understood.[4] In this connection, we wish to report the first example of the thermally induced decarbonylations of cage ketones **1**, in which a concomitant cleavage of the strained cyclobutyl σ-bond (C_2–C_3) occurred to give tricyclic dienes **2**. In addition, it was found that the irradiation of **2** led to the quantitative formation of cage compounds **3**. Thus, this reaction series offers an advantageous route to strained cage molecules **3**.

Starting ketones **1** were synthesized[5] by the irradiation of tricyclic dienones **4** which were obtained by Cope rearrangement of the cycloadducts of the corresponding dienes and 2,5-dimethyl-3,4-diphenylcyclopentadienone.[6,7] When a benzene solution of **1** was passed through a quartz column preheated at 450 °C for **1b** or 320 °C for **1c–e**, tricyclic dienes, **2b**, mp 55–56 °C, **2c**, mp 80–81 °C, **2d**, mp 113–114 °C, and **2e**, oil, were obtained in nearly quantitative yields. Contrary to **1b–e**, **1a** was completely stable at 420 °C, but it decomposed at 480 °C without decarbonylation affording an isomeric ketone in 30% yield which may be formed by the cleavage of the C_3–C_4 bond followed by complex rearrangements.[8] The structures of **2** were deduced on the basis of the spectroscopic data[9] along with chemical evidence. Particularly, the fact that the dienes, e.g., **2b** or **2d**, upon irradiation, provided a quantitative yield of the cage compounds, **3b**, mp 63–64 °C, or **3d**, mp 78–79 °C, which reverted to **2b** or **2d** by heating at 80 °C supports the structure of **2** and **3**. On the other hand, the irradiation of the ketones, e.g., **1b** or **1d**, resulted in inefficient decarbonylation to give the corresponding cage compounds, **3b** or **3d** in 16 or 17% yield, respectively. The thermal decarbonylations of **1** to **2** involving a cyclobutane ring cleavage are novel ones, and are in sharp contrast with the thermal decarbonylation of pentacyclodecanone **5** which is the only report in the thermolysis of pentacyclic ketones.[10]

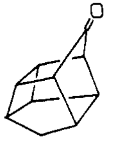
Table I. Thermolysis Rate Data and Mass Spectral Intensity Data for Cage Ketones **1**

Compd	Temp, °C	10^5k, s^{-1}	E_a,[a] kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate[b]	$M^+/(M - CO)$,[c] %
1a	...	...	...	...	...	37
1b	230.0	2.60	44.3 ± 1.1	5.7 ± 2.2	1	6
1c	184.5	11.2	39.1 ± 0.6	6.0 ± 1.2	214	1
1e	185.0	5.07	39.2 ± 1.1	4.6 ± 2.4	95.6	...

[a] Kinetic study was carried out in *o*-dichlorobenzene in the temperature range 220–250 °C for **1b**, 175–205 °C for **1c**, and 180–205 °C for **1e**. [b] At 230 °C. [c] The M − CO peaks were base peaks in all cases.



1 **2** **4** **3**



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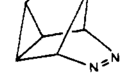

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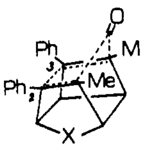
In order to clarify the mechanism and the relationship between the ease of decarbonylation and the structure of the cage ketones, the decarbonylation rates of **1b**, **1c**, and **1e** were determined by measuring the depletion of their methyl signals in the NMR spectrum. Good first-order kinetics were observed and the rate and activation parameters are summarized in Table I. It is revealed that the rate of decarbonylation strongly depends on the length of the carbon bridge, increasing as the bridge becomes longer. This same trend is observed in the mass spectrometer, where the relative intensity of the M − CO peak increases as the length of the carbon bridge increases. A similar structural influence was observed for an extrusion reaction involving the elimination of nitrogen from cyclic azo compounds **6**.[11]

Inspection of the molecular models of the ketones reveals that the cyclobutyl C_2–C_3 bond becomes strained and bends towards the ketonic group when the number of carbons in the chain (X) increases or when there is no bridge, while the C_3–C_4 bond is rather strained in **1a**. The magnitude of the strain of the C_2–C_3 bond is well correlated with the reactivity of the ketones **1**, i.e., the more strained, the easier the decarbonylation. Two pathways for the decarbonylation can be postulated; one is a concerted path in which the σ-bonds of the ketonic group interact with the cyclobutyl C_2–C_3 bond in the transition state **7**, six electrons being involved; the other is a stepwise path in which an initial cleavage of the cyclobutyl bond gives the diradical intermediate **8**, which, in turn, leads to **2**. The E_a values seem a little high for concerted reactions, but they are lower than those for the ring cleavage of 1,2-diphenylcyclobutanes.[12] The $\Delta S^{\ddagger}$ values are comparable to those reported for the cheletropic decarbonylation of tricyclo[3.2.1.0^{2,4}]-octan-8-ones.[13] Furthermore, the ethylene ketal of **1b**, **9**, which would be expected to decompose if a diradical like **8** is initially formed,[14] was found to be stable under a pyrolyzing condition at 550 °C. The formation of ring opening products such as **10** was not observed in the decomposition of **1b–e**. These facts



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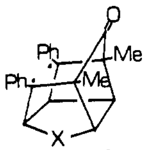

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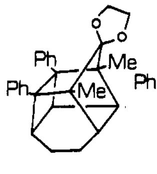

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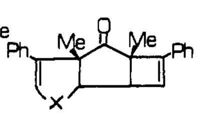

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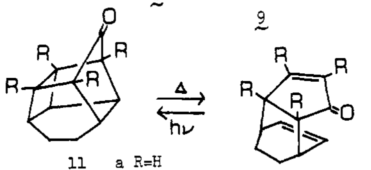

11 a R=H
b R=Cl

12 a R=H
b R=Cl

seem to support that a preferential cleavage of the C_2–C_3 bond of the cyclobutane ring is not essential for the decarbonylation of the cage ketones. It is rather more plausible that efficient overlapping of the developing p orbitals at the C_2–C_3 carbons with those of the ketonic bridge is a major factor. However, the effect of the phenyl groups should not be overlooked. Cage ketones like **11** with no phenyl substituents were synthesized by the irradiation of the corresponding dienones **12**,[15] and their pyrolytic reactions were investigated. Around 450 °C, the ketones **11** underwent a rather simple pyrolysis without decarbonylation reverting to the starting dienones **12** in nearly quantative yields. This reaction is analogous to that of **5**, implying that the phenyl groups participate in the decarbonylation reaction by weakening the C_2–C_3 bond in **1**. It is conceivable that the phenyl groups raise the π-character of the C_2–C_3 bond, resulting in an efficient perturbational interaction in the transition state **7**. Further studies are in progress to investigate the definite nature of the decarbonylation.

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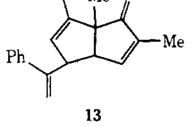
(8) The structure of the product is considered to be a five-membered α,β-unsaturated ketone **13** (ν_{CO} 1700 cm^{-1}). Details will be reported elsewhere soon.



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(9) NMR spectra (in $CDCl_3$, 100 MHz) of **2b, 2c, 2d,** and **2e** were similar to each other and chemical shifts of their methyl signals (δ 1.63–1.93) are compatible with that of sp^2-bound methyl groups. One of these signals (Me) splits into doublet–doublet by long-range coupling with H_B and H_C. Especially small values of the coupling constant between H_A, H_B, H_C, and H_D (2.1–4.2 Hz) support the tricyclic structure.
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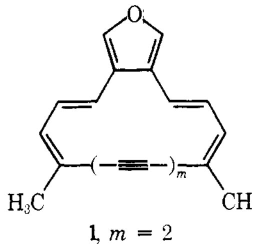
A Reactivity Criterion of Aromaticity and Antiaromaticity in Macrocyclic Annulenes[1]

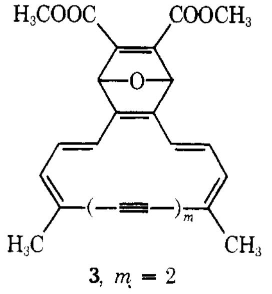
Sir:

The determination of the aromaticity of macrocyclic "Hückel"[2] ($4n + 2$) π-electron systems and the antiaromaticity of ($4n$) systems has been mainly based on their magnetic properties, as measured by ^1H NMR spectrometry.[3] By contrast, the classical concept of aromaticity of benzenoid compounds, developed in the last century, was based on reactivity considerations (retention of type, ease of formation). We now report a related reactivity criterion of aromaticity in macrocyclic "Hückel" [$4n + 2$]annulenes, as well as antiaromaticity in macrocyclic [$4n$]annulenes.

The Diels–Alder reaction of dimethyl acetylenedicarboxylate with the dimethylbisdehydro[14]annuleno[*c*]furan (**1**)[4-6] at room temperature to give the adduct **3** (90% yield) has been described previously.[7] Surprisingly, the corresponding reaction with the closely related dimethylmonodehydro[12]annuleno[*c*]furan (**2**)[8] to give **4** could not be effected, even in boiling benzene. We suspected that this lack of reactivity of **2** was due to the potential formation of an antiaromatic [$4n$]annulene derivative, although strain factors might also have played a part. It was therefore decided to synthesize the [16]- and [18]annuleno[*c*]furans (**12**[9a] and **13**[9b]), and to study their Diels–Alder reactions.



1, $m = 2$
2, $m = 1$



3, $m = 2$
4, $m = 1$

Wittig reaction of the dialdehyde **5**[5,10] with 1 mole equiv of carbethoxymethylenetriphenylphosphorane[11] in CH_2Cl_2 (20°, 20 h) yielded 30% of the monoester **6**[12a] as pale yellow prisms, mp 91–93°.[13] Reduction of **6** with *i*-Bu_2AlH in benzene (20°, 1 h), followed by oxidation of the resulting diol with MnO_2 in CH_2Cl_2 (20°, 2 h), led to the dialdehyde **7** as pale yellow prisms, mp 114–116°,[13] in 55% yield. Treatment of **7** with an excess of the Mg derivative of 3-bromo-1-butyne[14] in ether–THF (−30 to 0°, 15 min) gave a stereoisomeric mixture of **10**, which on successive coupling with anhydrous $Cu(OAc)_2$ in pyridine–ether (50°, 3.5 h), conversion to the dimesylate with mesyl chloride and $N(C_2H_5)_3$[15] (0°, 1 h), and elimination with 1,5-diazabicyclo[4.3.0]non-5-ene (20°, 4 h), afforded the dimethylbisdehydro[16]annuleno[*c*]furan (**12**)[12b] as orange prisms, mp 137–140°[13] (17% yield based on **7**). The ^1H NMR spectrum of **12** ($CDCl_3$, 100 MHz) had bands, inter alia, at