reaction[7] leading to the $(M - C_3H_6)\cdot^+$ ion. The lower frequency factor is consistent with the increased steric requirements of reaction 1.

Other examples are shown in Table II; in most cases, these are compounds whose normal spectra exhibit the characteristic rearrangement of a γ hydrogen through a six-membered-ring intermediate.[7] In the spectrum of hexanoic acid the metastable which would correspond to reaction 1 is even more abundant than the molecular ion. Competing metastable decompositions are also observed, some of which are analogous to those observed in other rearrangement reactions.[7,8] Cleavage of the β–γ bond is apparently enhanced by substituents on the β- and γ-carbon atoms. Anomalies such as the $(M - 29)^+$ metastable in 5-methyl-2-hexanone indicate that even more unexpected reactions are possible. The small abundance of metastables from reaction 1 in the spectrum of butylbenzene is inconsistent with the substantial abundance of $(M - C_3H_6)\cdot^+$ ions from rearrangement of γ-H and with the metastables exhibited by the alkenes of Table II. Several new reactions become competitive with reaction 1 in higher molecular weight compounds; for example, the loss of the α-methyl group yields abundant metastables in the spectra of higher 2-alkanones, consistent with the surprisingly abundant normal ions formed by this pathway at low ionizing voltages.[9]

Table II. Abundances[a] of Metastable Ions Corresponding to Those Expected in Ring Formation Reactions

	Number of ring atoms		
Compound	4	5	6
Hexanal	0.16	6.0[k,l]	0.04
2-Hexanone[b,c]	0.04	1.2	*d*
5-Methyl-2-hexanone[c,e]	0.06	0.02	
2-Octanone[c,f]	0.05	0.14	0.07
4-Methyl-2-heptanone[c,g]	0.27	0.36	0.05
6-Methyl-2-heptanone[h]	<0.02	5.6[l]	<0.02
5-Nonanone[c]	0.06	1.12	
Hexanoic acid	7.8	120[l]	0.48
Butyl formate	<0.15	25[i]	0.4
sec-Butyl acetate	2.4	0.3	
1-Chlorohexane	<0.07	24	0.09
1-Bromohexane	<0.05	31	<0.05
1-Thioheptane	<0.0002	0.0033	0.0005
1-Hexene	0.017	2.1	
4-Penten-1-ol[j]	<0.2	0.4	
n-Butylbenzene	0.083	0.024	

[a] $[m^*]/[M\cdot^+] \times 10^2$. Metastable abundances were determined by the Barber–Elliott defocusing method with a Hitachi RMU-7 mass spectrometer using the modification suggested by Major in which the electrostatic analyzer energy is lowered: F. W. McLafferty, J. Okamoto, H. Tsuyama, Y. Nakajima, T. Noda, and H. W. Major, *Org. Mass Spectrom.*, **2**, 751 (1969). [b] See Table I. We thank J. C. Tou and L. B. Westover, Dow Chemical Co., for a generous sample of this compound. [c] Based on the completely α-deuterated derivative. Not corrected for the partial H/D scrambling which is observed. [d] Values not measured for products due to loss of H. [e] $(M - 30)^+ = 1.6$; $(M - 31)^+ = 2.4$.[a,l] [f] $(M - \alpha\text{-Me})^+ = 1.0$.[a,c] [g] $(M - \alpha\text{-Me})^+ = 1.1$; $(M - 44)^+ = 1.2$; $(M - 45)^+ = 1.4$; $(M - 58)^+ = 0.21$.[a,l] [h] $(M - 29)^+ = 0.12$.[a] [i] High resolution shows that 95% of the $(M - 29)^+$ ion is due to the loss of ethyl at 13 eV. [j] $(M - 18)^+ = 6.3$.[a] [k] At 70 eV only 60% is loss of terminal ethyl: R. J. Liedtke and C. Djerassi, submitted for publication. We thank Professor Djerassi for communication of these results prior to publication. [l] See footnote 8a.

In normal mass spectra of *n*-alkyl chlorides and bromides[10] reaction 1 often accounts for the most abundant fragment ions, so that it is not surprising that the corresponding metastable ions are so important. In mass spectra of aliphatic thiols[11] this rearrangement is of only moderate importance (7% of base peak in 1-thioheptane), and is very substantially reduced in the corresponding metastable ions. Reaction 1 is of relatively little importance in both metastable and normal spectra of other common saturated functional groups such as alcohols, ethers, and amines.

Although further work is necessary to define the scope and limitations of this rearrangement, the data indicate that this, and other new metastable decompositions, will provide new structural information. In the normal mass spectra of the isomeric octanones simple cleavage at the carbonyl group and the γ-H rearrangement[7] indicate the substituents on the carbonyl group and on the α-C atoms, respectively; the β-CH_3 group of 4-methyl-2-heptanone is now indicated by the $(M - 29)^+$ metastable of reaction 1.

The ubiquitous existence of such reactions emphasizes that the energetically most-favored processes are often not those producing the most abundant fragment ions in ordinary mass spectra, and that metastable spectra offer a superior way of studying these processes.

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(7) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

(8) N. C. Rol, *Rec. Trav. Chim.*, **84**, 413 (1965).

(8a) NOTE ADDED IN PROOF. Further study of labeled derivatives has defined additional low energy pathways that contribute to some of these peaks. Losses of the α,β-carbon atoms as C_nH_{2n+1} and C_nH_{2n} are generally favored by β or γ branching. Pentanoic acid-2,2-d_2 exhibits these reactions as well as reaction 1, indicating an additional source of the abundant metastable in hexanoic acid. Loss of α,β,γ carbon atoms as C_nH_{2n+1} is noted for some higher molecular weight compounds.

(9) W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 6167 (1967).

(10) F. W. McLafferty, *Anal. Chem.*, **34**, 2 (1962).

(11) E. J. Levy and W. A. Stahl, *ibid.*, **33**, 707 (1961).

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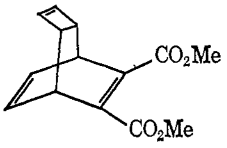
A Photochemical Precursor to Cyclobutadiene

Sir:

The Diels–Alder adducts of cyclooctatetraene with acetylene dicarboxylates are obvious potential sources of cyclobutadiene. However, the pyrolysis of 7,8-dicarbomethoxytricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (**1**)[1] has been reported to involve mainly rearrangement accompanied by a minor amount of fragmentation to 1,3-butadiene and dimethyl phthalate. In contrast, we have found that photolysis of **1** does lead to products which can be more convincingly ascribed to a cyclobutadiene intermediate.[2]



1

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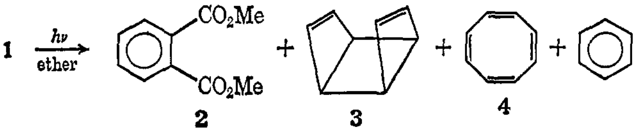
(1) M. Avram, G. Mateescu, and C. D. Nenitzescu, *Ber.*, **90**, 1857 (1957).

The 7,8-dicarbomethoxytricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (**1**) was prepared from cyclooctatetraene and dimethyl acetylenedicarboxylate.[3,4] The initial irradiations were performed on degassed 0.5% solutions of **1** (250 mg/35 ml) in anhydrous ether at 10° using a 450-W Hanovia immersion lamp (Vycor filter). Monitoring by glpc indicated >90% conversion after 48 hr.[5]

The isolated products of the photolysis were identified by spectral comparison with authentic samples and were determined by glpc: dimethyl phthalate (**2**, 37–40%), *syn*-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene (**3**, 16–18%),[6] cyclooctatetraene (**4**, 5–7%), a small amount of

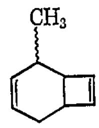


benzene, and some much higher boiling, presumably free-radical-derived products. The ratio **3**:**4** after 48 hr of irradiation, was *ca.* 3:1, having steadily decreased during the course of the photolysis.[7]

The photochemistry of **1** exhibited no striking temperature dependence. Low-temperature nmr analysis of the reaction mixture after 4-hr irradiation (−20°) indicated a starting material–dimethyl phthalate ratio of *ca.* 2:1 and provided no indication of products, other than those of fragmentation, thermally labile or otherwise.[8]

The irradiation (2537 Å) of **1** (3.3×10^{-2} *M*) at 77°K in a 1:1 ether–isopentane glass and subsequent warming with the lamps off produced **2**, **3**, and **4**. This result, considered concurrently with the stereospecific formation of the *syn* dimer, renders unlikely the production of **3** by initial dimerization of **1** and subsequent fragmentation. Similarly, the presence of **2** and absence of dimethyl acetylenedicarboxylate in this photolysis mixture imply that **3** is not produced directly from **1** by a retro Diels–Alder reaction.

Consistently, *trans*-piperylene and isoprene proved to be effective traps for the proposed cyclobutadiene intermediate. When the irradiation (2537 Å) of **1** was performed in the presence of varying concentrations of *trans*-piperylene and isoprene, a dramatic drop occurred in the yield of **3** accompanied by the appearance of another product in each case with a slightly longer glpc retention time than **3**.[10,11] Analytical and spectral characterization left little doubt that the new products isolated (preparative glpc) from the irradiation of **1** in *trans*-piperylene and isoprene were the expected diene



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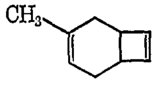

8

adducts with cyclobutadiene (**7** and **8**, respectively). Compound **7** showed the following spectral characteristics: nmr (CDCl$_3$), τ 4.08 (q, 2, $J = 2.5$ Hz), 4.5 (m, 2), 6.98 (m, 2), 7.87 (m, 3), and 8.99 (d, 3, $J = 7$ Hz);[12] partial mass (70 eV), *m/e* 120 parent),[14] 105 (base peak), 92, 91, 79, 78, 77, 68, 65, 63, 53, 52, and 51. Spectral characteristics of **8** were: nmr (CDCl$_3$), τ 4.11 (s, 2), 4.59 (m, 1), 7.0 (m, 2), 8.02 (m, 4), and 8.31 (br s, 3). The mass spectrum of **8** showed, in addition to the parent mass at *m/e* 120, a fragmentation pattern quite similar to (but not identical with) that of **7**. The adducts were produced in *ca.* 12–15% yield based on reacted starting material when the diene concentration was 0.4 *M*. Lower diene concentrations result in poorer yields of the adducts and correspondingly increased amounts of *syn* dimer **3**.[10]

In contrast, the irradiation of **1** in neat 2-butyne produced the *syn* dimer **3** and cyclooctatetraene **4** in over-all yields of 17 and 6%, respectively. Although a number of volatile products were produced in very low yield, none could conclusively be assigned to 2,3-dimethylbicyclo[2.2.0]hexa-2,5-diene or *o*-xylene.[15]

Further characterization and chemical study of the adducts **7** and **8** together with the application of the reaction to other diene systems is proceeding, as are attempts to spectrally characterize the proposed cyclobutadiene intermediate in the photolysis.

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(2) (a) E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. O. Schissel, *J. Amer. Chem. Soc.*, **91**, 1875 (1969); (b) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, 87, 3253 (1965).

(3) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948).

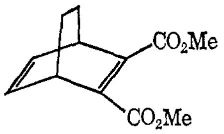
(4) The cyclooctatetraene was distilled under vacuum before use as a violent explosion occurred one time when this step was omitted.

(5) Similar conversions were obtained after only 20–23 hr of irradiation using low-pressure mercury resonance lamps.

(6) None of the corresponding *anti*-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene could be detected in the irradiation mixture.

(7) Product 3 was stable under the reaction conditions in the dark and was found to be similarly unaffected during the removal of the solvent by distillation (bath temperature 55°).

(8) H. Prinzbach and coworkers[9] have recently shown that 5 and 6 undergo efficient intramolecular cycloaddition to produce thermally labile dimethyl tetracyclo[4.2.0.$0^{2,8}$.$0^{5,7}$]octane-1,6-dicarboxylate and dimethyl pentacyclo[5.2.0.$0^{2,9}$.$0^{3,5}$.$0^{6,8}$]nonane-1,7-dicarboxylate, respectively, under these conditions.



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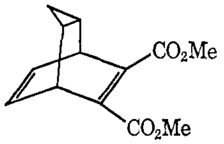

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(9) H. Prinzbach, W. Eberbach, and G. Philippossian, *Angew. Chem. Intern. Ed. Engl.*, 7, 887 (1968).

(10) The yield of 3 fell from 16 to 18% in the absence of any diene to 12% in 0.1 *M* and finally 4% in 0.4 *M trans*-piperylene. In each case, the conversions were >90%. The yield of cyclooctatetraene dropped markedly with the addition of diene and was not measurable at a diene concentration of 0.4 *M*. The amount of dimethyl phthalate produced was essentially unchanged by the addition of the diene trapping agents.

(11) 1 was inert to *trans*-piperylene and isoprene in the dark under the reaction conditions.

(12) The chemical shifts reported for 7 and 8 are extremely similar to those observed by Roth and coworkers[13] for the parent bicyclo[4.2.0]-octa-3,7-diene.

(13) W. Roth and B. Peltzer, *Ann.*, **685**, 56 (1965).

(14) The isotopic ratios indicated an empirical formula C$_9$H$_{12}$.

(15) The failure of 2-butyne to serve as an efficient cyclobutadiene trap is not unexpected based on the poor yields of alkyl Dewar benzenes obtained from the oxidation of cyclobutadieneiron tricarbonyl in the presence of dialkylacetylenes.[16]

(16) R. Pettit, private communication.

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