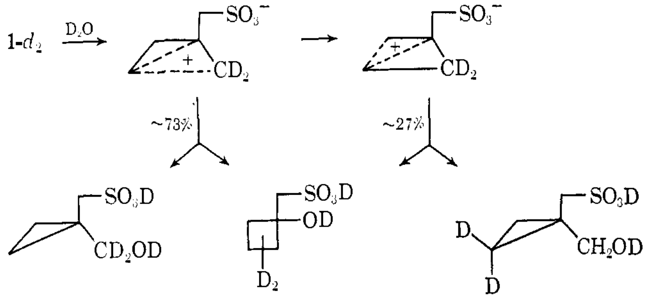
clopropane ring (11%), indicating cyclopropylcarbinyl to cyclopropylcarbinyl rearrangement. No internal return to scrambled **1**-d_2 was observed, although 2–3% should have been detectable. Again the product proportions remained constant during hydrolysis and were only slightly affected by the presence of urea.

The rate of hydrolysis of sultone **1** (*ca.* 0.007 *M*) was determined in 70% aqueous acetone by aliquot titration: $k_{50°} = 2.48 \times 10^{-5}$, $k_{70°} = 18.2 \times 10^{-5}$ sec^{-1} ($\Delta H^{\ddagger} = 21.4$ kcal/mol, $\Delta S^{\ddagger} = -14$ eu at 50°). For comparison, the hydrolysis rate of 3-hydroxypropanesulfonic acid sultone (**7**) was measured under the same conditions: $k_{50°} = 1.62 \times 10^{-5}$, $k_{70°} = 9.32 \times 10^{-5}$ sec^{-1} ($\Delta H^{\ddagger} = 18.7$ kcal/mol, $\Delta S^{\ddagger} = -23$ eu at 50°), *i.e.*, $k_1/k_7 = 1.53$ at 50°. Nilsson[15] reports that 2,2-dimethyl-3-hydroxypropanesulfonic acid sultone (**8**) undergoes hydrolysis at a considerably reduced rate ($k_8/k_7 = 0.0035$, 40° in water).[17]

From the kinetic data it appears that the hydrolysis of sultone **1** proceeds with a modest amount of assistance. Although an accurate estimate of the magnitude would be premature, the rate enhancement is evidently well below the usual level. The hydrolysis of cyclopropylcarbinyl tosylate, for example, is some 1550 times faster than ethyl tosylate (90% aqueous acetone, 25°).[19]

The kinetic data, products, and scrambling results can be economically explained in terms of a bicyclobutonium ion intermediate[8] which reacts with water to give **5** and **6** about 2.7 times faster than it rearranges.[20] However, some (16.5%) rearrangement *via* a tricyclonium ion is not excluded by the data. Although there could be an SN2 component in the hydrolysis of **1**, the partial label scrambling in the formation of **5**-d_2 demonstrates that a substantial fraction (41 or 55% depending upon the scrambling mechanism) of the cyclopropyl product **5** results from an SN1 pathway.



The reduced rate enhancement in the hydrolysis of **1** indicates that 2,3 participation probably contributes at most a small factor to the high solvolytic reactivity of cyclopropylcarbinyl derivatives and that the magnitude of the kinetic acceleration depends markedly upon the orientation of the leaving group.[3] This conclusion is in line with the theoretical calculations concerning the relative instability of the in-plane cyclopropylmethyl cation.[1b,7,11]

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for partial support of this research.

Robert M. Coates, Andrew W. W. Ho[21]
Department of Chemistry and Chemical Engineering
University of Illinois, Urbana, Illinois 61801

Received August 28, 1969

---

[15] T. Nilsson, Ph.D. Dissertation, University of Lund, 1946, quoted by Bordwell, Osborne, and Chapman.[16]

[16] F. G. Bordwell, C. E. Osborne, and R. D. Chapman, *J. Am. Chem. Soc.*, **81**, 2698 (1959).

[17] The low rate of solvolysis of **8** is apparently not entirely a result of steric hindrance since the relative rate of neopentyl benzenesulfonate in water at 40° is 0.10 compared to propyl benzenesulfonate as 1.0.[16,18] Bordwell, *et al.*, have suggested that the increased barrier to rotation about the 2,3 bond in the heterolytic ring opening of substituted sultones is an important factor in determining the hydrolysis rate.[16]

[18] P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **33**, 1207 (1955).

[19] D. D. Roberts, *J. Org. Chem.*, **30**, 23 (1965).

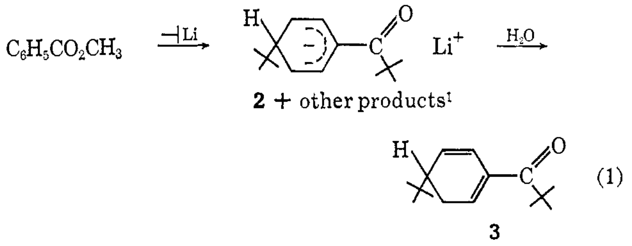
[20] A mechanism involving distinct cyclopropylcarbinyl (*e.g.*, the "bisected" conformation) and cyclobutyl (or C_s bicyclobutonium[1b]) intermediates interconverting through a bicyclobutonium-like transition state will satisfy the results described here equally well. At present we prefer the equilibrating bicyclobutonium ions since this scheme will accommodate as well the apparent stereochemical integrity maintained in the cyclopropylcarbinyl rearrangements.[4]

[21] National Science Foundation Undergraduate Research Participant, summer, 1969.

Electrocyclic Addition of a Cyclohexadienylic Anion to a Diene. Route to Polycyclic Compounds

Sir:

One of the consistent products of reaction of methyl benzoate with *t*-butyllithium (eq 1) was a compound, **1**, which can be formally represented as a dimer of two pivaloyl-*t*-butylcyclohexadienes.[1] *A priori* one can imagine a large number of electrocyclic reactions of the neutral dienes that would result in dimer formation or Michael addition of an anion **2** to a diene. None of these structures is, however, consistent with the spectroscopic and chemical data obtained for the material. The diene dimer **1** could be isolated only under specific conditions. A solution of 85 ml of *t*-butyllithium, 2 *M* in pentane, was added to 10 g of methyl benzoate in 35 ml of isooctane at such a rate that the mixture refluxed gently. The mixture was brought to 95° and 10 ml of water was added over 10 min. After cooling, an additional 30 ml of water was added and compound **1** immediately precipitated, 0.6 g (mp 244–244.5) from this hydrolysate. Heating the mixture of products (dienones, carbinols, and aromatic ketones) from the above reaction had no effect on the yield of **1**, nor did varying the reaction temperature. On the other hand, the yield of **2** increased markedly with the temperature of the hydrolysis reaction, ~0% at −10–0°, 1% at 35°, and 5% at 100°. Evidently, compound **1** is only formed during the hydrolysis reaction.



Infrared (2980 s, 1650 s, 1640 s, 1608 w, 1272 m, 1142 s, 764 cm^{-1}) and ultraviolet (234 mμ (ϵ 1400)) spectra indicate the presence of a conjugated ketone chromophore.[2] The nmr spectrum shows four different *t*-butyl resonances at τ 8.78, 8.83, 9.20, 9.26, and two

---

[1] G. Fraenkel and E. Pecchold, *Tetrahedron Letters*, in press. The main products are pivalophenone and di-*t*-butylbenzyl alcohol.

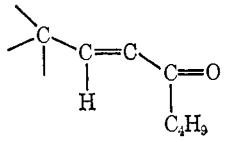
[2] E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3766 (1955).

Table I. Positive and Negative Ion Mass Spectra of **1**[a]

m/e	Negative ion intensity, %	Positive ion intensity, %	Elemental composition[b]
57		100	C_4Hg
58		6	
69		8	
72	7		
73	10		
74	8		
77	14	6	
79		8	
83		5	
85		9	C_5HgO
87		7	
91		5	
105		38	C_7H_5O
106		2	
107		9	
121	16		
135		4	
151		6	
161		4	
163		15	$C_{11}H_{15}O$
164		6	
165		10	
219	44		
220	2		
221	7	10	$C_{15}H_{25}O$
222		4	
269		3	$C_{20}H_{29}$
299		2	$C_{21}H_{31}O$
327		24	$C_{22}H_{31}O$
328		4	
355	9	2	$C_{25}H_{39}O$
356	2		
382	5		
383	20	59	$C_{26}H_{39}O$
384	9	18	
425		3	$C_{29}H_{45}O$
439	100		
440	39	3	$C_{30}H_{48}O_2$
441	16	1	

[a] Obtained at ±8 kV in an AEI MS-902 mass spectrometer. Emission 485 μA at 70 eV. Source temperature 200°. The relative intensities in the spectrum were highly dependent on the source temperature. [b] Elemental compositions were obtained from measured masses for the peak in question; all reported compositions agreed with the measured masses within less than 0.003 mass unit. Mass measurement was accomplished by peak matching against known perfloro-tri-*n*-butylamine peaks; resolution was set to greater than 1 part in 15,000.

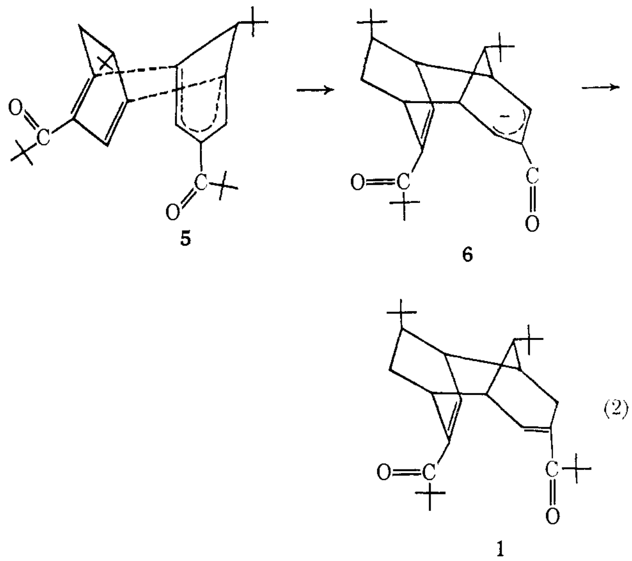
single vinyl protons, each part of a separate AX system, at τ 3.22 and 3.55.[3] The rest of the spectrum contains single lines, 1 H each, at τ 7.68 (3 H), doublets (J = 7 Hz) at 7.39, 7.959, and 8.036 (1 H each), and a multiplet at 8.08–8.36.[4] The spectrum does not change with temperature. These results clearly indicate the presence of the unit **4** in each half of the dimer.



4

Heating the various 1-pivaloyl-4-*t*-butylcyclohexadienes obtained from reaction of *t*-butyllithium with methyl benzoate singly or in mixtures, at 110°, for 3 hr results only in aromatization, no dimer being formed. Furthermore, **1** is stable for 2 weeks at 100° in the dark. Evidently, **1** is not the result of a normal Diels–Alder process.

The data for **1** are not consistent with any product of a Diels–Alder reaction involving 1-pivaloyl-4-*t*-butylcyclohexadienes or a Michael reaction of anion **2** with a diene. On the other hand, the results are in accord with the product of the allowed thermal ten-electron nine-orbital addition of anion **2** to diene **3** (eq 2).[5]



5

6

(2)

1

The positive ion and nitrogen-enhanced[6] negative ion mass spectra of **1** (Table I) strongly support the proposed structure and mode of formation. The positive ion mass spectrum may be interpreted on the basis of an initial *t*-butyl cleavage followed by fragmentation and/or rearrangement of the m/e 383 ion. The formation of m/e 221 can be rationalized as an electrocyclic process in the cation, 4 + 2 electrons, seven orbitals.

The corresponding negative ion process does not occur; however, we have observed a variable intensity metastable at m/e 109.3 (439 → 219) in the negative ion mass spectrum. This metastable was almost certainly collision induced since its intensity was strongly dependent on the nitrogen pressure. We tentatively propose that the reaction responsible for this metastable is the reverse of reaction 2.

An electrocyclic addition of a pentadienylic anion to a diene was proposed to account for the biosynthesis of glauconic acid.[7] Another electrocyclic reaction of a carbanion is the five-orbital six-electron cyclization of

---

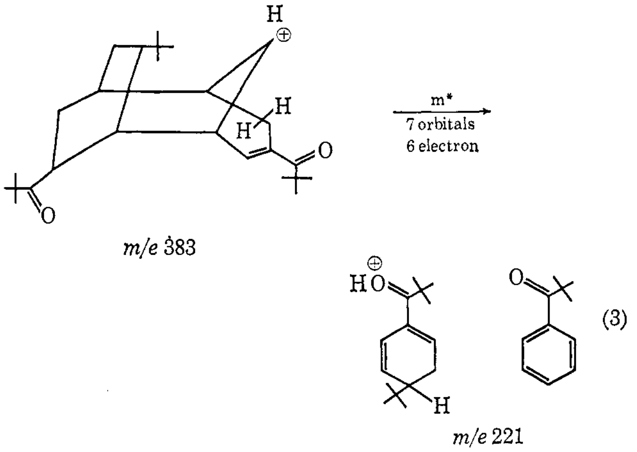
(3) Dr. Stephen Topey, Dow Chemical Co., private communication.

(4) Proton spectra were obtained at 60, 100, and 220 MHz. We thank Dr. Marion Habibi, Central Research Laboratory, E. I. du Pont de Nemours and Co., for running the 220-MHz spectrum.

(5) (a) M. J. S. Dewar, "Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969; M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966); (b) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2511 (1965); (c) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4388, 4389 (1965); (d) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

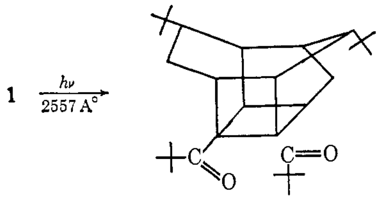
(6) R. C. Dougherty and C. R. Weisenberger, *ibid.*, **90**, 6570 (1968).

(7) C. E. Moppett and J. K. Sutherland, *Chem. Commun.*, 772 (1966).



cyclooctadienyl anion to, after hydrolysis, *cis*-bicyclo[3.3.0]oct-2-ene.[8]

Compound **1** undergoes an irreversible transformation in the solid state in sunlight over 2 weeks in Pyrex or in pentane solution irradiated for 5 min at 2557 Å (medium-pressure mercury lamp) to **6**, mp 146–147.5°. Compound **6** has no double bonds, and its positive ion mass spectrum is very similar to that of **1**. This result determines the stereochemistry of the double bonds in **1** and excludes structures in which intramolecular 2 + 2 photoprocesses are geometrically impossible.



6

The sequence of reactions from methyl benzoate to **7** is a fast, efficient route to pentacyclic compounds.

Acknowledgment. This research was supported by Air Force Office of Scientific Research Grant 253-65 and National Science Foundation Grant GP-8567.

---

(8) P. R. Stapp and R. F. Kleinschmidt, *J. Org. Chem.*, **30**, 3006 (1965); L. H. Slaugh, *ibid.*, **32**, 108 (1967); R. B. Bates and D. A. McCombs, *Tetrahedron Letters*, 977 (1969).

Charles Cottrell, Ralph C. Dougherty
Gideon Fraenkel, Englebert Pecchold
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received June 30, 1969

A Stable Complex of Heptafulvene

Sir:

Many unstable organic species have been isolated as metal complexes, including trimethylenemethane,[1] norbornadienone,[2] and certain sesquifulvalene and calicene systems.[3] Heptafulvene is a conjugated, nonbenzenoid hydrocarbon which is nonisolable and stable only in dilute solution at −170°;[4] only a few moderately stable monosubstituted derivatives have been reported.[5,6] We here report the preparation of the first stable transition metal derivative of unsubstituted heptafulvene, prepared by a method previously used to generate ethylene and propylene complexes.[7] This complex may prove to be a convenient source of heptafulvene for the further investigation of its reactions and properties.

Modification of an earlier preparation of 7-(carbethoxy)cycloheptatriene,[4] using G.E. 250-W infrared heat lamps and a room-temperature workup, gave the desired ester in 35% yield with up to 95% isomeric integrity. Inverse addition of $LiAlH_4$ at 0° to the ester in diethyl ether afforded a 90% yield of 7-(hydroxymethyl)-cycloheptatriene, apparently identical with that recently prepared by another route.[8] Reaction with benzenesulfonyl chloride at 0° in γ-collidine gave the corresponding ester (I) as a heat-sensitive oil;[9] the methylene group appears as a doublet in the nmr spectrum (τ 5.85, J = 6 Hz, CCl_4), confirming retention of the 7-substituted cycloheptatriene skeleton.

Addition under nitrogen of sodium π-cyclopentadienyliron dicarbonyl to I in dry, degassed tetrahydrofuran at −70°, warming to room temperature, removal of solvent, and chromatography on neutral alumina yielded 45% of the σ-bonded C_8H_9Fe-π-$Cp(CO)_2$ (II) as an air-sensitive orange-yellow liquid. Its nmr spectrum is characteristic of the 7-substituted cycloheptatriene skeleton: τ 3.45 (t, H_γ), 3.95 (m, H_β), 4.85 (four-line m, H_α), 5.38 (s, H_{Cp}), 8.20 (m, CH and CH_2), in the ratio 2:2:2:5:3 (CS_2). The infrared spectrum displayed strong absorptions at 1953 and 2008 cm^{-1} (CS_2), characteristic of σ-alkyl-π-cyclopentadienyliron dicarbonyl complexes.[7]

When II was treated with trityl salts ($(C_6H_5)_3C^+BF_4^-$, $(C_6H_5)_3C^+PF_6^-$, or $(C_6H_5)_3C^+SbF_6^-$) in methylene chloride at 0°, a deep red product formed immediately. Triphenylmethane could be isolated in nearly quantitative yields. The tetrafluoroborate and hexafluorophosphate salts were not readily crystallized; the hexafluoroantimonate derivative was an air-stable, nonhygroscopic dark red crystalline salt (III or IV), mp 98–100° (recrystallized from CH_2Cl_2-Et_2O). *Anal.* Calcd for $C_{15}H_{13}FeO_2SbF_6$: C, 34.8; H, 2.51; Fe, 10.80. Found: C, 35.1; H, 2.57; Fe, 10.68. Its nmr spectrum showed a peak, theoretically an $A_2B_2C_2$ multiplet, at τ 2.20, a sharp singlet at 4.73, and a sharp singlet at 6.51, in the ratio 6:5:2 (acetone-d_6).[10] The carbonyl groups of the product absorbed at 1986 and 2033 cm^{-1} in the infrared (CH_2Cl_2).[11] The nearly equivalent chemical shifts appearing in this case at τ 2.20 are frequently observed in symmetrical fully conjugated seven-membered rings,

---

(1) G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Am. Chem. Soc.*, **88**, 3172 (1966).

(2) J. M. Landesberg and J. Sieczkowski, *ibid.*, **90**, 1655 (1968).

(3) M. Cais and A. Eisenstadt, *ibid.*, **89**, 5468 (1967).

(4) W. von E. Doering and D. W. Wiley, *Tetrahedron*, 11, 183 (1960).

(5) (a) 8-Vinylheptafulvene has been synthesized: D. Bertelli, C. Golino, and D. Dreyer, *J. Am. Chem. Soc.*, 86, 3329 (1964). (b) The nmr spectra of several heptafulvenes have recently been analyzed: D. Bertelli, T. Andrews, and P. Crews, *J. Am. Chem. Soc.*, 91, 5286 (1969).

(6) (a) 8-Cyanoheptafulvene: M. Oda and Y. Kitahara, *Chem. Commun.*, 352 (1969); (b) 8-formyl and 8-carbethoxyheptafulvenes: M. Oda and Y. Kitahara, *Chem. Ind.* (London), 920 (1969).

(7) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963), and references contained therein.

(8) G. D. Sargent, N. Lowry, and S. Reich, *J. Am. Chem. Soc.*, **89**, 5985 (1967).

(9) The benzenesulfonate must be kept at temperatures lower than 15° to avoid spontaneous exothermic decomposition.

(10) No change was observed in the spectrum upon lowering the temperature to −60°.

(11) A small amount (<5%) of an unidentified impurity was present in all of our samples of this complex. The impurity exhibited a singlet in the nmr at τ 4.1 and weak carbonyl absorptions in the infrared at 2075 and 2128 cm^{-1}.