in the *trans* H-Ir-NCR complexes, the iridium atom can serve as a π donor into antibonding orbitals of the nitrile molecule, leading to the observed decreases in CN frequencies.[11] The assignment of the 2080-cm^{-1} absorption to the Ir-NC mode was confirmed by using deuterium hydrochloride instead of HCl to generate the five-coordinated intermediate **1**. Addition of the nitriles to the deuterated complex **1** gives products with the $\nu_{\mathrm{Ir-N\equiv C}}$ band (2083 cm^{-1}) unaltered, but with marked diminution of the 2190-cm^{-1} (Ir-H) band.

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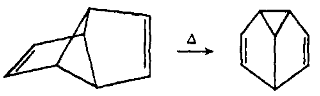
(CH)$_8$ Hydrocarbons. Photochemistry of Tricyclo[3.3.0.0^{2,6}]octa-3,7-diene[1]

Sir:

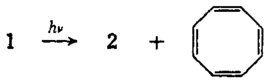
The highly strained tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (**1**), a valence isomer of cyclooctatetraene, has recently been prepared and characterized.[2,3] This diene undergoes remarkably facile thermal rearrangement to semibullvalene (**2**),[2,3] and in further examining its place on the (CH)$_8$ hydrocarbon energy surface we have explored its photochemistry. We now report the unusual electronic absorption spectrum of **1** as well as its photochemical conversion to cyclooctatetraene and semibullvalene.



1 2 (1)

The ultraviolet spectrum[4] of a solution of **1** in isopentane begins to show absorption at about 320 mμ, and the molar extinction at 300 mμ is *ca.* 190. While this absorption seems remarkable for a simple nonconjugated diene, it should be noted that the related monoolefin, tricyclo[3.3.0.0^{2,6}]oct-3-ene,[5,6] shows a long-wavelength ultraviolet absorption in isooctane with a molar extinction of 150 at 250 mμ. This abnormal electronic spectrum undoubtedly merits further investigation.

Solutions of a mixture of **1** and semibullvalene (**2**) (55~60 mg/0.3~0.4 ml of solvent; **1**:**2** = 0.6~1.2) placed in a Pyrex nmr sample tube were irradiated at $-60°$, using a 450-W Hanovia medium-pressure lamp through a Vycor immersion well. Under these conditions, the thermal rearrangement of **1** was shown to have a negligible rate. Monitoring the reaction mixtures by means of their nmr spectra showed the appearance of one new component as evidenced by the development of an nmr singlet at τ 4.3; at the same time there was an increase in area of the peaks in the nmr spectrum due to **2**. The new component was identified as cyclooctatetraene (**3**) by infrared and nmr spectral comparisons and by its gas chromatographic retention time. After 80 min of irradiation, the amounts of **2**, **3**, and unchanged **1** reached the values shown in Table I. No nmr spectral peaks beyond those accounted for by **1**, **2**, and **3** were observed.



3 (2)

Table I. Results of Low-Temperature Irradiation of Tricyclo[3.3.0.0^{2,6}]octa-3,7-diene[a]

Solvent	1, %	2,[b] %	3, %
Toluene	62	12	26
Isopentane	52	19	29
Dimethyl ether	91	~4[c]	~5[c]

[a] Reaction temperature was maintained at $-60°$ and the reaction time was 80 min. [b] Increase in semibullvalene. [c] The small conversion makes these yields inaccurate.

Since the cyclooctatetraene formed in these experiments might have arisen from photochemical reaction of semibullvalene[7] in addition to, or even instead of, from the diene (**1**), control experiments were performed as follows. Semibullvalene (**2**) was irradiated as previously described in isopentane and in toluene at $-60°$ and at -20 to $-30°$. No nmr singlet corresponding to **3** was observed in these experiments, confirming the formation of cyclooctatetraene[8] (**3**) from tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (**1**) itself.

In the pyrolysis of **1** to **2**, a concerted, suprafacial [1,3] sigmatropic process (observed in the thermal conversion of bicyclo[2.1.1]hexene derivatives to the corresponding bicyclo[3.1.0]hexenes)[9-11] seems unlikely, since the tricyclic structure does not permit inversion of the migrating center.[12] A two-step rearrangement by way of the doubly allylic diradical intermediate **4** seems to provide the best rationalization of this process.

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(1) The partial support of this research by grants from the National Science Foundation (GP-13085) and the National Institutes of Health (GM-10090) is acknowledged with pleasure.

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(4) The sample was a mixture of 1 and 2 (1:2 = 1.4:1) and the measurement was carried out on a Cary Model 14 at 1°. At this temperature the rearrangement of 1 to 2 is quite slow.

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(8) The possible formation of 2 from 3 was also excluded, since irradiation of 3 in isopentane under the same conditions described gave no nmr spectral peaks due to 2. A slow, sensitized conversion of 3 to 2, however, has been demonstrated by H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968).

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The photochemical rearrangements of **1** are subject to at least three interpretations: (i) initial formation of an *excited* diradical (**4**), which then serves as a common intermediate forming **3** by further bond cleavage and **2** by the appropriate radical recombination; (ii) formation of **2** *via* **4** as described above, accompanied by an independent process involving a retro (2 + 2) π reaction giving *cis,trans,cis,trans*-cyclooctatetraene[13] (**5**), which is converted to *all-cis*-cyclooctatetraene under the reaction conditions (even at −60°, attempts to detect the intermediate formation of **5** were unrewarded, although experiments at much lower temperatures might yield different results); (iii) formation of **2** from **1** *via* a concerted suprafacial [1,3] sigmatropic shift, and formation of **3** by one of the above-described paths. In any event, since the thermal rearrangement of **1** to **2** (unaccompanied by **3**) seems to proceed *via* the corresponding diradical intermediate, the photochemical production of **3** from **1** must involve either a different state of this diradical or else some alternative mechanism.


4


5

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[13] Known compounds similar to 5 include *trans,trans*-1,5-cyclooctadiene[14] and a *trans,cis,cis,cis*-cyclooctatetraene derivative.[15]

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Variation of Carbon-14 Isotope Effect with Substituent and the Mechanism of the *m*-Chloroperbenzoic Acid Oxidation of Labeled *para*-Substituted Acetophenones[1]

Sir:

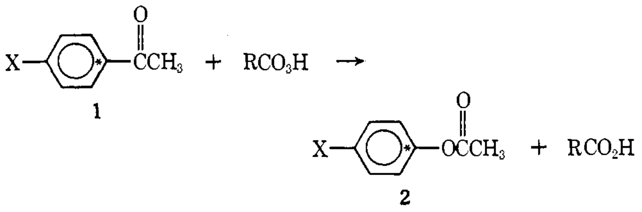
Small variations in heavy atom (nonhydrogen) isotope effects with ring substituents have been reported[2] in the past, but in no case has changing ring substitution resulted in an isotope effect change from near the lower detectable limit to near the maximum expected. Except for the recent work of Yukawa, *et al.*,[3] which was interpreted in terms of a changing mechanism with changing substituent, all previous studies of substituent effects on isotope effects have been carried out in systems in which the isotopic fractionation was taking place at an atom external to the ring bearing the substituent.

We wish to present here the results (see Table I) of a series of kinetic and isotope effect measurements on the *m*-chloroperbenzoic acid oxidation of *para*-substituted acetophenones-1-^{14}C (**1**) to *para*-substituted phenyl-1-^{14}C acetates (**2**) and to point out the implications of these results for the mechanism of the reaction.

Table I. Rates and Carbon-14 Kinetic Isotope Effects for the Oxidation of *para*-Substituted Acetophenones-1-^{14}C with *m*-Chloroperbenzoic Acid in Chloroform at 32°

para substituent	$k \times 10^3$,[a] l. mol^{-1} sec^{-1}	k^{12}/k^{14} ester[b]	k^{12}/k^{14} ketone[b]
CH_3O	40.3	0.998	0.998
CH_3	19.1	1.032	1.033
H	4.53	1.048	1.048
Cl	3.39	1.049	1.052
CN	0.50	1.084	1.085

[a] Reproducible to about 5%. [b] Calculated from the activity values of the starting ketone and the product ester or recovered ketone, respectively, at various fractions of reaction; average deviation of values from various fractions of reaction ±0.002–0.003 except for *p*-CN, ±0.006.



The labeled acetophenones were prepared from commercially available (ring labeled) benzoic-1-^{14}C acid and *p*-nitrobenzoic-1-^{14}C acid by standard methods[4–8] or as described elsewhere.[9] The kinetic and isotope effect measurements were carried out in chloroform at 32 ± 0.1°. The fraction of reaction was determined by standard iodometric methods and checked, with substantially identical results, by gas chromatographic or nmr analyses of the ketone/ester ratios. No trace of the methyl benzoate esters could be found, despite a careful search by gas chromatography. *p*-Nitroacetophenone could not be oxidized to the corresponding ester under these conditions.

All of the compounds studied displayed good second-order kinetics, in contrast to the observation of Friess and Soloway[10] that the related perbenzoic acid oxidation of substituted acetophenones displayed various kinetic orders depending on the substituent. It is clear the reaction is accelerated by electron-donating groups and slowed by electron-withdrawing groups, in general agreement with the results of Hawthorne and Emmons[11] on the related trifluoroperacetic acid oxidation of *para*-substituted acetophenones. In Hammett plots of the kinetic data, the linear fit is better with σ^+ ($\rho = -1.36$) than with σ, suggesting an activated complex which is electron deficient at a position capable of interaction with the *para* substituent. There is no indication of curvature in the Hammett plot, which supports the thesis that all of the compounds are reacting by the same mechanism.

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