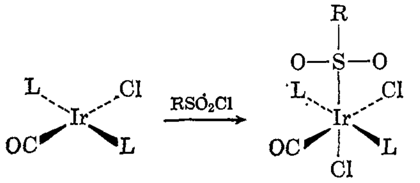
The average ratio of asymmetric to symmetric sulfonyl frequencies in Table I is 1.16. This is exactly the same ratio found in organic sulfones.[5] It is significant that the sulfonyl absorption modes are displaced by almost 100 cm^{-1} to lower frequency from the values typically found in the spectra of organic sulfonyl derivatives—even though this absorption is usually insensitive to conjugative effects.[6] This displacement is undoubtedly a reflection of $d\pi$–$d\pi$ back bonding from the metal to the sulfonyl group. The CO frequency is shifted from 1950 cm^{-1} in the starting material (**1**) to a value of about 2080 cm^{-1} in the sulfinates (**2**).

Table I. Infrared Frequencies[a] of $Ir(CO)Cl_2[P(C_6H_5)_3]_2RSO_2$[b]

R	SO_2 (asym), cm^{-1}	SO_2 (sym), cm^{-1}	CO, cm^{-1}
CH_3	1220	1070	2090
C_2H_5	1235	1070	2080
n-C_3H_7	1225	1070	2080
p-$CH_3C_6H_4$	1240, 1220	1065, 1055	2080
p-ClC_6H_4	1240, 1220	1060	2080
p-$NO_2C_6H_4$[c]	1245, 1225	1065	2080

[a] All compounds were measured as KBr pellets on a Perkin-Elmer Grating Infracord. [b] Satisfactory carbon and hydrogen analyses have been obtained for all compounds reported. Sulfur analyses were determined for aliphatic cases. [c] Aromatic NO_2 bands at 1525 and 1350 cm^{-1}.

In view of the obviously strong back-bonding properties of the sulfonyl group as a ligand, it is likely that it takes up a position *cis* to the carbonyl group. The disposition of the phosphine groups is *trans* as indicated by the proton nmr spectra of a series of octahedral adducts similar to **2** in which the ligand (L) is diphenylmethylphosphine. The nmr spectra of all such complexes reveal a methyl triplet (J = 4 cps) indicating virtual coupling of the two phosphorus nuclei in *trans* positions. The use of this phenomenon to establish the stereochemical relationship of phosphine ligands in diamagnetic complexes was first demonstrated by Shaw.[7] The *trans* disposition of phosphines and the probable *cis* arrangement of carbonyl and sulfonyl groups lead us to suggest the structure depicted for **2**. However, this stereochemical assignment must be considered tentative in the absence of more definitive evidence.



(1)

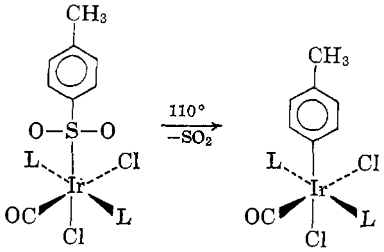
1 **2**

L = $(C_6H_5)_3P$

The alkyl iridium sulfinates are stable thermally and remain unchanged after boiling for 24 hr in solvents such as chloroform or toluene. However, certain of the arylsulfinates undergo loss of SO_2 upon heating 3 hr in boiling toluene. For example, the p-tolylsulfinate **3** is smoothly and quantitatively transformed into the p-tolyl derivative **4** (eq 2), in which the sulfonyl infrared absorptions are completely absent. *Anal.* Calcd for $C_{44}H_{37}OCl_2P_2Ir$: C, 58.28; H, 4.11; P, 6.87; Cl, 7.86. Found: C, 58.23; H, 4.39; P, 7.03; Cl, 8.24. This colorless crystalline compound is very stable as illustrated by its high melting point (259–260°) and represents the first known example of an iridium(III) aryl.[8] The CO frequency in **4** is at 2040 cm^{-1}.

This type of reaction did not prove to be a general method of preparing group VIII aryls inasmuch as other arylsulfinates such as p-chlorophenyl, p-nitrophenyl, and p-methoxyphenyl failed to lose SO_2 under our conditions. However, the benzenesulfinate does lose SO_2.

The elimination of SO_2 represents the third gas-forming elimination reaction whereby transition metal–carbon bonds are formed—the other two involving loss of CO[11] and N_2.[12] The reverse processes are known in the cases of CO and SO_2 but not N_2.



(2)

3 **4**

Experiments in progress are designed to elaborate this transition metal–carbon bond synthesis. For example, arylsulfinic acids have been found to add to ruthenium(0) and iridium(I) complexes.

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(5) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 863 (1957).

(6) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 54.

(7) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

(8) Aryls of the isoelectronic osmium(II) and platinum(IV) are well known from the work of Chatt and Hayter[9] and Chatt and Shaw.[10]

(9) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 6017 (1963).

(10) J. Chatt and B. L. Shaw, *ibid.*, 705, 4020 (1959).

(11) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964), and references therein.

(12) G. W. Parshall, *ibid.*, **87**, 2133 (1965).

(13) Alfred P. Sloan Foundation Fellow. This research was supported by the U. S. Army Research Office, Durham, Grant No. DA-ARO-(D)-318124-G185; by the Advanced Research Projects Agency, Contract SD-100; and by the National Science Foundation.

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Trimethylenecyclopropane

Sir:

We wish to report the synthesis and characterization of trimethylenecyclopropane (I), isomeric with benzene and the simplest member of the class of radialenes.[1,2] Pyrolysis of the appropriate trisquaternary hydroxide IIe has proved to be a superior route for the preparation of this elusive hydrocarbon in a form suitable for characterization, *i.e.*, with a minimum of contamination and dissolved in a solvent of choice; however, I, like

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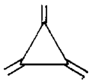
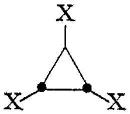
(1) This work was supported by grants from the National Science Foundation (G13759 and GP2543) and partially by the Army Research Office (Durham).

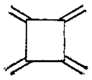
(2) Taken in part from the Ph.D. thesis of L. I. Peterson, Yale University, New Haven, Conn., 1963, and P. A. Waitkus, Tulane University, New Orleans, La., 1966 (in preparation).

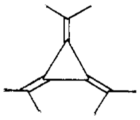
tetramethylenecyclobutane (III), also may be generated in dilute ethanolic solution by dehydrohalogenation of the corresponding trisiodomethylcyclopropane with base.[3] Singlet ground states were predicted for both I and III, and the calculated delocalization energies (HMO) are substantial (1.30 and 1.66 β, respectively).[4] At best only transient existence could be expected for I in view of the high free valency anticipated at the termini of the exomethylene groups in both systems (0.90 and 0.88) as well as the inherent strain associated with the presence of multiple trigonal centers in small ring systems. The tendency of I and II to polymerize has been confirmed by our experimental results and is in qualitative agreement with the semiempirical theoretical results.[4] Hexamethyltrimethylenecyclopropane (IV), a remarkably stable substituted derivative of I, recently has been reported.[5]

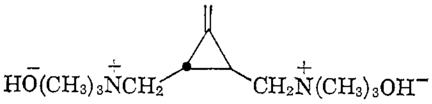

I



IIa, $X = CH_2\overset{+}{N}(CH_3)_3I^-$
b, $X = C(=O)N(CH_3)_2$
c, $X = CH_2N(CH_3)_2$
d, $X = CH_2I$
e, $X = CH_2\overset{+}{N}(CH_3)_2OH^-$
f, $X = CH_2OH$
g, $X = CH_2OTs$


III


IV



V

The *trans*-trisquaternary iodide IIa was prepared by reduction of the tris amide IIb[6] with lithium aluminum hydride in ether and subsequent quaternization of the resulting tris(dimethylaminomethyl)cyclopropane (IIc, bp 60° (0.19 mm)) with methyl iodide in ethanol. Alternatively trisiodomethylcyclopropane (IId, *vide infra*) may be treated with trimethylamine in ethanol to give IIa. The iodide IId was converted to the quaternary hydroxide IIe in the conventional manner, and the resulting aqueous solution was concentrated by lyophilization (1.0 mm) to a clear, colorless, viscous solution containing approximately 30% IIe.

Pyrolysis of the concentrated Hoffmann base solution at 170° (4.5 mm under nitrogen) according to the procedure described for the preparation of III[3] affords I, which was collected at −78° in carbon disulfide, Chromatoquality isopentane (Matheson Coleman and Bell), or carbon tetrachloride as required. After an initial short-path distillation under conditions selected to prevent codistillation of polymers with solvent and I, the dilute solution of the pyrolysis product in carbon disulfide was washed in turn with (1) 1.5 *N* hydrochloric acid (three times) to remove the volatile amines which were formed on pyrolysis, (2) water (three times), and (3) dilute aqueous sodium bicarbonate (three times). The washing operation as well as the drying procedure over anhydrous sodium sulfate were conducted at 0°. That I is indeed produced on pyrolysis of IIe is confirmed by the results of infrared, nmr, ultraviolet, and mass spectral analyses as well as hydrogenation.

The most striking feature of I is its ultraviolet spectrum $\lambda_{\max}^{\text{isopentane}}$ 295 and 305 mμ with a shoulder at about 322 mμ. Although the former peak is more intense, extinction coefficients cannot be reported at this time in view of the problems associated with establishing accurately the concentration of I in dilute solution. The long wavelength absorption band reported for IV is at $\lambda_{\max}^{\text{hexane}}$ 309.5 mμ (log ϵ 4.26), which is reassuringly close to that of I. Furthermore, Peterson[3] and Blomquist[7] report identical spectral characteristics for materials obtained in quantities insufficient for further characterization, derived from IId and V, respectively, by entirely different routes. It has been claimed in the case of IV that the long wavelength maximum in the ultraviolet spectrum is due to a transition which is allowed in I, but forbidden in radialenes of higher order such as III.[5]

The nmr spectrum of I in carbon disulfide consists of a single sharp peak at τ 4.86 which is consistent with the value of τ 4.81 observed for III in carbon tetrachloride. The nmr signal for I gradually decreases and disappears after 45 min when precautions are not exercised to cool the sample and exclude oxygen.

Compound I is sufficiently stable in the gas phase that it was possible to obtain a mass spectrum of sufficient quality that the molecular ion peak (m/e 78) is apparent. The sample was collected from a gas chromatograph operated at room temperature and equipped with a short glass column (5 ft × 0.25 in.) packed with Carbowax 20M on base-washed Chromosorb P. The collection vessel was purged with helium and evacuated prior to collection. By means of a needle valve, flow into the vessel was adjusted to equal precisely the flow from the chromatograph at the time of peak emergence. A by-pass bubble flow meter was employed as a sensitive detector to any flow imbalance.

Hydrogenation of I in isopentane employing palladium on charcoal (5%) as a catalyst may be controlled to avoid hydrogenolysis of the ring and is easily followed by the disappearance of the characteristic ultraviolet absorption spectrum of I. The major hydrogenation product was isolated by gas chromatography (Carbowax 20M on Chromosorb P in a 10 ft × 0.4 in. copper tubing column) and collected in the specially designed evacuated receiver in quantities sufficient for mass spectral analysis. The mass spectrum shows a parent

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(3) G. W. Griffin and L. I. Peterson, *J. Am. Chem. Soc.*, **84**, 3398 (1962); G. W. Griffin and L. I. Peterson, *ibid.*, **85**, 2268 (1963).

(4) (a) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *ibid.*, **74**, 4579 (1952). (b) For comparison it should be noted that the predicted index for *p*-xylylene is 0.92 and, while this compound is stable in the gas phase, it polymerizes in solution.

(5) G. Köbrich and H. Heinemann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 594 (1965).

(6) G. Maier, *Ber.*, **95**, 611 (1962); H. A. Hoffman and A. Burger, *J. Am. Chem. Soc.*, **74**, 5485 (1952). The tris amide IIb (mp 117.5–118°) was prepared from the corresponding acid chloride by treatment with dimethylamine in ether. Satisfactory elemental analyses were obtained on all new compounds described in this paper.

(7) It is clear that Professor A. T. Blomquist and the Cornell University group deserve credit for having first observed trimethylenecyclopropane. D. J. Connolly (Ph.D. Thesis, Cornell University, 1962) found that 1-methylene-*trans*-2,3-bis(trimethylammoniummethyl)cyclopropane dihydroxide (V) and the related amine oxide upon pyrolysis gave a product possessing an ultraviolet spectrum with two maxima at 295 and 305 mμ which is remarkably similar to ours. Connolly also established that this product possessed infrared absorption characteristic of unsubstituted exomethylene groups and established that it had a six-carbon skeleton. See also A. T. Blomquist and D. T. Longone, *J. Am. Chem. Soc.*, **81**, 2012 (1959), and other papers in this series.

peak at m/e 84, clearly demonstrating that I readily absorbs three moles of hydrogen.

The infrared spectrum of a dilute solution of I in carbon tetrachloride shows intense absorption at 881 cm^{-1}, which is near the characteristic region for the hydrogen out-of-plane deformations in terminal disubstituted olefins.[8] Other characteristic bands in the infrared spectrum of I appear at 910, 928, 992, 1026, and 2950 cm^{-1}. It is noteworthy that the infrared spectrum of III[3] shows strong absorption at 880 cm^{-1}.

trans-1,2,3-Triiodomethylcyclopropane (IId) was prepared from *trans*-1,2,3-tricarbomethoxycyclopropane.[6] The latter compound was reduced with lithium aluminum hydride in ether. Several attempts to convert the resulting triol IIf directly to the desired triiodide with phosphorus triiodide gave only unpromising oils. Consequently the alcohol was first converted to the corresponding tritosylate IIg (mp 101–102.5°) with *p*-toluenesulfonyl chloride in pyridine at −5°. The nmr spectrum of IIg exhibits resonance peaks (in addition to peaks for the aromatic protons) at τ 6.10 (CH_2O), 7.56 ($ArCH_3$), and 7.91 (cyclopropyl CH), whose areas are in the anticipated ratio of 2:3:1. Treatment of IIg with sodium iodide in acetone under reflux gave the unstable triiodide IId, mp 80–81.5°, which can be stored indefinitely at 0° in an opaque container. The nmr spectrum of IId shows two multiplets at τ 8.92 (1) and 8.42 (2) assigned to the cyclopropyl hydrogens, and signals centered at τ 6.88 for the methylene protons. When IId is subjected to treatment with sodium ethoxide in ethanol under nitrogen within a few hours the characteristic ultraviolet spectrum of I appears. The product readily codistils with ethanol, and the distinct absorption bands disappear overnight and are replaced by intense absorption over a broad region of the spectrum.

Other studies on the physical and chemical properties of I, including its reaction with dienophiles, are in progress.

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(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 31.

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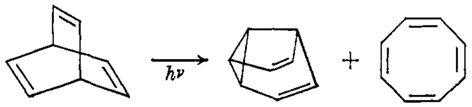
Received November 2, 1965

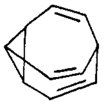
The Chemistry of Barrelene. III. A Unique Photoisomerization to Semibullvalene

Sir:

Previously we have reported the synthesis and some ground-state chemistry of barrelene[1] (I). We now communicate a most intriguing photochemical isomerization of barrelene to afford cyclooctatetraene and a C_8H_8 isomer whose structure is shown to be that of II, a compound reminiscent of bullvalene (III)[2,3] but lacking one of bullvalene's three ethylenic bridges. We term II "semibullvalene."



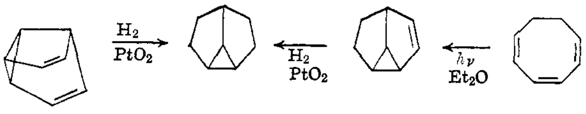
I II (1)



III

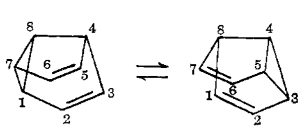
Thus, photolysis[4] of 1–2% isopentane solutions of barrelene containing 3–8% acetone as a photosensitizer afforded 25–40% yields of semibullvalene (II) and 1–2% of cyclooctatetraene, all based on 55–70% unrecovered barrelene. Barrelene, cyclooctatetraene, and semibullvalene were separated by Apiezon vpc and 25% silver nitrate–ether liquid–liquid partition chromatography.[5]

The structure of semibullvalene was established by elemental analysis, mass spectral molecular weight determination (parent ion 104), hydrogenation, and nmr. Hydrogenation of semibullvalene with PtO_2 in ether yielded as the major product the known tricyclo[5.1.0.0^{4,8}]octane (IV)[6–8] which we synthesized for comparison by photolysis[6,7,9] of 1,3,5-cyclooctatriene (V) to VI followed by PtO_2 hydrogenation. Tetrahydrosemibullvalene (IV) from photolysis of barrelene followed by hydrogenation proved identical (nmr, infrared, vpc) with IV prepared from the literature routes, and the spectral data agreed with that reported.[6,8]

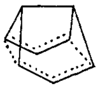


II IV VI V (2)

As the name implies, semibullvalene is in rapid equilibrium with its degenerate valence tautomer (IIa $\rightleftharpoons$ IIb), more rapid in fact than any of the previously reported degenerate Cope interconversions. The nmr (note Table I) showed only three varieties of hydrogens in a ratio of 2:4:2. Thus hydrogens 1, 3, 5, and 7 become equivalent, as do 4 and 8, while the set 2 and 6 remain unchanged but equivalent. Despite the nmr similarity in chemical shift of semibullvalene with the related compounds barbaralone (VII)[2a,10] and di-



IIa IIb (3)



X

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(1) (a) For paper I describing the synthesis of barrelene (bicyclo-[2.2.2]-2,5,7-octatriene) *cf.* H. E. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960); (b) paper II: H. E. Zimmerman and G. L. Grunewald, *ibid.*, **86**, 1434 (1964).

(2) (a) W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963); (b) *Tetrahedron*, **19**, 715 (1963).

(3) G. Schröder, *Chem. Ber.*, **97**, 3140, 3150 (1964).

(4) Photolysis in Vycor tubes external to a 450-w Hanovia medium pressure lamp for 45–80 min.

(5) Lack of $AgNO_3$ and vpc isomerization was established by nmr.

(6) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).

(7) O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Am. Chem. Soc.*, **86**, 2660 (1964).

(8) M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).

(9) W. R. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964).

(10) J. B. Lambert, *Tetrahedron Letters*, 1901 (1963).