Table II. Effect of Excitation Wavelength on the Photochemistry of 2 in Cyclohexane at Room Temperature

Excitation wavelength (nm)	% of 8 in product mixture	5:6:7
254[a]	76.2	1.00:0.06:0.17
280–330[b]	89.6	1.00:0.06:0.28
325–385[c]	41.2	1.00:0.07:0.28
>285[d]	12.3	1.00:0.08:0.32
313[e]	99.4	
313[e] plus 366[f]	29.6	1.00:0.06:0.29

[a] Rayonet reactor, RPR-2537 Å lamps, vycor vessel. [b] Rayonet reactor, RPR-3000 Å lamps (broad emmission maximum at 300 nm) Pyrex vessel. [c] Rayonet reactor, RPR-3500 Å lamps (broad emission maximum at 350 nm) Pyrex vessel. [d] Hanovia 450 W mercury lamp, Pyrex vessel. [e] As in footnote *d* but with a filter solution of basic potassium chromate. [f] Osram super pressure mercury lamp with a Bausch and Lomb high intensity monochromator.

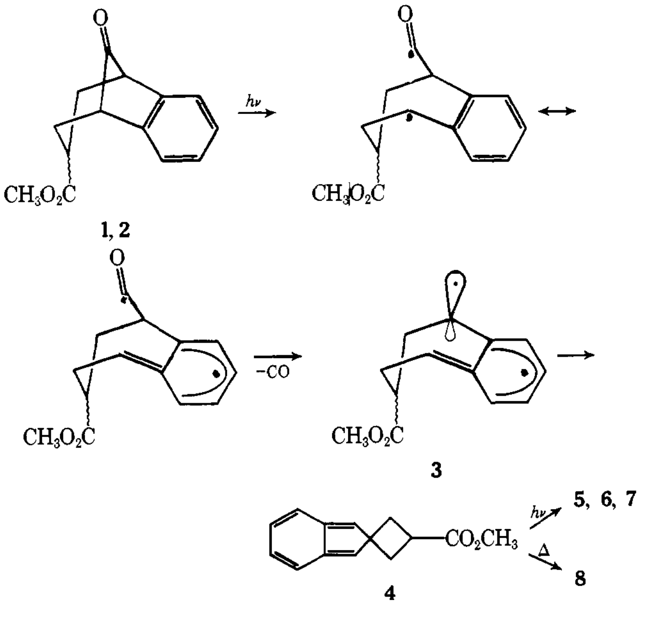
This effect could be duplicated by using a Rayonet reactor with one or two 3000 Å lamps, the rest being 3500 Å.

The simultaneous dual excitation experiments require the presence of an intermediate capable of absorbing light of wavelengths greater than 350 nm since this is not absorbed by **1** or **2**. We believe this intermediate to be the strained *o*-quinodimethane, **4**. Independent evidence for **4** comes from the formation of a one to one Diels–Alder adduct on irradiation of **2** in the presence of maleic anhydride.[10,11]

In view of these results we propose the mechanism shown in Scheme I[5] to explain the photochemistry of **1** and **2**. The most likely primary photochemical process is a singlet state (vide supra) α-cleavage producing the acyl-alkyl radical pair shown, followed by loss of carbon monoxide to biradical **3** which relaxes to the *o*-quinodimethane, **4**. The observed wavelength dependence (Table II) indicates that **5**, **6**, and **7** are produced in a secondary photochemical reaction of **4** by absorption of light (longer wavelengths) not absorbed by **1** or **2**. At low conversions it is unlikely that **4** will be able to compete successfully with the starting ketone for short wavelength light. The decreases observed in the relative yield of **8** with lowered reaction temperature (Table I) indicate that it is probably derived from **4** in a thermal reaction.

The unexpected stability as well as subsequent thermal and photochemical reactions of **4** are explicable in terms of orbital symmetry requirements[12] in product formation. Thermally allowed conrotatory closure of **4** cannot occur as this would lead to a very strained trans-fused bicyclic benzocyclobutene. Instead an allowed 1,5-suprafacial hydrogen shift takes place yielding **8**. With simultaneous irradiation at long wavelengths or photolysis at low temperatures where the 1,5-hydrogen shift is slowed down or stopped, **4**, absorbs light giving rise to the allowed disrotatory cyclization to the cis-fused bicyclic benzocyclobutenes, **5** and **6**, as well as a photochemical Diels–Alder reaction to **7**.

Scheme I



We have shown that the twisted and strained *o*-quinodimethane, **4**, is the only primary photoproduct formed on irradiation of the 2-indanones, **1** and **2**; however it undergoes competing thermal and photochemical reactions to produce the isolated products **5–8**. The surprising stability of **4**, even at room temperature, is no doubt due to a structural prohibition for the orbital symmetry allowed conrotatory ring closure, and the observed thermal and photochemical reactions of **4** apparently do not proceed via biradical intermediates but are instead concerted reactions governed by orbital symmetry.

Acknowledgment. Financial support from the University of Michigan, College of Literature, Science and the Arts and the Horace H. Rackham School of Graduate Studies is gratefully acknowledged. We would like to thank Professor C. H. Bushweller for his aid in interpreting NMR spectra and Professor R. G. Lawton for generous supplies of compound **1**.

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(1) (a) G. Quinkert, J. Palmowski, H.-P. Lorenz, W.-W. Wiersdorff, and M. Finke, *Angew. Chem., Int. Ed. Engl.*, **10**, 198 (1971), and references therein; (b) D. W. Jones and G. Kneen, *Chem. Commun.*, 1356 (1971); *J. Chem. Soc., Chem. Commun.*, 1038 (1972), and references therein.

(2) The synthesis of these compounds was carried out by R. G. Lawton and coworkers using a method developed previously. *J. Org. Chem.*, **35**, 690 (1970). A description of the synthesis will be provided in a future publication by these workers.

(3) In cyclohexane with nitrogen bubbling using a Rayonet reactor and RPR-3000 Å lamps.

(4) Assigned structures are consistent with observed spectroscopic and chemical properties. Products were shown to be isomeric by chemical studies as well as a combination of elemental analysis and high resolution mass spectroscopy, the details of which will be given in a future publication.

(5) Molecular conformations have been idealized.

(6) Quantum yield of product formation from **1** is 0.39 ± 0.05 in degassed (four freeze-pump-thaw cycles) benzene. Hanovia 450-W mercury lamp, with a basic potassium chromate filter solution (transmission maximum about 313 nm) was used for excitation.

(7) Stern-Volmer slopes 0.4 in benzene and 0.5 in cyclohexane. Product ratios were unchanged in the presence of *trans*-1,3-pentadiene.

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Dicarbonyltetraiodorhodate(III). An Example of a Thermodynamically Stable Trans Dicarbonyl Species

Sir:

The rationalization of the structures adopted by metal complexes containing two or more different types of ligand is a fundamental goal in inorganic chemistry. Some years ago Chatt and Heaton[1] noted that "groups of high trans effect, as ethylene in $Pt(C_2H_4)Cl_3^-$, render the position in mutual trans position more susceptible to bonding by what are now known as hard bases." Recently Pearson[2] framed this suggestion in somewhat different terms, "two soft ligands in mutual trans positions will have a destabilizing effect on each other when attached to class b metal atoms." Among the best evidence in favor of these ideas have been the thermodynamically stable structures adopted by transition metal halocarbonyl complexes. All halocarbonyl species containing two or more carbonyls on the metal have been shown to contain the minimum number of trans dicarbonyl groupings.[3] Thus species of the type $M(CO)_2X_2$, e.g., $Ru(CO)_2X_2$,[4] $Rh(CO)_2X_2^-$,[3] $Ir(CO)_2X_2^-$,[3] and $Pt(CO)_2Cl_2$[5] have cis square-planar structures. Species of the type $M(CO)_4X_2$, e.g., $Mn(CO)_4X_2^{2-}$ [6] and $Fe(CO)_4X_2$[7] adopt cis structures. Species of the type $M(CO)_3X_3$, e.g., $Ru(CO)_3X_3^-$ and $Os(CO)_3X_3^-$ [8] adopt the C_{3v} fac structure. Previously characterized species of the type $M(CO)_2X_4^-$, e.g., $Ru(CO)_2X_4^{2-}$,[8] $Os(CO)_2X_4^{2-}$ [8] and $Ir(CO)_2I_4^-$ [9] adopt the cis configuration.

Some years ago one of us reported[10] the preparation of the anions *cis*-$Rh(CO)_2X_4^-$, by oxidative addition of halogens to the *cis*-$Rh(CO)_2X_2^-$ ions. The compounds were unstable and decomposed to species containing only one CO stretching frequency in the infrared spectrum and they were presumed to be monocarbonyl species. In the case of $Rh(CO)_2I_4^-$ the new species has now been isolated in the form of Ph_4As^+, Bu_4N^+, and Pr_4N^+ salts and shows the following surprising reactions: (a) it reacts with excess triphenylphosphine to give $[Rh(Ph_3P)_2(CO)_2I]$ and (b) it reacts with excess iodide ion to give $Rh(CO)I_5^{2-}$ with evolution of approximately 1 mol of gas. More definitive characterization was clearly required and black crystals of $[(n\text{-}Pr)_4N][RhI_4(CO)_2]$ suitable for X-ray crystallographic investigation were grown by slow cooling of a solution in CH_2Cl_2-CCl_4 under 3 atm of CO pressure (ν_{CO} in CH_2Cl_2 is 2091 cm^{-1}). Two different monoclinic crystalline forms of $[n\text{-}Pr_4N][Rh(CO)_2I_4]$, $M = 852.9$, were observed, needles and octahedra. The needles have the following: $a = 12.764$ (8), $b = 12.695$ (8), $c = 7.737$ (5) Å, $\beta = 90.0$ (2)°; $Z = 2$; $d_{calcd} = 2.259$, $d_{measd} = 2.263$ g/cm^3; space group $P2_1$. The octahedra have the following: $a = 9.537$ (6), $b = 15.551$ (9), $c = 18.218$ (11) Å; $\beta = 108.4$ (2)°; $Z = 4$; $d_{calcd} = 2.210$, $d_{measd} = 2.222$ g/cm^3; space group $P2_1/c$. Intensity data from one of the needle crystals were collected on a linear diffractometer using Mo K_α radiation and were corrected for absorption. The structure was solved by Patterson and Fourier methods and refined to a final R value of 0.054 for 2051 planes above 2 σ. The X-ray analysis confirms the existence of the *trans*-$[Rh(CO)_2I_4]^-$ ion (see Figure 1). This anion has, to a good approximation, $4/mmm$ (D_{4h}) symmetry with Rh-C = 1.89 (2), Rh-I = 2.69, and C-O = 1.13 (4) Å; these values do not differ greatly from those found in the $[Rh_2I_6(MeCO)_2(CO)_2]^{2-}$ ion where Rh-C (carbonyl) = 1.86 (2) (trans to I), Rh-I = 2.67 (trans to I), and C-O (carbonyl) = 1.06 (3) Å.[11] Thus any weakness in the Rh-C bond trans to carbon in $[Rh(CO)_2I_4]^-$ is not accompanied by a significant increase in its length.[12]

This novel trans structure is not the result of solid state effects since we find that the trans form is stable in solution (CH_2Cl_2, CH_3NO_2) for many days under CO pressure whereas the cis isomer[10] isomerizes to the trans form within minutes at room temperature.

It is possible to invoke steric crowding as the reason for the finding of a preference for the trans structure in this system and in considering this we checked the stability of *cis*-$Ir(CO)_2I_4^-$ in solution over extended periods and could not detect any evidence for a trans species. This difference between the rhodium and iridium systems should be considered in conjunction with the knowledge that the reported Ir(III)-I bond lengths[13] are 2.67 and 2.68 Å (iodides trans to each other), 2.67 Å (iodide trans to CO), and 2.73 Å (iodide trans methyl, i.e., a strong trans influencing ligand) and thus are very close to those reported here for the Rh-I distances in *trans*-$Rh(CO)_2I_4^-$. Therefore steric repulsions are expected to be very similar in the two systems. Apparently the forces[1,2] responsible for the adoption of the cis structure in the iridium compound are more powerful than those operating in the rhodium case where the structure which minimizes steric repulsions is found.

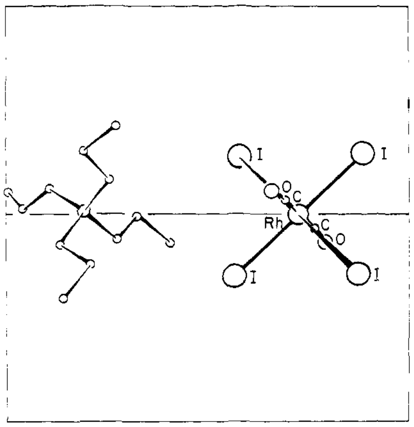

Figure 1. The $[n\text{-}Pr_4N]^+$ and $[Rh(CO)_2I_4]^-$ ions projected down the c axis.

In addition, preliminary results on the $Rh(CO)_2Br_4^-$ system indicate that (a) a trans form also exists and (b) it appears to be slightly the more stable form in solution in CH_2Cl_2.[14]

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Supplementary Material Available. A listing of structure factor amplitudes and atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-2551.

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(9) (a) M. J. Cleare and W. P. Griffith, *J. Chem. Soc. A*, 2788 (1970); (b) D. Forster *Synth. Inorg. Metal-Org. Chem.*, **1**, 221 (1971).
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appendix to this communication. See paragraph at end of paper regarding supplementary material.

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(14) D. Forster and G. F. Schaefer, to be submitted for publication, the trans form can be generated by carbonylation of $[Rh(CO)Br_5]^{2-}$. A solution of this trans form in the presence of excess bromine, slowly reverts (over 6 days at 22° and 1 atm of CO) to a mixture of the trans and cis isomers containing ~60% of the trans form. The same position can be reached by adding excess bromines to the *cis*-$Rh(CO)_2Br_2^-$ ion (which immediately generates the *cis*-$Rh(CO)_2Br_4^-$ ion) and allowing this solution to stand for 6 days under 1 atm of CO at 22°. The excess bromine is necessary to prevent decomposition to Rh^I and it is not known at this time whether this excess of bromine affects the equilibrium position in any way. It should be stressed that excess iodine was not present in the solution experiments involving the establishment of the equilibrium position in the $Rh(CO)_2I_4^-$ system.

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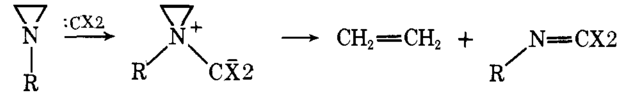
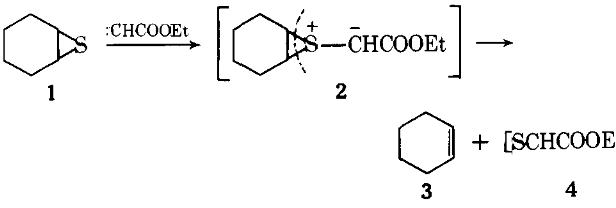
Fragmentation Reaction of Ylides. IV.[1] Reaction of Sulfide and Carbene

Sir:

We previously observed that aziridines react with carbenes to give the corresponding olefins by the simultaneous breaking of two C-N bonds in the aziridine ring.[2] The reactions should be preceded by the initial formation of aziridinium ylide followed by fragmentation of the three-membered ring. This observation was very different from the expected one in the ordinary reactions of ammonium ylide which usually include Stevens rearrangement or degradation into carbene and tertiary amine.[3] We are now interested in extending our research to other hetero three-membered rings. Sulfur compounds especially attract us as they might act to stabilize the ylide by their d-orbital resonance with an anion on an adjacent carbon. We studied the reaction between sulfides and carbenes and report here on the stereospecific fragmentation of *S*-ylide.

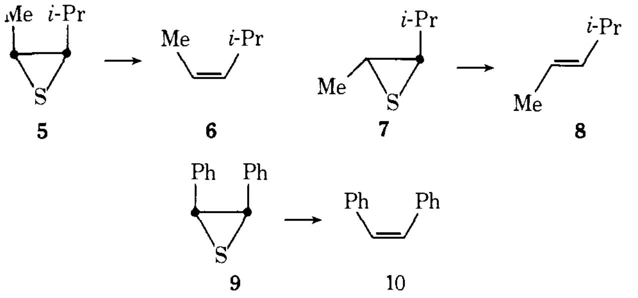


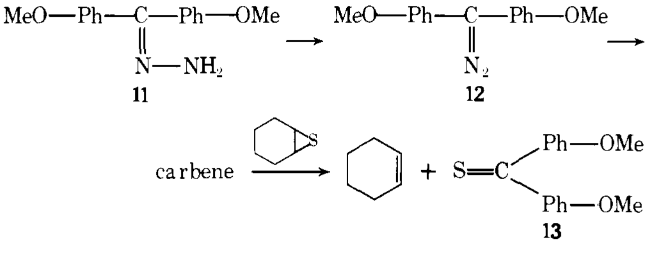
Cyclohexene sulfide and an equimolar amount of ethyl diazoacetate were dissolved in *p*-cymene, and a small amount of Cu(acac)$_2$ was suspended as a catalyst.[4] On heating the solution at 110°, vigorous reaction occurred with the evolution of a gas. After the reaction had ceased, distillation gave 70% cyclohexene. The reaction can be indicated as



The formation of *S*-ylide from cycloalkyl sulfide and carbene is generally accepted.[5] Episulfide likewise probably formed ylide **2** as an initial intermediate, which then decomposed by fragmentation into cyclohexene and thioglyoxalic ester. The manner of this reaction is the same as that of the reaction of aziridinium ylide. Recently, however, Kondo and his coworkers proposed that the decomposition of alkyl sulfoxide, which is considered to be a kind of ylide, proceeds by stepwise bond cleavage through the formation of a diradical intermediate, and that, as a result, the olefin formed does not retain the stereospecificity of the starting material.[6] This reasoning is contrary to the prediction from the fragmentation of aziridinium ylides. Thus, it seemed of interest to us to examine the stereochemistry of olefin formed from the fragmentation of *S*-ylide, and we carried out the reaction using *cis,trans*-4-methyl-2-pentene sulfide and *cis*-stilbene sulfide.[7]

A mixture of *cis*-4-methyl-2-pentene sulfide (**5**), 2 mol of ethyl diazoacetate, and Cu(acac)$_2$ in ether was heated under reflux for a short time. Olefin isolated at the end of the reaction was examined by VPC. The yield was 72%, and the product was entirely cis isomer **6**, no trans olefin being detectable at all. Thus, the fragmentation of *cis*-4-methyl-2-pentene sulfide ylide proceeded with >99.5% retention of stereochemistry. Another experiment showed that *trans*-4-methyl-2-pentene sulfide (**7**) gave 70% trans olefin **8**, and *cis*-stilbene sulfide (**9**) gave 94% of *cis*-stilbene (**10**) with complete retention of conformation, respectively. Attempts to isolate thioglyoxalic ester, whose formation is predicted by the proposed mechanism, completely failed, perhaps because it is very unstable. However, to understand the reaction, the compound containing the S atom leaving the ylide should be studied. Thus, we next used 4,4′-dimethoxybenzophenone hydrazone (**11**) as the source of carbene. The reaction was carried out using a large excess of cyclohexene sulfide without catalyst or solvent at 50–80°. As the reaction proceeded, the mixture showed the characteristic color of thio ketone **13**, which was isolated at the end of the reaction and identified by uv and ir absorption spectra and by TLC in comparison with an authentic sample. The only olefin produced was cyclohexene.





Nozaki and his coworkers have reported that the reaction of epoxide with carbene also gives olefin, although the yield is poor.[8] Thus, we propose that hetero three-membered ylides have a strong tendency to undergo α-fragmentation as shown in **14.** Four-membered *S*-ylide and four-membered *N*-ylide reportedly give a Stevens rearrangement product but no fragmentation.[2,5] Therefore, α-fragmentation is a