$$\begin{tikzcd}
\mathrm{Hg[Co(CO)_4]_3^-} \arrow[r] & \mathrm{Hg[Co(CO)_4]_2} \arrow[d, "\mathrm{PPh_3}"] & + \\
& \mathrm{Hg[Co(CO)_3PPh_3]_2} & \mathrm{Co(CO)_4^-} \arrow[d, "\mathrm{excess} \atop \mathrm{Ni(1,10\text{-}phen)_3^{2+}}"] \\
& & \mathrm{{}^1/_2Ni(1,10\text{-}phen)_3[Co(CO)_4]_2}
\end{tikzcd} \qquad (3)$$

The infrared spectrum of **2** in THF, as observed in a sealed Fluorite cell, showed strong bands at 2039 and 1963 $cm^{-1}$ for the complex, in addition to weak bands at 2069 and 1996 (sh) $cm^{-1}$ from $Hg[Co(CO)_4]_2$ and at 1887 $cm^{-1}$ for $Co(CO)_4^-$. In Nujol mulls of **1** only the absorptions attributable to the complex are observed. These spectra together with those of the THF reaction mixture confirm the reversible nature of the complex ion formation.[8] The approximately 30-$cm^{-1}$

$$Hg[Co(CO)_4]_2 + Co(CO)_4^- \rightleftharpoons Hg[Co(CO)_4]_3^- \qquad (4)$$

shift to lower energies on going from $In[Co(CO)_4]_3$[9] to $Hg[Co(CO)_4]_3^-$ is similar to that observed[10] between $Co_4(CO)_{12}$ and $FeCo_3(CO)_{12}^-$. Absorptions at 130 $cm^{-1}$ in the far-infrared and Raman and at 100 $cm^{-1}$ in the Raman spectra of $Hg[Co(CO)_4]_3^-$ can be attributed respectively to the antisymmetric and symmetric HgCo stretching vibrations of the $HgCo_3$ moiety. The reduction of the energies of the HgCo modes on going from $HgCo_2(CO)_8$[11] to $HgCo_3(CO)_{12}^-$ is expected for the increase in coordination number. Analogous shifts are observed in mercuric halides upon formation[12] of $HgX_3^-$ from $HgX_2$.

Mercury(II) complexes of the type $HgX_3^-$ have been characterized with halides,[13] pseudohalides,[13] main group elements,[14] transition metals and halides,[15] and carbon,[16] but not previously with transition metals alone. A related cadmium(II) halide–metal carbonyl complex has been described.[17] The most likely structure for $Hg[Co(CO)_4]_3^-$ would involve a planar arrangement of the four metal atoms. With the carbonyl groups staggered an ion of $C_{3h}$ symmetry would result, for which seven infrared active carbonyl stretching vibrations would be expected. In an elegant study of the vibrational spectrum of $Hg[Co(CO)_4]_2$, Bor[18] recently showed that coupling of the stretching vibrations of CO ligands on different cobalt atoms was quite small except for that of the *trans*-axial groups acting through a linear sequence of bonds. Since no linear arrangement of ligands exists in the proposed structure of $Hg[Co(CO)_4]_3^-$, it is reasonable to expect that local symmetry will adequately describe the carbonyl stretching vibrations. For $C_{3v}$ local symmetry three infrared-active bands are predicted. That only two of these are observed is probably a result of broadening due to the polar solvent necessary to dissolve the complex. An X-ray structure determination is currently in progress to provide more complete structural information.

The susceptibility of $Hg[Co(CO)_4]_2$ to nucleophilic attack by halide ions has recently been reported in these letters.[19] Attack of halides on $Hg[Co(CO)_4]_3^-$, like that on $Hg[Co(CO)_4]_2$, leads to displacement of $Co(CO)_4^-$. In a similar reaction, equimolar amounts of $(Ph_3PCH_2Ph)^+X^-$ ($X$ = Cl, I) and $Hg[Co(CO)_4]_2$ lead to the formation of new species, $(Ph_3PCH_2Ph)^+\{XHg[Co(CO)_4]_2\}^-$, for which satisfactory elemental analyses have been obtained. The infrared spectrum of the chloride complex in $CH_2Cl_2$ exhibits bands at 2052 m and 1983 vs $cm^{-1}$ in addition to a weak band at 2070 $cm^{-1}$ attributable to $Hg[Co(CO)_4]_2$. The shifts of the CO stretching peaks to lower frequencies indicate the $Co(CO)_4$ groups bear a fractional negative charge.

We are presently extending our study of complex anions to other transition metal carbonyl groups as well as to other main group elements. Preliminary studies have demonstrated the existence of such complexes as $Hg[Fe(CO)_2C_5H_5]_3^-$, $Cd[W(CO)_3C_5H_5]_3^-$, and $In[Co(CO)_4]_4^-$. Other derivatives of gallium, indium, and thallium such as $Br_2In[Co(CO)_4]_2^-$ and $Tl[Fe(CO)_2C_5H_5]_2^+$ have been independently observed.[20]

**Acknowledgment.** We are pleased to acknowledge financial support of this work from the National Science Foundation, the Petroleum Research Fund administered by the American Chemical Society, and the Advanced Research Projects Agency.

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[8] Preliminary investigations on the zinc and cadmium analogs of the complex ion indicate that the equilibrium (eq 4) is shifted toward the right in noncoordinating solvents; only infrared absorptions due to the complex were observed.

[9] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966).

[10] P. Chini, L. Colli, and M. Peraldo, *Gazz. Chim. Ital.*, **90**, 1005 (1960).

[11] H. Stammreich, K. Kawai, O. Sala, and P. Krumholz, *J. Chem. Phys.*, **35**, 2175 (1961).

[12] D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968.

[13] D. Grdenic, *Quart. Rev.* (London), **19**, 303 (1965).

[14] T. F. Schaaf and J. P. Oliver, *J. Amer. Chem. Soc.*, **91**, 4327 (1969).

[15] K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, *J. Chem. Soc., A*, 2851 (1968).

[16] L. M. Seitz and S. D. Hall, *J. Organometal. Chem.*, **15**, P7 (1968).

[17] J. K. Ruff, *Inorg. Chem.*, **7**, 1499 (1968).

[18] G. Bor, *Inorg. Chim. Acta*, **3**, 196 (1969).

[19] J. M. Burlitch, *J. Amer. Chem. Soc.*, **91**, 4563 (1969).

[20] W. A. G. Graham, private communication to J. M. B.

[21] Author to whom communications should be addressed.

[22] National Defense Education Act, Title IV, Fellow, 1966–1969.

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*Received November 17, 1969*

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## Stereochemistry of the Oxidation of the *cis*- and *trans*-1-Amino-2,3-diphenylaziridines

*Sir:*

The thermal fragmentation of episulfones,[1] nitrosoaziridines,[2] and ethyleneazamines[3] has been observed to be stereospecific in contrast to the nonstereospecific decomposition of episulfoxides[4] and contrary to the initial conclusions of Woodward and Hoffmann based

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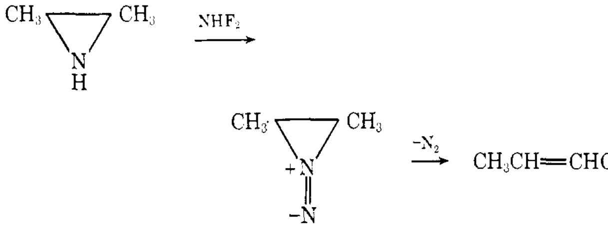
[1] (a) N. P. Neureiter and F. G. Bordwell, *J. Amer. Chem. Soc.*, **85**, 1209 (1963); (b) N. P. Neureiter, *ibid.*, **88**, 558 (1966); (c) L. A. Carpino and L. V. McAdams, III, *ibid.*, **87**, 5804 (1965); (d) N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966); (e) F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *J. Amer. Chem. Soc.*, **90**, 429 (1968).

[2] R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964).

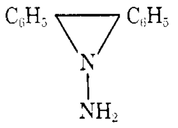
[3] J. P. Freeman and W. H. Graham, *J. Amer. Chem. Soc.*, **89**, 1761 (1967).

[4] G. E. Hartzell and J. N. Paige, *J. Org. Chem.*, **32**, 459 (1967).

on orbital symmetry considerations.[5] The azamine case is particularly interesting although it has not previously been studied using a substrate having a preformed N–N bond. Freeman and Graham[3] generated an appropriate pair of azamines by reaction of *cis*- and *trans*-2-butenimines with difluoramine and found that the conversion to olefin was cleanly stereospecific (eq 1). This observation, as well as the analogous results in the nitrosoaziridine and episulfone cases, has led to considerable confusion in view of the lack of correspondence with the theoretical predictions. More recently the earlier theoretical speculations have been revised and it has been suggested that these fragmentations should in fact proceed stereospecifically by concerted mechanisms involving nonlinear transition states, in line therefore with the experimental results.[6] We now wish to report a lack of stereospecificity in the case of a related reaction which is also believed to proceed through an ethyleneazamine intermediate. By application of recently described synthetic routes we have been able to prepare and study the oxidation of the first isomeric pair of 1-aminoaziridines. *cis*-1-Amino-2,3-diphenylaziridine (*cis*-I) [mp 110–111° dec, nmr[7] ($CDCl_3$) $\delta$ 3.14 (s, CH, 2 H), 3.80 (broad s, $NH_2$, 2 H), 7.12 (s, phenyl, 10 H)] was obtained in 32% yield by reaction of *meso*-hydrobenzoin dimesylate (*meso*-II), mp 122° dec, with 95% hydrazine.[9,10] It was not possible to obtain *trans*-I by the same technique since *rac*-II, mp 99–100°, gave only desoxybenzoin hydrazone under these conditions.[11] However the *trans* isomer could be obtained by adaptation of Rees' azamine-trapping reaction.[13] Oxidation of N-aminophthalimide (III) with lead tetraacetate in a methylene dichloride solution of *trans*-stilbene gave the adduct IV,[10] mp 165°, nmr ($CDCl_3$) 7.5 (m, aryl, 14 H), 4.99 and 3.96 (AB quartet, $J_{AB}$ = 6 cps, CH, 2 H), in 50% yield. Cleavage of the phthaloyl protective group by means of ethanolic hydrazine[14] gave in 40% yield *trans*-I,[10] mp 90° dec, nmr[7] ($CDCl_3$) 7.33 (m, phenyl, 10 H), 3.33 and 3.19 (AB quartet, $J_{AB}$ = 5 cps, CH, 2 H), and 3.00 (broad s, $NH_2$, 2 H).



(1)



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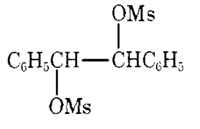
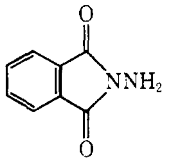
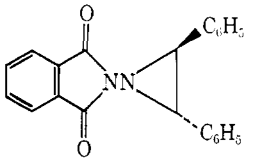


$C_6H_5\underset{OMs}{CH}-\overset{OMs}{CH}C_6H_5$

II



III



IV

Oxidation of *trans*-I by means of activated manganese dioxide[15] in methylene dichloride at 0° gave only *trans*-stilbene whereas oxidation of *cis*-I gave a mixture consisting of 85% *trans*- and 15% *cis*-stilbene (analysis by glpc). *cis*-Stilbene was shown not to be isomerized under the conditions of the oxidation. If one assumes similar intermediates[16] in the deamination of the 2-butenimines and our oxidation of *cis*- and *trans*-I, one can rationalize the results by postulating that the azamine fragmentation may occur through a range of mechanisms with a concerted transition state at one end of the scale and a two-step process, involving phenyl stabilization of radical or ionic species, at the other.[17] Alternatively isomerization might occur during the reaction.[17] Although it has been demonstrated that

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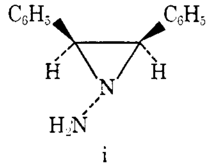
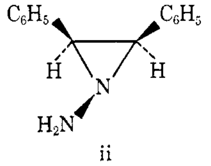
[5] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965); Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 8-S.

[6] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969). We are indebted to Professor Hoffmann for informative correspondence and a preprint on cheletropic reactions in advance of publication.

[7] The nmr spectra of *cis*- and *trans*-I are consistent with the expected hindrance to nitrogen inversion caused by the N-amino substituent.[8] If the N-amino group were not configurationally stable the *trans* isomer should exhibit only a singlet for the methine protons rather than the observed AB quartet. In the case of the *cis* isomer observation of a single peak suggests that only one of the two possible geometric isomers (i and ii), presumably i, was isolated.



i



ii

[8] S. J. Brois, *Tetrahedron Lett.*, 5997 (1968).

[9] H. Paulsen and D. Stoye, *Angew. Chem.*, **80**, 120 (1968).

[10] All new compounds gave satisfactory elemental analyses (±0.3%) and infrared and nmr spectra consistent with the indicated structures.

[11] The difference between the two mesylates in their reaction with hydrazine can be explained on the basis that competing $\beta$ elimination of methanesulfonic acid is sterically favored in the case of the racemic isomer. Hydrolysis of the resulting vinyl mesylate would yield desoxybenzoin and finally the corresponding hydrazone.[12]

[12] *Cf.* P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **90**, 6515 (1968).

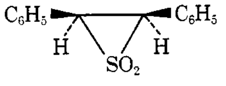
[13] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Commun.*, 146 (1969); R. S. Atkinson and C. W. Rees, *ibid.*, 1230 (1967).

[14] H. R. Ing and R. H. F. Manske, *J. Chem. Soc.*, 2348 (1926).

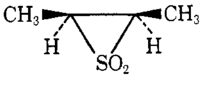
[15] The oxidant used was a special mixture obtained by precipitation of manganese dioxide on activated carbon: L. A. Carpino, to be published.

[16] This assumption seems reasonable on the basis of analogy with earlier work although it must be emphasized that there is as yet no *direct* evidence for the involvement of azamine intermediates in either of these reactions. For a discussion of reactions believed to take place through such transient species see (a) C. G. Overberger, J.-P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen-Nitrogen Bonds," Ronald Press Co., New York, N. Y., 1966, pp 12–16, 89–94; (b) J. H. Boyer in "Mechanisms of Molecular Migrations," Vol. 2, S. Thyagarajan, Ed., Interscience Publishers, New York, N. Y., pp 305–310. Adaptation of the present techniques to the synthesis of the *cis*- and *trans*-1-amino-2,3-dimethylaziridines is under study.

[17] In previously studied cases in which the by-product is sulfur dioxide or nitrous oxide there does not appear to be any difference between alkyl and aryl substituents as far as the stereochemistry of the fragmentation is concerned.[1,2] However in the sulfone case it has been noted that *cis*-diphenylethylene sulfone (iii), if decomposed in the presence of aqueous sodium hydroxide, undergoes isomerization to the *trans* isomer prior to fragmentation. In the case of the corresponding



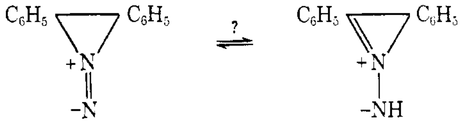
iii



iv

dimethyl derivative (iv) such isomerization occurs only in the presence of the stronger base, potassium *t*-butoxide.

*cis*-stilbene is not isomerized under the reaction conditions there is no certainty that the *cis*-azamine intermediate (V) is not isomerized to the *trans* isomer prior to fragmentation. A possible intermediate which could account for such an isomerization is the azirine imine VI. Related species have been implicated in other



V

VI

reactions of azamines,[18] although the mild conditions used in the present oxidation would appear to discount this possibility. Evidence on this point is being sought through deuterium-substitution studies as well as by generation of VI in other ways.

Of perhaps greater novelty than their oxidative behavior is the fact that both *cis*- and *trans*-I undergo thermal fragmentation readily. As expected[19] the *trans*-N-aminoaziridine is less stable than the *cis* isomer and undergoes decomposition to *trans*-stilbene on attempted recrystallization from ethanol or by brief heating at the melting point. Experiments are under way to determine whether the transient by-product of this fragmentation is the long-sought hydronitrogen, azamine ($H_2NN$).

**Acknowledgment.** This study was supported by a grant (GP-4283) from the National Science Foundation.

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[18] (a) L. A. Carpino, J. F. Ferrari, S. Göwecke, and S. Herliczek, *J. Org. Chem.*, **34**, 2009 (1969); (b) D. M. Lemal and T. W. Rave, *J. Amer. Chem. Soc.*, **87**, 393 (1965); (c) D. M. Lemal, F. Menger, and E. Coats, *ibid.*, **86**, 2395 (1964).

[19] A similar marked difference in stability has been observed for the corresponding episulfones.[1e] The difference can be rationalized on the basis of smooth fragmentation, in the case of the *trans* isomer, to the highly conjugated *trans*-stilbene system.

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*Received November 21, 1969*

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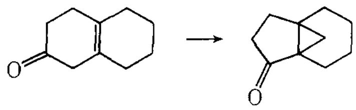
## Photochemical Rearrangement of an Acyclic $\beta,\gamma$-Unsaturated Ketone to a Conjugated Cyclopropyl Ketone. An Oxa-di-$\pi$-methane Rearrangement[1]

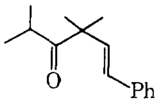
*Sir:*

The photochemistry of 1,3-dienes and their related $\alpha,\beta$-unsaturated ketone analogs has been studied in order to correlate the mechanistic aspects of the two chromophores.[2,3a] In continuation of this type of investigation, we wish to report the photochemical rearrangement of $\beta,\gamma$-unsaturated ketone (I) to $\alpha,\beta$-cyclopropyl ketone (VIII), a rearrangement which is directly analogous to the di-$\pi$-methane rearrangement found in 1,4-dienes (II to III).[3b] Furthermore, the rearrangement of I to VIII occurred only on sensitized irradiation, and the absence of acyl cleavage or decarbonylation products under such conditions suggests a mechanism involving initial vinyl–carbonyl bridging. In striking contrast, direct irradiation of I gave isomeric ketone IV and decarbonylation products V–VII. In ketone photochemistry, such a clean separation of reaction pathway depending upon method of excitation is rarely found.

Various $\beta,\gamma$-unsaturated ketones upon irradiation rearrange to cyclopropyl-conjugated ketones.[4–12] It



has been suggested[6,11] that such a rearrangement proceeds *via* initial ketonic $\alpha$ cleavage but doubts have been cast on the occurrence of *free radical* intermediates in the rearrangement step.[12] Recently, the rearrangement of benzobicyclo[2.2.0]octadienone has been suggested to proceed *via* carbonyl–vinyl bridging.[13] To investigate the possibility of the generality of an "oxa-di-$\pi$-methane" rearrangement pathway for all $\beta,\gamma$-unsaturated ketones, the photochemistry of the acyclic 1-phenyl-3,3,5-trimethylhex-1-en-4-one (I), a ketone structurally similar to the diene II which has been shown to undergo a di-$\pi$-methane rearrangement to III,[3b] has been examined.



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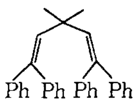

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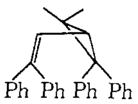

III

The starting ketone I was prepared in the following manner. Selective oxidation of 2,2,4-trimethyl-3-hydroxyvaleraldehyde (aldol of isobutyraldehyde) with a sixfold excess of isolated dry $CrO_3$–(pyridine)$_2$ complex in methylene chloride at room temperature[14,15] yielded 2,2,4-trimethyl-3-oxovaleraldehyde. This aldehyde upon reaction with benzylidenetriphenylphosphorane yielded a *cis–trans* (1:1) mixture of I; $I_c$ and $I_t$ were separately characterized by their uv, ir, nmr, and mass spectral properties.

The rearrangement of 1,4-diene II to cyclopropane ene III proceeded under both direct and sensitized irradiation conditions, the process being more efficient under direct irradiation conditions.[3b] The related "oxa-di-$\pi$-methane" rearrangement of ketone I would not be expected to proceed by direct irradiation, however, since under such conditions $\beta,\gamma$-unsaturated ketones are known to undergo facile ketonic $\alpha$ cleavage[7,12] and decarbonylation.[16] Indeed, when I was directly

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[1] This work was supported in part by Public Health Service Grant No. AM 00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

[2] H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **89**, 5971 (1967).

[3] (a) W. G. Dauben and W. A. Spitzer, *ibid.*, **90**, 802 (1968); (b) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969), and references cited therein.

[4] L. P. Tenney, D. W. Boykin, Jr., and R. E. Lutz, *ibid.*, **88**, 1835 (1966).

[5] J. R. Williams and H. Ziffer, *Chem. Commun.*, 194 (1967).

[6] J. R. Williams and H. Ziffer, *ibid.*, 469 (1967).

[7] L. A. Paquette, R. F. Eizember, and O. Cox, *J. Amer. Chem. Soc.*, **90**, 5153 (1968).

[8] J. Griffiths and H. Hart, *ibid.*, **90**, 5296 (1968).

[9] J. Ipaktschi, *Tetrahedron Lett.*, 215 (1969).

[10] K. Kojima, K. Sakai, and K. Tanabe, *ibid.*, 1925 (1969).

[11] J. Ipaktschi, *ibid.*, 2153 (1969).

[12] E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969).

[13] R. S. Givens and W. F. Oettle, *ibid.*, 1164 (1969).

[14] J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

[15] W. G. Dauben, M. Lorber, and D. S. Fullerton, *J. Org. Chem.*, **34**, 3587 (1969).

[16] J. E. Starr and R. H. Eastman, *ibid.*, **31**, 1393 (1966).