1,2-Anionic Rearrangement of Organosilylhydroxylamines[1,2]

Sir:

The 1,2-anionic rearrangement of hydrazines, in which organosilyl and aryl groups move from one nitrogen atom to another, was discovered in 1964[3] and has been described in a recent series of papers.[4] We now report the first 1,2-anionic rearrangement of a group from oxygen to nitrogen.

Pure N,O-bis(trimethylsilyl)hydroxylamine (**1**),[5] bp 65° (50 Torr), $n^{20}\text{D}$ 1.4120, was prepared by the reaction of excess hexamethyldisilazane with dry hydroxylamine in tetrahydrofuran (THF) at room temperature. That the product from this reaction has structure **1** is indicated by its nmr spectrum, which shows two sharp nmr peaks in the trimethylsilyl region at τ 9.85 and 9.92 and a broad resonance in the N–H region at τ 5.43, with relative intensity 9:9:1, respectively.

When **1** is converted to its lithium salt and added to a solution of methyl iodide in THF–pentane at room temperature, the rearranged anion of **1** is trapped as its methyl derivative **2** in high yield.

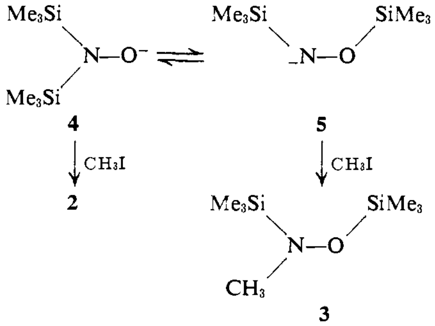
$$\underset{\mathbf{1}}{\mathrm{Me_3SiNHOSiMe_3}} \xrightarrow[\text{2. MeI}]{\text{1. } t\text{-BuLi}} \underset{\mathbf{2}}{\mathrm{(Me_3Si)_2NOMe}}$$

In a typical experiment, 4.05 g (22.9 mmol) of pure N,O-bis(trimethylsilyl)hydroxylamine was dissolved in 23 ml of pentane. To this was added at room temperature an equivalent amount of *t*-butyllithium dissolved in pentane, producing a white suspension and heat sufficient to reflux the pentane. The mixture was allowed to stir at room temperature for 24 hr to ensure complete reaction. The slurry was then added to a solution of 6.8 g (48 mmol) of methyl iodide in a mixture of 15 ml of pentane and 10 ml of THF and allowed to stir at room temperature for an additional 20 hr. Lithium iodide was separated from this reaction mixture by filtration under nitrogen. The clear filtrate was distilled to remove solvents and the residue afforded only one product, N,N-bis(trimethylsilyl)-O-methylhydroxylamine (**2**). Pure samples of **2** were obtained by preparative gas chromatography.

The nmr spectrum of **2** shows a single peak in the trimethylsilyl region, τ 9.90, and a single resonance at τ 6.57 assigned to the O-methyl protons, with relative areas 6.1:1, respectively, compared to the calculated ratio of 6:1. Unambiguous proof of the structure of **2** was obtained by synthesis of the compound by an independent route. The infrared and nmr spectra of the compound obtained from the reaction of hexamethyldisilazane with O-methylhydroxylamine hydrochloride are superimposable with those of **2**.

If the white suspension obtained from the reaction of **1** with *t*-butyllithium is derivatized immediately with methyl iodide, a mixture is obtained consisting of about 95% **2** with 5% of the unrearranged isomer, N,O-bis(trimethylsilyl)-N-methylhydroxylamine (**3**). Compound **3** shows two trimethylsilyl resonances in the nmr at τ 9.92 and 9.98, and an N-methyl resonance at τ 7.31, in the expected intensity ratio. The structure of **3** was further established by independent synthesis from N-methylhydroxylamine hydrochloride and hexamethyldisilazane.

The above results indicate that rearrangement of the anion of **1** is rapid under the conditions employed. However, when the white suspension of lithiated **1**, prepared at room temperature and stirred 24 hr, was slowly added to a methyl iodide–THF–pentane solution kept at −78°, *an approximately 1:1 mixture of* **2** *and* **3** *was obtained.* This finding suggests that the rearranged O anion **4** is in equilibrium with the unrearranged anion **5**, and that this equilibrium shifts toward **5** at lower temperatures.



The experiments described above provide conclusive evidence for a third kind of heteroatomic 1,2-anionic rearrangement, to be added to the known Wittig (O → C) and Stevens (N → C) rearrangements. The absence of mono- or trisilylated hydroxylamine derivatives in the products suggests that the rearrangement is intramolecular, like the hydrazine rearrangements described earlier.[4] Studies of the mechanism of the transformation are in progress.

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(1) Paper IX in the series, New Anionic Rearrangements. Previous paper in this series: R. West, M. Ishikawa, and S. Murai, *J. Amer. Chem. Soc.*, **90**, 727 (1968).

(2) This work was supported by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, U. S. Air Force, Grant No. AF-AFOSR 1061-66.

(3) R. E. Bailey and R. West, *J. Amer. Chem. Soc.*, **86**, 5369 (1964).

(4) R. West, H. F. Stewart, and G. R. Husk, *ibid.*, **89**, 5050 (1967); R. West, *Pure Appl. Chem.*, in press; and references given in these publications.

(5) The compounds reported in this communication all gave satisfactory analyses for C, H, Si, and N. Syntheses of **1**, **2**, and **3** have recently been described: U. Wannagat and O. Smrekar, *Monatsh. Chem.*, **100**, 750 (1963); O. Smrekar and U. Wannagat, *ibid.*, **100**, 760 (1969).

(6) Honorary Fellow in Chemistry, 1967–1968, on leave from Air Force Office of Scientific Research, Arlington, Va.

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Secondary Isotope Effects as Photochemical Mechanistic Criteria. Photosensitized *cis–trans* Olefin Isomerization Not Involving the Olefin Triplet State

Sir:

Simple olefins interact photochemically with carbonyl compounds possessing n–π^* lowest triplets to give both *cis–trans* isomerization and oxetane formation.[1] Until recently, it was thought that electronic energy transfer from the carbonyl triplet to give the olefin triplet (reactions 2–4) was the mechanism of isomerization.[2,3]

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(1) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

(2) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(3) D. R. Arnold, R. L. Hinman, and A. Glick, *Tetrahedron Letters*, 1425 (1964).

It is thought that a 1,4 biradical (I) is an intermediate in oxetane formation; it appears from the result of Arnold[2,4] that benzophenone gives the same initial *cis–trans* ratio of oxetanes with both *cis*- and *trans*-2-butene that either I or some other intermediate capable of losing stereochemical integrity must surely be involved. Recent work of Yang[5] and Saltiel[6] has suggested that I may also undergo cleavage to give back-isomerized olefin (eq 6 and 7); we picture fragmentation of I as giving ground-state olefin, in contrast to the triplet-state olefin proposed by Yang,[5] because we have recently shown[7] that another 1,4 biradical, generated photochemically as a triplet, fragments essentially exclusively to ground-state molecules.

$$R'_2C{=}O \xrightarrow{h\nu} \xrightarrow[\text{crossing}]{\text{intersystem}} R'_2C{=}O^{3n,\pi^*} \qquad (1)$$

$$R'_2C{=}O^{3n,\pi^*} + RCH{=}CHR \xrightarrow{k_2} R'_2C{=}O + RCH{=}CHR^3 \qquad (2)$$

$$RCH{=}CHR^3 \xrightarrow{k_3} cis\text{-}RCH{=}CHR \qquad (3)$$

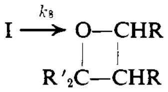
$$RCH{=}CHR^3 \xrightarrow{k_4} trans\text{-}RCH{=}CHR \qquad (4)$$

$$R'_2C{=}O^{3n,\pi^*} + RCH{=}CHR \xrightarrow{k_5} R'_2\dot{C}{-}O{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}\dot{C}HR \qquad (5)$$

I

$$I \xrightarrow{k_6} R'_2C{=}O + cis\text{-}RCH{=}CHR \qquad (6)$$

$$I \xrightarrow{k_7} R'_2C{=}O + trans\text{-}RCH{=}CHR \qquad (7)$$



$$I \xrightarrow{k_8} \begin{array}{l} O{-}CHR \\ |\quad\;\; | \\ R'_2C{-}CHR \end{array} \qquad (8)$$

We wish to present results at this time which demonstrate: (1) that some unconjugated olefins do, and some do not, undergo benzophenone-sensitized isomerization *via* energy transfer (reactions 2–4); (2) that secondary isotope effects[8] are useful mechanistic criteria even when quantum yield data are not reliable; and (3) that the Schenk[6,9] mechanism (eq 5–7) may not be complete enough to explain the true isomerization mechanism for 2-butene.

Photosensitized isomerization of the 1,2-dichloroethylenes in outgassed benzene solution proceeds efficiently, sensitized either by benzophenone at 3660 Å or propiophenone at 3130 Å. The quantum yields are: $Ph_2C{=}O$, $\phi_{t\rightarrow c} = 0.51 \pm 0.03$, $\phi_{c\rightarrow t} = 0.39 \pm 0.02$; $PhCOC_2H_5$, $\phi_{t\rightarrow c} = 0.44 \pm 0.02$, $\phi_{c\rightarrow t} = 0.46 \pm 0.02$; data have been extrapolated where necessary to 0% reaction and infinite olefin concentration. An energy transfer mechanism would require $\phi_{c\rightarrow t} = k_4/(k_3 + k_4)$ and $\phi_{t\rightarrow c} = k_3/(k_3 + k_4)$, independent of sensitizer. Reasoning similar to Saltiel's[6] would have led us to interpret the inapplicability of these relationships to our data as evidence for a possible Schenk mechanism. However, no oxetane was detected; material balance was always within a few per cent even at photostationary state. The expectation that reaction 8 should always accompany reactions 6 and 7 led us to study the isotope effect on the isomerization.

Preparation of 1,2-dichloroethylene-d_1 by the method of Leitch and Morse[10] afforded monodeuterated material of 98% isotopic purity. Isotope effects[11] on isomerization with benzophenone gave the following values: $k_2(cis\text{-}C_2H_2Cl_2)/k_2(cis\text{-}C_2HDCl_2) = 1.15 \pm 0.02$, $k_2(trans\text{-}C_2H_2Cl_2)/k_2(trans\text{-}C_2HDCl_2) = 1.18 \pm 0.02$; these values are in excellent agreement with the isotope effects previously observed[8,12] on triplet energy transfer to olefins. A Schenk mechanism is expected to show an inverse isotope effect, $k_H/k_D \sim 0.95$,[8,13] and thus appears to be ruled out. We have no explanation at present for the quantum-yield anomalies save to note that the propiophenone samples gave quantum yields that decreased with time, and these solutions became somewhat yellow when irradiated. One useful feature of secondary isotope effects as a mechanistic criterion is that they can be measured regardless of the presence of either photochemically generated or initially present quenchers or of competing reactions.

The interaction of 2-butene with benzophenone triplets appears to be of a fundamentally different nature. First, 2-butene gives an oxetane, in contrast to dichloroethylene.[3] Second, even though the triplet energy of 2-butene would be expected to be about 80 kcal/mol,[14a] *i.e.*, about 8 kcal higher than for *trans*-dichloroethylene,[14b] the rate constant for quenching of benzophenone triplets is six times larger for *cis*-2-butene than for *trans*-dichloroethylene; rate constants (relative to isoprene quenching as $5 \times 10^9\ M^{-1}\ sec^{-1}$) are respectively $8 \pm 1 \times 10^7\ M^{-1}\ sec^{-1}$ and $1.3 \pm 0.1 \times 10^7\ M^{-1}\ sec^{-1}$ in benzene. Third, there appears to be *essentially no isotope effect* on the rate of *cis–trans* isomerization of 2-butene.

Reduction of 2-butyne with D_2–Lindlar catalyst[15] gave, after preparative vpc, *cis*-2-butene-2,3-d_2; mass spectral analysis showed 93% d_2, 6% d_1, and traces of d_0, d_3, d_4. The nmr spectrum showed the methyl protons as a singlet, with no vinyl hydrogens detected. The isotope effect[11] on the conversion to *trans* was $k_{C_4H_8}/k_{C_4H_6D_2} = 1.02 \pm 0.01$.

The reaction of 2-bromo-2-butene with magnesium in THF, followed by D_2O quenching, afforded *trans*-2-butene-2-d_1 after preparative vpc. The nmr and mass spectral analyses indicated 92% deuteration in the vinyl position. The isotope effect on conversion to *cis* was $k_{C_4H_8}/k_{C_4H_7D} = 0.985 \pm 0.02$.

The *trans* to *cis* isotope effect may also be calculated for the dideuterated case as 0.993 ± 0.01 from the *cis* to *trans* value and the isotopic composition of mixtures at stationary state (73% *trans*); the difference from unity is not significant.

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(4) N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *J. Am. Chem. Soc.*, **89**, 3950 (1967).

(5) N. C. Yang, J. T. Cohen, and A. Shani, *ibid.*, **90**, 3264 (1968).

(6) J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969).

(7) R. A. Caldwell and P. M. Fink, *Tetrahedron Letters*, in press.

(8) R. A. Caldwell and G. W. Sovocool, *J. Am. Chem. Soc.*, **90**, 7138 (1968).

(9) G. O. Schenk and R. Steinmetz, *Bull. Soc. Chim. Belges*, **71**, 781 (1962).

(10) L. C. Leitch and A. T. Morse, *Can. J. Chem.*, **29**, 1034 (1951).

(11) Experimental procedures were analogous to those in ref 8.

(12) M. W. Scmidt and E. K. C. Lee, *J. Am. Chem. Soc.*, **90**, 5919 (1968).

(13) Mr. G. W. Sovocool has recently demonstrated an effect of this magnitude for thermal iodine-catalyzed isomerization of β-methylstyrene-β-d, which would appear to be a good model for a Schenk mechanism.

(14) (a) D. F. Evans, *J. Chem. Soc.*, 1735 (1960); (b) Z. R. Grabowski and A. Bylina, *Trans. Faraday Soc.*, **60**, 1131 (1964).

(15) H. Lindlar and R. Dubuis, *Org. Syn.*, **46**, 89 (1966).

These results clearly indicate that energy transfer is at most a very minor part of the isomerization mechanism; note that the dideuterated case (*cis* → *trans*) would be expected to have an isotope effect of the order of 1.30 or so. Furthermore, comparison of quenching rates and triplet energies with dichloroethylene suggests that the expected rate of triplet energy transfer from benzophenone to 2-butene would be far less than the quenching rate observed. We therefore also feel that the observed isotope effect is not reasonably interpretable on the basis of competing Schenk and energy-transfer mechanisms.

A simple Schenk mechanism appears not to fit the experiments particularly well either, since the isotope effect is not inverse. Furthermore, we would expect the rate of *t*-butoxy radical additions to an olefin to be a reasonable ballpark guess as to the rate of reaction 5,[16] and that rate is probably several orders of magnitude lower than our quenching rate.[16,17]

It is our present hypothesis that the anomalously high quenching rate for 2-butene and other oxetane-forming olefins,[5,18] our isotope effect, and the observations that 1,4-biradical stability is often distinctly mediocre as a predictive device for the direction of oxetane formation from unsymmetrical olefins[3,19] all may be better interpreted on the basis of some intermediate prior to I. Further work on isotope effects and rates of oxetane formation should suggest whether electron-transfer complexes or exciplexes do in fact intervene.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research through Grant 3031-A4.

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[16] C. Walling and V. Kurkov, *J. Am. Chem. Soc.*, **88**, 4727 (1966), and references therein.

[17] Note that the only reported addition of *t*-butoxy radical to an unconjugated olefin is to the strained olefin norbornylene [E. Tobler, D. E. Battin, and D. J. Foster, *J. Org. Chem.*, **29**, 2834 (1964)], that abstraction of (unactivated) H-5 and H-6 is competitive, and that abstraction rates appear to be of the order of 10^3–10^4 M^{-1} sec^{-1}; see ref 16, D. J. Carlsson, J. A. Howard, and K. U. Ingold, *J. Am. Chem. Soc.*, **88**, 4725 (1966), and W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 75, 167.

[18] P. J. Wagner, private communication.

[19] S. G. Schroeter and C. M. Orlando, Jr., *J. Org. Chem.*, **34**, 1181 (1969).

[20] National Science Foundation Undergraduate Research Participant, Summer 1968.

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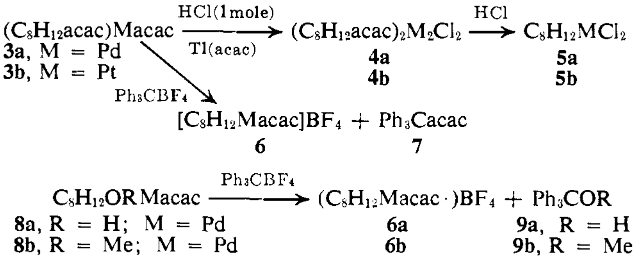
Cationic Transition Metal–Olefin Complexes

Sir:

Although many transition metal–olefin complexes are known, relatively few cationic derivatives have been reported.[1] This is possibly a reflection on the number of preparative methods at present available, and in general compounds of this type are prepared by the reaction of a suitable metal halide derivative in the presence of anhydrous aluminum trihalide and the appropriate olefin.[2] In connection with our studies of the reactivity of coordinated olefins,[3] we have examined the reaction of certain en-yl complexes of palladium(II) and platinum(II)[4] with electrophilic reagents such as triphenylmethyl tetrafluoroborate (**1**) and fluoroboric acid (**2**). These reactions led to the isolation of new cationic derivatives and suggested to us a convenient route to a variety of other cationic compounds of palladium(II), platinum(II), and rhodium(I).

Recently we reported the isolation and characterization of (acetylacetonato)(2-acetylacetonylcyclooct-5-en-yl)palladium(II) (**3a**), (Figure 1).[4] We have also shown previously that **3a** reacts with 1 mole of hydrochloric acid to produce di-μ-chloro-bis(2-acetylacetonylcyclooct-5-en-yl)palladium(II) (**4a**)[4] and with excess of that acid to generate (cycloocta-1,5-diene)dichloropalladium(II) (**5a**). We now wish to record that treatment of **3a** with triphenylmethyl tetrafluoroborate in methylene chloride, followed by the addition of ether, produces the yellow salt (acetylacetonato)(cycloocta-1,5-diene)palladium(II) tetrafluoroborate (**6a**) to which we assign the structure in Figure 2 on spectroscopic evidence (Table I) (see Scheme I). The other product from this reaction was identified as 3-triphenylmethylpentane-2,4-dione (**7**). This was initially assumed to arise by the attack of triphenylmethyl cation on the 2-acetylacetonylcyclooct-5-ene ligand, but the possibility that the initial attack by **1** occurred at the chelated acetylacetonato group followed by rearrangement cannot be ignored, and further attempts to determine the detailed mechanism operating in these reactions are currently in progress. Compound **6** was also obtained from the reaction of **1** with either (acetylacetonato)(2-methoxycyclooct-5-en-yl)palladium(II) (**8a**) or (acetylacetonato)(2-hydroxycyclooct-5-en-yl)palladium(II) (**8b**); in these reactions the organic products were methyl triphenylmethyl ether (**9a**) and triphenylmethanol (**9b**), respectively. The same cations have also been obtained by treatment of **3** or **8** with fluoroboric acid. By the above method a variety of cationic compounds of the general type [(β-diketonato)(diene)M^{II}]BF_4 (**10**) have been prepared.

Scheme I



In view of these results it appeared attractive to attempt the synthesis of other cationic derivatives by this method. The halogen-bridged dimers (**4**) react with cyclopentadienylthallium(I) to give unstable orange oils which rapidly decomposed on attempted purification. However, they are presumably the monomeric cyclopentadienyls (**11**) and on reaction with **1**, (cyclopentadienyl)(cycloocta-1,5-diene)palladium(II) (or -plat-

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[1] G. E. Coates, M. L. H. Green, and K. Wade in "The Transition Elements," Vol. 2, M. L. H. Green, Ed., Methuen and Co. Ltd., London, 1968.

[2] See, for example, E. O. Fischer and K. Ofele, Angew. Chem. Intern. Ed. Engl., **1**, 52 (1962).

[3] J. Lewis and A. W. Parkins, *J. Chem. Soc.*, *A*, 953 (1969), and references therein.

[4] B. F. G. Johnson, J. Lewis, and M. S. Subramanian, *ibid.*, 1993 (1968).