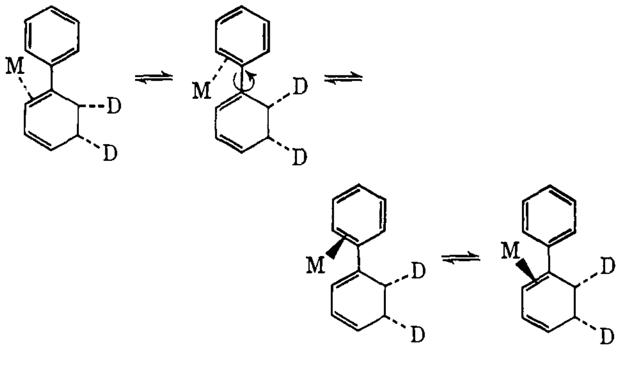
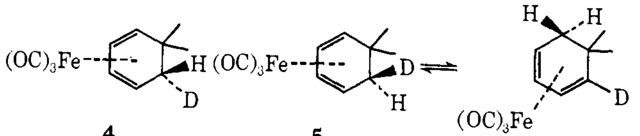
with phosphine by an unrelated path; in this case, the amount of isomerized product formed must be greater than 10%.[8]

Remaining is the question of deuterium scrambling in these complexes. We feel that this result does not require a pathway involving exo migration of hydrogen. Instead, the phenyl ring provides a way in which the iron atom can migrate from one side of the cyclohexadiene ring to the other. Victor, Ben-Shoshan, and Sarel[9,10] have shown that aromatic rings can coordinate Fe(CO)$_3$ to give diene complexes; our results indicate that an aromatic ring may coordinate the unsaturated Fe(CO)$_3$ fragment as well. In fact, the relative rate constants shown in Scheme II demonstrate that migration of the iron atom onto the aromatic ring is quite competitive with hydrogen abstraction.



That the presence of the aryl group is necessary for scrambling is consistent with the observation that no observable incorporation of deuterium into the vinyl region takes place in compound **4**,[11] while **5**[11] equilibrates readily with **6** at 145°. The rate of isomerization is at least 125 times faster than that of the rate of scrambling in these species.



4 **5** **6**

Whitlock and coworkers[12] have postulated intermediates analogous to **3** to account for hexatriene–iron tricarbonyl complex isomerization, which takes place under conditions similar to our hydrogen migration. The postulated metal hydride is the same kind of intermediate demonstrated[13] to account for double bond isomerization catalyzed by iron carbonyls again under similar conditions of thermal activation. An authenticated example of a concerted sigmatropic shift in the coordination sphere of a transition metal thus remains to be discovered.

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[8] If the (Ph$_3$P)$_2$Fe(CO)$_3$ is formed by an unrelated pathway (*i.e.*, ligand exchange), then the remainder of the complex should have undergone 35% isomerization. Thus, the amount of 2-phenyl isomer formed must be substantially greater than (0.35)(29) = 10%.

[9] R. Victor, R. Ben-Shoshan, and S. Sarel, *J. Org. Chem.*, 37, 1930 (1972).

[10] R. Victor, R. Ben-Shoshan, and S. Sarel, *Tetrahedron Lett.*, 4257 (1970).

[11] Compound **5** was prepared by sodium cyanoborodeuteride reduction of 6,6-dimethylcyclohexadienyliron tricarbonyl tetrafluoroborate, while **4** was prepared by corresponding reduction with sodium cyanoborohydride, followed by exchange with CF$_3$CO$_2$D.

[12] H. W. Whitlock and R. L. Markezich, *J. Amer. Chem. Soc.*, **93**, 5290, 5291 (1971); H. W. Whitlock, C. Reich, and W. P. Woessner, *ibid.*, **93**, 2483 (1971); H. W. Whitlock and Y. N. Chuah, *ibid.*, **87**, 3605 (1965).

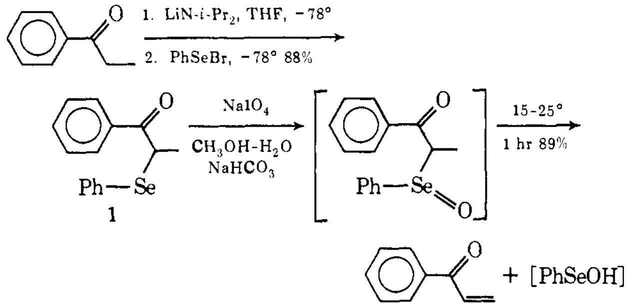
[13] C. P. Casey and C. R. Cyr, *ibid.*, **95**, 2248 (1973). We thank Professor Casey for a preprint of his manuscript.

Organoselenium Chemistry. α-Phenylseleno Carbonyl Compounds as Precursors for α,β-Unsaturated Ketones and Esters

Sir:

We report here a method for the conversion of ketones and esters to their α,β-unsaturated derivatives. The method is based on our observation that lithium enolates react rapidly and cleanly with benzeneselenenyl halides to give α-phenylseleno carbonyl compounds and on the report by Jones, Mundy, and Whitehouse[1] that aliphatic selenoxides readily undergo β-elimination to form olefins. Sharpless and Lauer[2] have recently applied this facile elimination in the synthesis of allyl alcohols from epoxides.

The method is illustrated for the conversion of propiophenone to acrylophenone,[3,3a] an olefin unusually sensitive to polymerization and nucleophilic attack. The selenide **1** can be isolated by crystallization in 88% yield (mp 36.5–37°, ir $\nu_{\mathrm{CCl_4}}$ 1675 cm^{-1}; nmr $\delta_{\mathrm{CCl_4}}$ 1.60 (d, J = 7.0 Hz, 3 H), 4.59 (q, J = 7.0 Hz, 1 H), 7.1–7.6 (m, 8 H), 7.88 (dd, J = 2, 8 Hz, 2 H)). Oxidation of **1** with sodium metaperiodate results in conversion to acrylophenone (89% yield).



1

The reaction of lithium enolates with benzeneselenenyl bromide or chloride[4] to give α-phenylseleno carbonyl compounds can be performed in high yield in a variety of esters and ketones. In all cases described here, this reaction was instantaneous at −78° and is

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[1] D. N. Jones, D. Mundy, and R. D. Whitehouse, *Chem. Commun.*, 86 (1970).

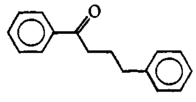
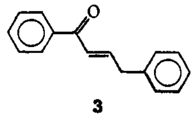
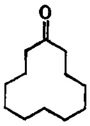
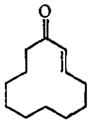
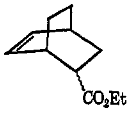
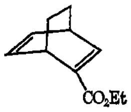
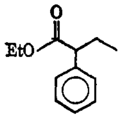
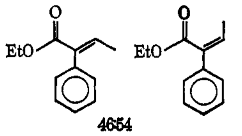
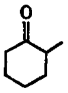
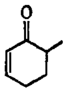
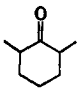
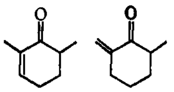
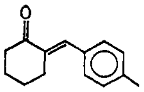
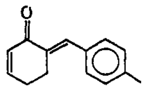
[2] K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, **95**, 2697 (1973).

[3] A related method involving β-elimination of α-methyl sulfinyl esters has been developed by B. M. Trost and T. Salzmann (private communication).

[3a] NOTE ADDED IN PROOF. Professor K. B. Sharpless has informed us of his independent work on the synthesis of α,β-unsaturated carbonyl compounds using organoselenium reagents.

[4] (a) Benzeneselenenyl bromide can be prepared by the addition of bromine to diphenyl diselenide in tetrahydrofuran or other nonhydroxylic solvents. This solution can be used directly. Benzeneselenenyl chloride works equally well but is not as conveniently prepared. (b) Enol acetates and enol silanes react with selenenyl derivatives to give α-arylseleno carbonyl compounds, and this provides an alternative synthesis. See also G. Hölzle and W. Jenny, *Helv. Chim. Acta*, **41**, 593 (1958).

Table I

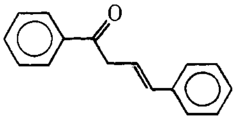
No.	Compound[a]	Product[a]	Oxidant	Yield[b]
	Propiophenone	Acrylophenone	$NaIO_4$	88, 89[c]
2		 3	H_2O_2[d]	84
5			H_2O_2[d]	72
6			H_2O_2[d]	79
7		 46:54	H_2O_2[d]	79
			H_2O_2[d]	36
		 67:33 80:20 89:11	H_2O_2-MeOH H_2O_2[d] H_2O_2-CCl_4	76 69
8			$NaIO_4$	68, 74[c,e]

[a] All compounds were adequately characterized by spectral methods. [b] Except for 2-methyl- and 2,6-dimethylcyclohexanones where yields were determined gas chromatographically, all yields quoted are for pure products isolated by crystallization, sublimation, or distillation. We normally find 2-8% of starting material in the crude product after one pot conversion. Actual yields are thus higher by this amount. [c] Intermediate selenide was purified by crystallization, followed by elimination. [d] Standard procedure described in text was used. [e] One equivalent of hexamethylphosphoramide was present to aid in proton transfer during formation of enolate ion from **8**.

probably more rapid than proton transfer since 2-methylcyclohexanone gave exclusively substitution at the six position and no disubstituted products were detected. Thus the methods developed for the preparation of specific enolate ions in unsymmetric ketones[4b,5] should be fully applicable here. Literature methods for the preparation of seleno substituted carbonyl compounds[6] lack generality and are often accompanied by undesirable side reactions.

The selenides need not be isolated, although this may be desirable for sensitive compounds or when traces of starting ketone in the product are objectionable and cannot be easily separated. The selenoxides normally undergo elimination during the oxidation (both steps proceed below room temperature for the compounds described here). The reaction mixture is usually mildly acidic since one of the products is benzeneseleninic acid, $pK_a = 4.79$.[7] A variety of oxidizing agents are effective. We have used hydrogen peroxide[2,8] for most compounds, although in especially sensitive cases (such as that described above) sodium metaperiodate[9a] gives higher yields of cleaner products. Low-temperature ozonolysis[9b] can be a useful alternative since it avoids the necessity for an aqueous work-up.

A second example illustrating the mildness of the conditions is the conversion of 1,4-diphenyl-1-butanone (**2**, Table I) to **3** in 84% yield after chromatography and sublimation. Less than 0.5% of the more stable phenyl-conjugated isomer **4** is formed, and no cis isomer



4

can be detected. Other systems where the reaction proceeds in excellent yields to give crude olefins essentially free of by-products are cyclododecanone (**5**) and the two esters **6** and **7**.

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(5) H. O. House, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **36**, 2361 (1971), and references therein.

(6) H. Rheinboldt in "Houben Weyl. Methoden der Organischen Chemie; Schwefel-, Selen-, Tellurverbindungen," Vol. IX, 1955, pp 976, 980, 986.

(7) J. D. McCullough and E. S. Gould, *J. Amer. Chem. Soc.*, **71**, 674 (1949).

(8) The hydrogen peroxide oxidation should be carried out under acidic conditions to avoid epoxidation of the enone formed.

(9) (a) M. Cinquini, S. Colonna, and R. Giovini, *Chem. Ind. (London)*, 1737 (1969); (b) G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 2089 (1962).

The standard procedure below results in high yields of the α-phenylseleno ketones from five-, six-, seven-, and eight-membered cyclic ketones, but the elimination reaction gives lower yields and less pure products than for the cases outlined above. Table I presents the results for the preparation of three cyclohexenones. The ratio of exo- and endocyclic olefins from 2,6-dimethylcyclohexanone depends on the elimination conditions, suggesting that stereochemical control may be possible in more complicated cases.

The experimental procedure is convenient. Of the selenium containing compounds involved, only benzeneselenenyl bromide is sufficiently volatile to have a detectable odor and, since it is prepared in solution and used directly, this does not present a problem. A solution of 3.0 mmol of lithium diisopropylamide (prepared from 0.42 ml of diisopropylamine and 1.47 ml of 2.05 *M* butyllithium in hexane) in 15 ml of THF was prepared under nitrogen at −78° and 0.56 g (2.5 mmol) of 1,4-diphenyl-1-butanone (**2**) in 3 ml of THF was added dropwise. The solution was stirred for 10 min and 3.0 mmol of benzeneselenenyl bromide (prepared by addition 0.081 ml of bromine to 0.47 g of diphenyl diselenide[10] in 3 ml of THF) was added rapidly dropwise. The solution was warmed to 0°, 1.5 ml of water, 0.3 ml of acetic acid, and 1.4 g of 30% hydrogen peroxide were added,[11] and the reaction temperature was maintained below 25° until the vigorous gas evolution had ended (30 min). The solution was poured into 50 ml of saturated sodium bicarbonate solution and 50 ml of 1:1 ether–pentane, and the organic layer was washed successively with water, 0.1 *N* hydrochloric acid, water, and saturated sodium chloride. The product was separated from 8% of starting ketone **2** by thin layer chromatography, and the enone was sublimed, giving 0.47 g of **3** (85% yield, 92% based on recovered starting material): mp 40–41°; ir ν_{CCl_4} 1672 cm^{-1}; nmr δ_{CCl_4} 3.58 (d, J = 5.9 Hz, 2 H), 6.8 (d, J = 15.7 Hz, 1 H), 7.0–7.5 (m, including a partially obscured dt, J = 15.7, 5.9 Hz, 9 H), 7.8–8.0 (m, 2 H).

Literature methods for the conversion of ketones to enones have involved bromination–dehydrobromination[12a] or direct oxidation of ketones using Collins reagent[12b] or other oxidizing agents.[12c] The method described here clearly has advantages in terms of yield, convenience, and mildness of reaction conditions.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. H. J. R. wishes to express his appreciation to the Du Pont Company for a Du Pont Young Faculty Grant.

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[10] Sharpless and Lauer[2] have discussed the use of diphenyl diselenide as a stoichiometric reagent.

[11] The oxidation is strongly exothermic, and for larger scale reactions slow addition of hydrogen peroxide at 10–15° is necessary.

[12] (a) T. A. Spencer, R. A. J. Smith, D. L. Storm, and R. M. Villarica, *J. Amer. Chem. Soc.*, **93** 4856 (1971); (b) W. G. Dauben, M. Lorber, and D. S. Fullerton, *J. Org. Chem.*, 34, 3587 (1969); (c) R. J. Theissen, *ibid.*, 36, 752 (1971).

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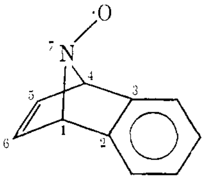
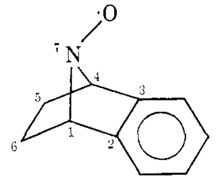
Electron Spin Resonance Spectra of Bicyclic Nitroxide Radicals. 7-Azabenzonorbornadiene-7-oxyl and 7-Azabenzonorbornene-7-oxyl

Sir:

It has been reported[1] that the mode of electron spin distribution depends quite sensitively on the conformation and geometry of a σ-bonded molecule. In order to gain further insight into stereospecificity of the electron spin transmission in the σ skeleton, we have studied here the esr spectra of new stable bicyclic nitroxide radicals, 7-azabenzonorbornadiene-7-oxyl (I)[2] and 7-azabenzonorbornene-7-oxyl (II)[2]. These spectra showed noteworthy features: (1) anomalously large nitrogen hyperfine splitting constants (hfsc's) as compared with other dialkyl nitroxides and (2) marked differences between the proton hfsc's of I and II. From these results stereospecific orientation of a nitroxide group is concluded.



I



II

I and II were prepared by hydrogen peroxide oxidation in an aqueous solution (in the presence of a small amount of ethanol) of parent amines[3] containing sodium tungstate and EDTA (ethylenediaminetetraacetic acid). Figure 1 presents the esr spectra of I (g value = 2.0061) and II (g = 2.0062) in dichloromethane solution at room temperature. The prominent feature of these spectra common to I and II is 1:1:1 triplet splitting (22.6 G for I and 23.1 G for II) which is, no doubt, due to hyperfine interaction with the nitrogen nucleus. These hfsc's are much larger than those for most of the dialkyl nitroxide radicals that have been reported so far.[4] These unusually large values of the nitrogen hfsc's could be attributed to the pyramidal structure around the nitrogen atom

In order to substantiate theoretically this feature, we carried out INDO–UHF MO calculations[5,6] for several conformations of dimethyl nitroxide (DMNO) as a model (Figure 2). ψ is the angle between the $C_\alpha NC'_\alpha$ plane and the N–O bond, and θ designates the angle between the two N–C_α bonds. Figure 2 shows that for the unstrained DMNO (θ = 120°) the

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[1] See, for instance, the following and the references cited therein: (a) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, **92**, 1267 (1970); (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *ibid.*, **93**, 3922 (1971); (c) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, **94**, 1425 (1972); (d) Z. Luz, *J. Chem. Phys.*, 48, 4186 (1968); (e) M. Barfield, *J. Phys. Chem.*, 74, 621 (1970).

[2] The derivatives of 7-azanorbornen-7-oxyl are expected to be stable, because nitron formation is prohibited in these nitroxide radicals by Bredt's rule; see A. R. Forrester, J. H. May, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, London and New York, Chapter 5.

[3] The parent amines were prepared by the method of L. A. Carpivo and D. E. Barr, *J. Org. Chem.*, 31. 764 (1966).

[4] For example, 16.2G for di-*tert*-butyl nitroxide (see ref 2) and 19.5 G for 1,5-dimethyl-8-azabicyclo[3.2.1]octan-3-one-8-oxyl; A. Rassat and J. Ronzaud, *J. Amer. Chem. Soc.*, **93**, 5041 (1971). In this paper, they reported pyramidal structure around the nitrogen atom in this bicyclic nitroxide.

[5] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

[6] In this calculation, the bond lengths (Å) are chosen as follows: N–O = 1.2, N–C = 1.47, C–C = 1.54, C–H = 1.09, and C=C = 1.33.