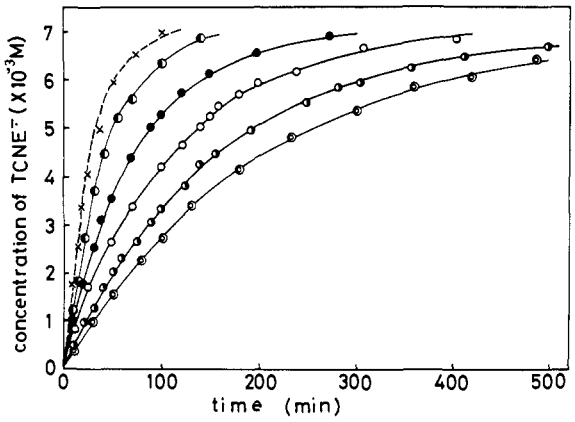

Figure 1. Concentration of TCNE radical anion formed in DMSO solution of TCNE (7×10^{-3} *M*) as a function of time after mixing TCNE into DMSO observed at (◎) 25°, (◑) 30°, (○) 35°, (●) 40°, and (◐) 45°C in the dark and (×) at 30°C under photoillumination.

sults do not agree with the previous ones in that the radical anion is so stable that its concentration remains unchanged after reaching the plateau value in the present investigation. The radical anion was found to be stable, even if the solution was exposed to air by breaking the sealed sample tube. The reason for this difference in the observed stability of the radical anion is not known at this moment, but we are wondering if some impurities in the reaction system might have reacted with the radical anion in the previous study.

The growth of the concentration of the radical anion agreed well with a first-order kinetics, which suggests that the radical anion results from a unimolecular dissociation of the EDA complex. Almost all TCNE is thought to be in complex with DMSO under the experimental conditions used.[5] The rate constant for the formation of radical anion was observed to be 1.1×10^{-4} sec^{-1} at 30°C and its temperature dependence agreed well with an Arrhenius relation, which gives an activation energy of 14 kcal/mol and a frequency factor of 2×10^{6} sec^{-1} in the temperature range examined (between 25 and 45°C). The temperature range was limited by the freezing point of DMSO (18.5°C) and its dissociation above 50°C.[5]

The slow formation of the radical anion observed in the present investigation is largely due to the small frequency factor for the formation process. As far as we know, this is the first success in determining the rate constant for the thermal ionic dissociation of an EDA complex. The observed slow ionic dissociation of the complex agrees with Mulliken's suggestion that in polar solvents dissociation of the complex into ions is governed by a slow, stabilizing solvation process.[8,9] Recently, Farrell and Ngô studied the spontaneous formation of TCNE radical anions in a TCNE-dimethylaniline system and found it to be apparently slow.[10] They interpreted this slow formation by the competition between the essentially fast formation process and the fast disappearance of the radical anion once formed. The present investigation indicates, however, that the ionic dissociation of the EDA complex occurs much more slowly than the complex formation does, at least in the TCNE-DMSO system.

References and Notes

(1) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).
(2) R. Vars, L. A. Tripp, and L. W. Pickett, *J. Phys. Chem.*, **66**, 1754 (1963).
(3) R. Ward, *J. Chem. Phys.*, **39**, 852 (1963).
(4) D. F. Ilten and M. Calvin, *J. Chem. Phys.*, **42**, 3760 (1965).
(5) F. E. Stewart, M. Eisner, and W. R. Carper, *J. Chem. Phys.*, **44**, 2866 (1966).
(6) F. E. Stewart and M. Eisner, *Mol. Phys.*, **12**, 173 (1967).
(7) W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.*, **32**, 626 (1960).
(8) R. S. Mulliken and W. B. Person, "Molecular Complexes: A Lecture and Reprint Volume", Wiley, New York, N.Y., 1969.
(9) N. H. Kolodny and K. W. Bowers, *J. Am. Chem. Soc.*, **94**, 1113 (1972).
(10) P. G. Farrell and P. N. Ngô, *J. Chem. Soc., Perkin Trans. 2*, 552 (1974).

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Allylic Amination of Olefins and Acetylenes by Imido Selenium Compounds

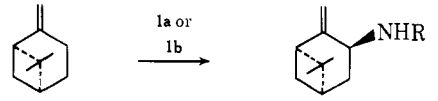
Sir:

In our recent report[1] on the vicinal oxyamination of olefins by imido osmium compounds we suggested that it might be the first example of a new class of reactions involving nitrogen and carbon analogues of known oxygen insertion processes. By finding that aza analogues (**1**) of selenium dioxide (**2**)[2] effect allylic amination of olefins, we have now extended this concept to a main group oxidant.

1a, R = *t*-Bu
1b, R = Ts

2

Imido selenium compounds such as **1** have not been described previously. Reaction of selenium tetrachloride with 2 equiv of *tert*-butylamine or of *p*-toluenesulfonamide[3] in methylene chloride in the presence of 4 equiv of an amine base produces solutions thought to contain **1a** and **1b**, respectively. Both **1a** and **1b** reacted with β-pinene (**3**) to afford the desired allylic amination products **4a** and **4b**. With



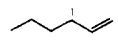
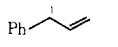
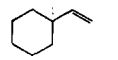
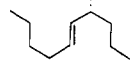
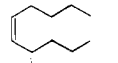
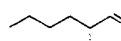
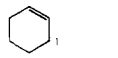
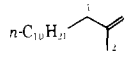
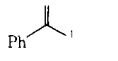
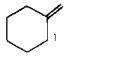
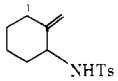
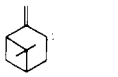
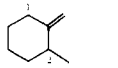
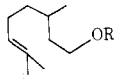
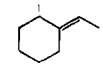
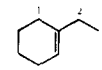
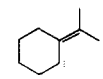
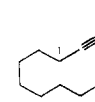
3

4a, R = *t*-Bu, 62%
4b, R = Ts, 82%

less reactive olefins than β-pinene the alkyl imido reagent **1a** gave much poorer yields than the sulfonimido reagent **1b**. It was then found by one of us (T.H.) that an even more reactive aminating species was formed when 2 equiv of anhydrous Chloramine-T (TsNClNa) were stirred with selenium metal in methylene chloride (this reagent will be designated **1b′**). Due to its ease of preparation and superior reactivity this Chloramine-T derived reagent was used for most of the aminations described here.

Examination of the examples in Table I reveals that this new nitrogen insertion reaction has much in common with the allylic insertion of oxygen into olefins by selenium dioxide. These aminations very likely occur via the same sequence of ene and [2,3]-sigmatropic reactions which we have established as the mechanism of the analogous oxoprocess.[4] Detailed comparison of these new allylic oxidants with selenium dioxide must be postponed, but several important points can be made now. Most olefins react readily with the imido reagent **1b′** at or below room temperature; thus it is much more reactive than SeO_2[5] and gives better yields with less reactive olefins, e.g., cases 1–7 Table I, but an even more striking feature of these allylic aminations is the almost complete absence of allylic rearrangement[6] products in situations where SeO_2 gives principally the abnormal, rearranged products (cases 1 and 2) or diene (case 25). The usual side reactions of SeO_2 oxidations appear to be suppressed by the milder conditions. The positional se-

Table I. Allylic Amination[a]

	Olefin or acetylene	1b'/substrate[c]	% yield[b] Site[d] 1	% yield[b] Site[d] 2
1		1.25, *0.83*	54	
2		1.25, *0.63*	40 (89)	
3		*0.63*	45 (106–107)	
4		1.25, *0.83*	53[e] (50–52)	
5		1.25, *0.83*	57[e] (50–52)	
6[g]		1.25, *0.83*	51	11
7		0.63, *0.83*	45 (101–102)	
8		*0.63*	45	15
9		1.25, *0.83*	57 (82–84)	
10		*0.63*	74[f] (120–121)	
11		0.63	58 (201–202)	
12		*0.63*	82[f] (192–193)	
13		0.63	30[h]	14
14a	 R = CH_3	0.63	58	
14b	R = H	*1.25*	65	
15		0.63	68 (98–99)	
16		0.63	84[f] (72–73)	
17		0.63	8 (105–106)	38 (86–87)
18		*0.63*	35 (77–78)	20 (68–69)
19		0.63	39[f]	43
20		0.63	8[i]	57
21		1.1	4[j]	64
22		0.63	43[k]	13
23a	cholesteryl acetate	2.5[l]	44[m] (238–239)	
23b	cholesterol	3.75	46[m] (198–199)	
24		1.25, *0.83*	60	
25		1.25, *0.83*	50	10
26		*0.63*	32	19
27		*1.25*	23 (65–66)	
28		0.63	51 (60–61)	
29		0.63	43	24

[a] With the appropriate differences in stoichiometry, all reactions were carried out as described in detail for cyclohexene. In most cases the allylic sulfonamides were crystalline (melting points given in parentheses) and in all cases they were characterized by spectral and combustion analyses. [b] All yields were determined by isolation, usually involving chromatography and/or recrystallization. [c] In those cases where the optimum of the three (0.63, 0.83, and 1.25) most commonly explored molar ratios was determined, it is italicized. In several instances the optimum ratio was determined by GLC, in which case it appears after the ratio actually used to obtain the isolated yields reported. When there is only one entry and it is not italicized, no effort was made to determine the optimum ratio. [d] Site of amination as indicated on original olefin. When only one amination product is indicated it generally means the other possible regioisomers were not detected. However, lacking authentic samples for many of the possible isomers, some of the minor (<5%) products were not identified. [e] As expected, the product from the *E* and *Z* olefins is identical and appears to be the *E*-isomer. [f] In these cases 0.4 equiv of dry NEt_3 was added to the reaction mixture a few minutes after addition of the olefin, with the result that the yield was increased by as much as 30%. However, in other cases (e.g., cyclohexene) NEt_3 decreases the yield. [g] In this and other cases where two products were formed, the ratio of the products varied with the amount of reagent 1b employed. [h] A 4:1 mixture of epimers. [i] Reagent 1b' was modified by addition of 8 equiv of triethylamine hydrochloride. [j] Reagent 1b' was used (i.e., $SeCl_4$, $2TsNH_2$, $4Et_3N$). [k] This reagent was formed by stirring Se^0 with TsNClAg in CH_2Cl_2. [l] The reaction mixture was refluxed for 48 hr. [m] The product is the 4β-toluenesulfonamido derivative.

lectivity for these aminations is in general reminiscent of that detailed by Guillemonat[5,7] for allylic oxygenation by selenium dioxide. However, there are some interesting differences, especially with cyclic olefins (e.g., cases 17, 18, and 25). Moreover, in the case of 1-methylcyclohexene the selectivity changes dramatically as the means of preparing the imidoreagent is changed (cases 18–22).

It was found that these oxidations can be quite sensitive to the mole ratio of reagent **1b'** to olefin (see Table I). Although this variable has not yet been explored for all the substrates studied, it appears that in most cases less than 1 mole equiv of the reagent is optimum. This indicates that more than one of the sulfonamido moieties of reagent **1b'** is available and suggests that disproportionation of selenium II intermediates is occurring. As revealed in Table I, principally three molar ratios (0.63, 0.83, and 1.25) were investigated, and the majority of olefins faired better with the lower (0.63 and 0.83) ratios. Since multiple amination is often the cause of poor yields, it seems best to begin with the 0.63 ratio and add more reagent if starting olefin remains after the usual reaction period.

In a typical experiment a dry 50-ml flask was charged with 0.52 g (6.6 mmol) of powdered selenium, 2.50 g (11 mmol) of anhydrous Chloramine-T,[8] and 22 ml of dry (passed through alumina) methylene chloride. The gray mixture was stirred (magnetically) under nitrogen for about 24 hr and a white-gray slurry[9] was produced. This slurry was cooled to 0° in an ice bath and 0.722 g (8.8 mmol) of cyclohexene (mole ratio of **1b'** to olefin = 0.63) was added. The ice bath was allowed to melt and warm to room tem-

perature (~1 hr) and stirring was continued for about 24 hr.[9] The yellow-green suspension was then diluted with 120 ml of ether and 30 ml of 1 *N* sodium hydroxide solution.[10] After stirring for 15 min the red mixture was filtered through a fine Celite pad and the organic layer of the filtrate was washed with 50 ml of 1 *N* NaOH,[10] 50 ml of 0.1 *N* hydrochloric acid, water, and brine, and was dried ($MgSO_4$) and concentrated to give a yellow oil. The crude product was chromatographed on 100 g of activity III (6% H_2O) basic alumina; elution with 5–10% EtOAc–hexane afforded 1.14 g of a white solid. Recrystallization from CCl_4–hexane gave 1.00 g (45%) of the allylic sulfonamide, mp 100–101; one more recrystallization produced crystals of mp 101–102°.

This new reaction provides the first instance of direct allylic amination of olefins[11] and also the most reliable[12] procedure for insertion of an atom into an allylic carbon–hydrogen bond in which the olefinic linkage retains its position. We are exploring new variations in the substituent on nitrogen in the hope of further increasing the reactivity of these selenium imido reagents (**1**); this important variable is of course not present in the case of the corresponding oxo reagents. We are also pursuing the obvious extension of these unique bond forming processes with the goal of inserting carbon into allylic carbon–hydrogen bonds.[15]

Acknowledgment. We are grateful to the National Institutes of Health (GM21686) for support of this research.

References and Notes

(1) K. B. Sharpless, D. W. Patrick, L. K. Truesdale, and S. A. Biller, *J. Am. Chem. Soc.*, **97**, 2305 (1975).

(2) For convenience both the new imidoselenium compounds (**1**) and selenium dioxide (**2**) are shown as monomers. Selenium dioxide is known to be a polymer and the new substances (**1**) are almost certainly oligomerized as well. However, the reactive entity in both cases may well be the monomer.

(3) Four other substituted benzene sulfonamides (4-Cl, 4-H, 4-OCH_3, and 2,4,6-trimethyl) were tried successfully in these reactions (see also ref 6).

(4) (a) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **94**, 7154 (1972); (b) D. Arigoni, A. Vasella, K. B. Sharpless, and H. P. Jensen, *ibid.*, **95** 7917 (1973); (c) H. P. Jensen and K. B. Sharpless, *J. Org. Chem.*, **40**, 264 (1975).

(5) For two recent reviews of selenium dioxide oxidation see (a) R. A. Jerussi in "Selective Organic Transformations", B. S. Thyagarajan, Ed., Wiley, New York, N.Y., 1970, pp 301–326; (b) E. N. Trachtenberg in "Oxidation", Vol. 1, R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1969, pp 119–187.

(6) In the early experiments with reagents derived from $SeCl_4$ (e.g., **1a** and **1b**) allylic rearrangement, giving rise to crossover products, sometimes was a problem, especially with olefins such as 1-methylcyclohexene and methylenecyclohexane. However, with the Chloramine-T derived reagent **1b′** crossover products were minimal (usually <5%) and therefore are not even indicated in Table I. Interestingly, methylenecyclohexane gave about 10–25% rearranged product with reagent **1b** and all of the other analogous reagents derived from the substituted sulfonamides described in ref 3 with the exception of mesitylene sulfonamide which gave exclusively the unrearranged amination product. It will be interesting to try this mesitylene sulfonamide derived reagent on olefins (e.g., case 6, 8, 17, and 25) where reagent **1b′** gives mixtures.

(7) A. Guillemonat, *Ann. Chim. (Rome)*, **11**, 143 (1939).

(8) The commercially available trihydrate was dried to constant weight at 80° under vacuum. *Caution.* On one occasion while drying about 500 g in a vacuum oven at a setting of 90° (?) the entire sample deflagrated with enough force to blow open the oven door but not violently enough to be called an explosion. For this reason we recommend a drying pistol or a rotary evaporator (under high vacuum) where the temperature can be controlled accurately. Chloramine-T is reported to be stable well above 100° (F. D. Chattaway, *J. Chem. Soc.*, **87**, 153 (1905)).

(9) Only about one-sixth of the reagent is in solution. The long reaction time (24 hr) is probably unnecessary for all but the least reactive olefins. The more reactive olefins are consumed quickly and the solvent will reflux unless cooling is employed.

(10) Most of the *p*-toluenesulfonamide by-product is extracted into the aqueous base.

(11) Allylic sulfonamides have been reductively cleaved with sodium naphthalene (S. Ji, L. B. Gortler, A. Waring, A. Battisti, S. Bank, and W. D. Closson, *J. Am. Chem. Soc.*, **89**, 5311 (1967)). Applying this procedure to sulfonamide **4b** we obtained the corresponding amino pinene in 98% yield. Thus a variety of unique amines can be made in two steps from olefins.

(12) Even at this early stage it is clear that these allylic aminations are more reliable than the related processes with SeO_2.

(13) Camille and Henry Dreyfus Teacher-Scholar Grant recipient; Alfred P. Sloan Fellow, 1973–1975.

(14) NATO Postdoctoral Fellow, 1973–1974.

(15) Note Added in Proof. We have now found that the related sulfur species (e.g., TsN=S=NTs) also effect allylic amination of olefins (K. B. Sharpless and T. Hori, *J. Org. Chem.*, in press).

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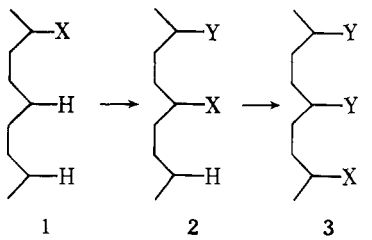
A Reiterative Functionalization of Unactivated Carbon–Hydrogen Bonds. Photolysis of α-Peracetoxynitriles

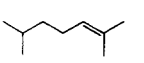
Sir:

Synthetically useful methodology for the introduction of functionality at unactivated carbon–hydrogen bonds should combine a high degree of efficiency and regioselectivity. Various approaches to this problem have relied on intramolecular free radical reactions to transfer a daughter functional group to a site distant from the parent functional group.[1] Additional advantage, however, would accrue to methodology in which the parent functional group (X) migrated in course of the photoreaction (**1** → **2**) and the daughter functional group (Y) remained at the original site.



1 2 3

Table I. The Yields of α-Peracetoxynitriles RR′C(OOAc)CN **4** from Secondary Nitriles RR′CHCN

	R	R′	% isolated yield of **4**
a	CH_3	$CH_2CH_2CH(CH_3)_2$	64
b	CH_3		63
c	CH_3		67
d	CH_3	CH_2Ph	89
e	CH_3		60
f	CH_2Ph	CH_2Ph	90
g	$-(CH_2)_5-$		72
h	Ph	CH_2CH_3	49
i	Ph	$CH_2CH_2CH_3$	57
j	Ph	$CH(CH_3)_2$	81
k	Ph	$CH_2CH_2CH_2CH_3$	72
l	Ph	$CH_2CH_2CH(CH_3)_2$	63
m	Ph	$CH_2CH_2C(CH_3)_3$	73
n	Ph	$CH_2CH_2CH_2Ph$	77
o	Ph	$CH_2CH_2CH(CH_3)Ph$	72
p	Ph	c-C_6H_{11}	74
q	*p*-FPh	CH_3	65
r	*p*-ClPh	CH_3	56
s	Ph	Ph	85