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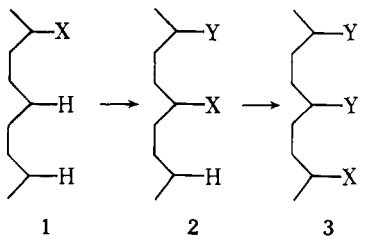
A Reiterative Functionalization of Unactivated Carbon-Hydrogen Bonds. Photolysis of α-Peracetoxynitriles

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

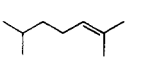
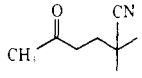
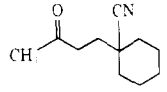
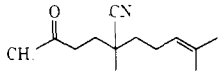
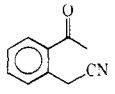
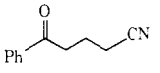
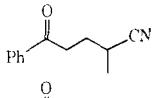
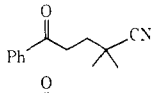
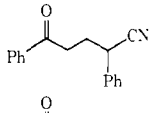
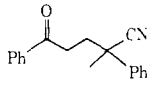
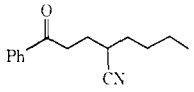
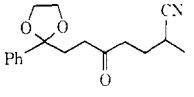
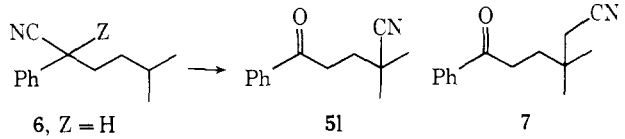
	R	R′	% isolated yield of **4**
a	CH_3	$CH_2CH_2CH(CH_3)_2$	64
b	CH_3		63
c	CH_3		67
d	CH_3	CH_2Ph	89
e	CH_3		60
f	CH_2Ph	CH_2Ph	90
g	$-(CH_2)_5-$		72
h	Ph	CH_2CH_3	49
i	Ph	$CH_2CH_2CH_3$	57
j	Ph	$CH(CH_3)_2$	81
k	Ph	$CH_2CH_2CH_2CH_3$	72
l	Ph	$CH_2CH_2CH(CH_3)_2$	63
m	Ph	$CH_2CH_2C(CH_3)_3$	73
n	Ph	$CH_2CH_2CH_2Ph$	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

Table II. The Photolysis of α-Peracetoxynitriles **4** in 0.25 *M* Benzene for 1 hr

α-Peracetoxy-nitrile	δ-Ketonitrile 5	% isolated yield
4a		50
4b		47
4c		28
4e		18
4i		15
4k		22
4l		52
4n		10
4o		9
10		20
13		26

Subsequent repetition of this reaction (**2** → **3**) would lead to polyfunctional molecules in a regioselective fashion. We now wish to report that the photolysis of α-peracetoxynitriles incorporates this latter advantage.

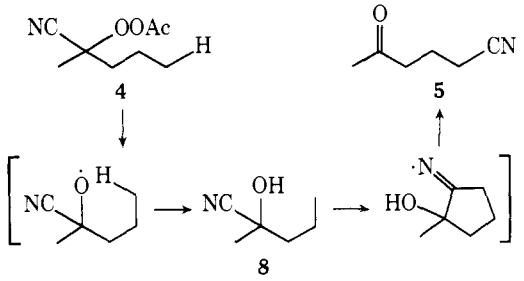
Trapping anions of secondary nitriles with molecular oxygen and quenching the intermediate α-cyanohydroperoxide anion with acetyl chloride provided α-peracetoxynitriles **4** in good yield[2] (Table I). The photolysis of **4** in benzene or *tert*-butyl alcohol using a high-pressure 450-W Hanovia lamp furnished δ-ketonitriles **5** regioselectively (Table II).[3] For example, the photolysis of the α-peracetoxynitrile **4l** prepared from 5-methyl-2-phenylhexanenitrile (**6**) provided the δ-ketonitrile **5l** in 52% yield. Under the same conditions, the photolysis of the benzoyl, phenacetyl, and pivaloyl peresters derived from **6** afforded **5l** in 57, 56, and 31% yield, respectively.[4] α-Peracetoxynitriles **4** lacking δ-hydrogens failed to produce ketonitriles of any type with the exception of **4m** which afforded the ε-ketonitrile **7** in 10% yield. α-Peracetoxynitriles **4** possessing δ-hydrogens which are not oriented properly for an intramolecular hydrogen transfer (e.g., **4p**) also failed to give δ-ketonitriles **5.**



6, Z = H
4l, Z = OOAc

5l 7

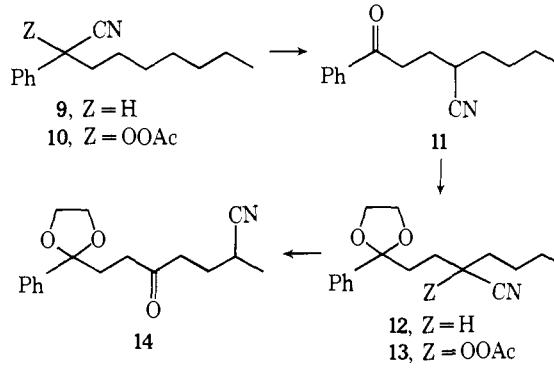
A mechanism[5] consistent with the observed products involves (1) the homolysis of the oxygen-oxygen bond in the α-peracetoxynitrile **4,** (2) δ-hydrogen atom abstraction, and (3) intramolecular cyano group transfer to the radical site in **8** to provide ultimately the δ-ketonitrile **5.** In general, the yields of δ-ketonitriles **5** paralleled the stability of the presumed free radical intermediate **8.** For example, α-peracetoxynitriles **4i, 4k,** and **4l** afforded δ-ketonitriles **5i, 5k,** and **5l** in 15, 22, and 52% yields, respectively. However, α-peracetoxynitriles **4n** and **4o** possessing benzylic δ-hydrogens underwent a competitive photodecarboxylation to give α-methoxynitriles. In defense of the low yields encountered in certain cases, it should be noted that (1) δ-ketonitriles **5** are not photostable but undergo Norrish type II photocleavage[6] and (2) the cyanohydrin-ketonitrile reaction of Kalvoda[7] fails for acyclic cases where the α-peracetoxynitrile-ketonitrile reaction has succeeded.



4 5

8

To illustrate the reiterative feature of this process the monofunctional nitrile **9** was transformed to the trifunctional nitrile **14** in five steps. The photolysis of the α-peracetoxynitrile **10** derived from **9** in 75% yield furnished the δ-ketonitrile **11** in 20% yield. An independent synthesis of **11** involving the alkylation[8] of hexanenitrile with β-bromopropiophenone ethylene ketal and the subsequent hydrolysis of the ketal moiety confirmed this structural assignment. The introduction of an α-peracetoxy group in the ketal nitrile **12** in 65% yield and the photolysis of the ketal α-peracetoxynitrile **13** provided the ketal δ-ketonitrile **14** in 26% yield. The appearance of a doublet at δ 1.31 in the NMR spectrum of **14** for the terminal methyl group confirmed that the conversion of **9** to **14** had involved two successive δ-migrations of a cyano group.[9]



9, Z = H
10, Z = OOAc

11

14

12, Z = H
13, Z = OOAc

Application of this methodology to the functionalization of a steroid nucleus is presently under investigation.

Acknowledgment. We wish to thank the Research Corporation and the Colorado Heart Association for their generous financial support and the University of Colorado for a Biomedical Sciences Support Grant used to purchase the photolysis equipment.

References and Notes

(1) (a) W. Carruthers, "Some Modern Methods of Organic Synthesis", Cambridge University Press, London, 1971, pp 172–206; (b) K. Heusler and J. Kalvoda, *Angew. Chem., Int. Ed. Engl.*, **3**, 525 (1964); (c) J. Kalvoda and K. Heusler, *Synthesis*, 501 (1971).
(2) S. J. Sellkson and D. S. Watt, *J. Org. Chem.*, **40**, 267 (1975).
(3) The yields in Table II were not optimized. For example, the yield of **5l** var-

ied as a function of irradiation time (in benzene): 15 min, 19%; 30 min, 39%; 1 hr, 52%; 3 hr, 58%; and 6 hr, 50% and solvent (for 1 hr): benzene, 52%, *tert*-butyl alcohol, 56%; cyclohexane, 21%; and toluene, 33%.
(4) The benzoyl, pivaloyl, and phenacetyl peresters were prepared from **6** in 63, 21, and 24% yields, respectively.
(5) J. Kalvoda, *Helv. Chim. Acta*, **51**, 267 (1968).
(6) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p 382.
(7) (a) Ch. Meystre, K. Heusler, J. Kalvoda, P. Wieland, G. Anner, and A. Wettstein, *Experientia*, **17**, 475 (1961); (b) J. Kalvoda, Ch. Meystre, and G. Anner, *Helv. Chim. Acta*, **49**, 424 (1965); (c) A. Kasal and V. Cerney, *Collect. Czech. Chem. Commun.*, **31**, 2759 (1966); (d) K. van Moorselaar and S. J. Halkes, *Recl. Trav. Chim. Pays-Bas*, **88**, 737 (1969).
(8) D. S. Watt, *Tetrahedron Lett.*, 707 (1974), and references therein.
(9) All new compounds reported in this study had ir, NMR, mass spectra, and elemental analyses in accord with assigned structures.

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Received July 14, 1975

Alkyl Substituent Effects in Electrophilic Substitution at Saturated Carbon. Inapplicability of Taft σ^* Values

Sir:

Electrophilic displacement at saturated carbon is an important process, characteristic for organometallic intermediates. Despite extensive studies, however, there is only limited knowledge concerning the mechanism of cleavage of the alkyl–metal bond, particularly with regard to structural variations.[1-3]

We wish to report the use of alkyl substituents as sensitive probes for examining electronic effects in electrophilic cleavages. Mercury compounds are ideal models for organometals since they are substitution-inert and less subject to steric effects than other metals (due to the relatively large radius and two-coordination of mercury). Acetolysis of the dialkylmercury compounds in Table I proceeds according to eq 1 and 2,

$$\text{R-Hg-R}' + \text{HOAc} \xrightarrow{k} \text{R}'\text{HgOAc} + \text{RH} \quad (1)$$

$$\text{R-Hg-R}' + \text{HOAc} \xrightarrow{k'} \text{RHgOAc} + \text{R}'\text{H} \quad (2)$$

where R, R′ = Me, Et, *i*-Pr, *t*-Bu, and follows first-order kinetics to high conversions. The pseudo-first-order rate constants, k and k', are determined individually by following the rate of alkane liberation by gas chromatography and alkylmercuric acetate by its proton NMR spectrum. A large deuterium kinetic isotope effect in the range of 9–11 (in HOAc and DOAc), depending on the organomercurial, suggests that a substantial positive charge is developed on mercury in the transition state.[4]

Examination of the complete series of dialkylmercurials allows the effects of alkyl groups to be separated into two classes, namely, the cleaved alkyl group R and the departing alkyl group R′ in eq 1. The importance of steric effects is shown in Table I by the reactivity of various alkyl groups under the conditions of a *common leaving group*.[5] More importantly, when a *particular alkyl group R is cleaved*, the dependence of log k on the nature of the departing group R′Hg is in good agreement with eq 3.

$$(\log k/k_{\text{Me}}) \quad \text{Me:Et:}i\text{-Pr}:t\text{-Bu} = 0:0.76:1.31:1.44 = 0:\mathbf{0.10}:\mathbf{0.17}:\mathbf{0.19} \quad (3)$$

where boldface numbers represent values after normalization of Et = 0.10 to conform to Taft σ^* in eq 4. The relationship is independent of the cleaved group R as shown by

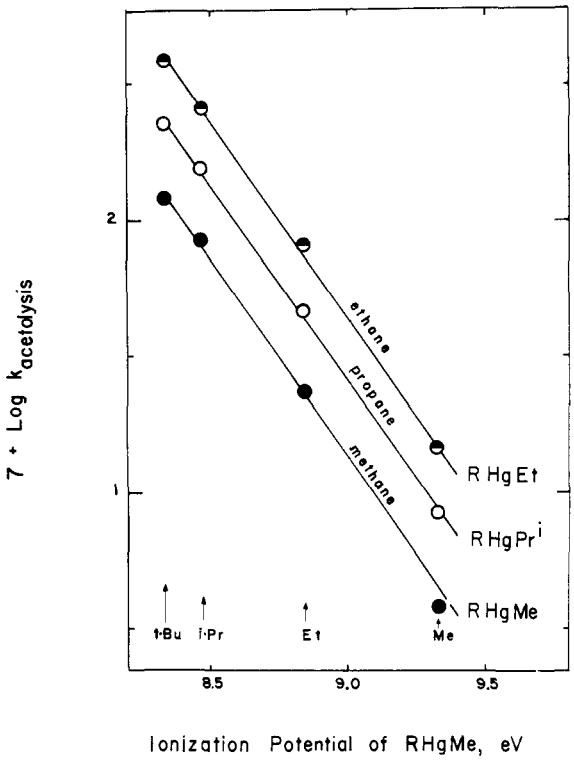

Figure 1. Correlation of the rates of acetolysis of MeHgR (●), EtHgR (◓), and *i*-PrHgR (○) with the vertical ionization potentials of RHgMe measured by He(I) photoelectron spectroscopy.

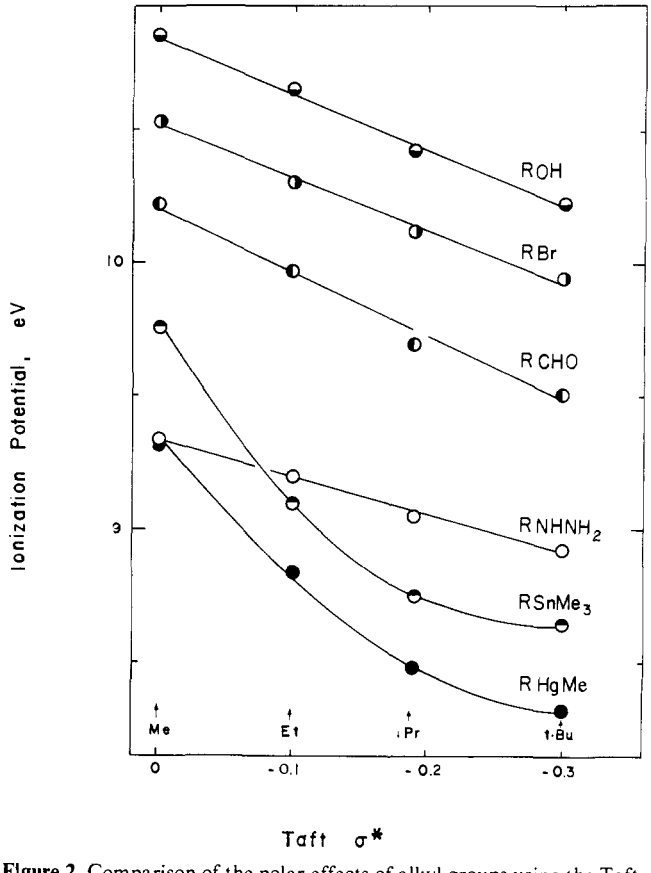

Figure 2. Comparison of the polar effects of alkyl groups using the Taft σ^* values and those obtained from ionization potentials. *Additivity* effects in alkylhydrazines (○), alkyl bromides (◑), aldehydes (◐), and alcohols ( ) are from ref 8. *Saturation* effects in alkylmethylmercury (●) and alkyltrimethyltin (◓) from ref 9. (Note that linearity in the additivity effect would be further improved in every case by the use of $\sigma^* = -0.20$ for *i*-Pr.)