70702-68-0; **8h**, 70702-69-1; **8i**, 70702-70-4; **8j**, 70702-71-5; **8k**, 70702-72-6; **9d**, 70702-73-7; **9e**, 70702-74-8; **9f**, 70702-75-9; **9g**, 70702-76-0; **9h**, 70702-77-1; **9i**, 70702-78-2; **9j**, 70702-79-3; **9k**, 70702-80-6; **10**, 288-32-4; **11**, 616-47-7; **12a**, 70702-81-7; **12b**, 70702-82-8; **12b** *p*-nitrobenzoate, 41507-39-5; **12c**, 70702-83-9; **12d**, 45786-14-9; **13**, 70702-84-0; **14**, 70702-85-1; **15**, 70702-86-2; **16a**, 1072-82-8; **16b**, 932-62-7; **16c**, 62128-46-5; **17**, 70702-87-3; **18**, 5202-71-1; 2-acetyl-1-methylpyrrole, 932-16-1; 2-(α-hydroxyethyl)-1-methylpyrrole, 56423-58-6; 2-(β-hydroxypropyl)-1,5-dimethylpyrrole, 70702-88-4; 2-(β-hydroxypentyl)-1,5-dimethylpyrrole, 70702-89-5; 2-(2-hydroxy-2-methylpropyl)-1,5-dimethylpyrrole, 70702-90-8.

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Base Decomposition of Azides Leading to Nitriles

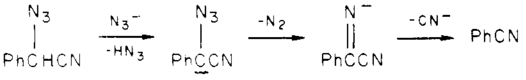
Summary: α-Azido sulfides, sulfoxides, sulfones, and nitriles bearing an α-hydrogen atom react with base to give nitriles.

Sir: We wish to point out a generally unrecognized property of the azide group: its ability to function under basic conditions as an intramolecular oxidizing agent.

There are scattered reports in the literature[1] of the reactions of α-azido ketones with base to give α-diketones (or α-imino ketones) and one report of the reaction of an allylic azide with strong base to give (upon aqueous workup) an α,β-unsaturated aldehyde.[2] It was suggested that these reactions involved the intermediacy of α-azido carbanions which lose molecular nitrogen to give imines that are readily hydrolyzed to ketones or aldehydes. We now present results which are consistent with the above proposed pathway and further extend these reactions by noting that when the electron-withdrawing group attached to the α-carbon atom of a primary or secondary azide is a leaving group, nitriles are produced. This is most dramatically illustrated by the conversion of phenylacetonitrile to benzonitrile in 90% yield in a simple two-step procedure.

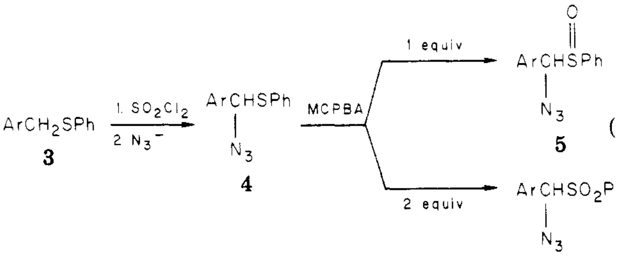
$$\mathrm{PhCH_2CN} \xrightarrow[\text{2. excess } N_3^-/\mathrm{Me_2SO}]{\text{1. NBS/CCl}_4} \mathrm{PhCN} + \mathrm{N_2} + \mathrm{CN^-} \quad (1)$$

The crude α-bromophenylacetonitrile is added to a solution of excess sodium azide in Me_2SO at room temperature, whereupon copious amounts of gas (presumably N_2) are evolved. The α-azido nitrile (**1**) presumably is formed, but under the reaction conditions, azide ion is sufficiently basic to deprotonate **1** giving carbanion **2** which then ejects nitrogen and cyanide ion (eq 2).



$$\underset{\mathbf{1}}{\mathrm{PhCH(N_3)CN}} \xrightarrow[-\mathrm{HN_3}]{\mathrm{N_3^-}} \underset{\mathbf{2}}{\mathrm{Ph\overset{-}{C}(N_3)CN}} \xrightarrow{-\mathrm{N_2}} \mathrm{PhC(=N^-)CN} \xrightarrow{-\mathrm{CN^-}} \mathrm{PhCN} \quad (2)$$

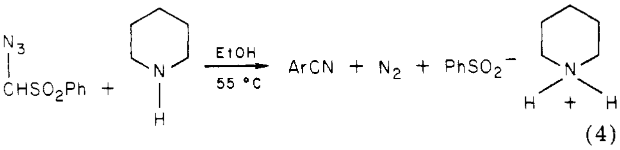
We have prepared a series of α-azido sulfur compounds[3] (eq 3) and have studied in detail the reactions of α-azido sulfones with base which give nitriles. The syntheses of the α-azido sulfides were accomplished in good yields except in the case where the aryl group was *p*-nitrobenzyl. Although α-chlorination proceeded smoothly,[4] treatment of the resulting α-chloro-*p*-nitrobenzyl phenyl sulfide with sodium azide gave *p*-nitrobenzonitrile, a reaction analogous to that observed with α-bromophenylacetonitrile (eq 2).



(3)

a, Ar = C_6H_5
b, Ar = *m*-ClC_6H_4
c, Ar = *p*-ClC_6H_4
d, Ar = *p*-CNC_6H_4
e, Ar = *p*-$CH_3C_6H_4$

Azides **4**, **5**, and **6** all react with base to give the corresponding benzonitriles, although as expected stronger bases are required as one goes from sulfone to sulfoxide to sulfide.[5] Because of the ease of reaction of azido sulfones with base, the scope of this reaction was investigated. The α-azidobenzyl phenyl sulfones **6** react readily with piperidine in ethanol at 55 °C to give benzonitriles in 70–90% yield. Benzenesulfinate was methylated (CH_3I) and isolated as methyl phenyl sulfone (eq 4).



(4)

a, Ar = C_6H_5
b, Ar = *m*-ClC_6H_4
c, Ar = *p*-ClC_6H_4
d, Ar = *p*-CNC_6H_4
e, Ar = *p*-$CH_3C_6H_4$

Treatment of α-azido-β-phenethyl phenyl sulfone (**7**) with sodium methoxide at 60 °C gave phenylacetonitrile in 85% yield. Similarly, the adamantylazido sulfone **8** gave 1-adamantanecarbonitrile in 90% yield when treated with potassium *tert*-butoxide in THF. Weaker base systems proved less effective with these azides presumably due to their lower acidity. On the other hand, typical α-azidoalkyl phenyl sulfones, e.g. **9** and **10**, reacted with these stronger base systems liberating nitrogen, but gave no isolable nitriles. Control experiments showed that the expected nitriles did not survive the strongly basic reaction conditions.

In conclusion, we note that when an azido group is attached to a carbon bearing both a hydrogen atom and an electron-withdrawing group, the carbon atom is readily oxidized ($-N_3$ being reduced to molecular nitrogen) under basic conditions. If the electron-withdrawing group is also a potential leaving group (e.g. $-CN$ or $-SO_2Ph$), then

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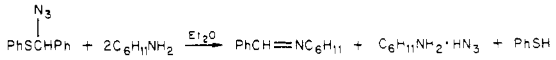
(1) (a) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **87**, 826 (1903); **91**, 867 (1907); (b) J. H. Boyer and F. C. Canter; *Chem. Rev.*, **54**, 1 (1954); (c) O. E. Roberts and K. K. Purushothaman, *Can. J. Chem.*, **42**, 712 (1964).

(2) A. Hassner and J. S. Teeter, *J. Org. Chem.*, **35**, 3397 (1970).

(3) The details of the syntheses and thermal reactions will be presented in a full paper. Analytical data and physical properties of compounds **6a–e**, **7**, **8**, **9**, and **10** are presented in the supplementary table.

(4) Chlorination of *p*-methoxybenzyl phenyl sulfide resulted in the formation of benzenesulfenyl chloride and benzyl chloride (carbon–sulfur bond cleavage). Based on previous work, this result was not unexpected: see B. B. Jarvis and M. M. Evans, *J. Org. Chem.*, **39**, 643 (1974), and references cited therein.

(5) Although the α-azidobenzyl sulfones reacted with relatively weak bases, α-azidobenzyl sulfides required significantly stronger base systems (e.g. potassium *tert*-butoxide) in order to lose molecular nitrogen. Use of milder bases (e.g. cyclohexylamine) typically gave substitution reactions:



$$\mathrm{PhS\overset{N_3}{\overset{|}{C}}HPh} + 2\mathrm{C_6H_{11}NH_2} \xrightarrow{\mathrm{Et_2O}} \mathrm{PhCH{=}NC_6H_{11}} + \mathrm{C_6H_{11}NH_2\cdot HN_3} + \mathrm{PhSH}$$

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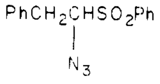
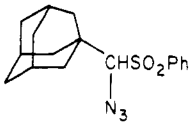
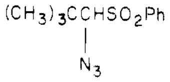
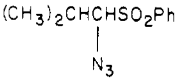

$PhCH_2\underset{N_3}{\underset{|}{C}}HSO_2Ph$

7


8


$(CH_3)_3C\underset{N_3}{\underset{|}{C}}HSO_2Ph$

9


$(CH_3)_2CH\underset{N_3}{\underset{|}{C}}HSO_2Ph$

10

nitriles are produced. These reactions are somewhat limited in that many alkyl nitriles may not be stable under strongly basic conditions.[6]

Registry No. 3a, 831-91-4; **3b**, 51229-52-8; **3c**, 7693-30-3; **3d**, 51229-54-0; **3e**, 5023-65-4; **4a**, 70891-83-7; **4b**, 70891-84-8; **4c**, 70891-85-9; **4d**, 70891-86-0; **4e**, 70891-87-1; **5a**, 70891-88-2; **5b**, 70891-89-3; **5c**, 70891-90-6; **5d**, 70891-91-7; **5e**, 70891-92-8; **6a**, 70891-93-9; **6b**, 70891-94-0; **6c**, 70891-95-1; **6d**, 70891-96-2; **6e**, 70891-97-3; **7**, 70891-98-4; **8**, 70891-99-5; **9**, 70912-36-6; **10**, 70892-00-1; benzonitrile, 100-47-0; *m*-chlorobenzonitrile, 766-84-7; *p*-chlorobenzonitrile, 623-03-0; *p*-cyanobenzonitrile, 623-26-7; *p*-methylbenzonitrile, 104-85-8; 1-adamantanecarbonitrile, 23074-42-2.

Supplementary Material Available: Analytical and spectral data on compounds **6–10** (1 page). Ordering information is given on any current masthead page.

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[6] The scope of this reaction may be limited by other problems. For example, α-iodo nitriles bearing two carbon atoms at the α center give α,β-unsaturated nitriles rather than α-azido nitriles when treated with azide ion under a variety of conditions: A. D. Barone, D. L. Snitman, and D. S. Watt, *J. Org. Chem.*, 43, 2066 (1978).

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Oxidative Rearrangements of Tertiary Cyclopropylcarbinols Leading to β,γ-Unsaturated Ketones. A Simple Approach to 1,4-Carbonyl Transposition

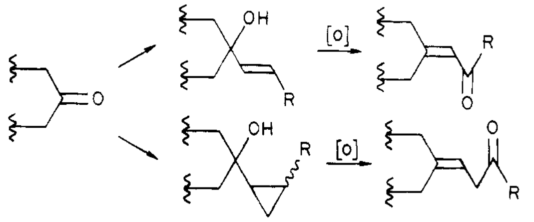
Summary: Oxidation of tertiary 2-alkylcyclopropylcarbinols with pyridinium chlorochromate results in oxidative homoallylic rearrangement to the corresponding β,γ-unsaturated ketones, making the overall process a synthetically useful method for 1,4-carbonyl transposition.

Sir: Recent communications[1] have described the direct oxidation of tertiary allylic alcohols with pyridinium chlorochromate (PCC)[2] yielding the corresponding α,β-unsaturated aldehydes or ketones,[3] which provides an efficient method for directed aldol condensation[4] and 1,3-carbonyl transposition[5] as depicted in eq 1. Despite the well-known similarity in rearrangement behavior of cyclopropylcarbinyl systems to that of allylic ones, direct oxidation of tertiary cyclopropylcarbinols has received only scant attention.[6-8] In our continuing investigation of synthetic applications of cyclopropane rearrangements,[9] we have now found that the modified use of PCC can effect direct oxidation of tertiary 2-alkylcyclopropylcarbinols to the corresponding β,γ-unsaturated ketones as depicted in eq 2.

Table I

method	reagent/reaction time^a	% yield^b	
		4a	5a
A	PCC (5 equiv)/6 h	48	15
B	PCC (5 equiv) + $AgNO_3$ (10 equiv)/6 h	53	*c*
C	$C_5H_5NHCrO_3BF_4$^{d} (5 equiv)/20 h	50	*c*
D	PCC (5 equiv) + H_2O (8 equiv)/6 h	60	5

^{a} Time required for completion. ^{b} Isolated yields via column chromatography. ^{c} Not detected by VPC or NMR. ^{d} For preparation, ref 15.

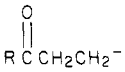


(1)

(2)

The interesting oxidative rearrangement appears to be an excellent method for converting ketones to the trishomologous β,γ-enones,[10,11] since the tertiary alcohols serving as substrates can be prepared by reactions of ketones with cyclopropyl organometallic reagents. The net effect of the process is an efficient method for effecting 1,4-carbonyl transposition and allows cyclopropyl anion **1** to serve as an equivalent of ketone homoenolate anion **2**.[12,13]

1


$R\overset{O}{\overset{\|}{C}}CH_2CH_2^-$

2

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[1] (a) J. H. Babler and M. J. Coghlan, *Synth. Commun.*, 6, 469 (1976); (b) W. G. Dauben and D. M. Michno, *J. Org. Chem.*, 42, 682 (1977); (c) P. Sundraraman and W. Herz, *ibid.*, 42, 813 (1977).

[2] Available from the Aldrich Co. For use of this reagent for oxidation of alcohols to aldehydes or ketones, see E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2674 (1975).

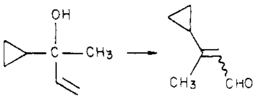
[3] For multistep transformations of allylic alcohols including secondary ones to the rearranged α,β-unsaturated carbonyl compounds, see B. M. Trost and J. L. Stanton, *J. Am. Chem. Soc.*, 97, 4018 (1975); T. Nakai, T. Mimura, and A. Ari-izumi, *Tetrahedron Lett.*, 2425 (1977), and references cited therein.

[4] Reviews: H. Reiff, *Newer Methods Prep. Org. Chem.*, 6, 48 (1971); A. T. Nielsen and W. J. Houlshan, *Org. React.*, 16, 1 (1968).

[5] For a general review on carbonyl transpositions, see T. Nakai and T. Mimura, *Yuki Gosei Kagaku Kyokaishi* (*J. Synth. Org. Chem., Jpn.*), 35, 964 (1977).

[6] Dauben and Michno (ref 1b) have briefly reported that attempted oxidation of cyclopropyldimethylcarbinol with PCC resulted in the formation of 5-chloro-2-methylpent-2-ene as the major product. In our hands, the yield of the chloro olefin was 40%.

[7] Most recently the PCC oxidation of carbinol i was found to result in oxidative allylic rearrangement to α,β-enal ii. We thank Mr. M. Nozomi in our laboratory for carrying out this experiment.



i ii

[8] For oxidation of secondary cyclopropylcarbinols with $Me_2SO–BF_3$ leading to the rearranged α,β-enals, see S. Nishida and F. Kataoka, *Chem. Lett.*, 1297 (1976).

[9] E. Wada, T. Nakai, and M. Okawara, *Chem. Lett.*, 1121 (1977), and our earlier papers cited therein.

[10] For a recent method for converting ketones to the trishomologous β,γ-enals, see E. J. Corey and P. Ulrich, *Tetrahedron Lett.*, 3685 (1975). This method is based on the solvolytic rearrangement of tertiary 2-methoxycyclopropylcarbinyl mesylates.

[11] For different routes to β,γ-enones, see C. Broquet and M. Simalty, *Tetrahedron Lett.*, 933 (1972); A. Pelter, C. R. Harrison, and D. Kirkpatrick, *ibid.*, 4491 (1973); K. Uehara, F. Kitamura, and M. Tanaka, *Chem. Lett.*, 279 (1973); R. Calas, J. Dunogues, J.-P. Pillot, C. Biran, F. Disciotti, and B. Arreguy, *J. Organomet. Chem.*, 85, 149 (1975), and references cited therein.

[12] For leading references of various homoenolate anion equivalents and related species, see E. Nakamura and I. Kuwajima, *J. Am. Chem. Soc.*, 99, 7360 (1977).