mol) vs. **1c** ($\Delta G^{\ne}$ = 31 kcal/mol[2]), since a tertiary radical site is generated at the α carbon in the activated complex C.[8]

The β-peroxy lactones **1c** and **1d** were also employed to determine the secondary isotope effect during the 1,2-shift of the β-methyl migrant, i.e., in the destruction of the 1,5-diradical **2** into products. For this purpose, by means of quantitative GLC the migratory aptitudes of methyl (k_{Me}) vs. phenyl (k_{Ph}) as a function of methyl deuteration were measured by determining the amount of β-methyl vs. β-phenyl migration product. From β-peroxy lactones **1c** and **1d** the migratory ratios $k_{\mathrm{CH_3}}/k_{\mathrm{Ph}}$ and $k_{\mathrm{CD_3}}/k_{\mathrm{Ph}}$, respectively, were obtained from which $k_{\mathrm{H}}/k_{\mathrm{D}}$ was calculated. A negligible secondary isotope effect was found. This implies, as expected, that the slow step of the decomposition of β-peroxy lactones is the peroxide bond cleavage into diradical **2**. Subsequently, this diradical **2** decarboxylates with β-alkyl migration via a fast step with a low activation barrier. In such cases the secondary isotope effect is expected to be very small.[9] The error in our product data is too large to pick up such small effects.

The product distribution derived from **1a** was found to be insensitive to solvent polarity. Thus, pinacolone was formed essentially quantitatively (>99% yield) and only small amounts (<0.5%) of acetone and tetramethyloxirane (stable to the thermolysis conditions) could be detected in the various solvents. Consequently, also the destruction of the diradical **2** into pinacolone exhibits negligible dipolar character.

In conclusion, our present solvent and isotope effect data substantiate the previously proposed diradical mechanism (eq 1).[2,3] The intervention of the 1,5-diradical is established; however, we have no information on its lifetime. Experiments to trap **2** have failed so far, which implies that the 1,5-diradical must be shorter lived than 10^{-7} s. A carbonyl-^{18}O labeling experiment is in progress to estimate the lower lifetime limit of this 1,5-diradical.

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References and Notes

(1) Paper No. 62 in the Cyclic Peroxide series.

(2) W. Adam and Y. M. Cheng, *J. Am. Chem. Soc.*, **91**, 2109 (1969).
(3) (a) W. Adam, Y. M. Cheng, C. W. Wilkerson, and W. A. Zaidi, *J. Am. Chem. Soc.*, **91**, 2111 (1969); (b) W. Adam and C. Wilkerson, *Chem. Commun.*, 1569 (1971); (c) W. Adam and J. Baeza, *J. Chem. Soc., Chem. Commun.*, 103 (1972).
(4) W. Adam and J. Arce, *J. Am. Chem. Soc.*, **97**, 926 (1975).
(5) R. Huisgen, *Acc. Chem. Res.*, **10**, 117, 199 (1977).
(6) T. W. Koenig and W. D. Brewer, *Tetrahedron Lett.*, 2772 (1965).
(7) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).
(8) C. I. Rojas, M. S. Thesis, University of Puerto Rico (1972). A detailed discussion of the α effect on the migratory aptitudes and activation parameters is reserved for a full paper.
(9) V. P. Vitullo and E. A. Logue, *J. Am. Chem. Soc.*, **98**, 5906 (1976).

(10) NIH Career Development Awardee (1975–1980).
(11) M. S. Thesis, University of Puerto Rico (1975).
(12) Graduate Participant in the Support for University Biomedical Education (SUBE) program, sponsored by NIH.

Waldemar Adam,*[10] Omar Cueto, Luis N. Guedes[11]
Luis O. Rodriguez[12]

Department of Chemistry, University of Puerto Rico
Río Piedras, Puerto Rico 00931

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Superoxide in Organic Synthesis: A New Mild Method for the Oxidation of Amines to Carbonyls via *N*-Chloramines

Summary: Conversion of amines to their chloramines followed by reaction with potassium superoxide is a mild method of oxidizing amines to carbonyl compounds.

Sir: *N*-Chloramines have been used as effective intermediates for converting amines to their carbonyl derivatives in a number of synthetic schemes.[1,2] We wish to report here a new, mild method employing potassium superoxide and the results of our study on seven representative amines, including several unsymmetrical secondary amines.

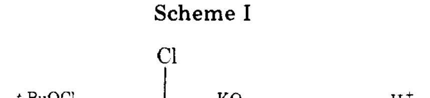
We have converted a series of amines to their corresponding *N*-chloramines in ether solution utilizing the method of Bachmann[2] and without prior isolation reacted the chloramines with potassium superoxide (see Scheme I). In a typical experiment *N*-methylbutylamine (**1g**) (20 mmol) in ether (50 mL) was converted to its chloramine. Additional ether (50 mL) was then added and the solution washed with water (1 × 50 mL), 1.5 M sulfuric acid (1 × 50 mL), and again with water (2 × 50 mL). It was then dried for at least 1 h over a mixture of magnesium sulfate, potassium carbonate, and molecular sieves.[3] After filtration the ether solution was slurried at room temperature with potassium superoxide (2.2 equiv) in the presence of 18-crown-6 polyether (80 mg). When the yellow superoxide color had completely faded (4–6 h), the mixture was filtered and the filtrate was poured into 2,4-dinitrophenylhydrazine reagent.[4] The ether was evaporated on a rotary evaporator and the crude 2,4-dinitrophenylhydrazone (2,4-DNP) of *n*-butyraldehyde was isolated (82% yield). Analysis of the product by TLC (silica, ether/petroleum ether, 20:80) showed only a minor trace of a material with an R_f similar to that of formaldehyde 2,4-DNP.[5] After recrystallization the melting point and mixed melting point confirmed the product to be *n*-butyraldehyde 2,4-DNP. See Table I for other examples.

The aldimines derived from diisobutylamine, di-*n*-pentylamine, and di-2-methylbutylamine have been isolated and their structures confirmed by IR (C=N stretch, 1670 cm^{-1}) and NMR (δ 7.6, 1 H, aldiminic). In the case of diisobutylamine pure *N*-chloramine was isolated and found to react in anhydrous ether to give imine[6] in 88% yield by analytical VPC, showing the reaction of KO$_2$ with *N*-chloramines is a clean, high-yield reaction.

An interesting result of our studies is our observation that elimination from unsymmetrical chloramines shows a preference for the more highly alkylated double bond, especially in the case of secondary methylamines. Thus *N*-chloro-*N*-methylbutylamine gives an overwhelming predominance of butylidenemethylamine on reaction with KO$_2$. Although imines have been shown to form from *N*-choramines, very little work has been done with chloramines of secondary amines and we are unaware of any studies on product yields from unsymmetrical amines. We believe the high regioselectivity we have observed, the mild conditions required, and the easy workup may have valuable synthetic applications in the removal of NCH$_3$ units from secondary methylamines.

Although the yield of carbonyl product from *n*-hexylamine was only moderate, no attempt was made to maximize the yield. Reaction of *N*-chlorohexylamine with KO$_2$ was more vigorous than with the secondary *N*-chloramines. Lowering the temperature of the reaction might enhance the yield.

Scheme I



$$\mathrm{R_2CHNHR'} \xrightarrow{t\text{-BuOCl}} \mathrm{R_2CH\overset{Cl}{N}R'} \xrightarrow{\mathrm{KO_2}} \mathrm{R_2C{=}NR} \xrightarrow{\mathrm{H^+}} \mathrm{R_2C{=}O}$$

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Table I. KO_2 Reaction with *N*-Chloramines

	Amine (1)	Product (3)	% yield
a	Diisobutylamine	$(CH_3)_2CHCH=NCH_2CH(CH_3)_2$	88[a]
b	Di-*n*-pentylamine	$CH_3(CH_2)_3CH=N(CH_2)_4CH_3$	73[b]
c	Di-2-methylbutylamine	$EtCHCH_3CH=NCH_2CHCH_3Et$	71[b]
d	Dibenzylamine	$PhCH=NCH_2Ph$	77[b]
e	*N*-Ethylcyclohexylamine	$C_6H_{10}=NCH_2CH_3$	40[b]
f		$C_6H_{11}N=CHCH_3$	23[b]
g	*N*-Methylbutylamine	$CH_3(CH_2)_2CH=NCH_3$	76[b]
h		$CH_3(CH_2)_3N=CH_2$	Trace[b]
i	*n*-Hexylamine	$CH_3(CH_2)_4CH=NH$	49[b]

[a] VPC yield of aldimine; see ref 6. [b] Isolated as 2,4-dinitrophenylhydrazone; see ref 7.

In an attempt to elucidate the mechanism we considered the possibility of a base-catalyzed reaction similar to Bachmann's.[2] However, KO_2 is no more basic than potassium acetate[8] and potassium acetate gave no imine when reacted under conditions used with KO_2. Using Na_2O_2 under these conditions, peroxide ion, a suspected product[9] of the reaction of KO_2 with *N*-chloramines, also gave no imine. When KOH was reacted with *N*-chloro-*N*-methylbutylamine, less than a 26% yield of imine was formed in the same time KO_2 gave an 82% yield. The KOH reaction was also considerably dirtier, giving several as yet unidentified products. We are therefore examining the reaction in detail for other possible intermediates.

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References and Notes

(1) G. Ehrhart, H. Ruschig, and W. Aumüller, *Angew. Chem.*, **52,** 363 (1939); H. Ruschig, W. Fritsch, J. Schmidt-Thomé, and W. Haede, *Chem. Ber.*, **88,** 883 (1955); J. Schmidt-Thomé, *ibid.*, **88,** 895 (1955); L. Labler and F. Sorm, *Collect. Czech. Chem. Commun.*, **24,** 2975 (1959); E. J. Corey, N. H. Anderson, R. M. Carlson, J. Paust, E. Vedejs, I. Vlattas, and R. E. K. Winter, *J. Am. Chem. Soc.*, **90,** 3245 (1968); E. J. Corey, I. Vlattas, N. H. Anderson, and K. Harding, *ibid.*, **90,** 3247 (1968).

(2) W. E. Bachmann, M. P. Cava, and A. S. Drieding, *J. Am. Chem. Soc.*, **76,** 5554 (1954).

(3) Thorough drying of the ether solution is required because KO_2 decomposes in the presence of water.

(4) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y.. 1967, p 330.

(5) We estimate that the crude product is >95% pure.

(6) Satisfactory elemental analysis (within 0.3%) was obtained on this compound. The yield of **3a** is based on amount of *N*-chloramine used.

(7) The structures of compounds **3b–i** were confirmed by comparison of the melting points and mixed melting points of their 2,4-dinitrophenylhydrazones with those of authentic compounds. Yields are based on amount of starting amine used.

(8) The pK_a's of the conjugate acids of superoxide and acetate are the same (4.8): see D. Behar, G. Czapski, J. Rabani, L. M. Dorfman, and H. A. Schwarz, *J. Phys. Chem.*, **74,** 3209 (1970).

(9) The white solid material at the end of the reaction appears to be a 50:50 mixture of KCl and KOOH. Acidification gave within 10% the theoretical amount of oxygen to be expected from decomposition of KOOH.

Frank E. Scully, Jr.,* Richard C. Davis

Department of Chemical Sciences
Old Dominion University
Norfolk, Virginia 23508

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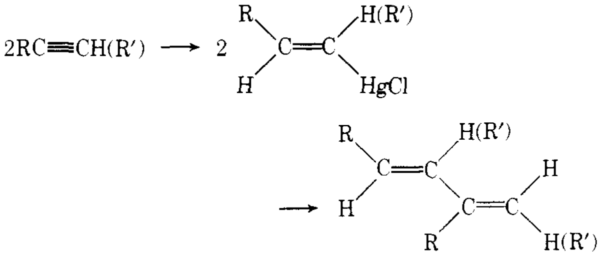
Mercury in Organic Chemistry. 15.[1] A Novel Stereospecific Synthesis of 1,3-Dienes via "Head-to-Tail" Dimerization of Alkynes

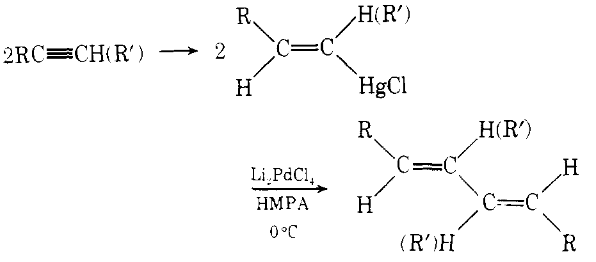
Summary: Terminal and internal alkynes can be dimerized in a "head-to-tail" fashion to provide excellent yields of unsymmetrical 1,3-dienes by preparing the corresponding vinylmercurial and treating it with palladium chloride and triethylamine in benzene at room temperature.

Sir: 1,3-Dienes have proven very valuable as intermediates in organic synthesis. Recently a number of interesting new organometallic methods have been reported for the stereospecific dimerization of terminal alkynes to 1,4-disubstituted 1,3-dienes.[2-9] For example, utilizing intermediate vinylboranes one can now prepare in a highly stereospecific manner cis,cis,[4] cis,trans,[5-7] or trans,trans[8,9] 1,4-disubstituted 1,3-dienes at will. We wish to report a novel new method employing vinylmercurials which produces unsymmetrical 1,3-dienes via "head-to-tail" dimerization of terminal and internal alkynes (eq 1).

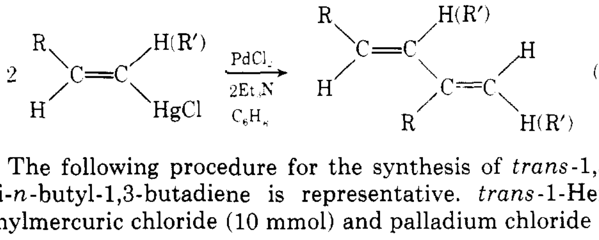


(1)

A while ago we reported a procedure for the symmetrical dimerization of vinylmercurials derived from both internal and terminal alkynes (eq 2).[10] Although the original procedure required stoichiometric amounts of lithium chloride and palladium chloride in hexamethylphosphoramide (HMPA) at 0 °C in order to obtain high yields, we have more recently found that all of the disadvantages of that procedure can be overcome by using only catalytic amounts of $[ClRh(CO)_2]_2$ to effect the dimerization.[11] Upon closer examination of the palladium reactions we have observed that "head-to-tail" dimerization can occur in these same reactions simply by varying the reaction conditions. In fact, by omitting lithium chloride and employing less polar solvents, we are able to obtain the unsymmetrical 1,3-dienes in excellent yield. Best results are obtained by using 0.5 equiv of $PdCl_2$ and employing benzene as the solvent. It was also observed that HCl is generated during the course of these reactions and the addition of triethylamine improves the yields dramatically (eq 3).



(2)



(3)

The following procedure for the synthesis of *trans*-1,3-di-*n*-butyl-1,3-butadiene is representative. *trans*-1-Hexenylmercuric chloride (10 mmol) and palladium chloride (5