New Syntheses of Alkenes and Alkynes from Amines[1]

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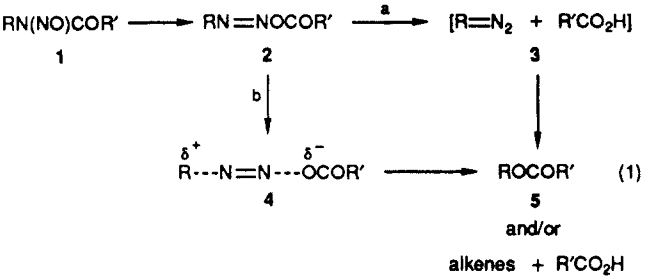
N-Nitrosocarboxamides **1** undergo a highly-solvent-dependent thermal rearrangement at 80–100 °C via diazenes **2** to products derived either from diazoalkanes **3** (path a) or carbocationic intermediates **4** (path b, eq 1).[2-4] Nitrosamides of primary *n*-alkylamines follow path a almost exclusively in nonpolar solvents where the initially formed diazoalkane and carboxylic acid rapidly recombine to ester **5** in high yield.[5,6]



Amine groups are notoriously difficult to remove or replace with other functionality. Diazo compounds, on the other hand, enjoy a fascinating variety of chemistry[7] by which the latent primary amine group in **1** might be eliminated or replaced. We therefore became intrigued with the possibility of intercepting and exploiting the diazoalkane intermediate **3** for such synthetically useful purposes.[1] Here we report efforts in this area that have culminated in new and apparently general constructions of alkenes, enol acetates, and monosubstituted alkynes from aliphatic amines and vicinal amino alcohols.

While transition metals promote numerous reactions of α-diazocarbonyl compounds,[7] little is known about how such catalysts affect unstabilized diazo compounds.[8] Ordinarily all but the simplest diazoalkanes are difficult or tedious to prepare in pure form. Azine byproducts and carbene dimers poison most useful transition-metal catalysts and complicate synthetic applications.[9] However, by thermally decomposing *N*-nitrosoacetamides in the presence of rhodium(II) catalysts, it proved possible to intercept **3** before ester formation and generate transient, rhodium-stabilized carbenoids **6**, which undergo 1,2-hydrogen migration[10] leading to alkenes **7** (eq 2). The overall transformation thus constitutes a milder, nonbasic alternative to the classical Hofmann elimination of amines.

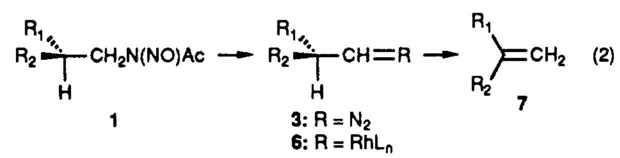
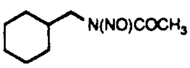
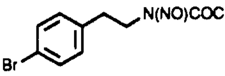
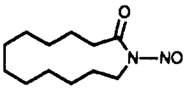
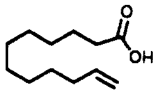
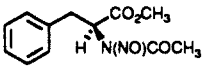
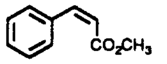
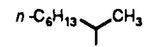


Table I. Rearrangement of *N*-Nitrosamides to Alkenes in the Presence of $Rh_2(OAc)_4$

entry	nitrosamide[a]	product (yield)
1	$n\text{-}C_9H_{19}CH_2N(NO)COCH_3$	1-decene (72%) *n*-pentylcyclopentane (10%)[b]
2	$n\text{-}C_{11}H_{23}CH_2N(NO)COCH_3$	1-dodecene (76%) *n*-heptylcyclopentane (10%)
3		methylenecyclohexane (78%)
4		*p*-bromostyrene (68%)
5		 (87%)
6		 (71%) *E*:*Z* = 1:9
7		1-octene (52%) 2-octene (26%) others (10%)

[a] Nitrosamides were prepared from the corresponding primary amines by acetylation (Ac_2O–pyr) then nitrosation (N_2O_4–CH_2Cl_2). [b] Identified by GC–MS with use of an authentic sample of product.

The scope and generality of this new transformation are depicted in the table. Reactions were generally performed by dropwise addition of a dilute benzene solution of nitrosamide to a suspension of $Rh_2(OAc)_4$ (1–2 mol %) in benzene at reflux. Essentially identical results were obtained with rhodium butyrate or rhodium octanoate. Virtually no catalyst poisoning was detected and simple *n*-alkylnitrosamides (entries 1 and 2) afforded terminal alkenes in high yield. By contrast, a distilled sample of diazo-*n*-decane rapidly turned the green $Rh_2(OAc)_4$ catalyst red-brown (azine complexation) with concomitant formation of 1-decene (20–30%) and decyl acetate (30–40%). Other common catalysts [e.g. $Pd(OAc)_2$ or $Cu(OAc)_2$] gave complex product mixtures also favoring esters.

Chain length permitting (entries 1 and 2), minor amounts of cyclopentanes can be formed by intramolecular C–H insertion, as previously noted with stabilized rhodium carbenoids.[11] Entry 5 illustrates a new synthesis of ω-unsaturated fatty acids from readily available macrocyclic lactams. Further evidence for the mechanism in eq 2 comes from entry 6, since the same *E*:*Z* ratio of cinnamates was obtained directly from the premade α-diazoester and has been attributed to orientational constraints for hydrogen migration in the metal–carbene intermediate.[10]

When similarly treated with $Rh_2(OAc)_4$, acetoxynitrosamides[12] **8** of 1,2-amino alcohols unexpectedly decomposed to rearranged enol acetates of predominantly *E* configuration (eq 3). The observed stereochemistry is best explained by invoking the preferred, trans-substituted dioxolonium ion intermediate **10** during acetate migration in the electrophilic carbenoid **9**.[9] Since *vic*-amino alcohols can be prepared from cyanohydrins, this reaction represents a new homologation of aldehydes to latent carbonyl compounds in a form suitable for enolate generation and alkylation.

Surprisingly, the thermal rearrangement of nitrosamides like **8** takes an entirely different course in the absence of rhodium catalyst (eq 4). When **8** (R = Ph) was brought to reflux in THF, smooth evolution of N_2 led to phenylacetylene as the only detectable product in 80% yield. Both aryl- and alkyl-substituted terminal alkynes could be synthesized in this fashion.[13]

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[1] Part 3 in the series: New Chemistry of Amines. For Part 2, see: Nikolaides, N.; Ganem, B. *Tetrahedron Lett.* **1990**, *31*, 1113.

[2] (a) Huisgen, R.; Horeld, G. *Liebigs Ann. Chem.* **1948**, *567*, 137. (b) Huisgen, R.; Krause, L. *Liebigs Ann. Chem.* **1951**, *574*, 157. (c) Huisgen, R.; Reimlinger, H. *Liebigs Ann. Chem.* **1956**, *599*, 183.

[3] Hey, D. H.; Stuart-Webb, J.; Williams, G. H. *J. Chem. Soc.* **1952**, 4657.

[4] (a) White, E. H. *J. Am. Chem. Soc.* **1955**, *77*, 6011, 6014. (b) White, E. H.; Aufdermarsh, C. A. *J. Am. Chem. Soc.* **1961**, *83*, 1174, 1179.

[5] (a) Streitweiser, A., Jr.; Schaeffer, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 2893.

[6] Nikolaides, N.; Ganem, B. *J. Org. Chem.* **1989**, *54*, 5996.

[7] (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (b) Fink, J.; Regitz, M. *Synthesis* **1985**, 569.

[8] Very recently 3-alkyl-3-phenyldiazirines were reported to form alkenes when decomposed in the presence of rhodium(II) perfluorobutyrate: Doyle, M. P.; High, K. G.; Oon, S.-M.; Osborn, A. K. *Tetrahedron Lett.* **1989**, *30*, 3049.

[9] Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75.

[10] Ikota, N.; Takamura, N.; Young, S. D.; Ganem, B. *Tetrahedron Lett.* **1981**, *22*, 4163.

[11] Taber, D. F.; Raman, K. *J. Am. Chem. Soc.* **1983**, *105*, 5935.

[12] Prepared by acetylation (Ac_2O–pyr) then nitrosation (N_2O_4–CH_2Cl_2) of the 1,2-amino alcohol.

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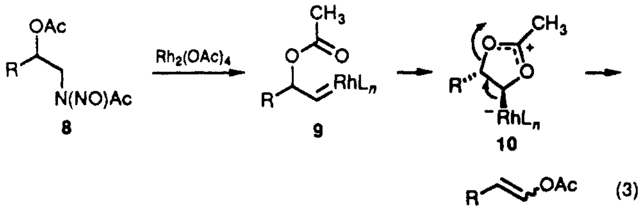
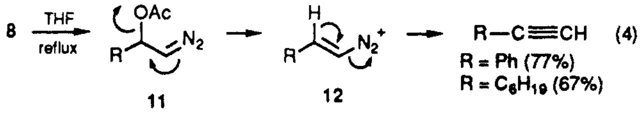


(3)

R (yield)	*E*:*Z*
Ph (69%)	2:1
C_6H_{19} (87%)	4:1



(4)

R = Ph (77%)
R = C_6H_{19} (67%)

Functionalized diazoalkanes like **11** are not easily prepared by other methods, and their unprecedented behavior deserves further comment. While structurally similar hydroxydiazoalkanes are involved in classical homologations of aldehydes or ketones (viz. Tiffeneau–Demjanov ring expansion),[14] the presence of an acetate leaving group in **11** apparently directs the intermediate to alkyne via diazonium ion **12**. Future work will address the synthetic utility of other unusually functionalized diazoalkanes available by mild nitrosamide fragmentation.

Acknowledgment. We thank the National Institutes of Health (GM 35712) for generous financial assistance. Support of the Cornell Nuclear Magnetic Resonance Facility by the NSF (CHE 7904825; PGM 8018643) and NIH (RR02002) is gratefully acknowledged.

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(13) With secondary-substituted amino alcohols like norephedrine, yields of disubstituted alkyne were low and several uncharacterized byproducts were also formed.

(14) (a) Gutsche, C. D. *Org. React.* **1954**, *8*, 364. (b) Krow, G. R. *Tetrahedron* **1987**, *43*, 3.

Book Reviews

Rigid-Chain Polymers: Hydrodynamic and Optical Properties in Solution. By V. N. Tsvetkov. Plenum: New York and London. 1989. xxii + 490 pp. $115.00. ISBN 0-306-11020-2.

This is the first book that is devoted entirely to semi-rigid polymer chain molecules in dilute solutions, the characterization of their conformation, and their hydrodynamic and optical properties. As such, it fills an important gap and should be well received.

The book consists of seven chapters with the first one setting the stage for the rest of the book by comparing the contrasting results (both experimental and theoretical) of semi-rigid-chain molecules and the much more thoroughly studied flexible-chain molecules. The distinction made between the two types of molecules is that flexible-chain molecules remain flexible and Gaussian in a Θ-solvent down to oligomeric size whereas the conformation of rigid-chain molecules differs over a wide range, from rodlike conformation to a Gaussian coil, depending on their molecular weight. Concepts such as Kuhn's segment length for flexible molecules, the persistence length of rigid molecules, excluded volume effects and rigidity effects on conformation are presented clearly in the first chapter. This clarity in exposition is reasonably well maintained throughout most of the book. There are two chapters on hydrodynamic properties, one on theory and the other on experimental data; and similarly, two chapters on flow birefringence. A chapter on transport methods describes the principles and methods of measurements of diffusion, sedimentation, and viscometry. The last chapter in the book is devoted to electric birefringence. Throughout the book, the author has tried successfully to integrate experimental results and theoretical predictions. The book presents compilations of experimental results on cellulose derivatives, polypeptides, polyisocyanates, aromatic polyamides, and aromatic polyesters, most of which are drawn from the author's own work in the Russian literature. Thus, the book makes available in English and in one source these important and extensive contributions with the original publications listed in the references.

The book suffers from a few defects. Newer experimental methods very relevant to the subject, such as dynamic light scattering (DLS), are not discussed; I noted only one passing reference (ref 39 in Chapter 6) to work using DLS. The discussion on the shear thinning of intrinsic viscosity with a heavy emphasis on "internal viscosity" is rather weak and outmoded. The approach taken, sometimes, of discussing different physical properties, e.g., intrinsic viscosity as a function of shear rate in Chapter 3 and dielectric increment versus frequency in Chapter 7 in terms of different models, is not very appealing from a theoretical view point, as the strength or weakness of a model must be based on experimental tests of theoretical predictions of all the physical properties based on this model. The latest references in the book date back to 1985 for the Russian literature and only to 1983 for the international literature; so that the book, due probably to delays in translation, is no longer up-to-date. Finally, despite the Library of Congress cataloging data printed in the book, which indicates the presence of an index, the book does not include an index.

Despite these shortcomings, the book fills a need and will be welcomed by researchers in the field and by those who want to learn about the dilute solution properties of semi-rigid chain polymers.

Claude Cohen, *Cornell University*

Chemical Resistance of Polymers in Aggressive Media. By Yu. V. Moiseev and G. E. Zaikov (Institute of Chemical Physics, Academy of Sciences of the USSR). Translated from Russian by R. J. Moseley. Consultant Bureau (Plenum): New York and London. 1987. xvii + 366 pp. $85.00. ISBN 0-306-10997-2.

This very specialized volume covers the area of chemical resistance of polymers to "aggressive media" such as solutions of acids, bases, and salts. The authors have attempted to cover both practical and theoretical aspects of the chemical degradation of polymers.

Early chapters include a physicochemical treatment of the mechanisms of degradation with a number of useful examples involving both model compounds and polymers. Subsequent chapters include a thorough theoretical treatment of the fundamental basis of chemical degradation of polymers with consideration of factors such as chemical reactivity, diffusion, morphology, and kinetics in the solid state. The last chapter of the book, containing a summary of the effect of aggressive media on polymer performance, is particularly useful.

Although the literature coverage extends only to the early 1980s, the book is particularly useful as it discusses in detail, with useful tables and figures, data which are not otherwise available to most readers.

While this book is directed primarily to those with an interest in the long-term *durability* of polymer materials, it may also provide valuable insight to those concerned with the design of *degradable* materials, both of which are topics of great current interest.

Jean M. J. Fréchet, *Cornell University*