partment of General and Organic Chemistry, University of Copenhagen, for loan of a Hitachi MPF-3 fluorescence spectrophotometer used in this work.

Jerzy W. Jaroszewski*
Department of Chemistry BC
Royal Danish School of Pharmacy
Universitetsparken 2
DK-2100 Copenhagen, Denmark

Martin G. Ettlinger
Department of General and Organic Chemistry
University of Copenhagen
Universitetsparken 5
DK-2100 Copenhagen, Denmark

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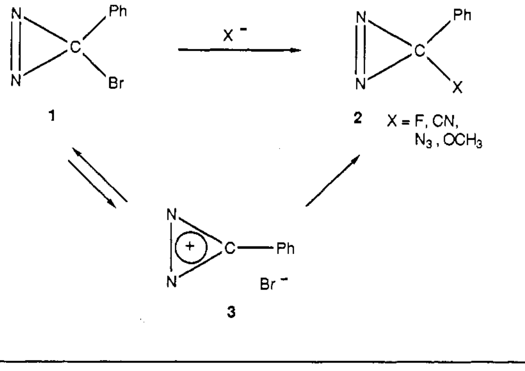
On the Intermediacy of Phenyldiazirinium Cation in Olefin Isomerizations

Summary: The phenyldiazirinium cation cannot be easily generated under solvolytic conditions. This study conflicts with the reported determination of an equilibrium constant for ionic dissociation of 3-bromo-3-phenyldiazirine while further studies indicate that the phenyldiazirinium cation is not involved in the diethyl maleate to fumarate isomerization as previously reported.

Sir: During the course of studies designed to prepare substituted methylenecyclopropanes, we wanted to prepare a series of substituted diazirines to use as cyclopropane precursors. We therefore prepared 3-bromo-3-phenyldiazirine, **1**, which is known to undergo reaction with certain nucleophiles to give the novel and interesting substitution products **2**.[1] It has been suggested that these products result from nucleophilic capture of a reversibly formed ion pair **3**.[1a] Subsequently, measurement of the equilibrium constant for dissociation of **1** in acetonitrile by a conductometric technique was reported.[2] It was also reported that **1** catalyzes the isomerization of diethyl maleate to diethyl fumarate, and it was further suggested that the ion pair **3** was the catalytic agent.[3] We now report studies that call into question the involvement of cation **3** in the maleate to fumarate isomerization.



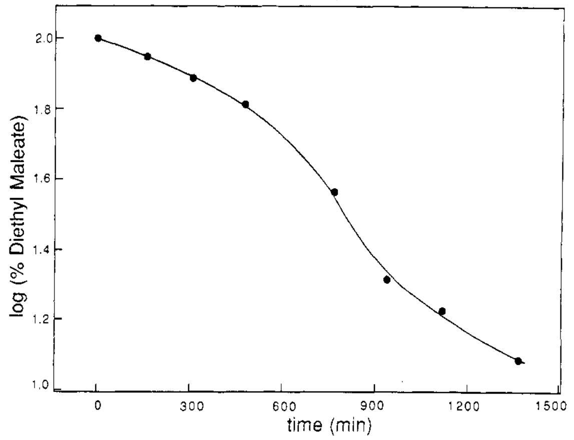
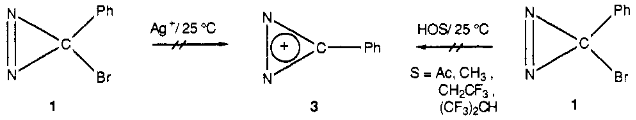


Figure 1. A plot of log (% unreacted diethyl maleate) vs time for isomerization of a 0.57 M solution of diethyl maleate in CCl_4 containing 0.13 M diazirine **1** at room temperature.

In an attempt to form the nitrate derivative, the bromodiazirine **1** was reacted with silver nitrate in acetonitrile. To our surprise the mixture only turned cloudy. There was no instantaneous copious precipitation of silver bromide as when triphenylmethyl bromide or benzyl bromide was reacted under the same conditions in acetonitrile.[4] This observation is inconsistent with the report that **1** is sufficiently ionized in acetonitrile to allow conductometric measurements.[5] Attempts to generate the cation **3** under solvolytic conditions were also unsuccessful. The bromodiazirine **1** was recovered unchanged after standing in acetic acid for 20 h at room temperature. The bromodiazirine **1** was also unreactive with silver acetate in acetic acid. In neutral methanol, **1** was unreactive over a period of 20 h. Bromodiazirine **1** was also recovered unchanged on standing in the more highly ionizing solvent trifluoroethanol for 20 h. Even the very highly ionizing solvent hexafluoroisopropyl alcohol doesn't lead to solvolysis of **1**. These attempted solvolyses suggest that the cation **3** is relatively unstable and cannot be easily formed under solvolytic conditions. Our findings are also consistent with Moss's report that reaction of methoxybromodiazirine with $AgNO_3$, $AlBr_3$, SbF_5/SO_2, H_2SO_4, $AlCl_3$, AgF, or FSO_3H "failed to provide evidence for diazirinium ions as spectroscopic entities or as chemical intermediates".[6]



In light of the apparent difficulty in generating the diazirinium cation **3**, we reinvestigated the reported isomerization of diethyl maleate to diethyl fumarate catalyzed by **1** where coordination of the cation **3** with the carbonyl oxygen is suggested to initiate the isomerization process.[3] We have found that freshly chromatographed and distilled diazirine **1** does indeed catalyze this interesting isomerization in the nonpolar solvent CCl_4 as reported. However, our lack of evidence for the cation **3** under solvolytic conditions in highly ionizing polar solvents caused us to

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[1] (a) Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 2743. (b) Wlostowska, J.; Moss, R. A.; Guo, W.; Chang, M. *Chem. Commun.* **1982**, 432. (c) Cox, D. P.; Moss, R. A.; Terpinski, J. *J. Am. Chem. Soc.* **1983**, *105*, 6513. (d) Moss, R. A.; Kmiecik-Lawrynowicz, G.; Cox, D. P. *Synth. Commun.* **1984**, *14*, 21. (e) Moss, R. A.; Cox, D. P.; Tomioka, H. *Tetrahedron Lett.* **1984**, *25*, 1023. (f) Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Lawrynowicz, G.; Wlostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 4341.

[2] Liu, M. T. H.; Paike, N. *Tetrahedron Lett.* **1987**, *28*, 3763.

[3] Liu, M. T. H.; Doyle, M. P.; Loh, K.-L.; Anand, S. M. *J. Org. Chem.* **1987**, *52*, 323.

[4] While **1** is recovered essentially unchanged after 1.5 h at room temperature in acetonitrile containing excess $AgNO_3$, under these conditions **1** is slowly converted over a period of 50 days to benzoic acid. The mechanism of this transformation is under investigation.

[5] The reported[2] dissociation constant for **1** in acetonitrile is 2×10^{-5}. If this were correct, then precipitation of AgBr should be instantaneous.

[6] Moss, R. A.; Wlostowska, J.; Guo, W.; Fedorynski, M.; Springer, J. P.; Hirshfield, J. M. *J. Org. Chem.* **1981**, *46*, 5050.

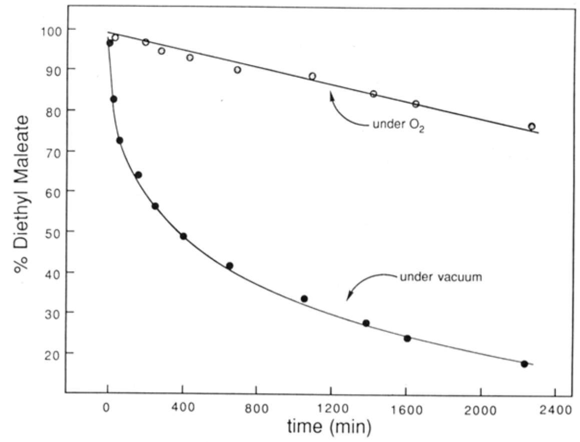
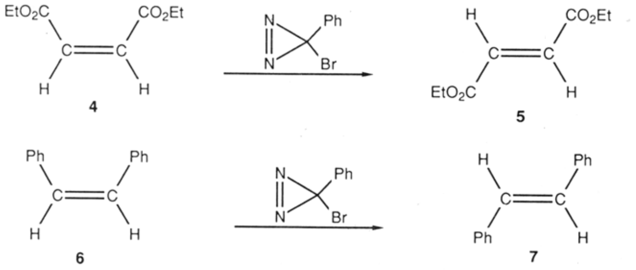


Figure 2. A plot of % unreacted diethyl maleate vs time for isomerization of a 0.44 M solution of diethyl maleate in CCl_4 containing 0.08 M diazirine **1** at 23 °C.

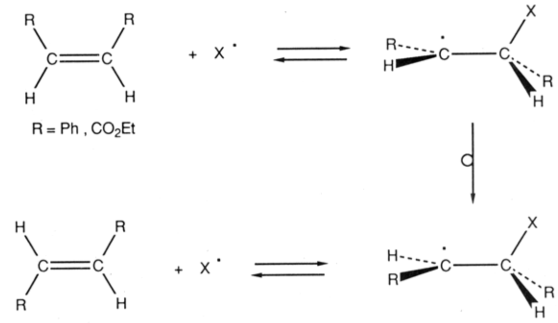
doubt the suggested mechanism for this isomerization which involves formation of the ion pair **3** in a very nonpolar solvent. When the reaction is monitored by NMR in CCl_4 under nitrogen, the disappearance of diethyl maleate is not first order. There is an induction period (which varies from run to run) as shown in Figure 1. In a separate experiment, brief exposure to light from a sunlamp initiates the reaction, which then continues smoothly. Figure 2 shows the result of a third set of experiments. When the reaction is carried out in a degassed solution in a sealed NMR tube under vacuum, there is no induction period. The reaction proceeds at a substantially slower rate under an oxygen atmosphere. In the degassed reaction under vacuum the disappearance of diethyl maleate is still not first order in diethyl maleate. In a fourth set of experiments, addition of thiophenol (PhSH) (which is not consumed during the reaction) also inhibited the reaction relative to the reaction carried out under a nitrogen atmosphere. If the ion pair **3** were involved in the isomerization of diethyl maleate to diethyl fumarate, there should be no induction period or inhibition by oxygen or thiophenol. Furthermore (since the diazirine is not consumed over the course of the reaction) the reaction should be first order in diethyl maleate over the course of the reaction if the ion pair **3** were the catalyzing agent. These experiments are therefore inconsistent with the involvement of the ion pair **3** in the isomerization.



4 **5** **6** **7**

We have found that **1** also catalyzes the isomerization of *cis*-stilbene to *trans*-stilbene.[7] The catalytic behavior is similar to (but not identical with) that observed in the maleate–fumarate isomerization. There is a nonreproducible induction period, and the reaction can be initiated by brief irradiation with a sunlamp. It is important to note that the suggested interaction of the ion pair **3** with the carbonyl group of diethyl maleate cannot occur with *cis*-stilbene. Yet the diazirine **1** catalyzes the isomerization.

These isomerization reactions of diethyl maleate and *cis*-stilbene have characteristics of a free radical chain process. We suggest that a more conventional mechanism initiated by some radical operates in these isomerizations. The nature of the chain-carrying radical is uncertain although bromine atom or phenyldiazirinyl radical initiated processes are likely possibilities. There is therefore no need to suggest the intermediacy of the ion pair **3** in olefin isomerizations.



In summary, our solvolytic studies show that the phenyldiazirinium cation, **3**, cannot be easily generated under solvolytic conditions even in highly ionizing solvents. Furthermore, isomerizations of diethyl maleate to fumarate do not appear to involve this cation. These observations suggest the need for further investigations of processes (such as the reported conductivity measurements) that purportedly involve this cationic intermediate.

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Xavier Creary,* Anthony F. Sky
Department of Chemistry
University of Notre Dame
Notre Dame, Indiana 46556

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(7) This classic isomerization has been observed under free radical, photochemical, acid, and basic conditions. See: (a) Kharasch, M. S.; Mansfield, J. V.; Mayo, F. R. *J. Org. Chem.* **1937**, *59*, 1155. (b) Saltiel, J.; Hammond, G. S. *J. Am. Chem. Soc.* **1963**, *85*, 2515. (c) Price, C. C.; Meister, M. *J. Am. Chem. Soc.* **1939**, *61*, 1595. (d) Noyce, D. S.; Hartter, D. R.; Miles, F. B. *J. Am. Chem. Soc.* **1968**, *90*, 4633. (e) Cram, D. J.; Hunter, D. H. *J. Am. Chem. Soc.* **1966**, *88*, 5765.

Cobaloxime-Mediated Radical Alkyl–Heteroaromatic Substitution

Summary: The first examples of cobaloxime-mediated radical alkyl–heteroaromatic cross-coupling, replacing a C–H in the protonated heteroaromatic with a C-alkyl, are accomplished via anaerobic visible light photolysis of 95% EtOH solutions of primary and secondary alkyl cobaloximes, $RCo^{III}(dmgH)_2py$ (dmgH = dimethylglyoxime monoanion), and pyridinium, quinolinium, 4-methylpyridinium, benzothiazolium, and benzimidazolium *p*-toluenesulfonate.

Sir: We recently reported radical alkyl–alkenyl cross-couplings via anaerobic visible light photolysis of solutions of $RCo^{III}(dmgH)_2py$ and alkenes activated for attack by nucleophilic alkyl radicals.[2,3] The reactivity of protonated

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(1) Fellow of the Alfred P. Sloan Foundation, 1987–1989.

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