Diazo Compounds

PROPERTIES and SYNTHESIS

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Properties and Synthesis

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Preface

The discovery of the chemistry of aliphatic diazo compounds was made a century ago: Theodor Curtius synthesized ethyl diazoacetate in 1883 for the first time and with this opened the wide field of diazo chemistry, which even today has not yet been exhausted. The solution of the long controversial problem of constitution, the development of general and facile syntheses, and the application of diazo compounds in organic synthesis, facilitated by their incredible reactivity, have made this field a truly exciting one. Novel methods of synthesis, such as diazo group transfer and electrophilic diazoalkane substitution, and the most valuable contribution of diazo compounds to the chemistry of carbenes and cycloadditions indicate the continued interest in these compounds.

This monograph deals only with the properties and syntheses of aliphatic diazo compounds. Discussions concerning their reactions—if not absolutely necessary to describe certain aspects of their preparation—have been intentionally omitted in order to maintain the format. The first chapters deal with structure, spectroscopic properties, thermal behavior, acidic decomposition, and photochemistry of diazoalkanes, followed by synthetic methods. Further initiatives and developments may be expected, especially from the discoveries of novel diazoalkane syntheses. The Bibliography is intended to make entry into the tremendously growing literature on the subject easier.

This monograph was primarily written to be used by chemists interested in the synthetic application of diazo compounds and for colleagues with an interest in the physical properties of these compounds. We hope to stimulate

those who, like the authors, believe that the chemistry of diazoalkanes will continue to be nourished by the imagination of its disciples.

Throughout the various chapters of the book, the literature up to the end of 1982 has been reviewed. The major developments published up to January of 1986 are compiled concisely in an Addendum.

We are grateful to Professor Peter Stang, University of Utah, on whose suggestion this monograph was written. Our thanks are also extended to the editors and staff of Academic Press for their patience and helpfulness.

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Part I

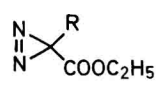
Properties of Aliphatic Diazo Compounds

Chapter 1

Structure and Spectroscopic Properties

1.1 The Constitution of Diazoalkanes

When Curtius first synthesized ethyl diazoacetate via amine diazotation in 1883, no suggestion was made as to whether the CN_2 group was in a cyclic [e.g., diazirine **1** (R = H)] or an open (**2**, R = H) configuration (*1*). Some years later, however, he postulated structure **1** for α-diazoesters, α-diazoamides, and the salts of the free acids (*1a*). The cyclic structure was adopted for diazomethane by v. Pechmann, who had synthesized the compound by base cleavage of *N*-methyl-*N*-nitrosourethane in 1894 (*2*).



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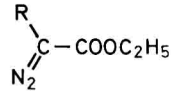

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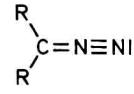

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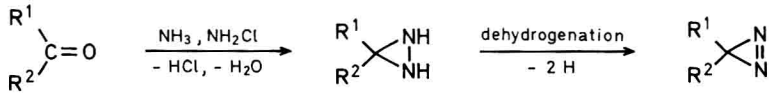
Thiele finally suggested open configuration **3** for diazoalkanes in 1911 (*3*); it contains, according to the valence theory accepted then, a pentavalent nitrogen atom. His reasoning is based on the experimental results that diazo compounds are formed by dehydrogenation of hydrazones, compounds whose open constitution was well known.

Neither chemical properties of diazo compounds nor measurements of the parachor or dipole moment of diazomethane could end the long-lived discussion over the "true" structure. An electron diffraction experiment by Boersch in 1935 finally decided the issue in favor of an open diazomethane

molecular structure with linear geometry of the CN_2 group (*4*). Only in 1957, did a chemical experiment prove the open structure for ethyl diazoacetate as well (*5*). Ethyl glycinate was diazotized with ^{15}N-labeled sodium nitrite, and the labeled ethyl diazoacetate reductively cleaved to glycine and ammonia. It was to be expected that in the case of a linear arrangement of the diazo group, ^{15}N would be released exclusively as ammonia, whereas for a cyclic arrangement a statistical distribution of the label between both reduction products should result. Analyses unambiguously decided in favor of the open structure.

Since 1960, straightforward routes to synthesize the cyclic valence isomer of diazomethane, diazirine **4** ($R^1 = R^2 = H$), and derivatives, have been discovered (*6,7*). This has made it possible to compare both classes of compounds directly: diazirines are (almost) colorless and most diazoalkanes are intensely yellow to red; diazirines are far less reactive than diazoalkanes (e.g. they are stable against acids), whereas sensitivity to acids is one of the most pronounced properties of most diazoalkanes (see Chapter 3, Section 1).



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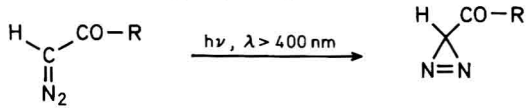
When suitable substituents are present, the valence isomerization diazoalkane–diazirine is possible in both directions. Upon irradiation of diazirine (*8*) ($\lambda = 320$ nm), 3-aryl-3*H*-azirines (*8a*) ($\lambda \geq 280$ nm), cycloalkanespirodiazirines (*8b*) ($\lambda \geq 310$ nm) or 3-*n*-butyl-3-phenyldiazirine (*8c*) ($\lambda \geq 330$ nm), isomerization to the corresponding diazoalkane competes with fragmentation into carbene and N_2. In these cases, diazoalkane formation was proved by trapping reactions, spectroscopically, or by the isolation of products that stem from diazoalkane reactions. In other examples, the intermediacy of diazoalkanes in thermal or photochemical reactions of diazirines was deduced from kinetic evidence or isotope labeling experiments (*8d*). 3,3-Diphenyldiazirine probably rearranges to diazodiphenylmethane in the presence of oxygen or mercury(II) oxide during its attempted synthesis (*9*). On the other hand, α-diazoamides (**5**) with a hydrogen atom at the diazo carbon will isomerize to the corresponding diazirinecarboxamides when irradiated with visible light (*10,11*).



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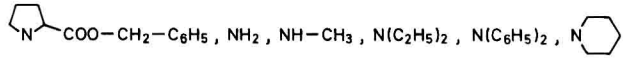
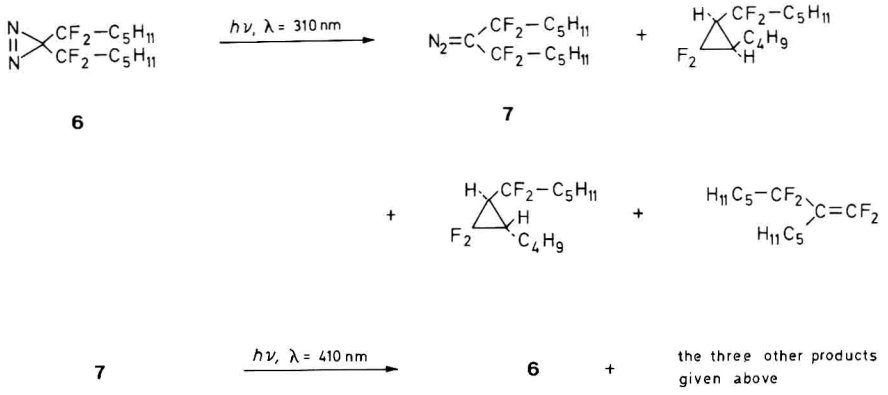
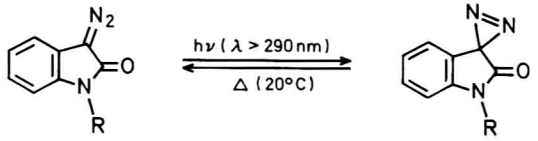
R = 

A reversible photochemical rearrangement of diazirine **6** and diazoalkane **7** is possible by selecting the appropriate wavelength. At 310 nm, **6** is converted to **7**; at 410 nm, the reverse reaction takes place. To some extent, carbenes are formed by N_2 elimination from the two valence isomers and undergo subsequent reactions (*12*).



6 **7**

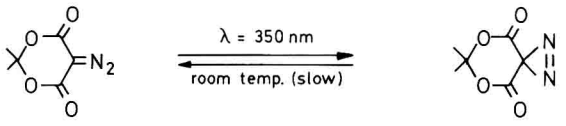
Examples of the thermal reversion of a photoisomerization are also known. Ultraviolet irradiation of 3-diazo-2,3-dihydro-2-indolone (3-diazo-2-oxoindoline) and its *N*-methyl derivative **8** leads to the pale yellow diazirines **9**, which rearrange, even at room temperature, to the red diazo compounds **8** (*13*). The activation parameters of **9** → **8** (R = CH_3) were determined as: $\Delta H^{\ddagger} = 110.9$ kJ mol^{-1} (26.5 kcal mol^{-1}), $\Delta S^{\ddagger} = 40.6$ J K^{-1} mol^{-1} (9.7 cal K^{-1} mol^{-1}).



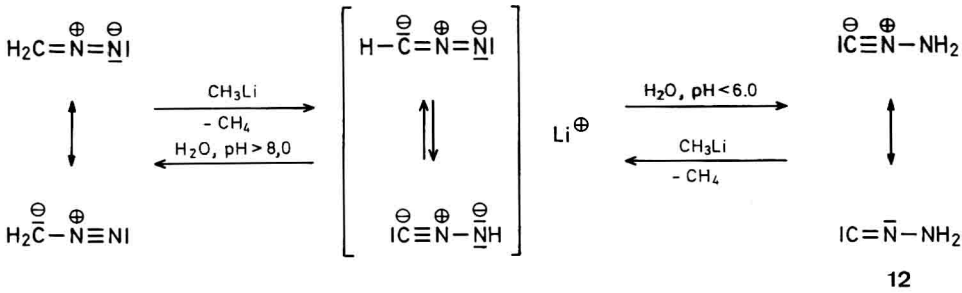
8 **9**

R = H, CH_3

Isopropylidene diazomalonate **10** and the isomeric diazirine **11** show similar behavior (*14*).



10 **11**



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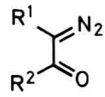
Scheme 1.1

It is not surprising that the thermal valence isomerization diazoalkane → diazirine has not yet been observed. Diazirine is higher in energy than diazomethane by a margin of ~126 kJ mol^{-1} (30 kcal mol^{-1}), according to the heats of formation obtained by mass spectrometric analysis (*15,15a*).

At a time when the structure of diazomethane was still in doubt, Müller and Kreutzmann (*16*) discovered another isomer. By treating the sodium salt of diazomethane in ether with acetic acid, a pale yellow solution is formed that no longer contains diazomethane but a new substance with unpleasant odor. The authors called the compound "isodiazomethane" but gave no suggested structure. Further investigations indicated the compound to be a tautomer of diazomethane, and it was finally characterized as *N*-isocyanoamine (**12**) because of the equivalency of both protons in the ^{1}H-NMR spectrum (*17–19*).

Scheme 1.1 demonstrates the reversible tautomerization of diazomethane and *N*-isocyanoamine, which takes place via a common tautomerizable anion.

For a long time there was a similar ambiguity in the constitution of α-diazocarbonyl compounds. Wolff (*20*) synthesized the compounds for the first time by diazotization of the α-amino derivatives of β-keto esters, or 1,3-diketones with sodium nitrite in dilute sulfuric acid solution. Because of their remarkable acid stability (see Chapter 3, Section 1), the open structure **13** seemed unlikely. Instead, Wolff suggested the structures of "diazoanhydrides," such as compounds of the type **14** (1,2,3-oxadiazoles). However, such heterocycles have not been isolated yet.



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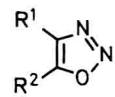

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