Reaction of Diphenyldiazomethane with *N*-Methyloxy- and *N*-Ethyloxycarbonyl-*N*-(2,2,2-trichloroethylidene)amines

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Reaction of the title imines with diphenyldiazomethane gives a Δ^3-1,3,4-triazoline, which leads, after loss of dinitrogen, to a transient azomethine ylide. Subsequent elimination of ethyl or methyl chloroformate gives the unexpected 1,1-diphenyl-4,4-dichloro-2-aza-1,3-butadiene.

Introduction

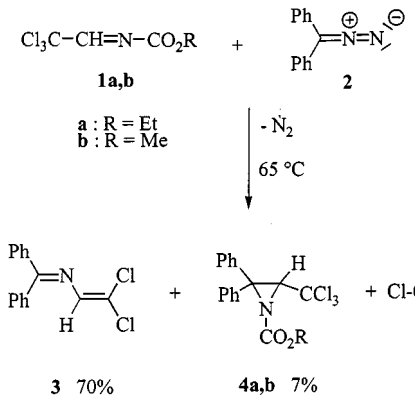
The known reactivity of the C=N double bond in various azomethines towards diazoalkanes leads to the regioselective formation of Δ^2-1,2,3-triazolines.[1–4] However, some examples of the formation of Δ^3-1,3,4-triazolines have also been reported.[1][4] It has often been observed that thermolysis of the triazolines gives the corresponding aziridines or other products resulting from the loss of dinitrogen.

We present here the reactions of diphenyldiazomethane **2** with *N*-ethyloxy- and *N*-methyloxycarbonyl-*N*-(2,2,2-trichloroethylidene)amines **1a** and **1b**. The 1,3-dipolarophilic reactivity of the electron-deficient imine **1a** has recently been assessed using 1,3-dipoles such as nitrones,[5] nitrilimines and nitriloxides,[6] as well as ethyl diazoacetate.[7] In this last case, the reaction involves nucleophilic addition of the ethyl diazoacetate with formation of a new 1,3-dipole.[7] This addition should not occur with diphenyldiazomethane since this 1,3-dipole has no mobile proton.

Results and Discussion

Reactions

After stirring a toluene solution of the imine **1a** or **1b** with diphenyldiazomethane **2** for 24 h at 65°C, a major product **3** (70%) was formed, together with a by-product **4** (7%). Elemental analysis, IR, and NMR data of **3** were not consistent with the structure of the expected triazoline. The structure of this product was later unambiguously established by an X-ray diffraction study (Figure 1). Elemental analysis and spectroscopic data showed **4** to be an aziridine commonly found as a secondary product of the expected triazoline.[1]



Scheme 1. Reaction of **1a**,**b** with **2** at 65°C

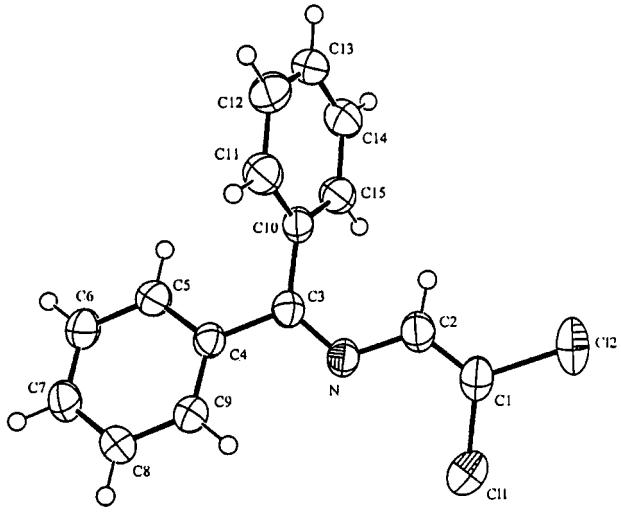


Figure 1. ORTEP plot (50% probability level) of the molecular structure of **3**

Formally, compound **3** is a secondary product formed by loss of dinitrogen and alkyl chloroformate from a triazoline 1,3-cycloadduct of **1** with **2**. Indeed, a quantitative gas-

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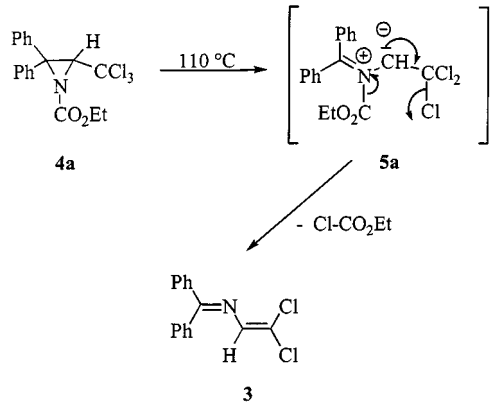
chromatographic analysis of the reaction mixture of **1a** with **2** led to the detection of >80% of the estimated stoichiometric amount of ethyl chloroformate.

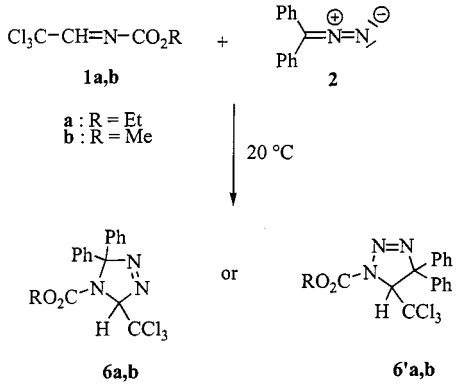
The 2-azadiene **3** may also be formed from the aziridine **4** following loss of alkyl chloroformate. According to literature data,[1] heating to a temperature >100°C allows cleavage of the C−C bond of an aziridine ring, leading to the corresponding azomethine ylide. Indeed, while **4a** is thermally stable at 65°C, refluxing a toluene solution of this compound results in quantitative conversion to the 2-azadiene **3** and ethyl chloroformate, this process certainly proceeding via the azomethine ylide **5a** (Scheme 2).



4a **5a** **3**

Scheme 2. Evolution of **4c** at 110°C

In order to identify some of the transient species leading to the 2-azadiene **3**, which should allow elucidation of the mechanism of the reaction, we carried out a study at room temperature. After 30 h at this temperature, a mixture of the imine **1a** or **1b** and diphenyldiazomethane **2** in toluene solution gave only one isolable product (yield: 70%), elemental analysis and spectrometric data of which showed it to be one of the two regioisomeric triazolines **6** or **6′** formed by 1,3-dipolar cycloaddition (Scheme 3).



6a,b **6'a,b**

Scheme 3. Reaction of **1a**,**b** with **2** at 20°C

With the aim of determining the direction of addition of this cycloadduct, we tried to undertake an X-ray crystal structure analysis. However, all attempts to obtain suitable single crystals were unsuccessful. Thus, the structure of the Δ^3-1,3,4-triazoline **6** was established on the basis of its ^{1}H-NMR data: The chemical shift of the 5-H proton (Cl_3CCH) at $\delta > 7.50$ is in good agreement with structure **6**, where the CH group resides between two deshielding nitrogen atoms. In the case of structure **6′**, this signal would be expected to appear below $\delta = 6.00$.[8] The signals of the alkyl ester groups are broadened (see Figure 2 for the case of **6a**), probably due to restricted rotation because of the steric hindrance imposed by the 2,2-diphenyl groups and the 5-CCl_3 moiety. Such hindrance should not be present in the triazolinic structure **6′**. Moreover, ^{1}H-NMR examination of the mother liquor of **6** did not reveal the expected signal of the 5-H proton ($\delta \approx 5.50-6.00$) of the regioisomer **6′**.

We attempted to rationalize the direction of the addition by carrying out some semi-empirical MO calculations (PM3 level, optimized geometries) on the starting reactants **1b** and **2**. The results of these calculations show that the cycloaddition occurs by interaction between the LUMO of **1b** and the HOMO of **2**. However, it is not possible to justify the observed direction of addition since the orbital coefficients of the C and N atoms of the LUMO of **1b** have equal weightings.

Study of the Evolution of Cycloadduct 6a

We observed that heating a solution of cycloadduct **6a** in toluene at 65°C furnished 2-aza-1,3-butadiene **3** in high yield (> 90%). Thus, we tried to follow this evolution in an NMR tube in $CDCl_3$ at 50°C over a period of 10 h (Figure 2).

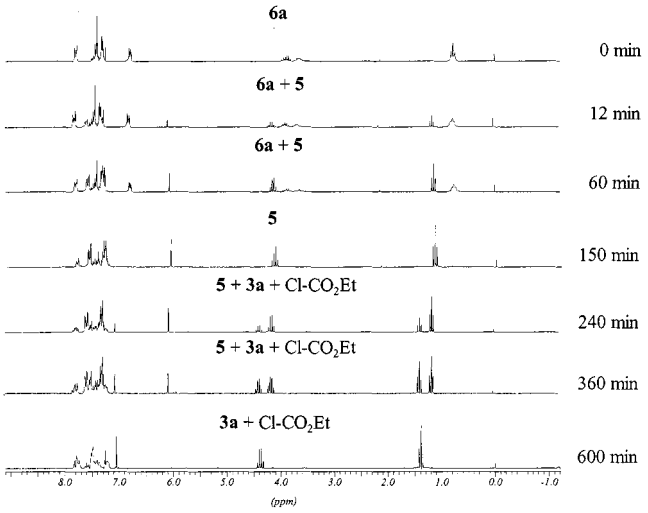
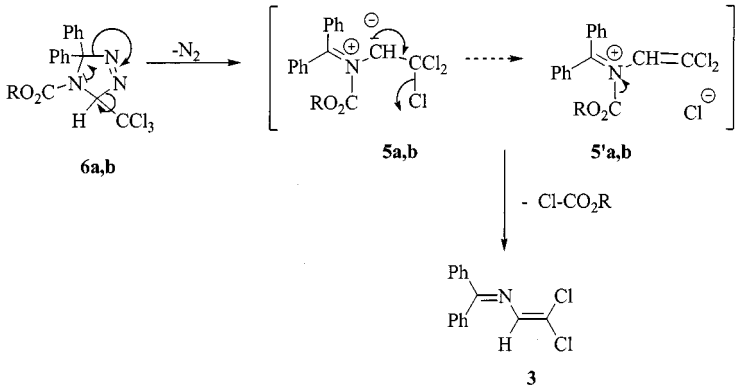


Figure 2. Evolution of the triazoline **6a** at 323 K

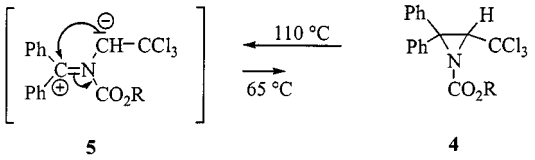
This study revealed that **6a** is not transformed directly to the final 2-azadiene **3**. In fact, a second intermediate **5** is involved. The ^{1}H-NMR spectrum of this transient species **5** features well-resolved signals for the ethyl group of the ester function. The absence of steric hindrance is probably due to a ring-opening of **6a**, leading to two possible transient species **5a** or **5′a**. The azomethine ylide structure **5a** would be formed from **6a** by 1,3-dipolar cycloreversion and loss of dinitrogen, while the *N*-(2,2-dichlorovinyl)iminium



Scheme 4. Evolution of **6a** at 323 K

salt **5′a** would arise by loss of one chloride ion[9] (Scheme 4).

We favour the azomethine ylide structure **5a** for the intermediate because in some of the recorded ^{1}H-NMR spectra the signals of aziridine **4a** appeared after the formation of the transient species **5**. Compound **4a** can only be derived from ring-closure of the azomethine ylide **5a** (Scheme 5). It is obtained at 50−65°C.



Scheme 5. Ring closure of **5**

The structure **5a** may be further supported by a transient orange coloration of the solution in the NMR tube. However, all attempts to trap this 1,3-dipole **5a** by cycloaddition with *N*-phenyl- or *N*-methylmaleimide or with DMAD proved unsuccessful. This may be attributable to the steric hindrance of the three atoms of the dipole **5a** rendering this species unreactive.

Conclusion

This study has established the successive steps of the mechanism of the title reaction. The primary cycloadduct **6a** leads, after loss of dinitrogen, to a transient azomethine ylide **5a**. Subsequent elimination of alkyl chloroformate gives the 1,1-diphenyl-4,4-dichloro-2-aza-1,3-butadiene **3**. To the best of our knowledge, this is the first example of the formation of a 2-azabutadiene as a secondary product of an azomethine ylide. Work is currently in progress aimed at extending this reaction to other disubstituted diazoalkanes and other conveniently substituted imines

Experimental Section

General: IR spectra (KBr) were recorded on a Bio-Rad FTS-7 spectrometer. − ^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker Spectrospin AC 200 spectrometer operating at 200 MHz for ^{1}H and at 50.3 MHz for ^{13}C. Chemical shifts were measured relative to TMS in $CDCl_3$ or [D_8]THF as solvents. − Analytical data were obtained at the Elemental Analysis Center, Dijon. − Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. − *N*-Ethyloxy- and *N*-methyloxycarbonyl-*N*-(2,2,2-trichloroethylidene)amines[10][11] and diphenyldiazomethane[12] were synthesized according to literature methods.

Reactions at 65°C. − General Procedure: A solution of diphenyldiazomethane (32 mmol) and *N*-ethyloxy- or *N*-methyloxycarbonyl-*N*-(2,2,2-trichloroethylidene)amine (32 mmol) in toluene (80 mL) was heated at 65°C for 24 h. The solvent was then evaporated and the residue was recrystallized from ethanol.

(a) Synthesis of 4,4-Dichloro-1,1-diphenyl-2-azabuta-1,3-diene (3): Yield: 70%, pale-yellow needles, m.p. 122°C. − ^{1}H NMR ($CDCl_3$): δ = 7.05 (s, 1 H, ethylenic CH), 7.15−7.80 (m, 10 H, arom. H). − ^{13}C NMR ($CDCl_3$): δ = 123.4 (s, $=CCl_2$), 128.2−131.0 (5 signals for 10 arom. CH), 135.2 (d, ethylenic CH), 135.4 (s, arom. C), 138.5 (s, arom. C), 168.3 (s, C=N). − $C_{15}H_{11}Cl_2N$ (276.18): calcd. C 65.24, H 4.01, N 5.07, Cl 25.68; found C 65.19, H 3.99, N 5.10, Cl 25.72.

X-ray Crystal Structure of 3: The structure was solved by direct methods using SHELXS-97. Hydrogen atoms were placed in calculated positions. Refinement was carried out by a full-matrix least-squares method based on F^2 values with 163 variables. Crystallographic data are collected in Table 1. Selected bond lengths [Å] and angles [°] for **3:** C1−C2 1.319(3), N−C2 1.392(3), N−C3 1.293(2); C1−C2−N 121.2(2), C2−N−C3 119.7(2), N−C3−C4 117.5(2), N−C3−C10 125.2(2), C4−C3−C10 117.3(2), Cl1−C1−Cl2 114.6(1). For further information see ref.[13]

(b) Synthesis of Aziridines 4a and 4b: The mother liquor from the above crystallization was concentrated and the newly obtained residue was crystallized from ethanol. Ethyl- and methyl 2,2-diphenyl-3-(trichloromethyl)aziridine-1-carboxylates **4a** and **4b** were obtained as pale-yellow needles (each 2.56 mmol, 7%).

Ethyl 2,2-Diphenyl-3-(trichloromethyl)aziridine-1-carboxylate (4a): Yield: 7%, m.p. 101°C. − IR (KBr): $\tilde{\nu}$ = 1720 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, ^3J = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 4.00 (AB part of ABX_3, ^3J = 7.1 Hz, ^2J = 10.7 Hz, 2 H, $CO_2CH_2CH_3$), 4.52 (s, 1 H, $CHCCl_3$), 7.20−7.65 (m, 10 H, arom. H). − ^{13}C NMR ($CDCl_3$): δ = 13.85 (q, J = 127 Hz, $CO_2CH_2CH_3$), 57.9 (d, J = 174 Hz, $CHCCl_3$), 60.5 (s, Cq), 63.0 (t, J = 148 Hz, $CO_2CH_2CH_3$), 96.2 (s, CCl_3), 127.7−129.0 (6 signals for 10 arom. CH), 135.8−136.8 (2 signals for 2 arom. Cq), 159.5 (s, CO). − MS (70 eV); *m/z* (%): 383 (3.6) [M$^+$], 348 (73.7) [M$^+$ − Cl], 275 (47.3) [M$^+$ − $ClCO_2Et$], 240 (45.0) [M$^+$ − Cl − $ClCO_2Et$]. −

Table 1. Crystallographic data for **3**[12]

Crystal data	
empirical formula	$C_{15}H_{11}Cl_2N$
molecular mass	276.15
crystal system	monoclinic
space group	$P2_1/n$
cell dimensions:	
a [Å]	9.874(1)
b [Å]	9.156(1)
c [Å]	15.032(2)
β [°]	98.03(1)
V [Å^3]	1345.7(3)
Z	4
ρ_{calcd} [g·cm^{-3}]	1.363
$F(000)$	692
Data collection	
diffractometer	Enraf-Nonius CAD4
radiation [Å]	λ(Mo-K_α) = 0.71073 Å
crystal size [mm]	0.40 × 0.20 × 0.20
monochromator	graphite
reciprocal lattice segment	$0 \le h \le 12$ $-11 \le k \le 0$ $-18 \le l \le 18$
scan type	ω−2θ scans
θ range [°]	2.33−26.29
linear abs., μ [cm^{-1}]	4.62
no. of refls. measd.	2881
no. of refls. unique	2721
cut-off for obsd. data	$I > 2\sigma(I)$
no. of unique obsd. data	2053
$R(F^2)$	0.0406
no. of parameters	163
$Rw(F^2)$	0.0652
G.O.F.	1.059
ρ_{max}/ρ_{min} [e/Å^3]	0.36/−0.47

$C_{18}H_{16}Cl_3NO_2$ (384.70): calcd. C 56.20, H 4.19, N 3.64, Cl 27.65; found C 55.98, H 4.22, N 3.50, Cl 27.78.

Methyl 2,2-Diphenyl-3-(trichloromethyl)aziridine-1-carboxylate (4b): Yield: 7%, m.p. 120°C. − IR (KBr): $\tilde{\nu}$ = 1725 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 3.65 (s, 3 H, CO_2CH_3), 4.55 (s, 1 H, $CHCCl_3$), 7.30−7.65 (m, 10 H, arom. H). − ^{13}C NMR ($CDCl_3$): δ = 53.6 (q, J = 148 Hz, CO_2CH_3), 58.2 (d, J = 174 Hz, $CHCCl_3$), 60.6 (s, Cq), 96.1 (s, CCl_3), 127.5−129.5 (6 signals for 10 arom. CH), 135.7 (s, arom. C), 136.9 (s, arom. C), 160.0 (s, CO). − $C_{17}H_{14}Cl_3NO_2$ (370.67): calcd. C 55.10, H 3.81, N 3.78, Cl 28.69; found C 55.19, H 3.76, N 3.81, Cl 28.76.

Reaction at 20°C: A solution of diphenyldiazomethane (10 mmol) and *N*-ethyloxy- or *N*-methyloxycarbonyl-*N*-(2,2,2-trichloroethylidene)amine (10 mmol) in toluene (15 mL) was stirred at room temperature for about 30 h. The solvent was then evaporated at room temperature, and the remaining white solid was collected by filtration. Methyl- and ethyl 2,2-diphenyl-5-trichloromethyl-Δ^3-1,3,4-triazoline-1-carboxylates **6a** and **6b** were obtained as white powders (each 7 mmol, 70%).

(a) Synthesis of Ethyl 2,2-Diphenyl-5-(trichloromethyl)-Δ^3-1,3,4-triazoline-1-carboxylate (6a): Yield: 70%, white powder, m.p.(dec) 103°C. − IR (KBr): $\tilde{\nu}$ = 1706 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 0.65 (br. s, 3 H, $CO_2CH_2CH_3$), 3.40−4.00 (2 br. s, AB part of ABX_3, 2 H, $CO_2CH_2CH_3$), 6.60−7.90 (m, 11 H, 10 arom. CH + $CHCCl_3$). − ^{1}H NMR ([D$_8$]THF): δ = 0.65 (br. s, 3 H, $CO_2CH_2CH_3$), 3.50−3.90 (2 br. s, AB part of ABX_3, 2 H, $CO_2CH_2CH_3$), 6.80−7.90 (m, 10 H, arom. H), 7.60 (s, 1 H, $CHCCl_3$). − ^{13}C NMR ($CDCl_3$): δ = 13.2 (q, J = 127 Hz, $CO_2CH_2CH_3$), 62.8 (t, J = 148 Hz, $CO_2CH_2CH_3$), 96.2 (s, CCl_3), 109.6 (d, J = 166 Hz, $CHCCl_3$), 115.8 (s, Cq, C-4), 125.0−131.0 (8 signals for 10 arom. CH), 135.8 (s, arom. C), 137.6 (s, arom. C), 155.5 (s, CO). − MS (70 eV); *m/z* (%): 412 (11.4) [M$^+$ + H], 348 (86.2) [M$^+$ − Cl − N$_2$]. − $C_{18}H_{16}Cl_3N_3O_2$ (411.71): calcd. C 52.39, H 3.91, N 10.18, Cl 25.77; found C 52.33, H 3.90, N 9.65, Cl 25.49.

(b) Synthesis of Methyl 2,2-Diphenyl-5-(trichloromethyl)-Δ^3-1,3,4-triazoline-1-carboxylate (6b): Yield: 70%, white powder, m.p.(dec) 109°C. − IR (KBr): $\tilde{\nu}$ = 1710 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 3.25 (br. s, 3 H, CO_2CH_3), 6.70−7.90 (m, 11 H, 10 arom. CH + $CHCCl_3$). − ^{13}C NMR ($CDCl_3$): δ = 53.0 (q, J = 148 Hz, CO_2CH_3), 96.0 (s, CCl_3), 109.3 (d, J = 166 Hz, $CHCCl_3$), 116.0 (s, Cq, C-2), 127.3−129.9 (4 signals for 10 arom. CH), 135.6 (s, arom. C), 137.2 (s, arom. C), 156.0 (s, CO). − $C_{17}H_{14}Cl_3N_3O_2$ (398.68): calcd. C 51.22, H 3.54, N 10.54, Cl 26.68; found C 51.17, H 3.62, N 10.32, Cl 26.65.

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[13] Crystallographic data for the structure **3** reported in this paper (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-104494. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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