Nucleophilic Additions of Sodium Alkoxides to 4,4-Dichloro-1,1-diphenyl-2-azabuta-1,3-diene

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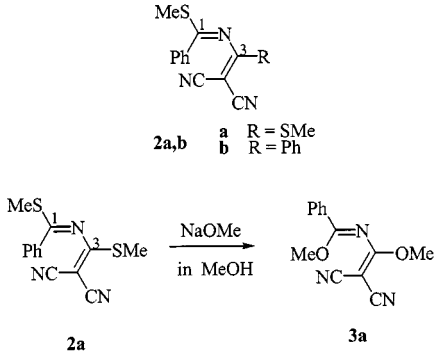
Keywords:

The reaction of some sodium alkoxides with 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene is described. Whereas sodium methoxide, ethoxide or isopropoxide leads to 1,3-bis(alkoxy)- and/or 1,3,4-tris(alkoxy)-2-azabut-2-enes, the sodium salt of ethyl glycolate gives a Δ^2-oxazoline. Mechanisms for the formation of these products are proposed.

Introduction

As a part of our research on the reactivity of some 1,3-dipoles with *N*-ethoxycarbonyl-*N*-(2,2,2-trichloroethylidene)amine,[1] we have reported[1c] the unexpected synthesis of 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene (**1**) from the reaction with diphenyldiazomethane. We subsequently undertook a study of the reactivity of this new azadiene.

Whereas nucleophilic substitutions at the C=N bond of imidoyl chlorides have been previously studied,[2–6] only one example of nucleophilic attack on substituted 2-azabuta-1,3-dienes **2** has been reported by A. Lorente et al.[7] (Scheme 1). In all cases, the authors observed nucleophilic substitutions of the methylthio group, on the C of the C=N, by a nucleophile (methoxide,[7a] pyrrolidine,[7a] methanethiolate,[7b] amines or hydrazines[7c]). These substitutions are accompanied by the isomerization of the C=N bond. Moreover, nucleophilic substitution at the C(3) has only been observed with the methoxide anion when the azabutadiene **2a** bears a good leaving group on this atom (Scheme 1).



Scheme 1. The work of Lorente et al.[7a][7b]

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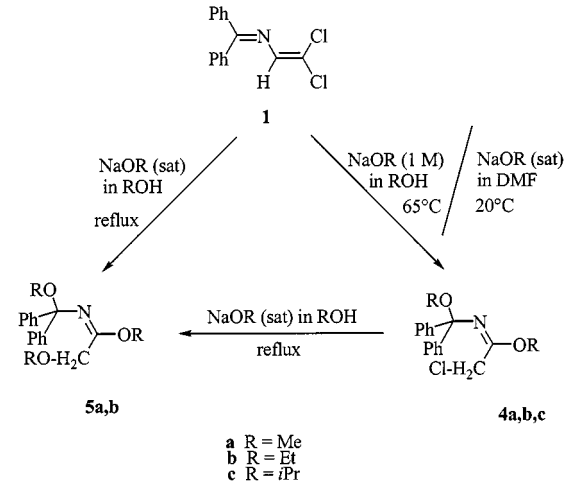
Herein we describe the reactions of 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene (**1**) with sodium salts of some alcohols: methanol, ethanol, 2-propanol and ethyl glycolate.

Results and Discussion

Azadiene **1** was placed in a refluxing saturated solution of sodium methoxide (24 hours) or ethoxide (48 hours) in the corresponding alcohol. After washing with water and ether extraction, the products **5a** and **5b** were isolated (Scheme 2).



Scheme 2. Reaction of azadiene **1** with sodium methoxide, ethoxide and isopropoxide

The structure of **5a** was unambiguously established by an X-ray diffraction study (Figure 1).

At lower temperature (65 °C) and lower alkoxide concentration (1 M), the compounds **4a, 4b** and **4c** were obtained after 3 hours (Scheme 2). The structure of **4b** was verified by an X-ray-crystallographic analysis (Figure 2).

Moreover, treatment of the compounds **4a** and **4b** with sodium methoxide or ethoxide affords the products **5a** and **5b** by a nucleophilic substitution of the chlorine atom (Scheme 2). Since the azabutenes **4** have two alkoxy groups

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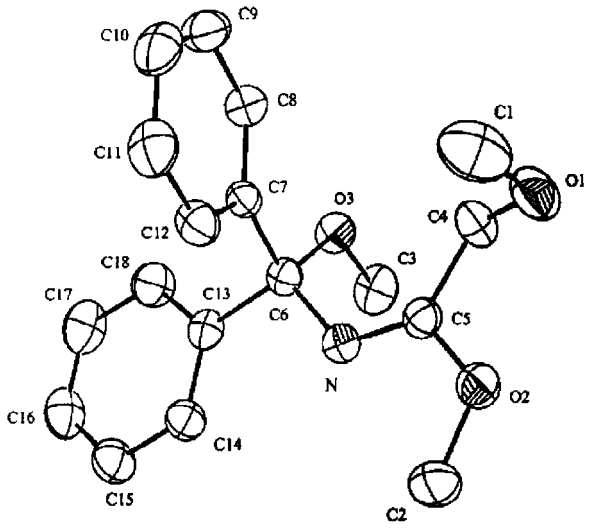


Figure 1. ORTEP plot (50% probability level) of the molecular structure of **5a**

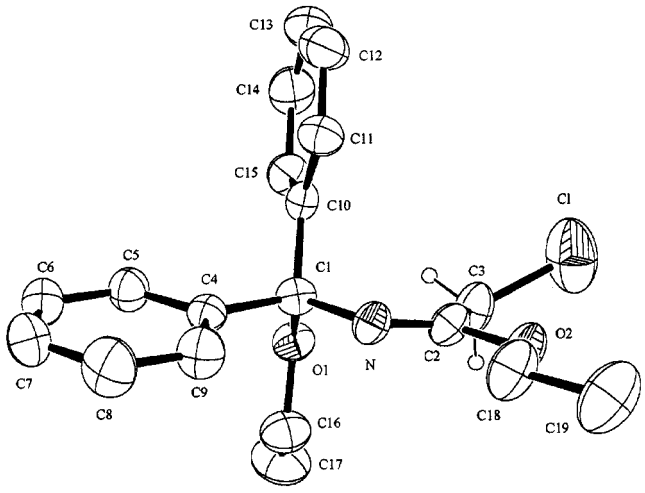
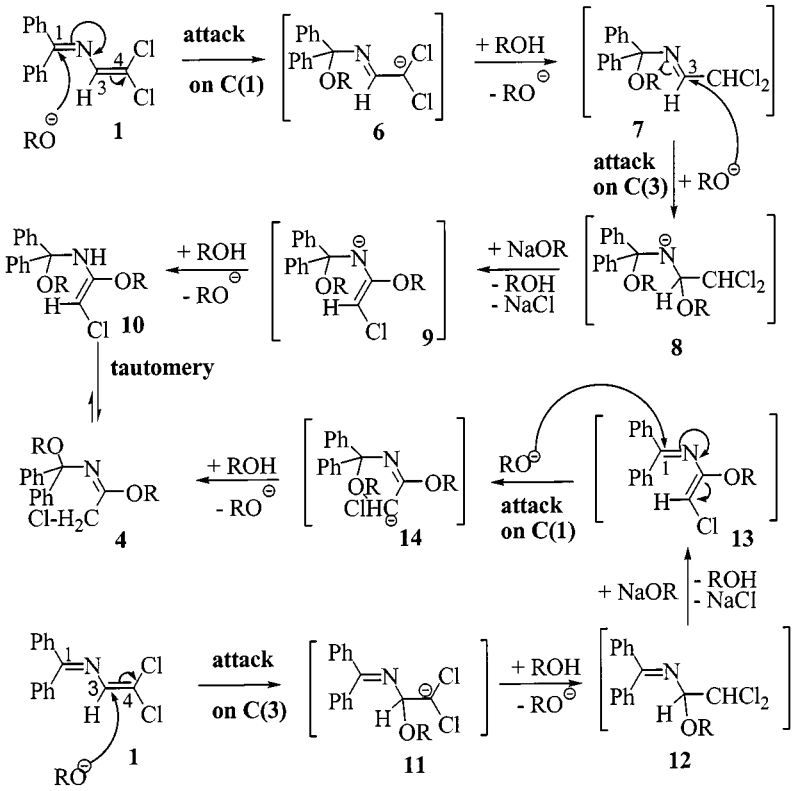


Figure 2. ORTEP plot (50% probability level) of the molecular structure of **4b**



Scheme 3. Possible mechanisms of formation of the azabutenes **4**

at the positions (1) and (3), two mechanisms for their formation are possible: either, the first nucleophilic attack occurs at C(1), or at C(3) of the azadiene **1** (Scheme 3).

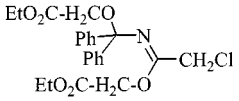
However, we cannot distinguish between these two pathways. The first mechanism would lead to the compound **10**, but since this compound presents an enamine with a secondary amine function, it is expected to tautomerise easily to its imine structure **4** which is the result of the alternative reaction sequence. Nevertheless, the results obtained with ethyl glycolate (vide infra) seem to indicate the second mechanism [nucleophilic attack at C(3), and then at the C(1) atom of the azadiene].

Moreover, the X-ray crystallographic determination of the structures of **5a** (Figure 1) and **4b** (Figure 2) shows that we obtained only the *E* stereoisomer. This observation implies that the configuration and conformation of the species **9** or **13** are these presented in Scheme 3 and are the structures which are less hindered.

Under the same conditions (solution of sodium salt in the corresponding alcohol), sodium isopropoxide gave only

compound **4c** with a poor yield (20%) and the sodium salt of ethyl glycolate was not soluble. So, we tried to work in anhydrous DMF (aprotic solvent), which dissolves the sodium salt of ethyl glycolate. The reaction of **1** with sodium methoxide, ethoxide or isopropoxide in anhydrous DMF gives, after the usual workup, the same products **4a**, **4b** and **4c**, respectively (Scheme 2). But, in this solvent, **5** has never been detected.

The reaction of azadiene **1** with the sodium salt of ethyl glycolate in anhydrous DMF leads, after the usual workup and chromatography on a column of neutral alumina, to a compound for which the spectroscopic data are not consistent with the expected structure **4d** (Figure 3).



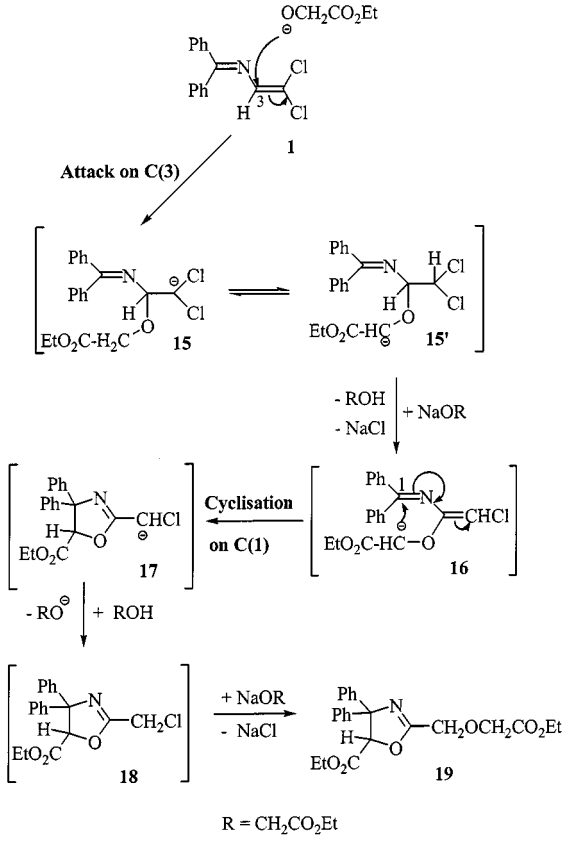
4d

Figure 3. Reaction of azadiene **1** with sodium salt of ethylglycolate: expected structure

In the ^{1}H NMR spectrum, we could see the signals of two ethoxycarbonyl groups. For structure **4d** the ^{1}H NMR spectrum would exhibit three singlets integrating for two hydrogens for the three methylene groups. But in our case, only two such signals are present and one other singlet integrating for only one H. Moreover, the hydrogen atoms of the methylene group of one of the ester functions are diastereotopic. This is not in agreement with the structure **4d**. In order to establish the structure and the mechanism of formation of this compound, we examined the different possibilities of successive nucleophilic attacks of the ethyl glycolate anion on the azadiene **1**. The first attack can take place at one of the three electrophilic centres C(1), C(3) or C(4) of azadiene **1**. However, the previous results with alkoxides indicated that the first addition never occurs at the C(4) position. So, we have only two possibilities for the first attack: either at the position C(1) or C(3). Examination of these two possibilities allows us to propose the mechanism which leads to the only structure which is in good agreement with the data (Scheme 4).

The first step yields the carbanion **15**, which is in equilibrium with its tautomeric form **15′**. The basicity of the solution makes possible the evolution of **15′** to the conjugated azadienic anion **16**. A second nucleophilic attack on the carbanion **16** by the alkoxide is disfavoured because of charge repulsion. However, **16** contains both nucleophilic and electrophilic centres, and so cyclisation may occur. The carbanionic intermediate **17** is formed by intramolecular attack at C(1). This intermediate is then protonated to the oxazoline **18** by the ethyl glycolate previously formed (step **15** → **16**). Finally, a nucleophilic substitution leads to the oxazoline **19**. This structure is in complete agreement with the NMR spectroscopic data.

So, the reaction sequence is very similar to that we have observed in the case of the alkoxides: first, a nucleophilic attack at C(3) of the azadiene **1**, followed by an attack at C(1) (intramolecular in this case), and, finally, a nucleophilic substitution at the carbon which was C(4) in the initial azadiene **1**.



Scheme 4. Mechanism leading to the oxazoline **19**

Conclusion

This work has established the mechanism of nucleophilic reaction of alkoxides with 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene. We have shown that it consists of a first nucleophilic addition at the C(3) of the azadiene **1**, then a second nucleophilic attack at C(1) (by the alkoxide or by the carbanion in the case of glycolate), and, finally, a nucleophilic substitution of the chlorine atom on the initial position (4) in **1**. So, while Lorente et al. have observed only substitutions of the thiomethyl group at the positions (1) and/or (3) by a nucleophilic species, we have here a particular behaviour bringing into the reaction the whole azadienic system.

Work is in progress to extend this study to thiolates, sodium salts of amines and other nucleophiles.

Experimental Section

General: IR spectra (KBr) were recorded with a Bio-Rad FTS-7 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker Spectrospin AC 200 spectrometer operating at 200 MHz for ^{1}H and at 50.3 MHz for ^{13}C. Chemical shifts are measured relative to TMS in $CDCl_3$ or [D_6]DMSO as solvent. Analytical data were obtained by the Elemental Analysis Centre of Dijon (France).

Melting points were determined with an Electrothermal 9200 and are not corrected. The synthesis of 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene was described in our previous paper.[1c]

Reactions in Alcoholic Solution at 65 °C. – General Procedure: 4,4-Dichloro-1,1-diphenyl-2-azabuta-1,3-diene (**1**) (1.1 mmol) was heated at 65 °C in a 1 M solution of sodium alkoxide (6 mmol) in the corresponding alcohol (6 mL) for 3 h. The reaction mixture was poured into water (100 mL) and then extracted with ether (150 mL). The organic phase was washed with water (3 × 50 mL), dried (Na_2SO_4) and the solvents evaporated. The crude product was purified by recrystallization or chromatography on a column of neutral Al_2O_3 with toluene as eluent.

(*E*)-4-Chloro-1,3-bis(methoxy)-1,1-diphenyl-2-azabut-2-ene (4a): Yield: 60%; colourless oil. – *Rf* = 0.95. – IR (film): $\tilde{\nu}$ = 1659 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 3.10 (s, 3 H, OCH_3), 3.97 (s, 2 H, CH_2Cl), 3.99 (s, 3 H, OCH_3), 7.10–7.70 (m, 10 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 38.0 (t, *J* = 153 Hz, *C*-4), 50.5 (q, *J* = 143 Hz, O*C*H$_3$), 54.0 (q, *J* = 146 Hz, O*C*H$_3$), 90.6 (s, *C*-1), 126.2–128.2 (3 signals for 10 aromatic *C*H), 145.8 (s, 2 aromatic *C*), 159.5 (s, *C*=N). – $C_{17}H_{18}ClNO_2$ (303.79): calcd. C 67.21, H 5.97, N 4.61; found C 67.55, H 6.09, N 4.52.

(*E*)-4-Chloro-1,3-bis(ethoxy)-1,1-diphenyl-2-azabut-2-ene (4b): Yield: 59%; colourless powder; m.p. 58 °C (EtOH). – IR (KBr): $\tilde{\nu}$ = 1659 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 1.20 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$–CH_3), 1.45 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$–CH_3), 3.25 (q, ^3J = 7.1 Hz, 2 H, OCH_2–CH$_3$), 3.97 (s, 2 H, CH_2Cl), 4.42 (q, ^3J = 7.1 Hz, 2 H, OCH_2–CH$_3$), 7.10–7.70 (m, 10 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (q, *J* = 145 Hz, *C*H$_3$), 15.2 (q, *J* = 127 Hz, *C*H$_3$), δ = 37.9 (t, *J* = 153 Hz, *C*-4), 58.0 (t, *J* = 144 Hz, O*C*H$_2$), 62.1 (t, *J* = 149 Hz, O*C*H$_2$), 90.1 (s, *C*-1), 126.0–128.0 (3 signals for 10 aromatic *C*H), 146.5 (s, 2 aromatic *C*), 159.2 (s, *C*=N). – MS (CI, chloroform); *m*/*z* (%): 332 (5) [M^+ + H], 296 (29) [M^+ – Cl], 286 (21) [M^+ – OEt], 254 (14) [M^+ – Ph], 211 (100) [$C_{15}H_{15}O^+$]. – $C_{19}H_{22}ClNO_2$ (331.84): calcd. C 68.78, H 6.68, N 4.22; found C 69.00, H 6.82, N 4.12.

(*E*)-4-Chloro-1,3-bis(isopropoxy)-1,1-diphenyl-2-azabut-2-ene (4c): Yield: 20%; colourless oil. – *Rf* = 0.90. – IR (film): $\tilde{\nu}$ = 1659 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 1.05 [d, ^3J = 6.0 Hz, 6 H, CH(CH_3)$_2$], 1.45 [d, ^3J = 6.3 Hz, 6 H, CH(CH_3)$_2$], 3.75 [sept, ^3J = 6.0 Hz, 1 H, OC*H*(CH$_3$)$_2$], 3.92 (s, 2 H, CH_2Cl), 5.42 [sept, ^3J = 6.3 Hz, 1 H, OC*H*(CH$_3$)$_2$], 7.10–7.70 (m, 10 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.5 [q, *J* = 125 Hz, OCH(*C*H$_3$)$_2$], 24.0 [q, *J* = 126 Hz, OCH(*C*H$_3$)$_2$], 39.0 (t, *J* = 153 Hz, *C*-4), 66.5 [d, *J* = 142 Hz, O*C*H(CH$_3$)$_2$], 68.3 [d, *J* = 147 Hz, O*C*H(CH$_3$)$_2$], 90.0 (s, *C*-1), 126.0–128.0 (3 signals for 10 aromatic *C*H), 147.0 (s, 2 aromatic *C*), 159.5 (s, *C*=N). – $C_{21}H_{26}ClNO_2$ (359.90): calcd. C 70.08, H 7.28, N 3.89; found C 70.22, H 7.36, N 3.83.

Reactions in Refluxing Alcohol. – General Procedure: 4,4-Dichloro-1,1-diphenyl-2-azabuta-1,3-diene (1.1 mmol) was stirred and refluxed in a saturated solution of sodium alkoxide (6 mmol) in the corresponding alcohol (3 mL) for the appropriate time (see below). The reaction mixture was then poured into water (100 mL) and extracted with ether (150 mL). The organic phase was washed with water (3 × 50 mL), dried (Na_2SO_4) and the solvents were evaporated. The crude product was purified by recrystallization or chromatography on a column of neutral Al_2O_3 with toluene as eluent.

(*E*)-1,3,4-Tris(methoxy)-1,1-diphenyl-2-azabut-2-ene (5a): Reaction time: 24 h; yield: 60%; colourless powder; m.p. 60 °C (EtOH). – IR (KBr): $\tilde{\nu}$ = 1658 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 3.04 (s, 3 H, OCH_3), 3.06 (s, 3 H, OCH_3), 3.97 (s, 2 H, CH_2OMe), 3.99 (s, 3 H, OCH_3), 7.10–7.70 (m, 10 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 50.2 (q, *J* = 142 Hz, O*C*H$_3$), 53.5 (q, *J* = 146 Hz, O*C*H$_3$), 58.8 (q, *J* = 142 Hz, O*C*H$_3$), 69.2 (t, *J* = 146 Hz, *C*-4), 90.5 (s, *C*-1), 126.5–128.0 (3 signals for 10 aromatic *C*H), 146.0 (s, 2 aromatic *C*), 162.5 (s, *C*=N). – $C_{18}H_{21}NO_3$ (299.38): calcd. C 72.22, H 7.07, N 4.68; found C 72.44, H 6.99, N 4.61.

(*E*)-1,3,4-Tris(ethoxy)-1,1-diphenyl-2-azabut-2-ene (5b): Reaction time: 48 h; yield: 60%; yellow oil. – *Rf* = 0.70. – IR (film): $\tilde{\nu}$ = 1658 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 1.01 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$–CH_3), 1.17 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$–CH_3), 1.44 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$–CH_3), 3.10 (q, ^3J = 7.0 Hz, 2 H, OCH_2–CH$_3$), 3.20 (q, ^3J = 7.0 Hz, 2 H, OCH_2–CH$_3$), 3.97 (s, 2 H, CH_2–OEt), 4.45 (q, ^3J = 7.1 Hz, 2 H, OCH_2–CH$_3$), 7.05–7.70 (m, 10 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.2 (q, *J* = 145 Hz, OCH$_2$–CH$_3$), 14.7 (q, *J* = 145 Hz, OCH$_2$–CH$_3$), 15.3 (q, *J* = 127 Hz, OCH$_2$–CH$_3$), 57.6 (t, *J* = 153 Hz, O*C*H$_2$), 61.5 (t, *J* = 144 Hz, O*C*H$_2$), 66.3 (t, *J* = 149 Hz, O*C*H$_2$), 67.2 (t, *J* = 148 Hz, O*C*H$_2$), 89.9 (s, *C*-1), 126.0–133.0 (5 signals for 10 aromatic *C*H), 137.4 (s, 2 aromatic *C*), 162.4 (s, *C*=N). – $C_{21}H_{27}NO_3$ (341.45): calcd. C 73.87, H 7.97, N 4.10; found C 74.20, H 7.85, N 4.18.

Isolation of 1,3,4-Tris(alkoxy)-2-azabut-2-ene (5) from 4-Chloro-1,3-bis(alkoxy)-2-azabut-2-ene (4). – General Procedure: 1,3-Bis(alkoxy)-1,1-diphenyl-2-azabut-2-ene (**4**) (1.1 mmol) was stirred and refluxed in a saturated solution of sodium alkoxide (6 mmol) in the corresponding alcohol (3 mL) for the appropriate times. The reaction mixture was then poured into water (100 mL) and extracted with ether (150 mL). The organic phase was washed with water (3 × 50 mL), dried (Na_2SO_4) and the solvents were evaporated. The crude product was purified by recrystallization or chromatography on a column of neutral Al_2O_3 with toluene as eluent.

(*E*)-1,3,4-Tris(methoxy)-1,1-diphenyl-2-azabut-2-ene (5a): Reaction time: 24 h; yield: 90%.

(*E*)-1,3,4-Tris(ethoxy)-1,1-diphenyl-2-azabut-2-ene (5b): Reaction time: 48 h; yield: 90%.

Reactions in Anhydrous DMF. – General Procedure: 4,4-Dichloro-1,1-diphenyl-2-azabuta-1,3-diene (**1**) (1.1 mmol) was placed at room temperature in a saturated solution of sodium alkoxide (6 mmol) in anhydrous DMF (4 mL) for the appropriate time (see below). The reaction mixture was poured into water (100 mL) and extracted with ether (150 mL). The organic phase was washed with water (3 × 50 mL), dried (Na_2SO_4) and the solvents were evaporated. The crude product was purified by recrystallization in ethanol or chromatography on a column of neutral Al_2O_3 with toluene or ether as eluent.

(*E*)-4-Chloro-1,3-bis(methoxy)-1,1-diphenyl-2-azabut-2-ene (4a): Reaction time: 30 min; eluent: toluene; yield: 45%.

(*E*)-4-Chloro-1,3-bis(ethoxy)-1,1-diphenyl-2-azabut-2-ene (4a): Reaction time: 30 min; yield: 20%.

(*E*)-4-Chloro-1,3-bis(isopropoxy)-1,1-diphenyl-2-azabut-2-ene (4c): Reaction time: 30 min; eluent: toluene; yield: 40%.

Ethyl 2-Ethoxycarbonylmethylenoxymethyl-4,4-diphenyl-(2-oxazoline-5-carboxylate (25): Reaction time: 5 h; yield: 40%; eluent: ether; pale yellow oil. – *Rf* = 1.0. – IR (film): $\tilde{\nu}$ = 1749 cm^{-1} (C=O). – ^1H NMR ([D$_6$]DMSO): δ = 0.9 (t, ^3J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.25 (t, ^3J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 3.65 (2 qd, *JAB* = 25 Hz, ^3J = 7.2 Hz, AB part of ABX_3, 2 H, CO_2CH_2–CH$_3$), 4.20 (q, ^3J = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 4.40 (s, 2 H, OCH_2), 4.55 (s, 2 H, OCH_2), 5.85 (s, 1 H, OC*H*), 7.00–7.70 (m, 10

Table 1. Crystallographic data for **4b** and **5a**[8]

Crystal data	**5a**	**4b**
Empirical formula	$C_{18}H_{21}NO_3$	$C_{19}H_{22}ClNO_2$
Molecular mass	299.36	331.83
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Cell dimensions:		
a, Å	14.216(4)	8.475(1)
b, Å	7.780(2)	10.949(2)
c, Å	16.321(4)	11.211(2)
α, °	90	98.56(1)
β, °	111.02(3)	104.37(1)
γ, °	90	106.89(1)
V, Å^3	1684.9(8)	936.5(3)
T, K	296(1)	293(2)
Z	4	2
$\rho_{calcd.}$, g·cm^{-3}	1.180	1.177
$F(000)$	640	352
Data collection		
Diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4
Radiation, Å	λ(Mo-K_α) 0.71073	λ(Mo-K_α) 0.71073
Crystal size, mm	0.30 × 0.20 × 0.13	0.25 × 0.20 × 0.20
Monochromator	graphite	graphite
Reciprocal lattice segment	$-16 \le h \le 17$ $-12 \le k \le 12$ $-13 \le l \le 12$	$0 \le h \le 9$ $-9 \le k \le 9$ $-20 \le l \le 0$
Scan type	ω-2φ scans	ω scans
φ range, °	2.37–26.30	2.43–24.64
Linear abs. μ, cm^{-1}	0.80	2.12
No. refl. measd.	5897	3397
No. refl. unique	3403	3160
Cut off for obsd. data	$I > 2\sigma(I)$	$I > 2\sigma(I)$
No. of unique obsd. data	1410	1316
$R(F^2)$	0.0471	0.0557
No. of parameters	199	208
$wR(F^2)$	0.1042	0.1405
G.O.F.	0.938	1.195
ρ_{max}/ρmin, e/Å^3	0.14/–0.23	0.33/–0.32

H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 13.4 (q, J = 127 Hz, CH_3), 14.0 (q, J = 127 Hz, CH_3), 60.9 (t, J = 148 Hz, CO_2CH_2), 61.3 (t, J = 148 Hz, CO_2CH_2), 64.9 (t, J = 145 Hz, OCH_2), 67.8 (t, J = 145 Hz, OCH_2), 83.5 (s, *C*-4), 85.7 (t, J = 157 Hz, *C*-5), 126.5–128.5 (6 signals for 10 aromatic *C*H), 140.3 (s, aromatic *C*), 143.9 (s, aromatic *C*), 162.3 (s, *C*=N), 167.8 (s, *C*=O), 169.3 (s, *C*=O). – $C_{22}H_{25}NO_6$ (399.45): calcd. C 66.15, H 6.31, N 3.51; found C 66.48, H 6.43, N 3.44.

X-ray Crystal Structures of 4b and 5a:[8] The structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97. Refinement was done by a full-matrix least-squares method based on F^2 values with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms are in calculated positions. Crystallographic data are given in Table 1.

Selected bond lengths (Å) and angles (°) for **4b:** C1–C3 1.752 (5), O1–C1 1.426 (4), O1–C16 1.427 (5), O2–C2 1.352 (4), O2–C18 1.437 (5), N–C2 1.257 (4), N–C1 1.458 (4), C2–C3 1.492 (5), C16–C17 1.489 (6), C18–C19 1.453 (5); C1–O1–C16 115.6 (3), C2–O2–C18 116.1 (3), C2–N–C1 121.2 (3), O1–C1–N 113.1 (3), O1–C1–C10 106.6 (3), N–C1–C10 110.8 (3), O1–C1–C4 109.4 (3), N–C1–C4 108.3 (3), C10–C1–C4 108.5 (3), N–C2–O2 120.2 (3), N–C2–C3 129.1 (4), O2–C2–C3 110.6 (4), C2–C3–Cl 114.2 (3), O1–C16–C17 108.2 (4), O2–C18–C19 108.8 (4).

Selected bond lengths (Å) and angles (°) for **5a:** O1–C4 1.402 (3), O1–C1 1.407 (4), O2–C5 1.356 (3), O2–C2 1.427 (3), O3–C3 1.427 (3), O3–C6 1.427 (3), N–C5 1.265 (3), N–C6 1.465 (3), C4–C5 1.506 (3); C4–O1–C1 111.5 (2), C5–O2–C2 116.6 (2), C3–O3–C6 115.25 (18), C5–N–C6 121.1 (2), O1–C4–C5 114.0 (2), N–C5–O2 119.4 (2), N–C5–C4 130.6 (2), O2–C5–C4 110.0 (2), O3–C6–N 112.30 (17), O3–C6–C7 106.60 (18), N–C6–C7 110.58 (19), O3–C6–C13 110.15 (19), N–C6–C13 108.50 (19), C7–C6–C13 108.66 (17).

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[8] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-129237 (**4b**) and -129238 (**5a**). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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