organic papers

4-Chloro-1,1-diphenyl-3-(1-pyrrolyl)-2-azabuta-1,3-diene

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.099
Data-to-parameter ratio = 16.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{19}H_{15}ClN_2$, is the sole stable product resulting from nucleophilic attack of the sodium salt of pyrrole on 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene. The mechanism of its formation is briefly discussed.
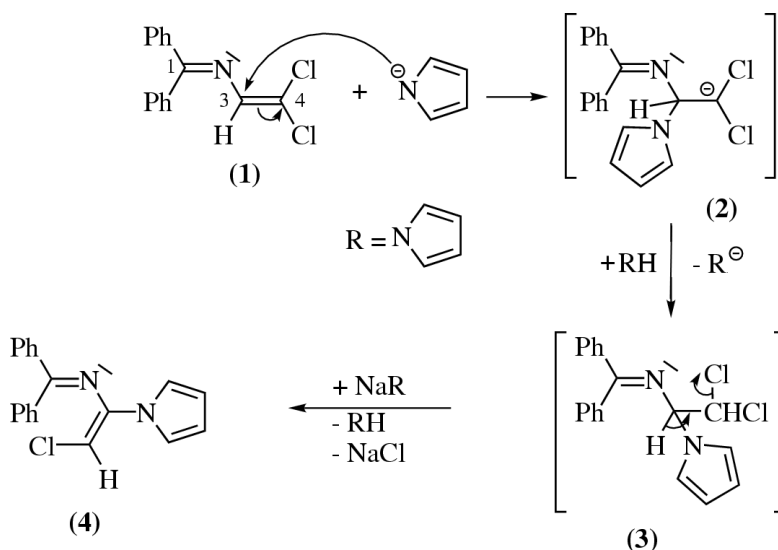
Comment

As a part of our research on the reactivity of 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene, (1), towards different nucleophiles, we have already described its reactions with some sodium alkoxides (Jacquot *et al.*, 2000). The reaction of the azadiene (1) with the sodium salt of pyrrole leads to a new product (4) through an addition–elimination process. X-ray structure analysis established that (4) is (*E*)-4-chloro-1,1-diphenyl-3-(1-pyrrolyl)-2-azabuta-1,3-diene, in which the chloro and the *N*-pyrrole substituents are in a *trans* configuration (Fig. 1). There are two independent organic molecules in the asymmetric unit of the centrosymmetric triclinic cell. They exhibit slightly different conformations, which may be due to the packing in the crystal.

This structure allows us to comment on the mechanism and the stereochemistry of formation of (4). Some semi-empirical calculations (extended Hückel and PM3) show that the electrophilic power of the C atoms of the azadiene linkage in (1) (estimated from calculated charges) increases in the order C4 < C3 < C1 (see Scheme above). Thus, the most electrophilic atom C1 should undergo the nucleophilic attack of the anion. However, this atom is protected by the presence of two rather bulky phenyl groups. Consequently, the pyrrolyl attack operates on C3, as already observed with alkoxide anions (Jacquot
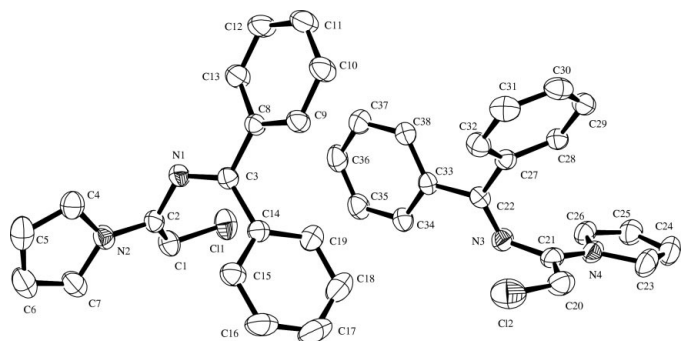
Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (4), shown with 50% probability displacement ellipsoids.

et al., 2000). Note, however, that the pyrrolyl action on (1) leads to the sole compound (4), while with the alkoxides it was possible to get up to three substitutions. The second step [leading to (4)] consists of *trans*-elimination of HCl from the favourable antiperiplanar conformation of H and Cl atoms [intermediate (3)], facilitated by the presence of sodium and pyrrole ions in the reaction mixture. There is only partial conjugation between the pyrrole and the C=C double bond as indicated by the values of the dihedral angles pyrrole/NC=CCl [21.1 (1)° for the molecule with atoms C1/C2, and 8.3 (3)° for the molecule with atoms C20/C21]. The total conjugation of the planar azadiene likage in (1) (Jacquot *et al.*, 1999) is broken in (4). The dihedral angles ClC=CN(pyrrole)/N=CC$_{ipso}$C$_{ipso}$ are close to 74° in both molecules.

Experimental

A mixture of 4.4 mmol of NaH, 8 ml of anhydrous DMF and 0.28 ml of pyrrole was stirred for 45 min. Then, a solution of 1.1 mmol of azadiene (1) in DMF was added. After 30 min of stirring, the mixture was poured into water and extracted with diethyl ether. The organic solution was washed three times with water, dried over anhydrous sodium sulfate and evaporated. The crude residue (4) was recrystallized from ethanol (70% yield).

Crystal data

C$_{19}$H$_{15}$ClN$_2$	$Z = 4$
$M_r = 306.78$	$D_x = 1.258$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.910\,(1)$ Å	Cell parameters from 25
$b = 10.411\,(1)$ Å	reflections
$c = 16.401\,(1)$ Å	$\theta = 4.8$–$18.6°$
$\alpha = 89.88\,(1)°$	$\mu = 0.23$ mm^{-1}
$\beta = 73.19\,(1)°$	$T = 293\,(2)$ K
$\gamma = 88.89\,(1)°$	Prism, yellow
$V = 1619.5\,(2)$ Å^3	$0.4 \times 0.3 \times 0.2$ mm

Data collection

Enraf–Nonius CAD-4	$\theta_{max} = 26.3°$
diffractometer	$h = -12 \rightarrow 0$
ω scans	$k = -12 \rightarrow 12$
6954 measured reflections	$l = -20 \rightarrow 19$
6557 independent reflections	3 standard reflections
4267 reflections with $I > 2\sigma(I)$	frequency: 120 min
$R_{int} = 0.013$	intensity decay: 1.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.049P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.3756P]$
$wR(F^2) = 0.099$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
6557 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
397 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cl1—C1	1.715 (2)	N3—C22	1.283 (2)
Cl2—C20	1.716 (3)	N3—C21	1.402 (2)
N1—C3	1.284 (2)	N4—C26	1.371 (2)
N1—C2	1.396 (2)	N4—C23	1.382 (3)
N2—C4	1.368 (3)	N4—C21	1.412 (3)
N2—C7	1.374 (3)	C1—C2	1.323 (3)
N2—C2	1.412 (2)	C20—C21	1.317 (3)
C3—N1—C2	121.5 (2)	C8—C3—C14	118.58 (15)
C22—N3—C21	121.5 (2)	C21—C20—Cl2	122.4 (2)
C2—C1—Cl1	121.9 (2)	C20—C21—N3	125.1 (2)
C1—C2—N1	124.7 (2)	C20—C21—N4	121.9 (2)
C1—C2—N2	120.8 (2)	N3—C21—N4	112.6 (2)
N1—C2—N2	113.9 (2)	N3—C22—C33	117.1 (2)
N1—C3—C8	117.1 (2)	N3—C22—C27	123.2 (2)
N1—C3—C14	124.3 (2)	C33—C22—C27	119.7 (2)

H atoms were included in calculated positions and treated in a riding model with isotropic displacement parameters set to 1.2 times those of the C atoms bearing them.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *PROCESS* in *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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