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Nitro Derivatives of 3-Acetamidobenzyl Acetate

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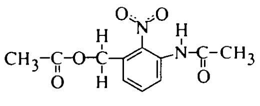
Abstract

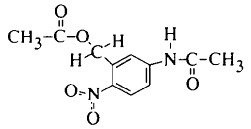
The structures of 3-acetamido-2-nitrobenzyl acetate, $C_{11}H_{12}N_2O_5$, (I), 3-acetamido-6-nitrobenzyl acetate, $C_{11}H_{12}N_2O_5$, (II) and 3-acetamido-6-nitrobenzyl acetate monohydrate, $C_{11}H_{12}N_2O_5.H_2O$, (III), have been determined at low temperature; 150 K for (I) and (III), and 100 K for (II). The molecules differ mainly in the conformation of the acetamide and acetate groups with respect to the aromatic ring plane: in (II) they are almost coplanar, in (I) they are markedly distorted from planarity, while in (III) they are intermediate. The nitro group is twisted with respect to the aromatic ring in (I), but is almost coplanar with it in (II) and (III). In all three structures, one of the nitro O atoms is directed towards a methylene C atom, approximately bisecting the H—C—H angles, and intramolecular C—H···O hydrogen bonds involving the aromatic H and carboxyl O atoms are observed. In all three cases, the crystal structures are stabilized by intermolecular N—H···O [and O—H···O in (III)], as well as weak C—H···O, hydrogen bonds.

Comment

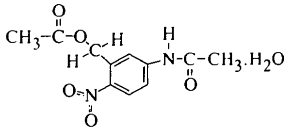
The electronic structure of nitrobenzene and its substituted derivatives has been the subject of longstanding interest for organic chemists. Conjugation between the nitro group and the aromatic system was suggested many years ago (Trotter, 1960). In recent years, many spectroscopic, structural and theoretical studies have shown that the quinoidal structure plays only a minimal role in the resonance structures (Butcher *et al.*, 1991; Vinson & Dannenberg, 1989; Bromilow *et al.*, 1980; Hiberty & Ohanessian, 1984). On the other hand, it is well known that the position of the nitro group in a nitrobenzene carrying one or more different substituents could strongly influence the conformation of the rest of the molecule (Butcher *et al.*, 1992). This paper describes two structural isomers of 3-acetamidobenzyl acetate with the nitro groups in positions 2 or 6. The structure of the 4-nitro isomer has been described previously (Rusek *et al.*, 1995).



(I)



(II)



(III)

The structures presented differ only in the position of the nitro group on the aromatic ring. Compound (III) is the monohydrate of compound (II). The molecules each have three different substituents connected to the benzyl skeleton, namely nitro, acetamido and acetate groups (Figs. 1, 2 and 3). In all three structures, the bond lengths in the aromatic and aliphatic parts are comparable within 3σ and similar to other aromatic nitro compounds (Allen *et al.*, 1991). The most significant difference observed is for the C4—C5 bond length [1.364 (4) Å in (II), but 1.386 (3) and 1.381 (2) Å in (I) and (III), respectively]. The bond angles are slightly different for all the structures, the biggest difference being observed for C2—C3—N1 [123.7 (2), 123.3 (3) and 115.8 (3)°, in (I), (II) and (III), respectively], probably as a result of the steric hindrance [in (I) and (II)] of the neighbouring nitro and acetamide groups in the aromatic ring. The widening of the C—C—N(amine) bond angle has been observed previously for other *o*-nitro amide aromatic compounds where the amide H atom is not involved in the intramolecular hydrogen bond (Allen *et al.*, 1991). In (III), the lower value of this angle is probably a consequence of the water molecule. The aromatic ring is slightly distorted from strict planarity, especially in (II), being slightly boat shaped, with C3 and C6 as the 'bows'; the largest deviation [0.021 (2) Å] from an aromatic ring plane occurs for C6 in (II).

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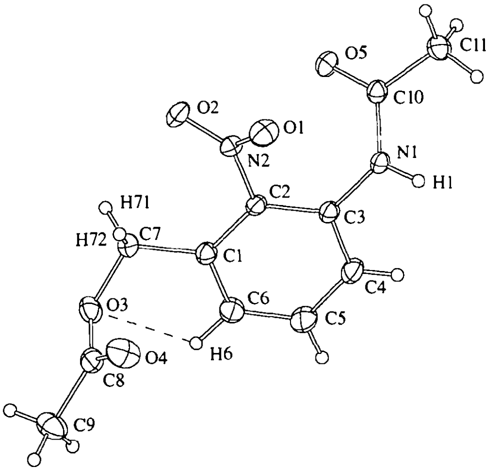

Fig. 1. The molecular structure and the numbering scheme of 3-acetamido-2-nitrobenzyl acetate, (I). Displacement ellipsoids are shown at the 50% probability level.

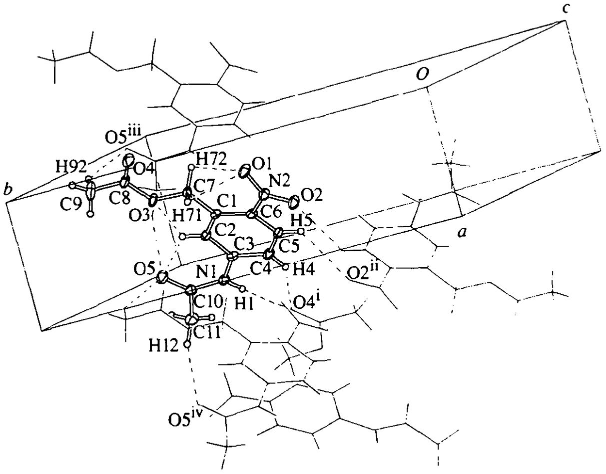

Fig. 2. The molecular structure, packing and numbering scheme of 3-acetamido-6-nitrobenzyl acetate, (II). Displacement ellipsoids are shown at the 50% probability level. The short intramolecular C—H···O interactions are shown as dashed and dotted lines.

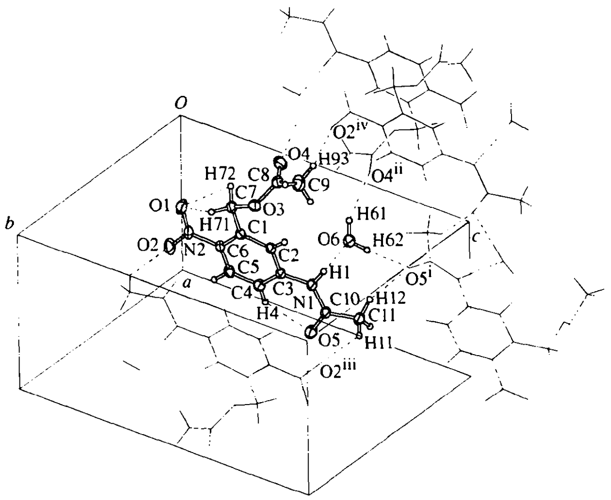

Fig. 3. The molecular structure, packing and numbering scheme of 3-acetamido-6-nitrobenzyl acetate monohydrate, (III). Displacement ellipsoids are shown at the 50% probability level.

The conformations of these molecules are rather different. Fig. 4 shows a superposition onto the aromatic rings of 2-, 4- and both 6-nitro forms. Molecule (II) is almost flat and its conformation is similar to the 4-nitro compound (Rusek *et al.*, 1995), while (I) and (III) are considerably distorted from planarity. In the case of molecule (I), the conformation is an effect of the steric hindrance of the substituent in the 2-position of the ring, between the amide and ester groups. The nitro substituent is twisted out of the ring plane by 43.5 (2)°. The neighbouring amine H atom does not participate in the intramolecular hydrogen bond to the nitro group. The acetate part is almost perpendicular, while the acetamide is *gauche* to the aromatic ring. In (II), the molecule is nearly planar, the largest deviation from the aromatic ring plane [0.502 (8) Å] occurring for the methyl C11 atom. The acetamide and ester chains are almost coplanar with the ring, with the same orientation of the acetamide as in the 4-nitro compound (Rusek *et al.*, 1995). Although the nitro O atoms do not participate in the intramolecular hydrogen bonds, the nitro group is almost coplanar with the aromatic ring, the angle between them being 15.9 (2)°. The conformation of molecule (III) is intermediate between those of (I) and (II). The acetamide part is almost coplanar with the ring and the furthest atom from the plane is O5 [0.478 (3) Å], while the acetate chain is twisted well out of the plane. The amide H atom is directed towards the acetate group, the opposite of the situation observed in (II) and in the

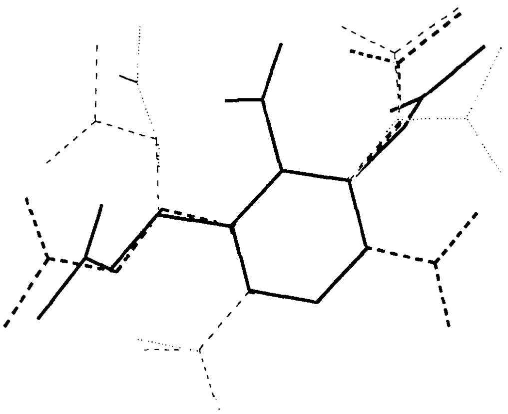

Fig. 4. Comparison of structures (I) (solid line), (II) (dashed thin line), (III) (dotted line) and 3-acetamido-4-nitrobenzyl acetate (Rusek *et al.*, 1995) (dashed bold line). The common feature is the aromatic ring.

4-nitro analogue. This is attributed to the water molecule, which makes fairly strong hydrogen bonds with the amide N and carbonyl O atoms. The nitro group is more coplanar with the ring than in (II), the angle between them being only 10.6 (2)°.

In all three structures, several intramolecular C—H···O hydrogen bonds with H···O ≤ 2.5 Å were found, and these are shown as dotted lines in Figs. 1, 2 and 3.

In (I) and (II), the molecules are arranged in three-dimensional networks *via* N—H···O and C—H···O hydrogen bonds (Tables 2 and 4). In these cases, there is one hydrogen bond between the amide H atom and the carboxyl O atom, O5 in (I) and O4 in (II) (Fig. 2). The C—H···O interactions are found between the aromatic H atoms, as well as between the aliphatic H atoms and the carboxyl and nitro O atoms. These interactions are particularly weak and the H···O distances are around 2.5 Å. In the crystals of (III), the water O6 atom is an acceptor of the H atom from the amide, while the carboxyl O4 and O5 atoms are acceptors of the H atoms from water. In this crystal, C—H···O intermolecular interactions are also observed, but in contrast to (I) and (II), only the aliphatic H atoms are involved in these interactions.

Experimental

The title compounds were prepared by the reaction of 3-acetamidobenzyl acetate with $Cu(NO_3)_2$ in acetic anhydride (Rusek *et al.*, 1995). 3-Acetamido-4-nitrobenzyl acetate was obtained as the major product (82%), while 3-acetamido-2-nitrobenzyl acetate and 3-acetamido-6-nitrobenzyl acetate were obtained as the minor ones (5 and 13%, respectively). The isomers were separated by liquid chromatography using ethyl acetate/chloroform (1:2) as eluent. Crystals of (I) were obtained by slow isothermal evaporation from ethyl acetate; those of (II) were obtained from absolute methanol, and for (III) they were obtained by slow evaporation from 97% ethanol.

Compound (I)

Crystal data

$C_{11}H_{12}N_2O_5$
$M_r = 252.23$
Triclinic
$P\bar{1}$
$a = 4.851\ (4)$ Å
$b = 6.288\ (5)$ Å
$c = 9.781\ (8)$ Å
$\alpha = 99.96\ (7)°$
$\beta = 101.26\ (7)°$
$\gamma = 91.04\ (7)°$
$V = 287.8\ (4)$ Å^3
$Z = 1$
$D_x = 1.455\ (2)$ Mg m^{-3}
D_m 1.42 Mg m^{-3} (at room temperature)
D_m measured by flotation in $CHCl_3/CH_2Cl_2$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 51 reflections
$\theta = 9–14°$
$\mu = 0.117$ mm^{-1}
$T = 150\ (1)$ K
Prism
0.5 × 0.4 × 0.1 mm
Yellow

Data collection

Kuma KM-4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
2011 measured reflections
1684 independent reflections
1504 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.060$
$\theta_{\rm max} = 30°$
$h = -6 \rightarrow 1$
$k = -8 \rightarrow 8$
$l = -13 \rightarrow 13$
3 standard reflections every 100 reflections intensity variation: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.105$
$S = 1.144$
1684 reflections
211 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.021$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: see *Experimental* below

Table 1. *Selected torsion angles for (I) (°)*

O1—N2—C2—C1	−43.4 (3)	C7—O3—C8—C9	−179.3 (2)
O2—N2—C2—C1	134.8 (2)	C3—N1—C10—O5	5.0 (3)
O1—N2—C2—C3	138.2 (2)	C3—N1—C10—C11	−175.2 (2)
O2—N2—C2—C3	−43.5 (3)	C8—O3—C7—C1	81.4 (3)
C2—C1—C7—O3	−164.4 (2)	C10—N1—C3—C4	124.8 (3)
C6—C1—C7—O3	14.4 (3)	C10—N1—C3—C2	−54.3 (3)
C7—O3—C8—O4	−0.5 (3)		

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O5$^{\rm i}$	0.88 (3)	1.95 (3)	2.813 (3)	168 (3)
C4—H4···O1$^{\rm ii}$	0.87 (4)	2.61 (3)	3.352 (4)	144 (2)
C5—H5···O4$^{\rm iii}$	0.98 (4)	2.55 (4)	3.282 (4)	131 (3)
C9—H93···O5$^{\rm iv}$	1.06 (4)	2.56 (4)	3.520 (4)	149 (3)
C11—H11···O3$^{\rm v}$	0.95 (4)	2.61 (4)	3.345 (4)	134 (3)
C11—H12···O4$^{\rm vi}$	0.90 (4)	2.54 (4)	3.398 (4)	160 (3)
C7—H71···O1	0.91 (2)	2.50 (3)	2.714 (3)	94 (2)
C7—H72···O1	0.98 (3)	2.55 (3)	2.714 (3)	89 (2)
C7—H71···O4	0.91 (2)	2.38 (3)	2.639 (3)	96 (2)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 + x, 1 + y, z$; (iii) $x, 1 + y, z$; (iv) $x, y - 1, z - 1$; (v) $1 + x, y, 1 + z$; (vi) $x, 1 + y, 1 + z$.

Compound (II)

Crystal data

$C_{11}H_{12}N_2O_5$
$M_r = 252.23$
Monoclinic
$P2_1/n$
$a = 4.874\ (7)$ Å
$b = 17.833\ (16)$ Å
$c = 13.277\ (15)$ Å
$\beta = 92.35\ (10)°$
$V = 1153\ (3)$ Å^3
$Z = 4$
$D_x = 1.453\ (2)$ Mg m^{-3}
D_m 1.40 (at room temperature)
D_m measured by flotation in aqueous KI

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 88 reflections
$\theta = 9–16°$
$\mu = 0.115$ mm^{-1}
$T = 100\ (2)$ K
Plate
1.0 × 0.6 × 0.03 mm
Dark yellow

Data collection

Kuma KM-4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
1914 measured reflections
1688 independent reflections
1400 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$
$\theta_{\rm max} = 30°$
$h = -6 \rightarrow 2$
$k = 0 \rightarrow 24$
$l = -18 \rightarrow 18$
3 standard reflections every 100 reflections intensity variation: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.122$
$S = 1.091$
1688 reflections
211 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.083P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.036$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected torsion angles for (II) (°)*

O1—N2—C6—C5	165.3 (3)	C7—O3—C8—C9	179.9 (3)
O2—N2—C6—C5	−16.2 (4)	C3—N1—C10—O5	5.9 (6)
O1—N2—C6—C1	−15.8 (5)	C3—N1—C10—C11	−173.5 (3)
O2—N2—C6—C1	162.7 (3)	C8—O3—C7—C1	−176.7 (3)
C2—C1—C7—O3	1.2 (4)	C10—N1—C3—C2	−6.7 (5)
C6—C1—C7—O3	−177.1 (3)	C10—N1—C3—C4	171.8 (3)
C7—O3—C8—O4	−0.9 (5)		

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4$^{\rm i}$	0.85 (4)	2.11 (4)	2.952 (4)	171 (4)
C2—H2···O5	0.93 (4)	2.25 (4)	2.859 (4)	123 (3)
C2—H2···O3	0.93 (4)	2.28 (3)	2.657 (4)	104 (3)
C7—H71···O1	0.97 (4)	2.43 (3)	2.631 (4)	91 (2)
C7—H72···O1	0.93 (4)	2.42 (4)	2.631 (4)	93 (3)
C7—H71···O4	0.97 (4)	2.66 (4)	2.611 (4)	77 (2)
C7—H72···O4	0.93 (4)	2.50 (3)	2.611 (4)	87 (3)
C4—H4···O4$^{\rm i}$	0.96 (4)	2.54 (4)	3.367 (5)	144 (3)
C5—H5···O2$^{\rm ii}$	0.93 (4)	2.54 (4)	3.153 (4)	124 (3)
C9—H92···O5$^{\rm iii}$	0.92 (5)	2.62 (5)	3.390 (6)	142 (4)
C11—H12···O5$^{\rm iv}$	1.08 (5)	2.40 (5)	3.423 (6)	156 (3)

Symmetry codes: (i) $\frac{3}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $x - 1, y, z$; (iv) $1 + x, y, z$.

Compound (III)

Crystal data

$C_{11}H_{12}N_2O_5.H_2O$
$M_r = 270.24$
Monoclinic
$P2_1/c$
$a = 7.453$ (3) Å
$b = 10.939$ (5) Å
$c = 15.473$ (9) Å
$\beta = 93.84$ (3)°
$V = 1258.7$ (11) Å^3
$Z = 4$
$D_x = 1.426$ (2) Mg m^{-3}
D_m 1.38 (at room temperature)
D_m measured by flotation in $CHCl_3/CH_2Cl_2$
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 61 reflections
$\theta = 10.0$–13.5°
$\mu = 0.117$ mm^{-1}
$T = 150$ (1) K
Parallelepiped
0.8 × 0.6 × 0.5 mm
Light yellow

Data collection

Kuma KM-4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
3800 measured reflections
3553 independent reflections
2488 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\rm max} = 30°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = -21 \rightarrow 21$
3 standard reflections every 100 reflections intensity variation: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.139$
$S = 1.058$
3553 reflections
229 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.081P)^2 + 0.38P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.063$
$\Delta\rho_{\rm max} = 0.45$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0033 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 5. *Selected torsion angles for (III) (°)*

O1—N2—C6—C5	−168.9 (2)	C7—O3—C8—C9	178.6 (2)
O2—N2—C6—C5	10.6 (2)	C3—N1—C10—O5	1.3 (3)
O1—N2—C6—C1	10.0 (2)	C3—N1—C10—C11	−176.6 (2)
O2—N2—C6—C1	−170.4 (2)	C8—O3—C7—C1	98.6 (2)
C2—C1—C7—O3	−12.5 (2)	C10—N1—C3—C4	−14.3 (3)
C6—C1—C7—O3	166.3 (2)	C10—N1—C3—C2	166.2 (2)
C7—O3—C8—O4	−2.5 (2)		

Table 6. *Hydrogen-bonding geometry (Å, °) for (III)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O6	0.90 (3)	1.96 (3)	2.857 (2)	176 (2)
C4—H4···O5	0.95 (3)	2.34 (3)	2.858 (2)	114 (2)
C7—H71···O1	0.98 (2)	2.37 (2)	2.625 (2)	94 (2)
C7—H72···O1	0.92 (3)	2.51 (2)	2.625 (2)	87 (2)
C7—H72···O4	0.92 (3)	2.32 (2)	2.682 (2)	103 (2)
O6—H62···O5$^{\rm i}$	0.82 (3)	1.93 (3)	2.743 (2)	174 (3)
O6—H61···O4$^{\rm ii}$	0.81 (3)	2.13 (3)	2.876 (2)	153 (3)
C11—H11···O2$^{\rm iii}$	0.88 (4)	2.59 (4)	3.278 (2)	136 (3)
C11—H12···O5$^{\rm i}$	0.94 (4)	2.47 (4)	3.338 (2)	154 (3)
C9—H93···O2$^{\rm iv}$	0.91 (4)	2.60 (4)	3.321 (4)	137 (3)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $-x, -y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x, y - 1, z$.

Preliminary oscillation and Weissenberg photographs showed that crystals of (I) are triclinic, and that those of (II) and (III) are monoclinic. In the case of (I), the absolute structure cannot be determined reliably since the values of anomalous dispersion for the heaviest O atoms in the case of Mo radiation are very small. Therefore, during the refinement, the measured Friedel pairs were averaged. In the case of (II), only those reflections for which the prescan procedure gave an intensity greater than zero were measured.

For all compounds, data collection: *Kuma KM-4 Users Guide* (Kuma Diffraction, 1989); cell refinement: *Kuma KM-4 Users Guide*; data reduction: *Kuma KM-4 Users Guide*; program used to solve structures: *SHELXS*86 (Sheldrick, 1990); program used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1149). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 867–870

Racemic 3-Methyl-*r*-2,*c*-3,*c*-5-triphenylpyrrolidine and 3-Methyl-*r*-2,*t*-3,*c*-5-triphenylpyrrolidine

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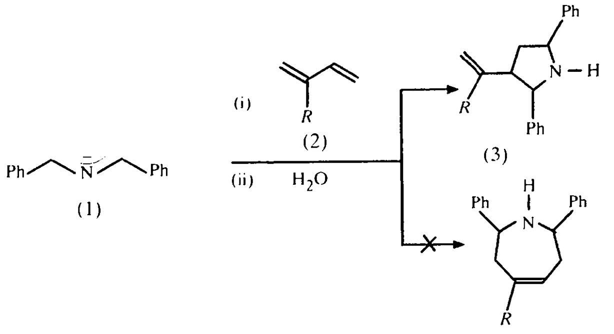
Abstract

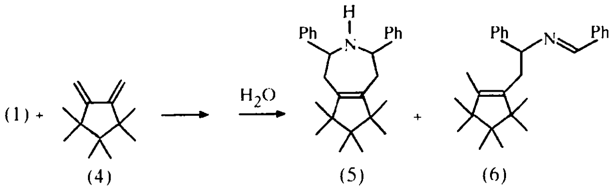
The 1,3-diphenyl-2-azaallyl anion adds almost quantitatively to 2-phenylpropene with retention of the conformation of the anion. Two racemic diastereoisomeric [3+2] cycloadducts, *i.e.* the corresponding pyrrolidines, are formed, in which both phenyl substituents derived from the anion are *cis* oriented. The structures of racemic 3-methyl-*r*-2,*c*-3,*c*-5-triphenylpyrrolidine, $C_{23}H_{23}N$, (I), and 3-methyl-*r*-2,*t*-3,*c*-5-triphenylpyrrolidine, $C_{23}H_{23}N$, (II), were determined by X-ray analysis. There is no intermolecular hydrogen bonding in either crystal.

Comment

The 1,3-diphenyl-2-azaallyl anion, (1), adds stereospecifically to *E*/*Z*-isomeric alkenes with retention of the configuration of the alkene and the conformation of the azaallyl anion (Kauffmann & Köppelmann, 1972). This result is in accord with a concerted process (Woodward & Hoffmann, 1969), where the anion behaves as a $_{\pi}4s$ cycloaddition partner. The mechanistic significance of this observation has been questioned (Huisgen, 1984), however, because the isolated yields of the cycloadducts were rather low. The exclusive formation (Scheme 1) of a single 3-vinylpyrrolidine, (3), in the reaction of this anion with 1,3-dienes, (2) (Kauffmann & Eidenschink, 1971), would be additional evidence for a concerted cycloaddition, but quite recently, [4+3]-cycloaddition and 1,4-addition products [(5) and (6), respectively] were found to be formed in moderate yields when the 1,3-diphenyl-2-azaallyl anion, (1), was combined with 3,3,4,4,5,5-hexamethyl-1,2-bis(methylene)cyclopentane, (4) (Mayr *et al.*, 1993) (Scheme 2). Both reaction partners showed $_{\pi}4$ reactivity resulting in the formation of a seven-membered ring. This last result can only be rationalized by a stepwise $_{\pi}4$ + $_{\pi}4$ cycloaddition process. A similar rather unusual result has been obtained for the reaction of the diene (4) with *C*,*N*-diphenylnitrone (Baran & Mayr, 1987). The sterically encumbered double bond and the allylic stabilization of the intermediate would be two reasons for the stepwise mechanism operating in these cases (Baran & Mayr, 1989; Mayr *et al.*, 1991).



Scheme 1



Scheme 2

Similar factors can operate in the reaction of the anion (1) with 2-phenylpropene, (7), which was investigated next (Scheme 3). The reaction is almost quantitative and results in the formation of only two diastereoisomers of the [3+2] cycloadducts, (I) and (II), the structures

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