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Structures of products of the reaction of dimethylsulfonium phenacylide with benzylidenecyanoacetamide

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Benzylidenecyanoacetamide reacted with dimethylsulfonium phenacylide to form 2-benzoyl-1-cyano-3-phenylcyclopropanecarboxamide and a product of its intramolecular cyclization, *viz.*, a derivative of 3-azabicyclo[3.2.1]hexan-2-one. The structures of the products were established by X-ray diffraction analysis.

Key words: benzylidenecyanoacetamide, dimethylsulfonium phenacylide, 2-benzoyl-1-cyano-3-phenylcyclopropanecarboxamide, 1-cyano-4-hydroxy-4,6-diphenyl-3-azabicyclo[3.2.1]hexan-2-one, intramolecular cyclization, X-ray diffraction analysis.

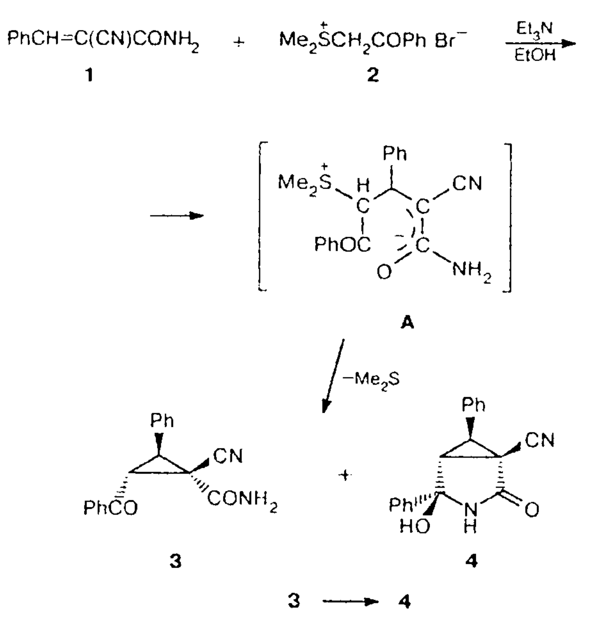
Previously,[1] we have demonstrated that stabilized sulfonium ylides $Me_2S^+C^-HCOR$ react with α,β-unsaturated thioamides $ArCH=C(CN)CSNH_2$ to form both compounds containing three-membered rings (cyclopropanes) and compounds containing five-membered rings (dihydrothiophenes). In all cases, the reactions proceeded stereoselectively. In this connection, it was of interest to study the direction and stereochemistry of reactions of this type of ylides with α,β-unsaturated amides. The reactions of unstabilized sulfur ylides with α,β-unsaturated amides afforded cyclopropanes and (or) 2-pyrrolidones.[2–4] However, the properties of stabilized ylides may be substantially different.[5,6]

In the present work, we found that the reaction of dimethylsulfonium phenacylide $Me_2S^+C^-HCOPh$ with benzylidenecyanoacetamide $PhCH=C(CN)CONH_2$ (**1**) yields cyclopropane **3** and bicyclic compound **4** (Scheme 1), which is a product of intramolecular cyclization of **3** (ylide was generated *in situ* upon addition of a base to the corresponding sulfonium acid **2**).

When the reaction time was increased from 10 min to 1 h, compound **4** was isolated as the only product. Moreover, compound **3** was partially converted into compound **4** (the conversion was 75% according to the ^{1}H NMR spectral data) upon prolonged storage (48 h) in an alcoholic solution at 20—25 °C. Recrystallization of **3** from alcohol, which involved rapid heating of the solution to boiling followed by immediate cooling to 10 °C, can be readily performed.

The structure of product **3** was confirmed by X-ray diffraction analysis. The overall view of the molecule is shown in Fig. 1. The bond lengths and bond angles are given in Tables 1 and 2, respectively.

Scheme 1



As can be seen from Fig. 1, the phenyl and benzoyl substituents in molecule **3** are in *trans* positions with respect to the three-membered ring (the C(6)—C(2)—C(3)—C(13) and H(2)—C(2)—C(3)—H(3) torsion angles are 137.7 and −161.7°, respectively). The carbamoyl and benzoyl fragments are on the same side of the plane of the cyclopropane ring (the C(5)—C(1)—C(2)—C(6) torsion angle is 7.2°).

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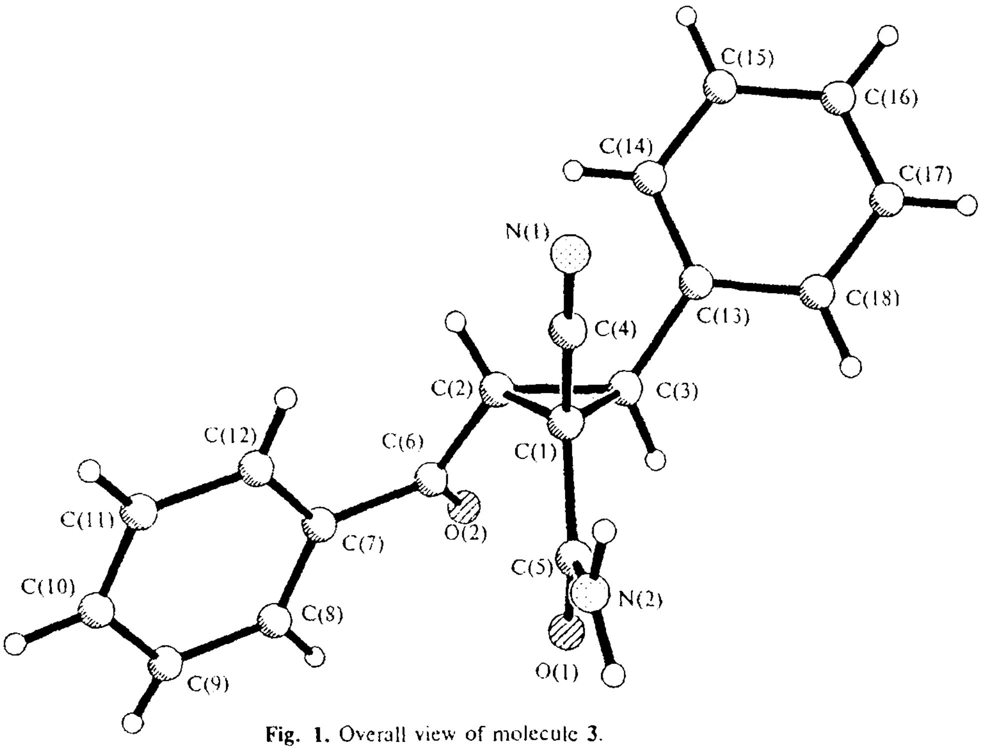


Fig. 1. Overall view of molecule 3.

The mutual arrangement of the substituents with respect to the carbocycle results in the following forced shortened nonbonded intramolecular contacts: O(1)...C(6), 2.752(3) Å; C(4)... C(13), 3.030(3) Å; and C(5)...C(6), 3.023(3) Å (the sums of the van der Waals radii[7] of O and C and of C and C are 3.35 and 3.54 Å, respectively). Apparently, steric interactions between the phenyl ring and the cyano group are responsible for the noticeable increase in the C(1)—C(3) bond length (1.559(2) Å) compared to the other bond lengths in the ring.

Table 1. Bond lengths (*d*) in compound 3

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
O(1)—C(5)	1.212(2)	C(1)—C(2)	1.529(2)	C(7)—C(12)	1.382(3)	C(13)—C(14)	1.383(3)
O(2)—C(6)	1.207(2)	C(1)—C(3)	1.559(2)	C(7)—C(8)	1.392(3)	C(13)—C(18)	1.392(3)
N(1)—C(4)	1.142(2)	C(2)—C(3)	1.478(2)	C(8)—C(9)	1.380(3)	C(14)—C(15)	1.385(3)
N(2)—C(5)	1.330(2)	C(2)—C(6)	1.505(3)	C(9)—C(10)	1.376(3)	C(15)—C(16)	1.380(4)
C(1)—C(4)	1.437(2)	C(3)—C(13)	1.488(2)	C(10)—C(11)	1.374(4)	C(16)—C(17)	1.366(4)
C(1)—C(5)	1.507(2)	C(6)—C(7)	1.491(2)	C(11)—C(12)	1.392(3)	C(17)—C(18)	1.382(3)

Table 2. Bond angles (ω) in compound 3

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(4)—C(1)—C(5)	117.51(14)	N(1)—C(4)—C(1)	178.5(2)	C(11)—C(10)—C(9)	120.8(2)
C(4)—C(1)—C(2)	116.9(2)	O(1)—C(5)—N(2)	123.6(2)	C(10)—C(11)—C(12)	119.4(2)
C(5)—C(1)—C(2)	118.34(14)	O(1)—C(5)—C(1)	119.5(2)	C(7)—C(12)—C(11)	120.0(2)
C(4)—C(1)—C(3)	117.78(14)	N(2)—C(5)—C(1)	117.0(2)	C(14)—C(13)—C(18)	119.1(2)
C(5)—C(1)—C(3)	115.31(14)	O(2)—C(6)—C(7)	121.7(2)	C(14)—C(13)—C(3)	122.9(2)
C(2)—C(1)—C(3)	57.20(11)	O(2)—C(6)—C(2)	119.8(2)	C(18)—C(13)—C(3)	117.9(2)
C(3)—C(2)—C(6)	120.3(2)	C(7)—C(6)—C(2)	118.3(2)	C(13)—C(14)—C(15)	119.9(2)
C(3)—C(2)—C(1)	62.43(11)	C(12)—C(7)—C(8)	120.0(2)	C(16)—C(15)—C(14)	120.6(2)
C(6)—C(2)—C(1)	120.9(2)	C(12)—C(7)—C(6)	122.0(2)	C(17)—C(16)—C(15)	119.6(2)
C(2)—C(3)—C(13)	124.7(2)	C(8)—C(7)—C(6)	118.0(2)	C(16)—C(17)—C(18)	120.6(2)
C(2)—C(3)—C(1)	60.38(11)	C(9)—C(8)—C(7)	119.5(2)	C(17)—C(18)—C(13)	120.1(2)
C(13)—C(3)—C(1)	122.30(14)	C(10)—C(9)—C(8)	120.2(2)		

In the crystal, molecules **3** are linked in infinite chains along the *c* axis *via* the following intermolecular hydrogen bonds: N(2)—H(2.2)...O(2) (*x*, *y*, 1+*z*) [N(2)...O(2), 2.944(3) Å; N(2)—H(2.2), 0.90(3) Å; H(2.2)...O(2), 2.25(3) Å; the N(2)—H(2.2)...O(2) angle is 133(3)°] and N(2)—H(2.1)...N(1) (0.5+*x*, 1.5−*y*, 1−*z*) [N(2)...N(1), 3.058(3) Å; N(2)—H(2.1), 0.88(3) Å; H(2.1)...N(1), 2.20(3) Å; the N(2)—H(2.1)...N(1) angle is 166(3)°].

Problems have been experienced in establishing the structure of compound **4** because the NMR spectral data are contradictory to the results of mass spectrometry. In the mass spectrum, the most intense peaks are those with masses of 105 (apparently, $PhCO^+$) and 44 (apparently, $CONH_2^+$). At the same time, the data of ^{13}C NMR spectroscopy do not confirm the presence of the PhCO group (there are no signals in the region of 180—200 ppm, typical of the carbonyl carbon atom attached to the benzene ring[8]). The structure of compound **4** was unambiguously established by X-ray diffraction analysis. Probably, the data of mass spectrometry are attributable to the fact that under conditions of mass-spectrometric study (the temperature of the ionization chamber was 250 °C and direct introduction of the sample into the ion source), compound **4**, apparently, underwent reverse conversion to **3**.

X-ray diffraction analysis of compound **4** demonstrated that there are two symmetrically independent molecules, **4a** and **4b**, per asymmetric unit. These molecules have similar structures. The overall view of molecule **4a** is shown in Fig. 2. The bond lengths and bond angles are given in Tables 3 and 4, respectively. (Hereinafter, the values for molecule **4b** are given in parentheses.)

According to the Cambridge Structural Database, data on the structures of analogous bicyclic compounds are unavailable in the literature.

Cyclization product **4** retains the same mutual arrangement of the substituents with respect to the cyclopropane ring as in molecule **3** (the C(2)—C(3)—C(4)—C(13), C(6)—C(5)—C(4)—C(13), H(4)—C(4)—C(5)—H(5), and C(13)—C(4)—C(3)—C(19) torsion angles are 154.2° (151.6°), −156.2° (−156.3°), 150.4° (153.1°), and 3.5° (−1.5°), respectively). It is interesting that in spite of the formation of the bicyclic system, the distribution of the bond lengths in the three-membered ring of molecule **4** coincides with that observed in molecule **3**.

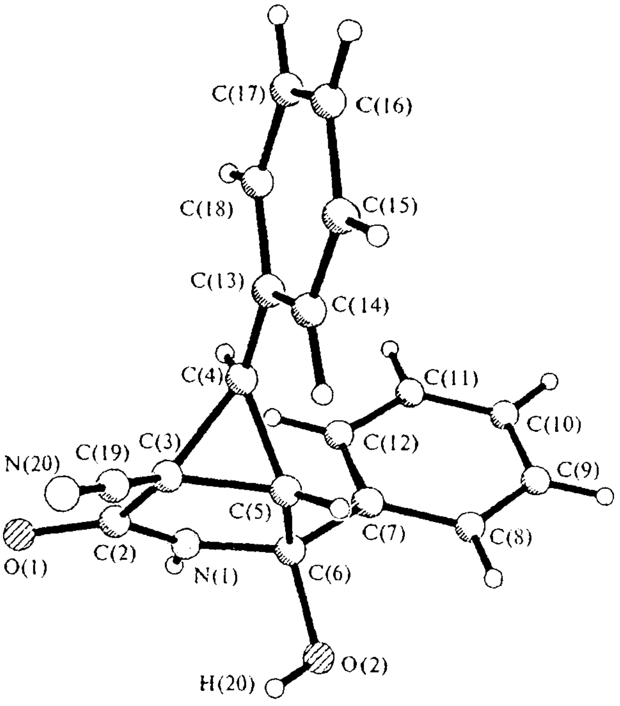


Fig. 2. Overall view of molecule **4a**.

The pyrrolidone fragment adopts a flattened envelope conformation. The N(1) atom deviates from the plane through the remaining four atoms (planar to within ±0.019 Å (±0.025 Å)) by 0.227 Å (−0.244 Å). The dihedral angle between the planar fragments of the bicycle is 110.9° (69.9°).

In the crystal, molecules **4a** and **4b** are linked to each other *via* an extensive network of hydrogen bonds: N(1)—H(1)...O(1′) (1−*x*, −*y*−1, 2−*z*) (N(1)...O(1′), 3.113(3) Å; N(1)—H(1), 0.83(3) Å; H(1)...O(1′),

Table 3. Bond lengths (*d*) in compound **4**

Bond	*d*/Å	
	Molecule **4a**	Molecule **4b**
O(1)—C(2)	1.233(3)	1.232(3)
O(2)—C(6)	1.419(3)	1.408(3)
N(1)—C(2)	1.339(3)	1.346(3)
N(1)—C(6)	1.462(3)	1.460(3)
N(20)—C(19)	1.140(3)	1.138(3)
C(2)—C(3)	1.491(4)	1.498(3)
C(3)—C(19)	1.433(4)	1.436(4)
C(3)—C(5)	1.525(4)	1.520(4)
C(3)—C(4)	1.565(4)	1.556(4)
C(4)—C(5)	1.490(4)	1.487(4)
C(4)—C(13)	1.486(4)	1.477(4)
C(5)—C(6)	1.525(4)	1.533(4)
C(6)—C(7)	1.525(4)	1.517(4)
C(7)—C(12)	1.375(4)	1.378(4)
C(7)—C(8)	1.385(4)	1.387(4)
C(8)—C(9)	1.382(5)	1.386(4)
C(9)—C(10)	1.361(5)	1.364(5)
C(10)—C(11)	1.374(5)	1.366(5)
C(11)—C(12)	1.392(5)	1.385(5)
C(13)—C(14)	1.385(4)	1.377(4)
C(13)—C(18)	1.388(4)	1.382(5)
C(14)—C(15)	1.380(5)	1.389(5)
C(15)—C(16)	1.387(6)	1.353(6)
C(16)—C(17)	1.360(6)	1.375(5)
C(17)—C(18)	1.383(5)	1.381(4)

Table 4. Bond angles (ω) in compound **4**

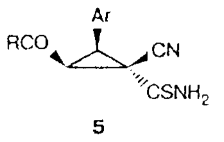
Angle	ω/deg	
	Molecule **4a**	Molecule **4b**
C(2)—N(1)—C(6)	114.8(2)	115.4(2)
O(1)—C(2)—N(1)	126.3(2)	127.4(2)
O(1)—C(2)—C(3)	125.9(2)	125.3(2)
N(1)—C(2)—C(3)	107.8(2)	107.3(2)
C(19)—C(3)—C(2)	118.4(2))	120.7(2)
C(19)—C(3)—C(5)	125.8(2))	123.3(2)
C(2)—C(3)—C(5)	105.7(2)	105.8(2)
C(19)—C(3)—C(4)	120.7(2))	120.5(2)
C(2)—C(3)—C(4)	114.1(2)	113.0(2)
C(5)—C(3)—C(4)	57.7(2)	57.4(2)
C(13)—C(4)—C(5)	122.1(2))	123.6(2)
C(13)—C(4)—C(3)	120.2(2))	120.1(2)
C(5)—C(4)—C(3)	59.8(2)	60.1(2)
C(4)—C(5)—C(3)	62.5(2)	62.6(2)
C(4)—C(5)—C(6)	117.5(2)	117.4(2)
C(3)—C(5)—C(6)	106.4(2)	106.7(2)
O(2)—C(6)—N(1)	109.8(2)	110.3(2)
O(2)—C(6)—C(5)	110.8(2)	107.6(2)
N(1)—C(6)—C(5)	102.3(2)	115.5(2)
O(2)—C(6)—C(7)	107.5(2)	111.4(2)
N(1)—C(6)—C(7)	114.7(2)	101.8(2)
C(5)—C(6)—C(7)	111.7(2)	110.3(2)
C(12)—C(7)—C(8)	119.2(3))	119.3(3)
C(12)—C(7)—C(6)	122.1(3))	123.2(3)
C(8)—C(7)—C(6)	118.6(3)	117.3(3)
C(9)—C(8)—C(7)	120.1(3)	119.9(3)
C(10)—C(9)—C(8)	120.7(4))	120.6(3)
C(9)—C(10)—C(11)	119.7(3)	120.1(3)
C(10)—C(11)—C(12)	120.3(4)	120.3(3)
C(7)—C(12)—C(11)	120.0(3)	119.9(3)
C(14)—C(13)—C(18)	118.3(3)	118.6(3)
C(14)—C(13)—C(4)	123.7(3)	123.2(3)
C(18)—C(13)—C(4)	118.0(3)	118.2(3)
C(15)—C(14)—C(13)	120.7(4)	120.1(4)
C(14)—C(15)—C(16)	120.1(4)	120.8(4)
C(17)—C(16)—C(15)	119.7(4)	120.0(3)
C(16)—C(17)—C(18)	120.3(4)	119.6(4)
C(17)—C(18)—C(13)	120.8(4)	121.0(3)
N(20)—C(19)—C(3)	178.5(3)	178.5(3)

2.35(3) Å; the N(1)—H(1)...O(1′) angle is 154(3)°), O(2)—H(O(2))...O(1)[*] (1−*x*, −*y*−2, 1−*z*) (O(2)...O(1), 3.146(3) Å; O(2)—H(O(2)), 0.86(3) Å; H(O(2))...O(1), 2.30(3) Å; the O(2)—H(O(2))...O(1) angle is 173(3)°), N(1′)—H(1′)...O(1′) (2−*x*, −*y*, 3−*z*) (N(1′)...O(1′), 2.953(3) Å; N(1′)—H(1′), 0.87(3) Å; H(1′)...O(1′), 2.10(3) Å; the N(1′)—H(1′)...O(1′) angle is 168(3)°), and O(2′)—H(O′(2))...O(1) (1−*x*, −*y*−1, 2−*z*) (O(2′)...O(1), 2.846(3) Å; O(2′)—H(O′(2)), 0.84(3) Å; H(O′(2))...O(1), 2.01(3) Å; the O(2′)—H(O′(2))...O(1) angle is 173(3)°).

The remaining geometric parameters of the compounds under study have the expected values.[9]

Unlike the reactions of sulfur ylides with α,β-unsaturated thioamides, which gave dihydrothiophenes as the major products,[1,10] the reactions under consideration did not afford their analogs, *viz.*, dihydrofurans. Undoubtedly, this is due to the fact that the O atom is a weaker nucleophile than the S atom, and, consequently, the O atom, unlike S, cannot close the five-membered ring in intermediate **A** through nucleophilic attack on the C atom bound to the Me_2S^+ leaving group (see Scheme 1).

The stereochemistry of the reactions under study also differs substantially from that observed previously.[1] Thus, the thioamide group in cyclopropanethiocarboxamides **5** is in the *trans* position with respect to the Ar and RCO groups, while the $CONH_2$ and PhCO groups in molecule **3** are on the same side of the ring (which makes possible cyclization of **3** to **4**), and the phenyl substituent is on the opposite side. It is reasonable that the cyclization of molecule **5**, analogous to the conversion of compound **3** into **4**, is not observed.



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Previously,[1] we proposed two possible explanations of the stereochemistry of molecule **5**. One explanation assumes thermodynamic control over the formation of compound **5** (and, consequently, assumes that **5** is the most stable stereoisomer). An alternative explanation assumes kinetic control, namely, the relative configurations of two atoms of the three-membered ring are fixed even in the stage of addition and the configuration of the third atom of this ring is fixed in the stage of elimination (see Scheme 1). More recently, calculations (the PM3 method, the HyperChem program (Hypercube Inc., 1996), version 5.01) demonstrated that isomer **5** (R = Ar = Ph) is not in fact the most stable one (the isomer with the opposite orientation of the PhCO group is more stable; the difference between the energies is 3.9 kcal mol^{-1}). Consequently, the formation of isomer **5** is the kinetically controlled process. Since the initial compounds and the reaction conditions are similar, there is good reason to believe that the formation of **3** is also governed by kinetic control. The difference in the stereochemistry is all the more surprising. The reasons for this difference remain unclear and call for additional studies.

However, complete stereospecificity is untypical of the reactions under study, unlike the reactions with α,β-unsaturated thioamides studied previously.[1] Thus, compound **4** contained about 20% of an admixture before recrystallization (according to the ^1H NMR spectral data). In the NMR spectra, most of signals of the protons of this admixture overlap with signals of the

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[*] H(O(2)) is the hydrogen atom attached to the O(2) atom.

Table 5. Atomic coordinates (×10^4) and isotropic equivalent (isotropic for H atoms) thermal parameters (U_{eq}) in compound **3**

Atom	x	y	z	U_{eq}
O(1)	3746(1)	7266(1)	1264(2)	55(1)
O(2)	2601(2)	7458(1)	−2388(2)	72(1)
N(1)	392(2)	8212(1)	4159(3)	61(1)
N(2)	3111(2)	7259(1)	3966(2)	50(1)
C(1)	1944(1)	7921(1)	1821(2)	30(1)
C(2)	1485(2)	7848(1)	−3(2)	34(1)
C(3)	2175(2)	8552(1)	437(2)	32(1)
C(4)	1073(2)	8090(1)	3112(2)	38(1)
C(5)	3020(2)	7451(1)	2333(2)	35(1)
C(6)	1999(2)	7252(1)	−1197(2)	41(1)
C(7)	1688(2)	6419(1)	−920(2)	38(1)
C(8)	2347(2)	5860(1)	−1788(3)	50(1)
C(9)	2050(2)	5085(1)	−1618(4)	61(1)
C(10)	1102(2)	4870(1)	−610(3)	57(1)
C(11)	457(2)	5415(1)	274(3)	52(1)
C(12)	758(2)	6197(1)	126(3)	45(1)
C(13)	1665(2)	9348(1)	552(2)	36(1)
C(14)	546(2)	9536(1)	−66(3)	50(1)
C(15)	157(2)	10299(1)	−21(4)	63(1)
C(16)	879(3)	10877(1)	629(3)	59(1)
C(17)	1979(2)	10691(1)	1261(3)	55(1)
C(18)	2377(2)	9931(1)	1242(3)	46(1)
H(2.1)	3799(25)	7081(14)	4341(33)	63(7)
H(2.2)	2598(24)	7444(16)	4747(33)	65(7)
H(2)	672(21)	7860(12)	−70(28)	45(6)
H(3)	3013(18)	8517(11)	127(24)	39(5)
H(8)	3007(20)	6004(13)	−2523(28)	54(6)
H(9)	2443(28)	4706(18)	−2197(39)	88(9)
H(10)	925(23)	4335(15)	−530(35)	70(7)
H(11)	−185(21)	5266(14)	988(34)	61(7)
H(12)	297(20)	6561(14)	703(29)	49(6)
H(14)	55(23)	9148(16)	−415(32)	68(8)
H(15)	−629(28)	10434(17)	−477(38)	86(9)
H(16)	629(23)	11424(15)	630(35)	71(7)
H(17)	2441(24)	11084(17)	1715(32)	74(8)
H(18)	3150(17)	9801(12)	1621(27)	40(5)

Table 6. Atomic coordinates (×10^4) and isotropic equivalent (isotropic for H atoms) thermal parameters (U_{eq}) in compound **4**

Atom	Molecule **4a**				Molecule **4b**			
	x	y	z	U_{eq}	x	y	z	U_{eq}
O(1)	4578(2)	−10087(2)	6180(2)	43(1)	8633(2)	−1194(2)	13706(2)	39(1)
O(2)	4739(2)	−7464(2)	4928(2)	50(1)	7477(2)	2048(2)	14227(2)	47(1)
N(1)	4353(3)	−8273(2)	6196(2)	38(1)	9055(2)	793(2)	14120(2)	33(1)
N(20)	8236(3)	−9946(2)	6224(2)	53(1))	5402(3)	−2120(2)	10944(2)	55(1)
C(2)	5078(3)	−9083(2)	6327(2)	33(1)	8471(3)	−351(2)	13442(2)	32(1)
C(3)	6605(3)	−8554(2)	6685(2)	32(1)	7592(3)	−430(2)	12273(2)	33(1)
C(4)	7177(3)	−7366(2)	7779(2)	35(1)	8440(3)	178(2)	11752(2)	33(1)
C(5)	6659(3)	−7366(2)	6600(2)	34(1)	7622(3)	829(2)	12399(2)	33(1)
C(6)	5129(3)	−7289(2)	6106(2)	36(1)	8415(3)	1615(2)	13683(2)	34(1)
C(7)	4896(3)	−6092(2)	6756(2)	37(1)	9444(3)	2662(2)	13824(2)	34(1)
C(8)	5277(3)	−5163(3)	6487(3)	49(1)	10882(3)	2753(3)	14155(3)	43(1)
C(9)	5180(4)	−4048(3)	7118(3)	63(1)	11744(4)	3692(3)	14176(3)	54(1)
C(10)	4716(4)	−3847(3)	8010(3)	63(1)	11182(4)	4529(3)	13871(3)	62(1)
C(11)	4323(4)	−4763(3)	8277(3)	65(1)	9758(4)	4448(3)	13541(3)	67(1)
C(12)	4410(4)	−5892(3)	7647(3)	53(1)	8878(4)	3517(3)	13514(3)	54(1)
C(13)	8701(3)	−6988(2)	8526(2)	39(1)	8021(3)	−245(2)	10478(2)	37(1)
C(14)	9783(3)	−6959(3)	8109(3)	52(1)	7020(4)	140(3)	9812(3)	62(1)
C(15)	11176(4)	−6562(3)	8855(4)	71(1)	6704(5)	−271(4)	8628(3)	76(1)
C(16)	11507(5)	−6169(3)	10038(4)	80(1)	7371(4)	−1052(3)	8113(3)	67(1)
C(17)	10454(5)	−6200(3)	10458(4)	73(1)	8375(4)	−1446(3)	8764(3)	62(1)
C(18)	9057(4)	−6616(3)	9711(3)	53(1)	8697(4)	−1041(3)	9942(3)	50(1)
C(19)	7521(3)	−9320(2)	6424(2)	34(1)	6380(3)	−1382(2)	11530(2)	37(1)
H(1)	3489(33)	−8365(25)	6026(26)	51(10)	9691(29)	1007(23)	14805(24)	40(8)
H(2O)	4882(43)	−8130(36)	4565(35)	97(15)	6929(28)	1446(23)	14134(22)	31(8)
H(4)	6520(27)	−7260(21)	8186(21)	34(7)	9427(27)	331(20)	12171(21)	28(7)
H(5)	7428(26)	−7063(20)	6341(20)	33(7)	6754(29)	1004(23)	12007(23)	43(8)
H(8)	5665(30)	−5310(24)	5850(25)	49(8)	11288(31)	2180(26)	14372(25)	56(9)
H(9)	5488(39)	−3417(33)	6928(32)	92(13)	12766(36)	3734(27)	14397(27)	65(10)
H(10)	4717(37)	−3041(33)	8502(31)	85(11)	11817(35)	5230(29)	13903(28)	75(10)
H(11)	3957(36)	−4612(29)	8916(30)	76(11)	9314(41)	5022(34)	13359(33)	94(13)
H(12)	4171(35)	−6525(29)	7850(28)	72(11)	7903(31)	3460(23)	13292(24)	45(8)
H(14)	9553(29)	−7191(24)	7253(26)	47(8)	6510(36)	658(29)	10156(29)	71(11)
H(15)	11829(43)	−6526(33)	8517(34)	91(14)	6070(40)	62(31)	8215(32)	85(12)
H(16)	12544(47)	−5936(34)	10529(35)	104(14)	7156(33)	−1297(27)	7354(30)	66(10)
H(17)	10683(40)	−5948(31)	11273(35)	88(13)	8868(36)	−2004(29)	8421(30)	73(11)
H(18)	8274(28)	−6662(21)	9999(21)	33(7)	9400(31)	−1309(24)	10402(25)	51(9)

protons of compound **4**. However, the following signals are clearly seen (δ): 3.68 (d, 1 H, J = 10.0 Hz), 3.96 (d 1 H, J = 10.0 Hz), 7.59 (t, 2 H, J = 7.9 Hz), 8.12 (d, 2 H, J = 7.9 Hz) (the relative integral intensities of the signals of the protons of the admixture are given).

The large values of the spin-spin coupling constants (10.0 Hz), typical of *cis*-protons in cyclopropanes,[1,8] as well as a doublet at δ 8.12 (which is similar in chemical shift and relative integral intensity to the doublet at δ 8.10 observed in the spectrum of compound **3** and which, undoubtedly, belongs to the protons of the PhCO group) suggest that the admixture is a cyclopropane, which is isomeric to **3** but contains the Ph and PhCO groups in *cis* orientations. Unfortunately, we failed to isolate the admixture in pure form either by crystallization or by chromatography.

Experimental

The NMR spectra were recorded on a Bruker AM-300 instrument in $(CD_3)_2CO$ (operating at 300.13 MHz for ^1H and at 75.47 MHz for ^{13}C). The IR spectrum was obtained on a Specord M-80 instrument in KBr pellets. The mass spectrum was measured on a Varian MAT 311A instrument.

***c*-2-Benzoyl-1-cyano-*t*-3-phenylcyclopropane-*r*-1-carboxamide (3) and (1*RS*,4*SR*,5*SR*,6*RS*)-1-cyano-4-hydroxy-4,6-diphenyl-3-azabicyclo[3.1.0]hexan-2-one (4).** Et_3N (0.11 g, 1.1 mmol) was added to a suspension of benzylidenecyanoacetamide (**1**) (1.1 mmol) and dimethylphenacylsulfonium bromide (**2**) (0.29 g) in EtOH (3 mL). The reaction mixture was kept at 30—40 °C for 10 min, during which time the mixture became homogeneous and then became turbid again. Then the reaction mixture was cooled to 20 °C and the precipitate of amide **3** that formed was filtered off, washed with water, and dried. The yield of amide **3** was 65 mg (20%). Water (1 mL) was added to the filtrate and the precipitate that formed was filtered off, washed with water, and dried. The yield was 205 mg (64%). According to the ^1H NMR spectral data, this precipitate was compound **4** containing about 20% of an admixture (see above), which can be removed by recrystallization from ethanol.

Amide 3, m.p. 228—231 °C (decomp.). ^1H NMR, δ: 3.79 (d, 1 H, H(3), J = 8.3 Hz); 4.18 (d, 1 H, H(2), J = 8.3 Hz); 7.00 (br.s, 1 H, NH_2); 7.30—7.70 (m, 9 H, Ph and NH_2); 8.10 (d, 2 H, Ph, J = 8.1 Hz).

Bicyclic compound 4 (t.decomp. > 160 °C). ^1H NMR, δ: 2.90 (d, 1 H, H(4), J = 5.1 Hz); 3.71 (d, 1 H, H(5), J = 5.1 Hz); 6.40 (br.s, 1 H, OH); 7.20—7.40 (m, 8 H, Ph); 7.69 (d, 2 H, Ph, J = 7.9 Hz); 8.20 (br.s, 1 H, NH). ^{13}C NMR, δ: 29.5 (C(3)); 38.6 (C(4)); 41.3 (C(5)); 88.2 (C(6)); 115.5 (CN); 126.7, 128.9, 129.0, 129.2, 129.3, 129.4, 137.7, 141.2 (all Ph); 169.3 (CO) (the atomic numbering scheme used in the description of the NMR spectra was identical with that given in Fig. 2). IR, ν/cm^{-1}: 3250—3450 (νNH and νOH); 2250 (νCN); 1690 (νCO). MS (EI, 70 eV, m/z (I_{rel}(%)): 290 $[M]^+$ (7.4); 185 $[M - PhCO]^+$ (61.1); 105 $[PhCO]^+$ (100); 77 $[Ph]^+$ (69.7); 44 $[CONH_2]^+$ (95.4). Crystals of **3** ($C_{18}H_{14}N_2O_2$) are orthorhombic, at 25 °C: a = 11.195(3), b = 17.215(5), c = 7.866(3) Å, V = 1515.8(7) Å^3, Z = 4, d_{calc} = 1.272 g cm^{-3}, space group $P2_12_12_1$.

Crystals of **4** ($C_{18}H_{14}N_2O_2$) are triclinic, at 25 °C: a = 10.220(4), b = 12.502(3), c = 13.290(3) Å, α = 110.60(2), β = 108.01(2), γ = 95.46(2)°, V = 1471.4(7) Å^3, Z = 4, d_{calc} = 1.311 g cm^{-3}, space group $P\bar{1}$. The unit cell parameters and intensities of 2022 and 5396 reflections (for compounds **3** and **4**, respectively) were measured on an automated four-circle Siemens P3/PC diffractometer (λ-Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, θ_{max} = 27°). The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal factors for nonhydrogen atoms. The positions of the hydrogen atoms were located from difference Fourier syntheses and refined isotropically. The final values of the R factors were as follows: R_1 = 0.035 based on 1653 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.086 based on 1966 independent reflections for **3**; R_1 = 0.056 based on 3244 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.120 based on 5031 independent reflections for **4**. All calculations were carried out on an IBM PC/AT-486 computer using the SHELXTL PLUS and SHELXL-93 program packages. The atomic coordinates and isotropic thermal parameters (equivalent thermal parameters for nonhydrogen atoms) for compounds **3** and **4** are given in Tables 5 and 6, respectively.

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