STEREOSELECTIVE $[\pi 4_s + \pi 2_s]$-DIPOLAR CYCLOADDITION OF PYRIDINIUM YLIDES TO NITRILES OF THE *trans*-1,3-BUTADIENE SERIES. CRYSTAL AND MOLECULAR STRUCTURE OF 3-BENZOYL-1-(2,2-DICYANO-1-CYCLOPROPYLVINYL)-2-PHENYL-6-CYANO-1,2-*trans*-2,3-*trans*-1,9-*trans*-1,2,3,9-TETRAHYDROINDOLIZINE

A. M. Shestopalov, Yu. A. Sharanin, V. N. Nesterov,
G. E. Khoroshilov, V. E. Shklover, Yu. T. Struchkov,
and V. P. Litvinov

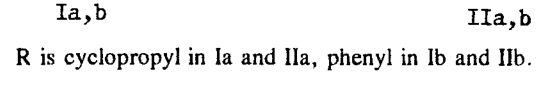
UDC 547.461:547.821.3:
547.831.1:548.737

The interaction of substituted trans-1,1-dicyano-4-phenyl-1,3-butadienes with pyridinium ylides proceeds through the path of $[\pi 4_s + \pi 2_s]$-dipolar cycloaddition, highly regioselective and stereoselective, with the formation of substituted 1-(2,2-dicyanovinyl)-2-phenyl-6-cyano-1,2-trans-2,3-trans-1,9-trans-1,2,3,9-tetrahydroindolizines. The stereoselectivity of these reactions is due to endo-addition of molecules of trans-1,3-butadienes to the anti form of the pyridinium ylides; it is confirmed by correlation analysis of the data from double PMR, mathematical calculations of torsion angles, and x-ray structural studies of the substituted tetrahydroindolizines.

In previous reports we examined reactions of azinium ylides with nitriles of the ethylene series [1-3]. It was established that the regioselectivity and stereoselectivity of these reactions depend on the structure of the original compounds; also, synthetic possibilities of the compounds were determined. The interaction of pyridinium carbamoylmethylide or phenacylmethylide [generated in the reaction mixture by the action of bases on halides of 1-(carbamoylmethyl)pyridinium or 1-phenacylpyridinium] with an arylmethylenemalononitrile proceeds stereoselectivity with the formation of substituted *trans*-cyclopropanes [1]. The introduction of arylmethylenecyanothioacetamides into this reaction is accompanied by a change in the regioselectivity of interaction, leading to substituted 4-aryl-2-hydroxy-3-(1-pyridinio)-5-cyano-3,4-*trans*-1,2,3,4-tetrahydropyridine-2-thiolates [2]. The interaction of isoquinolinium ylides, which are more π-deficient, with arylmethylenemalononitriles, proceeds with high stereoselectivity along the path of synchronous 1,3-dipolar cycloaddition with the formation of substituted 1,2-*trans*-1,2,3,4-tetrahydrobenzo[f]indolizines [3]. Here we are presenting results from an investigation of reactions of 3-cyano- and 3-ethoxycarbonylpyridinium ylides, for which the π-electron density in the ring is lower, with substituted *trans*-1,3-butadienes. Reactions of pyridinium ylides with butadienes had not been investigated previously [4-6].

The original butadienes were obtained by condensation of the unsaturated nitriles Ia, b with benzaldehyde in isopropanol in the presence of a base. The condensation proceeds stereoselectively with 68-71% yields of the substituted *trans*-1,3-butadienes IIa, b. In the IR spectra of these compounds, absorption bands of conjugated C≡N groups are present in the 2223-2224 cm^{-1} region. In the PMR spectra, the signals of the protons of the butadiene fragment are manifested in the form of doublets in the 6.47-6.97 and 7.18-7.68 ppm regions, with a characteristic transoid SSCC $^3J = 15.8\text{-}16.0$ Hz.

The pyridinium ylides were not segregated as such, but were generated in the reaction mixture by treatment of the corresponding pyridinium salts III with an equimolar quantity of triethanolamine in ethanol.



Ia,b IIa,b

R is cyclopropyl in Ia and IIa, phenyl in Ib and IIb.

T. G. Shevchenko Lugansk State Pedagogical Institute, Lugansk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1354-1360, October, 1991. Original article submitted January 12, 1990; revision submitted July 16, 1990.

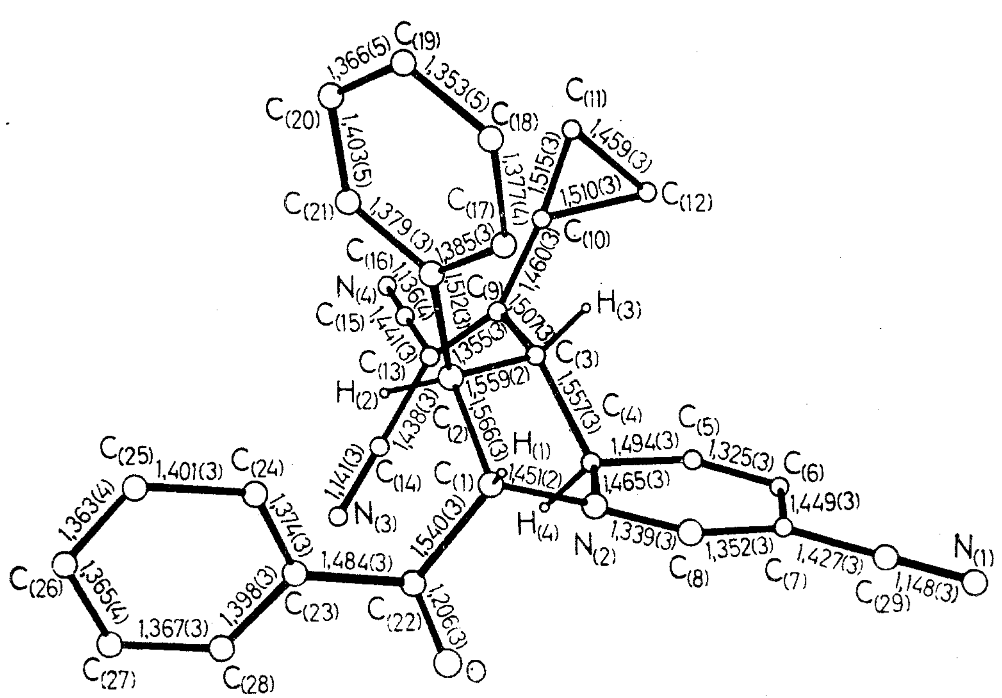


Fig. 1. General view of molecule Va and bond lengths in molecule. The *trans* position can be seen for the pairs of atoms $H_{(1)}$ and $H_{(2)}$, $H_{(2)}$ and $H_{(3)}$, and $H_{(3)}$ and $H_{(4)}$.

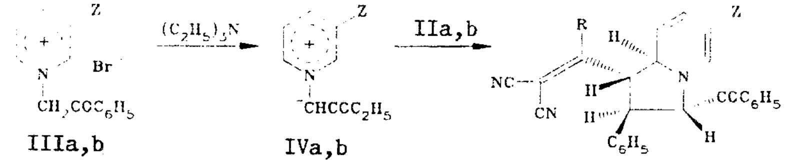
TABLE I. Characteristics of Substituted Tetrahydroindolizines Va-d

Compound	Empirical formula	mp, °C*	IR spectrum, ν, cm^{-1}			Yield, %
			C=C	C=O	C≡N	
Va	$C_{29}H_{22}N_4O$	150...152	1638	1697	2202, 2234	95
Vb	$C_{32}H_{22}N_4O$	148...150	1628	1686	2205, 2226	100
Vc	$C_{31}H_{27}N_3O_3$	134...136	1622	1672, 1686 sh.	2227	86
Vd	$C_{34}H_{27}N_3O_3$	122...124	1628	1678, 1687sh.	2232	84

---

*Compounds Va, c, d were crystallized from methanol, compound Vb from isopropanol.

The subsequent interaction of the ylides IV with the butadienes II proceeds along the path of synchronous 1,3-dipolar cycloaddition, regioselectively and stereoselectively, with the formation of the substituted tetrahydroindolizines V (Tables 1 and 2). Of the several possible products of regioselective addition with respect to the dipolarophile II, only one product is realized in practice, specifically, the product of $[\pi 4_s + \pi 2_s]$-cycloaddition [7] of the ylides (IV) at the $C_{(3)}{=}C_{(4)}$ bond of the molecules of the butadiene II



IIIa,b IVa,b Va-d

In compounds III and IV, Z is CN (a) or $COOC_2H_5$ (b). In compounds V, R and Z are (respectively) cyclopropyl and CN (a), C_6H_5 and CN (b), cyclopropyl and $COOC_2H_5$ (c) or C_6H_5 and $COOC_2H_5$ (d)

TABLE 2. PMR Spectra of Substituted Tetrahydroindolizines Va-d

Compound	Chemical shifts δ, ppm							SSCC, ^3J, Hz				Torsion angle φ, deg		
	1-H, dd	2-H, dd	8a-H, dt	8-H, d	3-H, d	7-H, dd	other protons	J_{H_1,H_2}	J_{H_2,H_3}	$J_{H_1,H_{8a}}$	J_{H_7,H_8}	$\overset{\varphi}{H_1CCH_2}$	$\overset{\varphi}{H_2CCH_3}$	$\overset{\varphi}{H_1CCH_{8a}}$
Va	3,27	3,56	5,08	5,18	5,80	6,03*	0,52, 0,97, 1,07, 1,18, 2,02 (5H, m, CH-cyclopropyl); 7,27...7,60 (11H, m, $(C_6H_5)_2$)	10,0	7,0	10,0	10,0	148	132	148
Vb	3,20	3,70	5,42	5,16	5,97	6,07	7,15...7,84 (16H, m, $(C_6H_5)_3$, 5-H)	10,2	7,3	9,8	9,5	149	133	147
Vc	3,10	3,55	5,11	5,11**	5,95	6,37	0,21, 0,94, 1,10, 2,02 (5H, m, CH-cyclopropyl); 1,18 (3H, t, CH_3, $J = 7,2$ Hz); 4,02 (2H, q, CH_2), 7,24...7,57 (10H, m, $(C_6H_5)_2$); 7,65 (1H, s, 5-H)	10,0	6,5	9,0	9,0	148	129	143
Vd	3,20	3,68	5,42	5,18	5,95	6,40	1,16 (3H, t, CH_3, $^3J = 7,3$ Hz); 4,06 (2H, q, CH_2); 7,17...7,82 (16H, m, (C_6H_5), 3,5-H)	10,0	7,0	10,0	9,2	148	132	148

---

*SSCC, $^4J = 3.0$ Hz.

**Signals overlap.

For this reason, the IR spectra of compounds V contain characteristic absorption bands of conjugated C≡N groups of the dicyanomethylene fragment in the 2226-2234 cm^{-1} region and an absorption band of the carbonyl group of the benzoyl fragment, related to the sp^3-hybrid carbon atom, in the 1686-1697 cm^{-1} region (see Table 1). Comparing the IR spectra of compounds Va, b and Vc, d, we can note that the band of the C≡N group connected to the pyridine ring is shifted toward higher frequencies, to 2202-2205 cm^{-1}. The bands of the $COOC_2H_5$ group of compounds Vc, d are observed in the 1672-1678 cm^{-1} region. These data are evidence of development of p—π conjugation in the $C_5C_6C_7(CN)C_8N$ fragment of the molecules of compound V.

The regioselective addition is accompanied by high stereoselectivity of the reaction, with preservation of orbital symmetry. This is confirmed by the retention of the *trans* position of the hydrogen atoms built into the original 1,3-butadienes when the transition is made to the tetrahydroindolizines, SSCC $^3J_{H_1,H_2}$ = 10.0-10.2 Hz (see Table 2). The regioselectivity of the reactions with respect to the asymmetric pyridinium ylide is also high. Of the two alternative directions of addition, only one is realized in practice — addition of the ylide molecules to the butadienes with participation of the C^-—N—C_6 fragment, with the formation of 6-cyano- or 6-ethoxycarbonyl derivatives of tetrahydroindolizines V. In the PMR spectra of the tetrahydroindolizines V, signals are observed from the 7-H and 8-H protons with characteristic $^3J_{H_7,H_8}$ = 9.0-10.0 Hz. The signal of the 5-H proton is overlapped by a multiplet of signals of the phenyl protons; only in the case of compound Vc is it manifested in the form of a singlet in the 7.65 ppm region.

Stereoselectivity of the reactions of the ylides with the butadienes is also evidenced by the multiplicity and SSCC ^3J of the other protons of the tetrahydroindolizines V. The signal of the 1-H proton is manifested in the 3.10-3.27 ppm region in the form of a double doublet with SSCC $^3J_{H_1,H_{8a}}$ = 9.0-10.0 Hz. The signals of the 2-H and 3-H protons are manifested in the form of a double doublet and a doublet at 3.55-3.70 and 5.80-5.97 ppm, respectively, with SSCC $^3J_{H_1,H_3}$ = 6.5-7.3 Hz (see Table 2). The signal of the nodal atom 8*a*-H is complicated by long-range spin—spin coupling and is manifested in the form of a double triplet with SSCC $^3J_{H_1,H_{8a}}$ = 9.0-10.0 Hz.

These assignments of the hydrogen atom signals were based on a double NMR experiment. In the PMR spectra of the tetrahydroindolizines Va-c upon irradiation at the frequency of the 3-H proton, the components of the double doublet signal of the 2-H proton in the 3.55-3.70 ppm region, with SSCC $^3J_{H_2,H_3}$ = 6.5-7.0 Hz, merge into a doublet with SSCC $^3J_{H_2,H_1}$ = 10.0-10.2 Hz. Irradiation at the frequency of the 8*a*-H proton is accompanied by merging of the components of the double doublet in the 3.10-3.27 ppm region into a doublet with SSCC $^3J_{H_1,H_2}$ = 10.0-1.2 Hz. Irradiation at the frequency of the 2H proton results in narrowing of the doublet of the 3-H proton signal in the 5.80-5.97 ppm region to form a singlet, and merging of the components of the double doublet of the 1-H proton signal into a doublet with SSCC $^3J_{H_1,H_{8a}}$ = 9.8-10.0 Hz.

On the basis of the Karplus—Conroe equation [8], we calculated the torsion angles φ, with allowance for the SSCC ^3J (see Table 2). It can be seen from these data that all of the hydrogen atoms in the hydrogenated pyrrole fragment of the molecules of compound V have the *trans*-pseudoaxial orientation, and the substituents connected to these atoms are in the *trans*-pseudoequatorial position relative to each other.

TABLE 3. Bond Angles in Molecule Va

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$C_{(1)}N_{(2)}C_{(4)}$	109,2(1)	$C_{(6)}C_{(7)}C_{(29)}$	121,5(2)	$C_{(17)}C_{(16)}C_{(21)}$	118,4(2)
$C_{(1)}N_{(2)}C_{(8)}$	124,9(2)	$C_{(8)}C_{(7)}C_{(29)}$	119,8(2)	$C_{(16)}C_{(17)}C_{(17)}$	121,4(2)
$C_{(4)}N_{(2)}C_{(8)}$	123,4(2)	$N_{(2)}C_{(8)}C_{(7)}$	122,4(2)	$C_{(17)}C_{(18)}C_{(19)}$	119,2(3)
$N_{(2)}C_{(1)}C_{(2)}$	105,0(2)	$C_{(3)}C_{(9)}C_{(10)}$	118,9(2)	$C_{(18)}C_{(19)}C_{(20)}$	121,9(3)
$N_{(2)}C_{(1)}C_{(22)}$	111,0(2)	$C_{(3)}C_{(9)}C_{(13)}$	122,0(2)	$C_{(19)}C_{(20)}C_{(21)}$	118,8(3)
$C_{(2)}C_{(1)}C_{(22)}$	112,4(2)	$C_{(10)}C_{(9)}C_{(13)}$	119,1(2)	$C_{(16)}C_{(21)}C_{(20)}$	120,3(2)
$C_{(1)}C_{(2)}C_{(3)}$	104,0(1)	$C_{(9)}C_{(10)}C_{(11)}$	121,1(2)	$OC_{(22)}C_{(1)}$	119,6(2)
$C_{(1)}C_{(2)}C_{(16)}$	115,0(2)	$C_{(9)}C_{(10)}C_{(12)}$	121,0(2)	$OC_{(22)}C_{(23)}$	121,9(2)
$C_{(3)}C_{(2)}C_{(16)}$	111,7(2)	$C_{(11)}C_{(10)}C_{(12)}$	57,7(1)	$C_{(1)}C_{(22)}C_{(23)}$	118,5(2)
$C_{(2)}C_{(3)}C_{(4)}$	104,2(1)	$C_{(10)}C_{(11)}C_{(12)}$	61,0(2)	$C_{(22)}C_{(23)}C_{(24)}$	123,2(2)
$C_{(2)}C_{(3)}C_{(9)}$	116,7(2)	$C_{(10)}C_{(12)}C_{(11)}$	61,3(2)	$C_{(22)}C_{(23)}C_{(28)}$	118,3(2)
$C_{(4)}C_{(3)}C_{(9)}$	114,5(2)	$C_{(9)}C_{(13)}C_{(14)}$	124,6(2)	$C_{(24)}C_{(23)}C_{(28)}$	118,6(2)
$N_{(2)}C_{(4)}C_{(3)}$	100,5(1)	$C_{(9)}C_{(13)}C_{(15)}$	120,8(2)	$C_{(23)}C_{(24)}C_{(25)}$	120,0(2)
$N_{(2)}C_{(4)}C_{(5)}$	111,9(2)	$C_{(14)}C_{(13)}C_{(15)}$	114,6(2)	$C_{(24)}C_{(25)}C_{(26)}$	119,7(2)
$C_{(3)}C_{(4)}C_{(5)}$	116,8(2)	$N_{(3)}C_{(14)}C_{(13)}$	178,4(2)	$C_{(25)}C_{(26)}C_{(27)}$	121,1(3)
$C_{(4)}C_{(5)}C_{(6)}$	122,7(2)	$N_{(4)}C_{(15)}C_{(13)}$	179,3(2)	$C_{(26)}C_{(27)}C_{(28)}$	119,6(3)
$C_{(5)}C_{(6)}C_{(7)}$	120,8(2)	$C_{(2)}C_{(16)}C_{(17)}$	121,5(2)	$C_{(23)}C_{(28)}C_{(27)}$	121,1(3)
$C_{(6)}C_{(7)}C_{(8)}$	118,6(2)	$C_{(2)}C_{(16)}C_{(21)}$	120,0(2)	$N_{(1)}C_{(29)}C_{(7)}$	178,4(2)

In order to obtain unambiguous confirmation of the structure of the compounds, we have carried out an x-ray structural study of compound Va.

The general form of the Va molecule and the bond lengths are shown in Fig. 1; bond angles are listed in Table 3. The values of the torsion angles $C_{(22)}C_{(1)}C_{(2)}C_{(16)}$ 121.6(4) and $H_{(1)}C_{(1)}C_{(2)}H_2$ 121(3)° indicate a transoid position of the pseudoequatorial phenyl and 2,2-dicyano-1-cyclopropylvinyl substituents, and also of the pseudoaxial atoms $H_{(1)}$ and $H_{(2)}$ in the molecule of Va. The hydrogen atoms $H_{(2)}$ and $H_{(3)}$, and also $H_{(3)}$ and $H_{(4)}$, have the *trans* position [torsion angles $H_{(2)}C_{(2)}C_{(3)}H_{(3)}$ 153(3) and $H_{(3)}C_{(3)}C_{(4)}H_{(4)}$ 173(3)°].

In the molecule Va, the five-membered pyrrolidine heterocycle has a conformation that is intermediate between the convert and the twist conformation, as indicated by values of the modified parameters [9] of Cremer Pople [10] (φ = 278°, q_2 = 0.571 Å). In the molecule of a compound that we had investigated previously, 1-carbamoyl-3,3-dicyano-2-(3-pyridyl)benzo[f]indolizine (VI), this heterocycle has the twist conformation (φ = 249.4°, q_2 = 0.614 Å) [3]. The change in conformation of the five-membered heterocycle in the molecule Va is probably due to steric factors — the presence of bulky substituents and the large number of shortened intramolecular nonvalence contacts. Connection of the five-membered heterocycle in the molecule Va with the six-membered dihydropyridinium ring through the $N_{(2)}—C_{(4)}$ bond is characterized by values of the torsion angles $C_{(3)}C_{(4)}N_{(2)}C_{(1)}$ 42.1(3), $C_{(5)}C_{(4)}N_{(2)}C_{(8)}$ 3.5(3), $C_{(5)}C_{(4)}N_{(2)}C_{(1)}$ 166.7(4), and $C_{(3)}C_{(4)}N_{(2)}C_{(8)}$ 121.1(4)°.

The rotation of the carbonyl group, i.e., rotation of the coordination plane of the $C_{(22)}$ atom [the $C_{(22)}$ deviates from the plane of the atoms $C_{(1)}OC_{23}$ by only 0.003(2) Å], relative to the plane of the $N_{(2)}C_{(1)}C_{(2)}$ of the five-membered heterocycle is 122.9°, and relative to the plane of the Ph substituent [$C_{(23)}$-$C_{(28)}$] it is 16.0°. The phenyl substituent [$C_{(16)}$-$C_{(21)}$] is almost perpendicular to the $C_{(1)}C_{(2)}C_{(3)}$ fragment of the five-membered heterocycle (dihedral angle 79.6°). The substituted dicyanovinyl fragment which is planar within 0.030(2) Å, is actually perpendicular to the other part of this same heterocycle $C_{(2)}C_{(3)}C_{(4)}$ (angle 90.9°) and also to the plane of the cyclopropyl substituent $C_{(10)}C_{(11)}C_{(12)}$ (angle 89.3°).

Conjugation of the unshared electron pair of the plane-trigonal atom $N_{(2)}$ (sum of bond angles 357°) with the π-system of the double bond $C_{(7)}{=}C_{(8)}$ tends to flatten the dihydropyridine heterocycle [it is planar to within 0.023(2) Å]. Conjugation brings about a shortening of the $N_{(2)}—C_{(8)}$ bond to 1.339(3) Å, in comparison with the standard length of the $C_{(sp^3)}—N_{(sp^2)}$ bond in pyridine, 1.337 Å [11]. At the same time, the length of the $N_{(2)}—C_{(4)}$ bond, 1.465(3) Å, is comparable to the length of the $N_{(2)}—C_{(1)}$ bond, 1.451(2) Å, and it coincides with the standard value of the length of an ordinary $C_{(sp^3)}—N_{(sp^2)}$ bond, 1.462 Å [11]. It should be noted that in the tetrahydroindolizine VI, the lengths of the analogous bonds are 1.461(7) and 1.458(6) Å (the nitrogen atom has a pyramidal coordination), but in the tetrahydropyrrole substituent of the molecule 2-(1-pyrrolidinyl)benzylidenemalononitrile (VII), the lengths are 1.475 and 1.468 Å [12]. However, in the pyrrolidine substituent of the molecule Va, the bond lengths are $C_{(1)}—C_{(2)}$ 1.566(3), $C_{(2)}—C_{(3)}$ 1.559(2), and $C_{(3)}—C_{(4)}$ 1.557(3) Å, slightly longer in comparison with the standard lengths of the bond $C_{(sp^3)}—C_{(sp^3)}$, for example in cyclopentane (1.543 Å [11]); they are considerably greater than the corresponding bond lengths in the molecule VII (1.502, 1.502, and 1.511 Å) and are close to the values observed in the molecule VI [1.673(5), 1.563(7), 1.578(6) Å]. The same as in the molecule VI, the increase of the indicated bond lengths in the pyrrolidine heterocycle in Va is probably due to ring strain and steric effects that arise in closing the ring.

We should note a certain increase in the length of the double bond $C_{(9)}{=}C_{(13)}$ to 1.355(3) Å in comparison with the standard value for $C_{(sp^2)}—C_{(sp^2)}$, 1.331 Å [11], apparently due to conjugation of CN groups with this double bond. However, no significant changes are observed in the lengths of the $C_{(sp^3)}—C_{(sp)}$ and $C{\equiv}N$ bonds.

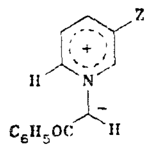
Here we must note the significant increase in length of the $C_{(1)}—C_{(22)}$ bond to 1.540(3) Å in comparison with the standard length of the $C_{(sp^3)}—C_{(sp^3)}$ bond, 1.507 Å [11]; this can be explained by induced steric contacts that exist in the molecule.

In the cyclopropyl substituent, the length of the distal $C_{(11)}—C_{(12)}$ bond, 1.459(3) Å, is considerably smaller in comparison with the vicinal bonds $C_{(10)}—C_{(11)}$ 1.515(3) and $C_{(10)}—C_{(12)}$ 1.510(3) Å, and also in comparison with the standard length of the C—C bond in cyclopropanes, 1.510 Å [11].

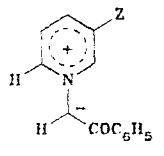
Comparing the calculated torsion angles with the experimental values, we can note that the basic conformation of the molecules of the compounds V does not change in DMSO-D_6 solution, and is similar in the entire series of substituted tetrahydroindolizines. This means that in the entire series, the reactions proceed with high stereoselectivity (analogous stereoselectivity was observed in a series of reactions of arylmethylenemalononitriles with isoquinolinium ylides [3]) through a mechanism of synchronous 1,3-dipolar cycloaddition. Of the two isomeric *syn* and *anti* forms of the pyridinium ylides (VIII, IX), one enters into reaction.

TABLE 4. Coordinates of Nonhydrogen Atoms (×10⁴)

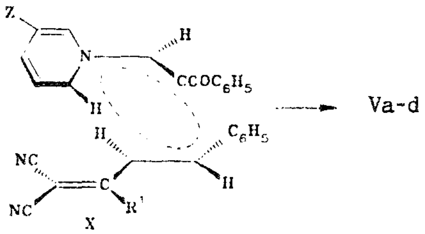
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O	658(2)	3496(2)	2913(1)	$C_{(13)}$	−4190(2)	4740(2)	1812(2)
$N_{(1)}$	1341(2)	9287(2)	−1096(2)	$C_{(14)}$	−2990(2)	3500(2)	2471(2)
$N_{(2)}$	−888(1)	6269(2)	1546(1)	$C_{(15)}$	−5226(2)	4331(2)	1610(2)
$N_{(3)}$	−2059(2)	2500(2)	3007(2)	$C_{(16)}$	−3970(2)	7474(2)	3229(1)
$N_{(4)}$	−6053(2)	4023(2)	1449(2)	$C_{(17)}$	−3775(2)	8761(2)	2985(2)
$C_{(1)}$	−1295(2)	5918(2)	2710(1)	$C_{(18)}$	4754(3)	9912(3)	3359(3)
$C_{(2)}$	−2940(2)	6244(2)	2772(1)	$C_{(19)}$	−5934(3)	9783(4)	3974(3)
$C_{(3)}$	−3285(2)	6647(2)	1560(1)	$C_{(20)}$	−6165(3)	8527(4)	4257(3)
$C_{(4)}$	−1763(2)	5982(2)	1002(1)	$C_{(21)}$	−5171(2)	7360(3)	3869(2)
$C_{(5)}$	−1656(2)	6648(2)	−224(1)	$C_{(22)}$	−332(2)	4270(2)	3374(2)
$C_{(6)}$	−873(2)	7423(2)	−733(1)	$C_{(23)}$	−661(2)	3678(2)	4570(2)
$C_{(7)}$	−72(2)	7667(2)	−112(1)	$C_{(24)}$	−1533(2)	4589(2)	5170(2)
$C_{(8)}$	−153(2)	7103(2)	1001(2)	$C_{(25)}$	−1803(2)	3949(3)	6297(2)
$C_{(9)}$	−4381(2)	6193(2)	1404(1)	$C_{(26)}$	−1198(3)	2421(3)	6792(2)
$C_{(10)}$	−5661(2)	7349(2)	758(2)	$C_{(27)}$	−313(3)	1499(3)	6211(2)
$C_{(11)}$	−6422(2)	8919(2)	821(2)	$C_{(28)}$	−54(3)	2115(2)	5110(2)
$C_{(12)}$	−5594(2)	8706(2)	−182(2)	$C_{(29)}$	721(2)	8556(2)	−645(2)



anti-VIII



syn-IX



X

Considering the nodal hydrogen atom 9*a*-H and the hydrogen atom 3-H in the molecules of compounds Va-d occupy the *trans*-pseudoaxial position relative to each other, we can note that the reaction in question proceeds as *endo*-addition of molecules of *trans*-1,3-butadiene to the *anti* isomer of the pyridinium ylide VIII through compound X as a transition state.

EXPERIMENTAL

The IR spectra were taken in a Perkin—Elmer 577 instrument in KBr tablets. The PMR spectra were recorded in a Bruker WM-250 instrument (250 MHz) in solutions in DMSO-D_6 with TMS as a standard.

X-ray Structural Study of 3-Benzoyl-1-(2,2-dicyano-1-cyclopropylvinyl)-2-phenyl-6-cyano-1,2,3,9-tetrahydroindolizine (Va). The crystals of compound Va are triclinic; at 20°C, a = 10.3865(9), b = 10.6914(10), c = 13.2295(10) Å, α = 66.602(6), β = 77.836(6), γ = 62.140(6)°, V = 1191.4(2) Å^3, d_{calc} = 1.23 g/cm^3, Z = 2, spacegroup P$\bar{1}$. The cell constants and intensities of 3267 independent reflections were measured in a Hilger—Watts four-circle automatic diffractometer (λ_{MoK_α}, graphite monochromator, $\theta/2\theta$ scanning up to θ_{max} = 30°). The structure was deciphered by the direct method using the MULTAN program and was refined by the full-matrix least squares method in the anisotropic approximation for the nonhydrogen atoms on the basis of 2835 reflections with $I \geq 3\sigma$. The hydrogen atoms were distinguished objectively by difference synthesis and were refined isotropically. The final values of the divergence factors were R = 0.039 and R_w = 0.045. All of the calculations were performed in an Eclipse S/200 computer, using INEXTL programs [14]. Coordinates of the nonhydrogen atoms are listed in Table 4.

Substituted *trans*-1,1-Dicyano-4-phenyl-1,3-butadienes (IIa, b). A mixture of 30 mmoles of compounds Ia, b, 30 mmoles of benzaldehyde, and 0.5 ml of triethylamine in 40 ml of isopropanol was refluxed for 0.5 h, after which it was cooled to room temperature and allowed to stand; after 5 h, the precipitate was filtered off and washed with isopropanol and hexane.

Compound IIa ($C_{15}H_{12}N_2$), mp 88-89°C (from ethanol). IR spectrum: 2223 cm^{-1} (C≡N). PMR spectrum: 1.10, 2.17 (m, 5H, CH of cyclopropyl); 6.97 (d, 1H, $C_{(3)}H$, ^3J = 15.8 Hz); 7.68 (d, 1H, $C_{(4)}H$), 7.46 ppm (m, 5H, C_6H_5). Yield 68%.

Compound IIb ($C_{19}H_{12}N_2$), mp 112-114°C (from ethanol). IR spectrum: 2224 cm^{-1} ($C\equiv N$). PMR spectrum: 6.47 (d, 1H, $C_{(3)}H$, $^3J = 16.0$ Hz); 7.18 (d, 1H, $C_{(4)}H$); 7.22-7.80 ppm (m, 10H, $(C_6H_5)_2$). Yield 71%.

Substituted Tetrahydroindolizines (Va-d). A mixture of 10 mmoles of the pyridinium salts IIIa, b, 10 mmoles of compound IIa, b, and 12 mmoles of triethylamine in 20 ml of methanol was stirred for 5-8 h at 20°C. The precipitate was filtered off and washed with ethanol and hexane.

The elemental analysis obtained on compounds IIa, b and Va-d are in agreement with the calculated values.

LITERATURE CITED

1. A. M. Shestopalov, Yu. A. Sharanin, V. P. Litvinov, and O. M. Nefedov, *Zh. Org. Khim.*, **25**, 1111 (1989).
2. A. M. Shestopalov, Yu. A. Sharanin, L. A. Rodinovskaya, V. Yu. Mortikov, V. P. Litvinov, and V. K. Promonenkov, in: Summaries of Papers from First All-Union Conference on the Chemistry and Technology of Pyridine-Containing Pesticides, Chernogolovka (1988), p. 122.
3. A. M. Shestopalov, Yu. A. Sharanin, V. N. Nesterov, L. A. Rodinovskaya, V. E. Shklover, Yu. T. Struchkov, and V. P. Litvinov, *Khim. Geterotsikl. Soedin.*, No. 9, 1248 (1991).
4. J. Zugravescu and M. N. Petrovanu, *Ylid Chemistry*, McGraw-Hill, New York (1976).
5. O. Tsuge, S. Kanemasa, and S. Takenaka, *Bull. Chem. Soc. Jpn.*, **58**, 3137 (1985).
6. O. Tsuge, S. Kanemasa, and K. Samato, *Bull. Chem. Soc. Jpn.*, **61**, 2513 (1988).
7. T. L. Gilchrist and R. C. Storr, *Organic Reactions and Orbital Symmetry*, Cambridge University Press (1972).
8. H. Guenther, *NMR Spectroscopy: An Introduction*, Wiley, New York (1980).
9. N. S. Zefirov and V. A. Palyulin, *Dokl. Akad. Nauk SSSR*, **252**, 111 (1980).
10. D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 1354 (1975).
11. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, No. 1, 1 (1987).
12. L. C. Groenen, W. Verboom, W. H. N. Nyhuis, D. N. Reinhoudt, G. J. van Hummel, and D. Feil, *Tetrahedron*, **44**, 4637 (1988).
13. A. Bondi, *J. Phys. Chem.*, **70**, 3006 (1966).
14. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, *Kristallografiya*, **28**, 1029 (1983).