Chemistry of Heterocyclic Compounds, Vol. 34, No. 6, 1998

SYNTHESIS OF 2,12-DIARYL-4-(ARYLMETHYLENEAMINO)-5,6,10,11,11-PENTACYANO-8-METHYL-1,3,8-TRIAZATRICYCLO[7,3,0,0^{3,7}]DODECA-4,6,9-TRIENES BY THE REACTION OF 2,5-DIARYL-3,3,4,4-TETRACYANOPYRROLIDINES WITH DIAZOMETHANE

A. N. Lyshchikov, O. E. Nasakin, P. M. Lukin,
A. B. Zolotoi, and A. I. Prokhorov

2,12-Diaryl-4-(arylmethyleneamino)-8-methyl-5,6,10,11,11-pentacyano-1,3,8-triazatricyclo[7,3,0,0^{3,7}]dodeca-4,6,9-trienes (VIIa-c) are synthesized on methylation of 2,5-diaryl-3,3,4,4-tetracyanopyrrolidines with diazomethane in dioxan. Their structure was confirmed by an x-ray structural investigation of a single crystal of compound (VIIa).

As was shown previously, the reaction of 3,3,4,4-tetracyanopyrrolidines (I) with alcohols and amines proceeds through initial fission of the pyrrolidine ring [1-3]. It is also known that N-acylated analogs of compound (I) are stable to such fission [4]. In addition, the properties of N-alkylated 3,3,4,4-tetracyanopyrrolidine are of interest since facile ring fission is known for the adducts of tetracyanoethylene with vinyl ethers in polar solvents [5-7]. However, on attempting to methylate 2,5-diaryl-3,3,4,4-tetracyanopyrrolidines (I) with diazomethane at the heterocyclic nitrogen in such an aprotic solvent as 1,4-dioxan, compound (I) reacted in a new way. Reaction took place with a small exothermic effect. 2,12-Diaryl-4-(arylmethyleneamino)-5,6,10,11,11-pentacyano-8-methyl-1,3,8-triazatricyclo[7,3,0,0^{3,7}]dodeca-4,6,9-trienes (VIIa-c) were isolated from the reaction mixture. Their structure was established by x-ray structural investigation of a single crystal of compound (VIIa) (Fig. 1).

The main factor leading to the formation of such a complex compound as (VII) is probably the initial methylation at nitrogen in the linear form (II), the formation of which is assisted by diazomethane. Methylation of the ketimine fragment makes recyclization to the pyrrolidine impossible since participation of the aldimine C=N bond of the methylated form (III) in subsequent conversions becomes feasible. This is put into effect by the addition of a second molecule of the linear form (II). Subsequent cyclizations, comprising formation of the pyrroline, 1,3,5-triazine, and pyrrole rings lead to the tricyclic (V). Re-

TABLE 1. Characteristics of Compounds (VIIa-c)

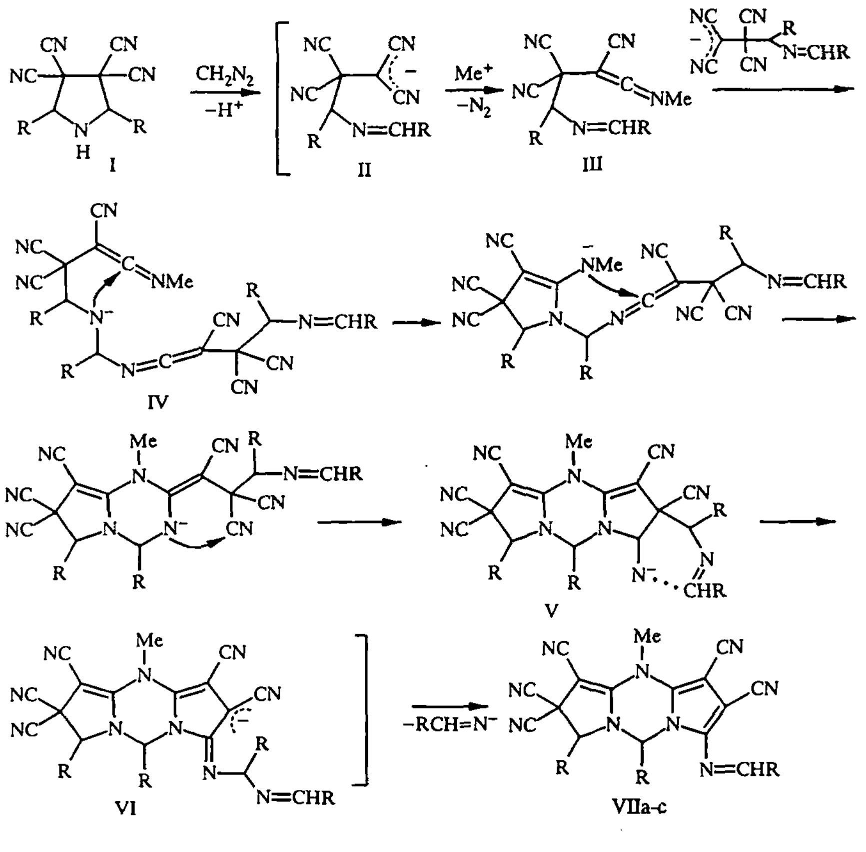
Compound	Empirical formula	Found, %			Calculated, %			mp, °C	R	IR spectrum, cm^{-1}			Yield, %
		C	H	N	C	H	N			$\nu_{C\equiv N}$	$\nu_{C=N}$	$\nu_{C=C}$	
VIIa	$C_{34}H_{21}N_9$	73,61	3,81	22,73	73,50	3,81	22,69	283...285 (dec.)	H	2235, 2225, 2205	1610	1590	54
VIIb	$C_{37}H_{27}N_9$	74,45	4,32	21,11	74,36	4,55	21,09	Dec. > 370	4-$H_3CC_6H_4$	2235, 2225, 2205	1610	1590	17
VIIc	$C_{34}H_{18}Cl_3N_9$	62,11	2,66	14,23	61,97	2,75	19,13	180...181 (dec.)	3-ClC_6H_4	2235, 2210	1610	1585	15

I. N. Ulyanov Chuvash State University, Cheboksary 428015. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 816-819, June, 1998. Original article submitted July 28, 1997.

TABLE 2. Coordinates of Atoms in the Molecule of Compound (VIIa)

Atom	x	y	z	Atom	x	y	z
$N_{(1)}$	0,1624(2)	0,0612(1)	0,4387(3)	$N_{(2)}$	0,2814(2)	0,1157(1)	0,6090(3)
$N_{(3)}$	0,2098(2)	0,1565(1)	0,4512(3)	$N_{(4)}$	0,1000(2)	-0,0345(1)	0,4069(3)
$N_{(5)}$	-0,1138(3)	-0,0373(2)	0,1289(4)	$N_{(6)}$	-0,0074(3)	0,1392(2)	0,1552(4)
$N_{(7)}$	0,2834(3)	0,2877(2)	0,7166(4)	$N_{(8)}$	0,2509(3)	0,1699(2)	1,0455(4)
$N_{(9)}$	0,5331(3)	0,2532(2)	0,8604(4)	$C_{(1)}$	0,0943(3)	0,0134(2)	0,3713(4)
$C_{(2)}$	0,0363(3)	0,0285(2)	0,2805(4)	$C_{(3)}$	0,0715(3)	0,0867(2)	0,2963(4)
$C_{(4)}$	0,1495(3)	0,1051(1)	0,3940(4)	$C_{(5)}$	0,2646(3)	0,1592(2)	0,5758(4)
$C_{(6)}$	0,3038(3)	0,2004(2)	0,6774(4)	$C_{(7)}$	0,3500(3)	0,1812(2)	0,8011(4)
$C_{(8)}$	0,3414(3)	0,1241(2)	0,7435(4)	$C_{(9)}$	0,2523(3)	0,0663(2)	0,5188(4)
$C_{(10)}$	0,0444(3)	-0,0804(2)	0,3491(4)	$C_{(11)}$	0,0516(3)	-0,1306(2)	0,3809(4)
$C_{(12)}$	0,1200(3)	-0,1310(2)	0,4820(4)	$C_{(13)}$	0,1283(3)	-0,1785(2)	0,5084(4)
$C_{(14)}$	0,0692(4)	-0,2260(2)	0,4398(5)	$C_{(15)}$	0,0011(4)	-0,2266(2)	0,3400(5)
$C_{(16)}$	-0,0082(3)	-0,1796(2)	0,3133(4)	$C_{(17)}$	-0,0460(3)	-0,0074(2)	0,1951(4)
$C_{(18)}$	0,0291(3)	0,1167(2)	0,2207(4)	$C_{(19)}$	0,2917(3)	0,2480(2)	0,6934(4)
$C_{(20)}$	0,2917(3)	0,2480(2)	0,6934(4)	$C_{(21)}$	0,2938(3)	0,1742(2)	0,9399(4)
$C_{(22)}$	0,4539(3)	0,2210(2)	0,8329(4)	$C_{(23)}$	0,4403(3)	0,1241(2)	0,7174(4)
$C_{(24)}$	0,5043(3)	0,1563(2)	0,6084(4)	$C_{(25)}$	0,5950(3)	0,1556(2)	0,5890(4)
$C_{(26)}$	0,6223(3)	0,1236(2)	0,6744(5)	$C_{(27)}$	0,5597(3)	0,0918(2)	0,7829(5)
$C_{(28)}$	0,4678(3)	0,0922(2)	0,8050(4)	$C_{(29)}$	0,3316(3)	0,0681(2)	0,4124(4)
$C_{(30)}$	0,3633(3)	0,1053(2)	0,2952(4)	$C_{(31)}$	0,4404(3)	0,1090(2)	0,2077(4)
$C_{(32)}$	0,4843(3)	0,0750(2)	0,2312(5)	$C_{(33)}$	0,4528(3)	0,0375(2)	0,3429(5)
$C_{(34)}$	0,3756(3)	0,0335(2)	0,4347(4)				

action probably occurs in such a way that each successive step is predetermined by the former. Migration of substituent to the imine nitrogen atom then occurs in (V) probably by a type of Claisen rearrangement with subsequent stabilization at compound (VII) by the direct elimination of a molecule of aldimine, as was shown in the reaction of pyrrolidines (I) with alcohols and amines [1-3].



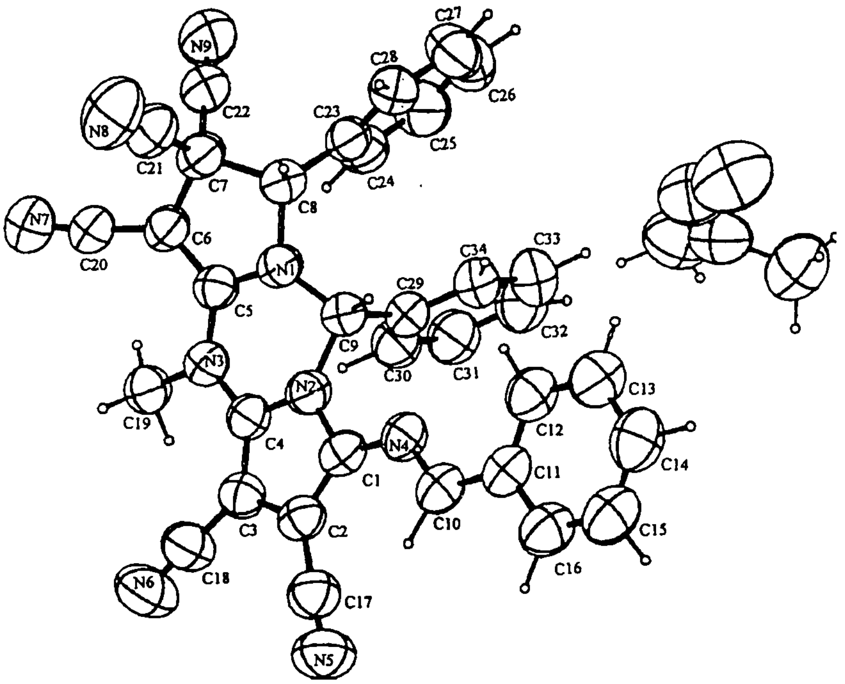


Fig. 1. Molecular structure of compound (VIIa) (bond lengths, Å): $N_{(1)}-C_{(1)}$ 1.377(5), $N_{(1)}-C_{(4)}$ 1.347(4), $N_{(1)}-C_{(9)}$ 1.476(6), $N_{(2)}-C_{(5)}$ 1.343(6), $N_{(2)}-C_{(8)}$ 1.463(5), $N_{(2)}-C_{(9)}$ 1.454(5), $N_{(3)}-C_{(4)}$ 1.374(4), $N_{(3)}-C_{(5)}$ 1.372(5), $N_{(3)}-C_{(19)}$ 1.460(5), $N_{(4)}-C_{(1)}$ 1.374(6), $N_{(4)}-C_{(10)}$ 1.256(5), $N_{(5)}-C_{(17)}$ 1.141(7), $N_{(6)}-C_{(18)}$ 1.146(7), $N_{(7)}-C_{(20)}$ 1.154(7), $N_{(8)}-C_{(21)}$ 1.124(6), $N_{(9)}-C_{(22)}$ 1.138(7), $C_{(1)}-C_{(2)}$ 1.380(7), $C_{(2)}-C_{(3)}$ 1.424(7), $C_{(2)}-C_{(17)}$ 1.406(6), $C_{(3)}-C_{(4)}$ 1.380(6), $C_{(3)}-C_{(18)}$ 1.397(7), $C_{(5)}-C_{(6)}$ 1.356(6), $C_{(6)}-C_{(7)}$ 1.520(6), $C_{(6)}-C_{(20)}$ 1.386(7), $C_{(7)}-C_{(8)}$ 1.579(7), $C_{(7)}-C_{(21)}$ 1.470(6), $C_{(7)}-C_{(22)}$ 1.467(7), $C_{(8)}-C_{(23)}$ 1.496(7), $C_{(8)}-H_{(8)}$ 0.98(1), $C_{(9)}-C_{(29)}$ 1.508(6), $C_{(9)}-H_{(9)}$ 0.97(1), $C_{(10)}-C_{(11)}$ 1.439(7), $C_{(10)}-H_{(10)}$ 0.87(1).

The structure of compounds (VIIb, c) was established by comparing their IR spectra with the IR spectrum of compound (VIIa) and also by data of elemental analysis.

EXPERIMENTAL

A check on the progress of reactions and the purity of synthesized compounds was carried out by TLC on Silufol UV 254 plates, visualizing with UV light or iodine vapor. The IR spectra were taken on a UR 20 spectrometer in a thin film (Nujol suspension). The x-ray structural investigation was carried out on a RED-4 diffractometer, CuKα radiation, $\mu(\text{CuK}\alpha) = 5.8\ \text{mm}^{-1}$.

2,12-Diaryl-4-(arylmethylamino)-5,6,10,11,11-pentacyano-8-methyl-1,3,8-triazatricyclo[7,3,0,0^{3,7}]dodeca-4,6,9-trienes (VIIa-c). Diazomethane was passed through a suspension of 2,5-diaryl-3,3,4,4-tetracyanopyrrolidine (I) (10 mmole) in 1,4-dioxan (30 ml) with stirring and cooling with water until complete solution of the initial pyrrolidine (I) and its disappearance from the reaction mixture. The solution obtained was then diluted with saturated aqueous sodium chloride solution. The dark oily mass which separated on dilution was separated and crystallized on trituration with 2-propanol. The solid obtained was filtered off, washed with 2-propanol, and recrystallized (Table 1). Mass spectrum of compound (VIIa), *m/z* (relative intensity, %): 555 (1), 528 (43), 425 (6), 352 (4), 324 (56), 310 (11), 281 (23), 255 (6), 222 (76), 104 (100), 77 (39) (the peak for the molecular ion and the ten most intense fragment ion peaks are given).

X-Ray Structural Investigation of Tricyclic (VIIa). Main crystallographic data: monoclinic, $C_{34}H_{21}N_9\cdot C_3H_7NO$, $d_{calc} = 1.27$ g/cm^3; $a = 14.940(3)$, $b = 27.057(5)$, $c = 9.010(2)$ Å; $\alpha = \beta = 90°$, $\gamma = 116.64(2)°$, $V = 3255.5$ Å^3, Z =

4, space group P $2_1/b$. The intensities of 2670 reflections with $I > 3\sigma(I)$ were measured in the range $2\Theta < 109.5°$. The structure of the molecule was solved by the direct least squares method in a full matrix approach allowing for the anisotropy of the nonhydrogen atoms and the isotropy of the hydrogen atoms and refined to $R_f = 0.59$ (SHELX 86 and SHELX 76 programs). The drawing of the molecule (Fig. 1) was obtained with the ELLIDS program [8].

The work was carried out with the financial support of the Scientific and Technical Program (NTP) "Fine Chemical Synthesis" (grant FT-22).

REFERENCES

1. O. E. Nasakin, A. N. Lyshchikov, P. M. Lukin, A. Kh. Bulai, V. A. Tafeenko, and P. A. Sharbatyan, Khim. Geterotsikl. Soedin., No. 11, 1502 (1991).
2. O. E. Nasakin, A. N. Lyshchikov, P. M. Lukin, V. A. Tafeenko, A. Kh. Bulai, and S. V. Medvedev, Khim. Geterotsikl. Soedin., No. 10, 1325 (1992).
3. O. E. Nasakin, A. N. Lyshchikov, P. M. Lukin, and V. A. Tafeenko, Khim. Geterotsikl. Soedin., No. 11, 1472 (1992).
4. O. E. Nasakin, A. N. Lyshchikov, P. M. Lukin, and A. Kh. Bulai, Khim. Geterotsikl. Soedin., No. 3, 353 (1994).
5. J. K. Williams, D. M. Wiley, and B. C. McKusik, J. Am. Chem. Soc., **84**, 2210 (1962).
6. R. Huisgen, R. Schug, and G. Steiner, Angew. Chem., **84**, 47 (1974).
7. I. Karle, J. Flippen, R. Huisgen, and R. Schug, J. Am. Chem. Soc., **97**, 5285 (1975).
8. A. N. Chekhlov, Kristallografiya, **26**, 596 (1981).