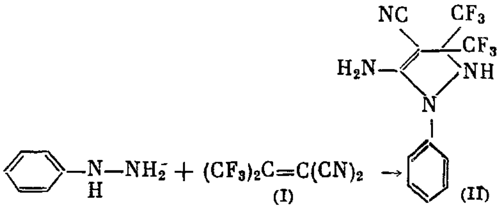
5-AMINO-3,3-BIS(TRIFLUOROMETHYL)-1-PHENYL-4-CYANO-4-PYRAZOLINE

K. V. Komarov, N. D. Chkanikov, S. V. Sereda,
M. Yu. Antipin, Yu. T. Struchkov,
A. F. Kolomiets, and A. V. Fokin

UDC 542.91:548.737:
547.772.2

In our previous work [1, 2], we described the reactions of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (I) with arylamines, leading to derivatives of fused six- and seven-membered nitrogen heterocycles. In the present work, we found that the reaction of alkene (I) with phenylhydrazine in absolute Freon-113 leads to 5-amino-3,3-bis(trifluoromethyl)-1-phenyl-4-cyano-4-pyrazoline in 89% yield.



Pyrazoline (II) is stable under ordinary conditions and has limited solubility in nonpolar organic solvents. The mass spectrum of (II) shows an M^+ peak. The major fragmentation involves the elimination of the CF_3 groups and the benzene ring. The chemical shifts in the ^{13}C and ^{19}F NMR spectra are given in the Experimental section.

The molecular structure of (II) was unequivocally proven by an x-ray diffraction structural analysis. The atomic coordinates are given in Table 1. The temperature factors may be obtained from the authors. Figure 1 shows a general view of this molecule with the numbering of the atoms. The most important bond lengths: C^3–C^4, 1.486(7); C^3–N^2, 1.477(6); C^4–C^5, 1.378(7); N^2–N^1, 1.441(6); and N^1–$C^{1'}$, 1.433(7) Å.

We note a number of features of the five-membered heterocycle. This ring is virtually planar (the maximal yield of the atoms from the mean plane is ±0.02 Å). The conjugation chain apparently includes C^4=C^5, N^1–C^5, C^5–N^3, and, to a lesser extent, C^4–C^8. In particular, significant extension of the C^4=C^5 bond is observed to 1.378(7) Å in comparison with 1.313 Å for ethylene [3]. Contraction is noted for C^5–N^1 (1.369(6) Å) and, to a greater extent, C^5–N^3 (1.316(7) Å) in comparison with the ordinary C_{sp^2}–N_{sp^3} bond length (1.45 Å) [4]. There

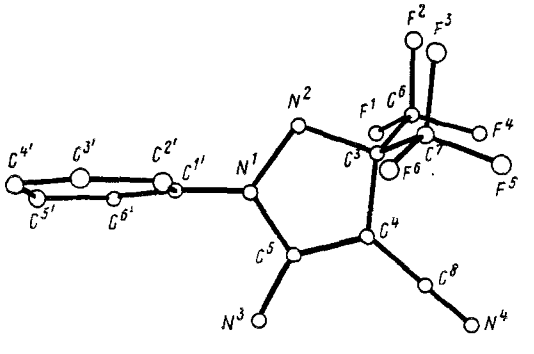


Fig. 1. General view of (II) with numbering of the non-hydrogen atoms. The most important bond lengths: C^3–C^4, 1.486(7); C^3–N^2, 1.477(6); C^4–C^5, 1.378(7); N^2–N^1, 1.441(6), and N^1–$C^{1'}$, 1.433(7) Å.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2417-2419, October, 1988. Original article submitted December 30, 1987.

0568-5230/88/3710-2180$12.50

TABLE 1. Coordinates of the Non-Hydrogen Atoms ($\times 10^4$) in the Structure of 5-Amino-3,3-bis(trifluoromethyl)-1-phenyl-4-cyano-4-pyrazoline

Atom	X	Y	Z	Atom	X	Y	Z
F^1	9672(5)	6389(1)	1444(4)	C^4	7038(8)	5744(2)	3467(6)
F^2	8235(6)	6828(1)	3269(4)	C^5	5789(7)	5779(2)	4760(6)
F^3	7137(6)	6920(2)	946(4)	C^6	7813(9)	6573(2)	1977(7)
F^4	7288(6)	5636(2)	66(4)	C^7	5623(10)	5843(3)	775(7)
F^5	4307(7)	5444(2)	1069(4)	C^8	11182(10)	4590(2)	6695(6)
F^6	4667(7)	6162(2)	−220(4)	$C^{1'}$	3162(8)	6444(2)	5619(6)
N^1	4122(7)	6117(2)	4471(5)	$C^{2'}$	1375(9)	6255(3)	6365(7)
N^2	4344(6)	6360(2)	2983(5)	$C^{3'}$	443(10)	6558(3)	7508(7)
N^3	5979(7)	5550(2)	6113(5)	$C^{4'}$	1194(12)	7042(3)	7833(8)
N^4	9717(9)	4867(2)	6813(6)	$C^{5'}$	2991(15)	7223(3)	7109(9)
C^3	6237(8)	6115(2)	2269(6)	$C^{6'}$	3969(12)	6915(3)	5991(8)

is considerable compression of the pyramidal configuration of N^1 (the sum of the bond angles is 349.5°, which exceeds the sum of the three ideal tetrahedral angles (328.2°) by 21.3°) as a result of conjugation of the unshared N^1 electron pair with the π-system of the $C^4{=}C^5$ double bond. Conjugation of the $C^4{=}C^5$ double bond with the cyano group, judging from the bond lengths, is less pronounced: the $C^4{-}C^8$ single bond is slightly shortened to 1.406(8) Å relative to the standard $C_{sp^2}{-}C_{sp}$ bond length (1.426 Å [5]), while the triple bond has the ordinary length (1.158(8) Å). There is no conjugation between the unshared electron pair of N^1 with the phenyl ring π-system due to rotation of the ring (the dihedral angle between the planes of the two rings is 73.4°). The other geometric parameters of (II) have the expected values.

EXPERIMENTAL

The ^{19}F and ^{13}C NMR spectra were taken on a Bruker WP-200SY spectrometer at 188.32 and 50.31 MHz, respectively, in acetone (^{19}F NMR) and DMSO (^{13}C NMR). The chemical shifts were determined relative to TMS as the internal standard (^{13}C NMR) and CF_3CO_2H as the external standard (^{19}F NMR). The mass spectrum was taken on an AEI MS-30 mass spectrometer. The R_f value is given for Silufol UV-254 plates with 10:1 benzene—acetone as the eluent.

A sample of (II) was recrystallized from octane—acetone from the x-ray diffraction study. The unit cell parameters for the monoclinic crystals of (II) at 20°C are as follows: $a = 6.256(1)$, $b = 25.272(2)$, $c = 8.699(1)$ Å, $\beta = 90.47(6)°$, $V = 1375.4(3)$ Å^3, $d_{calc} = 1.56$ g/cm^3, $Z = 4$, space group $P2_1/c$. The unit cell parameters and intensities of 1969 independent reflections were measured on a Hilger—Watts automatic four-circle diffractometer using λMoK_α radiation, graphite monochromator, and $\theta/2\theta$ scanning; $2\theta \leq 52°$. The structure was solved by the direct method using the MULTAN program and refined by the method of least squares in the anisotropic block diagonal approximation using 1148 reflections with $F^2 \geqslant 3\sigma$. The positions of all the hydrogen atoms were calculated geometrically and these atoms were included in the refinement with fixed thermal and positional parameters. The final R = 0.069 and $R_w = 0.056$. All the calculations were carried out on an Eclipse S/200 computer using the INEXTL programs [6].

5-Amino-3,3-bis(trifluoromethyl)-1-phenyl-4-cyano-4-pyrazoline (II). A sample of 1.09 g alkene (I) was added with stirring over 30 min to an emulsion of 0.5 g phenylhydrazine in 6 ml absolute freon-113. The reaction mixture was left for 4 h at 20°C. The crystals were filtered off and washed with pentane. Recrystallization from CCl_4 gave 1.3 g (89%) white crystalline (II), mp 151-153°C, R_f 0.13. ^{13}C NMR spectrum (δ, ppm): 162.4 (C^5), 142.7 ($C^{1'}$), 129.3 ($C^{3'}$, $C^{5'}$), 126.7 ($C^{4'}$), 124.1 ($C^{2'}$, $C^{6'}$), 123.1 (CF_3) ($^1J_{CF}$ 285 Hz), 116.3 (CN), 71.1 (C^3), 48.0 (C^4). ^{19}F NMR spectrum (δ, ppm): −2.4 s. Mass spectrum, m/z (relative intensity, %): 322 M^+ (1.55), 253 $[M{-}CF_3]^+$ (100), 77 $[C_6H_5]^+$ (73.36), 69 $[CF_3]^+$ (27.03). Found: C 44.77; H 2.25; N 17.59%. Calculated for $C_{12}H_8N_4F_6$: C 44.72; H 2.48; N 17.39%.

CONCLUSIONS

The reaction of phenylhydrazine with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene leads to 5-amino-3,3-bis(trifluoromethyl)-1-phenyl-4-cyano-4-pyrazoline, whose structure was proven by x-ray diffraction analysis.

LITERATURE CITED

1. K. V. Komarov, N. D. Chkanikov, S. V. Sereda, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1917 (1988).
2. K. V. Komarov, N. D. Chkanikov, S. V. Sereda, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1920 (1988).
3. G. J. H. Nes and A. Van Vos, Acta Crystallogr., 33, 1653 (1977).
4. M. Burke-Laing and M. Laing, Acta Crystallogr., 32, 3216 (1976).
5. A. I. Kitaigorodskii (Kitaigorodsky), Molecular Crystals and Molecules, Academic Press, New York–London (1973), p. 431.
6. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, Kristallografiya, 1029 (1983).

HOMOGENEOUS AND SUPPORTED PLATINUM COMPLEX CATALYSTS WITH NITROGEN-CONTAINING LIGANDS IN THE HYDROGENATION OF UNSATURATED HYDROCARBONS

E. G. Kliger, L. P. Shuikina,
O. P. Parenago, and V. M. Frolov

UDC 542.971.2:542.941:547.313:
547.314:547.315

Heterogeneous platinum catalysts are highly active in the hydrogenation of various classes of organic compounds [1, 2]. Information on the use of platinum complexes as hydrogenation catalysts is extremely limited [3, 4].

In our previous work [5], we reported on the synthesis of new platinum complexes with nitrogen-containing ligands, which display high activity in the hydrogenation of unsaturated hydrocarbons. In the present work, results are given for a study of the hydrogenation of unsaturated hydrocarbons in the presence of platinum complex catalysts containing higher aliphatic amines as ligands.

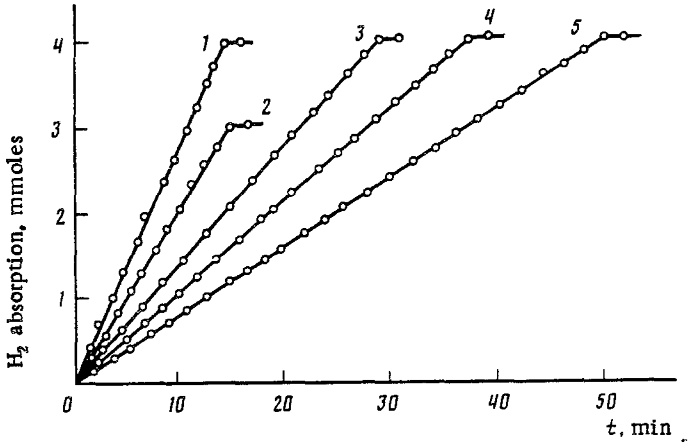


Fig. 1. The kinetic curves for the hydrogenation of 1-hexene (1), cyclopentene (2), 1,3-pentadiene (3), cyclopentadiene (4), and isoprene (5) in the presence of the catalyzer H_2PtCl_6–$(C_9H_{19})_3N$–$(i\text{-}C_4H_9)_2AlH$–C_2H_5OH at 20°C, P_{H_2} = 40 kPa, [Pt] = $5 \cdot 10^{-4}$ mole/liter, amine/Pt = 2, Al/Pt = 8, C_2H_5OH/Pt mole ratio = 8. Toluene served as the solvent. Substrate introduced, mmoles: 4 (1), 3 (2), 2 (3-5).

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2420-2422, October, 1988. Original article submitted January 25, 1988.

0568-5230/88/3710-2182$12.50