

SHORT
COMMUNICATIONS

Synthesis of Substituted Cyclopentenes by Reaction of Acrolein with $\beta,\beta,\gamma,\gamma$ -Tetracyanoalkanones

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In 1957, Middleton *et al.* [1] were the first to effect tetracyanoethylation of ketones. $\beta,\beta,\gamma,\gamma$ -Tetracyanoalkanones were obtained by mixing ketones with tetracyanoethylene in the presence of silver [1] or HCl [2]. Reactions of $\beta,\beta,\gamma,\gamma$ -tetracyanoalkanones with some acids (HCl, HBr, HI, CH_3COCOOH) lead to formation of cyano-substituted pyrroles and pyridines [3–5]. However, the ketones studied in [3–5] had relatively simple structures: they contained no multiple bonds or bulky substituents. Analogous reactions with more

complex ketones which are related to natural and biologically active compounds were not studied.

We have found that $\beta,\beta,\gamma,\gamma$ -tetracyanoalkanones **Ia–If** readily react with acrolein under mild conditions, affording cyanocyclopentene derivatives **IIIa–IIIc** in high yields (Scheme 1). The proposed procedure seems to be convenient for modification of natural and biologically active compounds containing CH_3COCR_3 and $\text{R}^1\text{CH}_2\text{COCR}_3$ fragments through transformation into cyano derivatives.

Scheme 1.

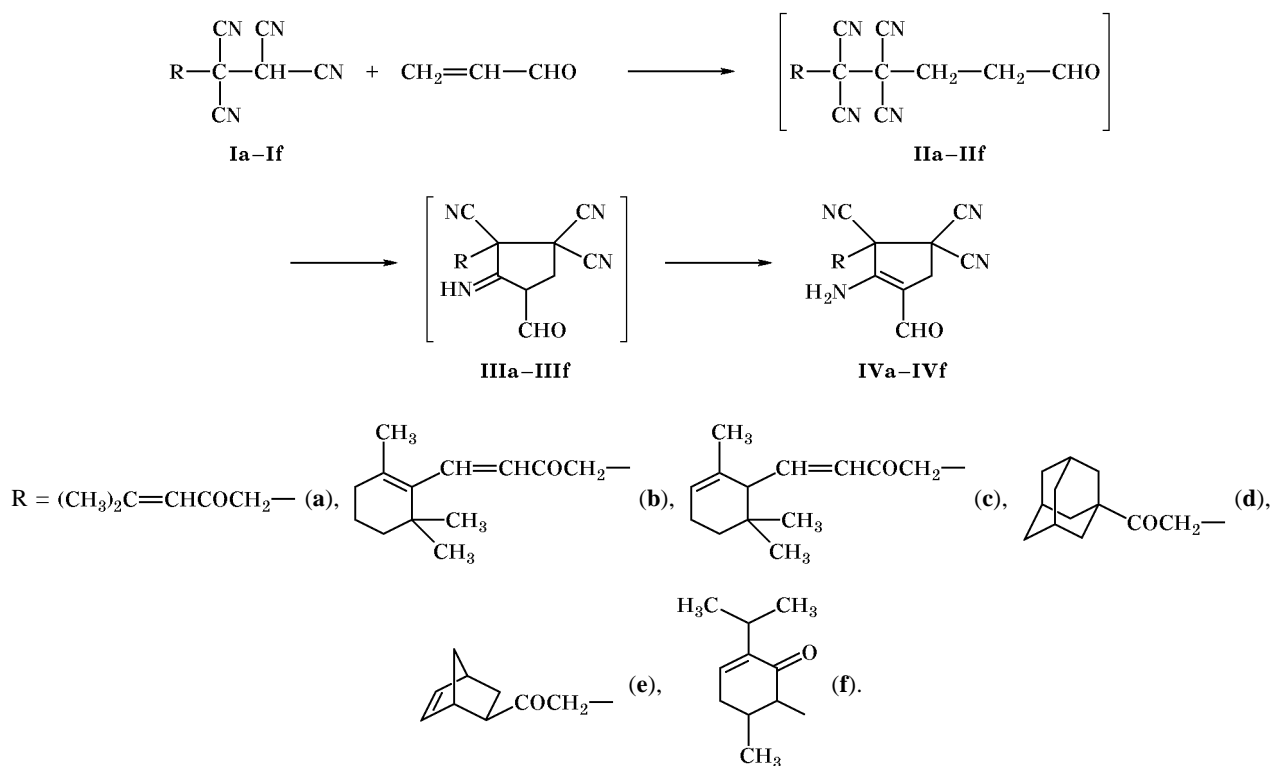


Table 1. Yields, melting points, IR spectra, and elemental analyses of compounds **IVa–IVf**

Comp. no.	Yield, %	mp, °C	IR spectrum, ν , cm^{-1}	Found, %			Formula	Calculated, %		
				C	H	N		C	H	N
IVa	67	138–139	3410, 3365, 2265, 1680, 1665, 1590	63.91	4.93	19.87	$\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_2$	63.82	5.00	19.85
IVb	65	192–193	3440, 3375, 2270, 1680, 1660, 1580	70.24	6.48	14.83	$\text{C}_{22}\text{H}_{24}\text{N}_4\text{O}_2$	70.19	6.43	14.88
IVc	69	194–195	3435, 3365, 2265, 1675, 1665, 1585	70.10	6.49	14.94	$\text{C}_{22}\text{H}_{24}\text{N}_4\text{O}_2$	70.19	6.43	14.88
IVd	92	175–176	3415, 3360, 2275, 1700, 1685, 1595	65.68	6.18	15.52	$\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_2$	65.59	6.12	15.46
IVe	78	171–172	3420, 3370, 2265, 1710, 1690, 1575	67.39	4.97	17.41	$\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_2$	67.48	5.03	17.48
IVf	84	179–180	3365, 3195, 2265, 1695, 1650, 1595	67.35	6.47	16.49	$\text{C}_{19}\text{H}_{22}\text{N}_4\text{O}_2$	67.43	6.55	16.55

Table 2. ^1H NMR spectra of compounds **IVa–IVf**

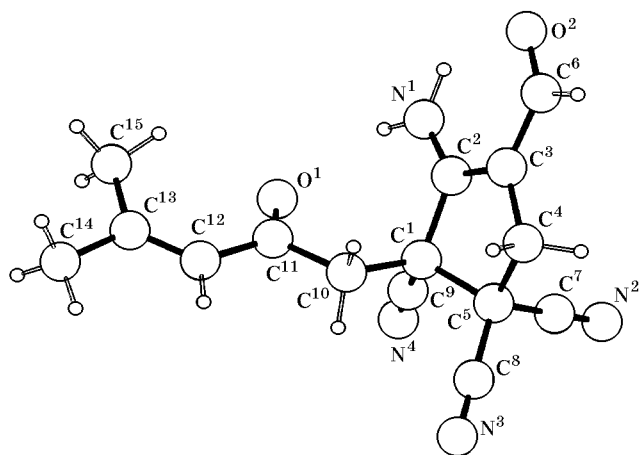
Comp. no.	Chemical shifts δ , ppm
IVa	9.56 s (1H, CHO), 7.94 s (2H, NH_2), 7.16 d [1H, $(\text{CH}_3)_2\text{C}=\text{CHCO}$], 4.13 d (1H, CH_2CO), 3.68 d (1H, CH_2CO), 3.65 d [1H, $\text{CH}_2\text{C}(\text{CN})_2$], 3.51 d [1H, $\text{CH}_2\text{C}(\text{CN})_2$], 1.8 s, [6H, $\text{C}(\text{CH}_3)_2$]
IVb	9.58 s (1H, CHO), 7.99 s (2H, NH_2), 7.47 d (1H, $\text{CH}=\text{CHCO}$), 6.24 d (1H, $\text{CH}=\text{CHCO}$), 4.18 d (1H, CH_2CO), 3.65 d (1H, CH_2CO), 3.61 d [1H, $\text{CH}_2\text{C}(\text{CN})_2$], 3.44 d [1H, $\text{CH}_2\text{C}(\text{CN})_2$], 2.13 m [2H, $\text{CH}_2\text{C}(\text{CH}_3)=\text{C}$], 1.82 s (3H, $\text{CH}_3\text{C}=\text{C}$), 1.63 m [2H, $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)=\text{C}$], 1.48 m [2H, $\text{CH}_2\text{C}(\text{CH}_3)_2$], 1.1 s [6H, $\text{C}(\text{CH}_3)_2$]
IVc	9.61 s (1H, CHO), 7.92 s (2H, NH_2), 7.32 d (1H, $\text{CH}=\text{CHCO}$), 6.08 d (1H, $\text{CH}=\text{CHCO}$), 5.17 d.d [1H, $\text{CH}=\text{C}(\text{CH}_3)$], 4.12 d (1H, CH_2CO), 3.66 d (1H, CH_2CO), 3.60 d [1H, $\text{CH}_2\text{C}(\text{CN})_2$], 3.52 d (1H, $\text{CHCH}=\text{CH}$), 3.43 d [1H, $\text{CH}_2\text{C}(\text{CN})_2$], 2.18 m [2H, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)$], 1.75 s (3H, $\text{CH}_3\text{C}=\text{C}$), 1.68 m [2H, $\text{CH}_2\text{C}(\text{CH}_3)_2$], 1.04 s [6H, $\text{C}(\text{CH}_3)_2$]
IVd	9.58 s (1H, CHO), 7.99 s (2H, NH_2), 4.14 d (1H, CH_2CO), 3.61 d [1H, $\text{CH}_2\text{C}(\text{CN})_2$], 3.53 d (1H, CH_2CO), 3.38 d [1H, $\text{CH}_2\text{C}(\text{CN})_2$], 2.08 m (3H, 3CH), 1.88 m (6H, 3 CH_2), 1.64 m (6H, 3 CH_2)
IVe	9.67 s (1H, CHO), 7.87 s (2H, NH_2), 5.87 m (2H, $\text{CH}=\text{CH}$), 4.1 d (1H, CH_2CO), 3.57 d [1H, $\text{CH}_2\text{C}(\text{CN})_2$], 3.5 d (1H, CH_2CO), 3.41 d [1H, $\text{CH}_2\text{C}(\text{CN})_2$], 3.35 m (1H, CHCO), 2.67 m (2H, CH), 1.61–1.78 m (6H, 3 CH_2)
IVf	9.5 s (1H, CHO), 7.87 s (2H, NH_2), 3.82 d [1H, $\text{C}(\text{O})\text{CHCH}$], 3.71 d (1H, CH_2), 3.53 d (1H, CH_2), 2.5 m [1H, $\text{CHCH}(\text{CH}_3)_2$], 2.18–1.58 m [5H, $\text{CH}(\text{CH}_3)_2$, CH_2CH_2], 1.48 d (3H, CH_3), 0.84 d [6H, $\text{CH}(\text{CH}_3)_2$]

A probable mechanism of the reaction (Scheme 1) includes initial addition of ketone **Ia–If** to acrolein with formation of intermediates **IIa–IIf**. The latter undergo intramolecular cyclization to 2-iminocyclopentane-1-carbaldehydes **IIIa–IIIf** whose prototropic isomerization yields aminocyclopentenes **IVa–IVf** (Tables 1, 2).

Reaction of tetracyanoalkanones Ia–If with acrolein. Acrolein, 0.015 mol, was added dropwise to 0.01 mol of tetracyanoalkanone **Ia–If** in 20 ml of

2-propanol, and the mixture was stirred until it became homogeneous. After 1–2 days, crystallization occurred, and the precipitate was filtered off and washed with 2-propanol. An additional amount of the product can be isolated by dilution of the filtrate with 40 ml of water. The precipitates were combined and recrystallized from 2-propanol.

The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates. The IR spectra were recorded on a UR-20 instrument



Structure of the molecule of 3-amino-4-formyl-2-(4-methyl-2-oxo-3-pentenyl)-3-cyclopentene-1,1,2-tricarbonitrile (**IVa**).

in mineral oil. The ^1H NMR spectra were obtained on a Bruker AM-300 spectrometer (300 MHz) in $\text{DMSO-}d_6$. The X-ray diffraction data for a single crystal of compound **IVa** were obtained on a Siemens P3/PC four-circle diffractometer (MoK_α irradiation,

graphite monochromator, $\theta/2\theta$ scanning). Unit cell parameters: $a = 9.144(2)$, $b = 19.216(4)$, $c = 8.365(2)$ Å; $\alpha = 90^\circ$, $\beta = 93.43(2)^\circ$, $\gamma = 90(2)^\circ$; $V = 1467.2(6)$ Å 3 ; $d_{\text{calc}} = 1.273$ g/cm 3 ; space group $P2_1/c$. All calculations were performed on a computer using SHELXTL PLUS software.

REFERENCES

1. Middleton, W.I., Heckert, R.E., Little, E.L., and Krespan, C.G., *J. Am. Chem. Soc.*, 1958, vol. 80, no. 11, pp. 2783–2788.
2. Nikolaev, E.G., Nasakin, O.E., Terent'ev, P.B., Khaskin, B.A., and Petrov, V.G., *Zh. Org. Khim.*, 1984, vol. 20, no. 1, pp. 205–206.
3. Nasakin, O.E., Sheverdob, V.P., Moiseeva, I.V., Ershov, O.V., Chernushkin, A.N., and Tafeenko, V.A., *Russ. J. Gen. Chem.*, 1999, vol. 69, no. 2, pp. 291–300.
4. Nasakin, O.E., Nikolaev, E.G., Terent'ev, P.B., Bulai, A.Kh., and Kalandriashvili, A.G., *Khim. Geterotsikl. Soedin.*, 1985, no. 8, pp. 1027–1030.
5. Nasakin, O.E., Nikolaev, E.G., Terent'ev, P.B., Bulai, A.Kh., and Zakharov, V.Yu., *Khim. Geterotsikl. Soedin.*, 1985, no. 9, pp. 1225–1228.