INTERACTION OF 1,1,2,2-TETRACYANOETHANE WITH α,β-UNSATURATED KETONES, ALKYLIDENEACETOACETIC ESTERS AND ALKYLIDENE(OR ARYLIDENE)ACETYLACETONES

O. E. Nasakin, P. M. Lukin, P. B. Terent'ev,
A. Kh. Bulai, V. D. Sheludyakov, A. B. Zolotoi,
A. I. Gusev, O. A. D'yachenko, G. M. Apal'kova,
and L. O. Atovmyan

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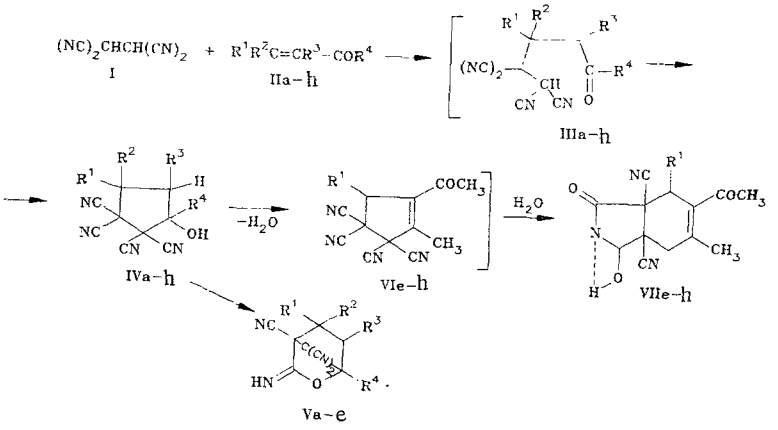
We found that 1,1,2,2-tetracyanoethane (I) undergoes a Michael reaction with compounds IIa-h, which contain an α,β-unsaturated ketone fragment, in aqueous isopropanol at 30-48°C with the initial fomration of β-tetracyanoethylated carbonyl compounds IIIa-h, which are then cyclized according to an aldol addition mechanism to carbinols IVa-h. Compounds IVa-e subsequently undergo intramolecular cyclization by means of the hydroxyl group and one of the cyano groups in position 3 to form bicyclic iminolactones Va-e. Carbinols IVf-h apparently quickly undergo dehydration to cyclopentenes VIf-h, which are converted into bicyclic imides VIIf-h as a result of the partial hydrolysis of one of the nitrile groups followed by the interaction of the carbamoyl fragment formed with the adjacent cyano group (see the scheme).

Compound, yield, %, mp °C: Va, 32, 158-159; Vb, 10, 162-163; Vc, 32, 131-132; Vd, 22, 120-121; Ve, 24, 143-144; VIIf, 51, 234-235 (with decomposition); VIIg, 52, 243-244 (with decomposition); VIIh, 48, 223-224 (with decomposition).



II—VII a $R^1=R^2=R^4=CH_3$; b $R^1=i\text{-}C_3H_7$, $R^4=CH_3$; c $R^1=R^4=CH_3$, $R^3=COOC_2H_5$; d $R^1=C_2H_5$, $R^3=COOC_2H_5$, $R^4=CH_3$; e $R^1=C_6H_5$, $R^4=C_2H_5$; f $R^1=R^4=CH_3$, $R^3=COCH_3$; g $R^1=C_6H_5$, $R^3=COCH_3$, $R^4=CH_3$; h $R^1=3\text{-}ClC_6H_4$, $R^3=COCH_3$, $R^4=CH_3$, not indicated R=H

The structures of all the compounds synthesized were confirmed by the data from elemental analysis and the ^1H NMR, ^{13}C NMR, IR, and the structures of Va and VIIf were confirmed by x-ray diffraction analysis.

I. N. Ul'yanov Chuvashskii State University, Cheboksary 428015. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, p. 1431, October, 1984. Original article submitted March 2, 1984.

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