on the strength of these bonds. The observed dependence of the intensity of the fragment ions on the spatial orientation of the substituents in the molecule can be used to establish the structures of new polynuclear benzo[f]quinoline derivatives.

EXPERIMENTAL

The mass spectra were obtained with a Varian MAT-311 spectrometer under the following conditions: the cathode emission current was 1.0 mA, and the ionizing-electron energy was 70 eV. The samples were introduced directly into the ion source of the mass spectrometer. The vaporization temperature of the samples was 150-200°C, and the ion-source temperature was 200°C. The benzo[f]quinolines were synthesized by the method in [8].

LITERATURE CITED

1. N. A. Klyuev, R. A. Khmel'nitskii, G. A. Mal'tseva, A. K. Sheinkman, V. A. Ivanov, and B. M. Zolotarev, Khim. Geterotsikl. Soedin., No. 7, 979 (1973).
2. P. B. Teret'ev, N. P. Lomakina, and A. N. Kost, Org. Mass Spectrom., 11, 281 (1976).
3. C. N. R. Rao, Electronic Spectra in Chemistry [Russian translation], Mir, Moscow (1964), p. 264.
4. F. Andreani, R. Andrisano, G. Salvadory, and M. Tramontini, J. Chem. Soc., C, No. 5, 1007 (1971).
5. V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, Dipole Moments in Organic Chemistry [in Russian], Khimiya, Leningrad (1968), p. 248.
6. R. Taylor, J. Chem. Soc., B, 2382 (1971).
7. G. T. Pilyugin, Ya. O. Gorichok, B. M. Gutsulyak, and S. I. Gorichok, Khim. Geterotsikl. Soedin., No. 6, 889 (1965).
8. N. S. Kozlov, L. K. Slobodchikova, and G. S. Shmanai, Dokl. Akad. Nauk SSSR, 187, 803 (1969).

CYCLOADDITION TO AMINOMETHYLENE DERIVATIVES OF 1-PHENYL-3-METHYLPYRAZOLE-5-THIONE AND 1-PHENYL-3-METHYLPYRAZOLE-5-SELENONE

G. K. Lebedeva, I. Ya. Kvitko,
and A. V. El'tsov

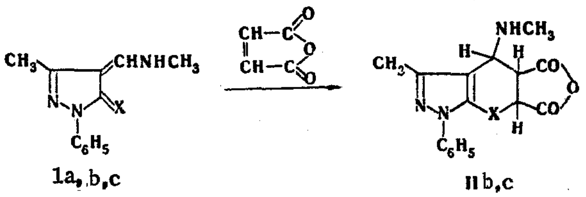
UDC 547.722.81

Addition products — anhydrides of 1-phenyl-3-methyl-4-alkylamino-4,5,6-tetrahydrothio(seleno)pyrano-3,2-pyrazole-5,6-dicarboxylic acids — were obtained by cycloaddition of maleic anhydride to aminomethylene derivatives of 1-phenyl-3-methylpyrazole-5-thione and 1-phenyl-3-methylpyrazole-5-selenone, while anhydrides of the corresponding dihydrothio(seleno)pyranopyrazoledicarboxylic acids were obtained by splitting out of an amine. The oxygen-containing analog does not undergo cycloaddition. An oxanol dye is formed from 1-phenyl-3-methyl-4-dimethylaminomethylene-5-pyrazolone, whereas the corresponding acyl derivative was isolated from the monomethyl derivatives.

In a continuation of our research on cycloaddition to aminomethylene derivatives of heterocyclic types [1, 2] we subjected maleic anhydride to reaction with monosubstituted derivatives of 1-phenyl-3-methyl-5-pyrazolone (Ia) and its sulfur (Ib) and selenium (Ic) analogs.

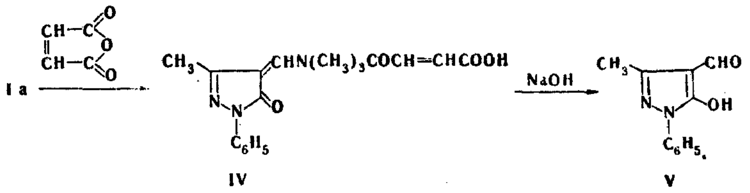
Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 527-529, April, 1979. Original article submitted December 21, 1977; revision submitted October 30, 1978.

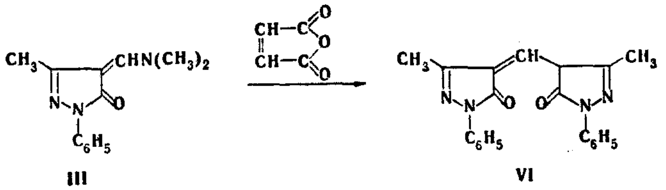
0009-3122/79/1504-0429$07.50



a X=O; b X=S; c X=Se

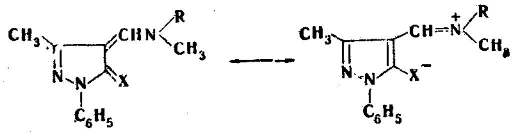
In the case of Ib the reaction in benzene or dioxane leads to the corresponding addition products (IIb, c). The reaction of the oxygen-containing compound (Ia), as well as 1-phenyl-3-methyl-4-dimethylaminomethylene-5-pyrazolone (III), takes place under more severe conditions and leads to substances with different structures (IV and VI).



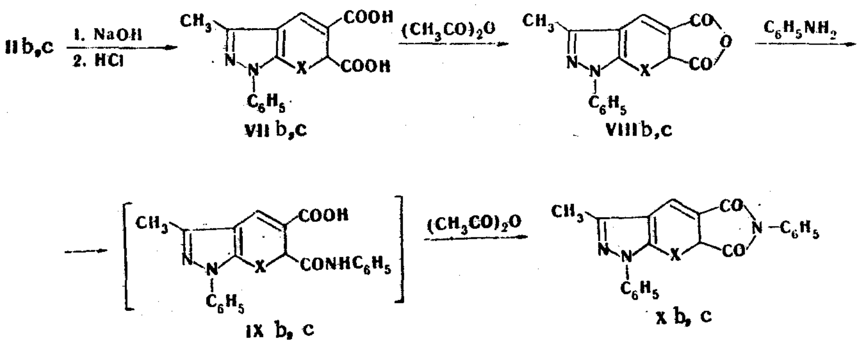


The ease of conversion of III and VI was noted in [3]. In this case the reaction is evidently accelerated by the presence of maleic anhydride. The structure of the product of acylation of 1-phenyl-3-methyl-4-methylaminomethylene-5-pyrazolone (IV) with maleic anhydride was confirmed by spectral data, the results of elementary analysis, and by alkaline hydrolysis, which leads to the corresponding formylpyrazole V [4].

The different behavior of the oxygen analog as compared with the sulfur- and selenium-containing enamines in the cycloaddition reaction is associated with the considerable polarization of the latter, as a consequence of which they readily undergo reaction by attaching the activated double bond of maleic anhydride.



When adducts IIb, c are heated in aqueous alcohol solutions of alkali, they readily split out an amine and are converted to the corresponding salts of thio(seleno)pyranopyrazoledicarboxylic acids VIIb, c.



When the latter are heated with acetic anhydride, they are converted to the corresponding anhydrides (VIIIb, c), which react with aniline to give monoamides IXb, c; the latter are dehydrated in acetic anhydride to imides Xb, c.

TABLE 1. Derivatives of Dihydrothio(seleno)pyranopyrazoledicarboxylic Acids

Compound	mp, °C	ν_{CO}, cm^{-1}	λ_{max}, nm (log ε) (in ethanol)	Found, %			Empirical formula	Calc., %			Yield, %
				C	N	S		C	N	S	
IIb	246—248[a]	1710	255 (4,16)		13,0	9,7	$C_{16}H_{15}N_3O_3S$		12,8	9,7	88
IIc	243—245[a]	1700	255 (4,08)	51,0	11,0		$C_{16}H_{15}N_3O_3Se$	51,0	11,2		75
VIIb	218—220[b]	1710	255 (4,04)		9,1	9,9	$C_{15}H_{12}N_2O_4S$		8,9	10,1	95
VIIc	115—117[b]	1710	258 (3,75)	49,4	7,6		$C_{15}H_{12}N_2O_4Se$	49,6	7,7		74
VIIIb	256—258[b]	1710	255 (4,04)		9,3	10,5	$C_{15}H_{10}N_2O_3S$		9,3	10,8	80
VIIIc	221—223[b]	1710	258 (3,75)	52,1	8,1		$C_{15}H_{10}N_2O_3Se$	52,1	8,1		94
IXb	210—212[b]	1710	257 (4,48)		10,5	7,9	$C_{21}H_{17}N_3O_3S$		10,7	8,2	78
Xb	248—250[c]	1710	257 (4,40)		11,1	8,4	$C_{21}H_{15}N_3O_2S$		11,3	8,6	74

a) From butyl acetate. b) From chlorobenzene. c) From acetic acid.

The cycloaddition of maleic anhydride to aminomethylene derivatives of pyrazolethione and pyrazoleselenone is accompanied by decolorization of the reaction solution. The hypsochromic shift is ~200 nm [5] and is associated with the formation of a new ring. In contrast to the starting compounds, all of the adducts are weakly colored, and an absorption maximum at 260 nm, which is associated with a $\pi-\pi^*$ transition in the phenylpyrazole ring, is observed in their electronic spectra. A comparison of the IR spectra of the starting [5] and final compounds also indicates sharp changes. The absorption bands at 1650 cm^{-1} vanish, and new bands appear at 1700-1710 (C=O) and 3450-3470 cm^{-1} (NH). The PMR spectra of IIb, c confirm the structures adopted for them.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with an SF-8 spectrophotometer. The PMR spectra of d_6-DMSO solutions of the compounds were recorded with a Perkin–Elmer spectrometer (60 MHz). The starting aminomethylene derivatives of pyrazolthione(selenone) were obtained by the method in [6].

1-Phenyl-3-methyl-4-methylamino-4,5,6-tetrahydrothiopyrano[2,3-d]pyrazole-5,6-dicarboxylic Acid Anhydride (IIb). A 0.23-g (1 mmole) sample of 1-phenyl-3-methyl-4-methylaminomethylene-5-thiopyrazolone in 20 ml of dioxane was added to a solution of 0.196 g (2 mmole) of maleic anhydride in 5 ml of dioxane, and the mixture was refluxed for 30 min. The excess dioxane was then removed by distillation, and the residue was diluted with butyl acetate. The resulting precipitate was removed by filtration and dried. Compound IIc was similarly obtained. PMR spectrum of IIb: 2.32; 2.7 (2s, 6H, $2CH_3$); 4.8; 4.3; 3.6; 3.4 (4H, 4s, 4-H, NH, 5-H, 6-H); 7.6 ppm (5H, m, C_6H_5); IIc: 2.4; 2.75 (6H, 2s, $2CH_3$); 4.8; 4.3; 3.4 (3H, 3s, 4-H, 5-H, 6-H); 7.6 ppm (5H, m, C_6H_5).

1-Phenyl-3-methylthiopyrano[3,2-d]pyrazole-5,6-dicarboxylic Acid (VIIb). A 0.329-g (1 mmole) sample of IIb was heated in 10 ml of a 10% NaOH solution with 5 ml of methanol at 60°C for 1 h, after which the mixture was cooled and acidified to pH 6 with 9% hydrochloric acid. The resulting precipitate was removed by filtration and dried. Compound VIIc was similarly obtained.

1-Phenyl-3-methylthiopyrano[3,2-d]pyrazole-5,6-dicarboxylic Acid Anhydride (VIIIb). A 0.316-g (1 mmole) sample of VIIb was refluxed in 10 ml of acetic anhydride for 30 min, after which the mixture was cooled and poured over ice. The resulting precipitate was removed by filtration, washed with water, and dried. Compound VIIIc was similarly obtained.

1-Phenyl-3-methyl[3,2-d]pyrazole-5,6-dicarboxylic Acid Monoanilide (IXb). A 0.316-g (1 mmole) sample of VIIb was fused with 0.14 ml (1.5 mmole) of aniline at 160°C for 2 h, after which the mixture was cooled and treated with 9% hydrochloric acid. The resulting precipitate was removed by filtration, washed with water, and dried.

1-Phenyl-3-methyl[3,2-d]pyrazole-5,6-dicarboxylic Acid N-Phenylimide (Xb). A 0.391-g (1 mmole) sample of monoanilide IXb was heated with 10 ml of acetic anhydride at 100°C for 30 min, after which the mixture was cooled and poured over ice. The resulting precipitate was removed by filtration and dried.

1-Phenyl-3-methyl-4-methylmalenoylaminomethylene-5-pyrazolone (IV). A solution of 0.215 g (1 mmole) of 1-phenyl-3-methyl-4-methylaminomethylene-5-pyrazolone in 20 ml of benzene was added to a solution of 0.196 g (2 mmole) of maleic anhydride in 10 ml of benzene, and the reaction mixture was refluxed for 2 h. The excess benzene was then removed by distillation, and the residue was treated with petroleum ether. Workup gave 0.23 g (74%) of a product with mp 128-130°C (from benzene with octane). IR spectrum: 1630 (C=C), 1685 (CO), and 3250 cm^{-1} (NH). UV spectrum (in ethanol), λ_{max} (log ε): 260 (4.29) and 290 nm (4.39). PMR spectrum (in $CDCl_3$): 2.2; 3.2 (6H, $2CH_3$); 8.0 (1H, $CH-NCH_3$): 6.4 (2H, CH=OH); 7.5 ppm (5H, C_6H_5).

1-Phenyl-3-methyl-4-formyl-5-hydroxypyrazole (V). A 0.313-g (1 mmole) sample of IV was heated with 10 ml of 10% NaOH and 2 ml of ethanol at 60°C for 1.5 h, after which the mixture was cooled and treated with 9% hydrochloric acid. The resulting precipitate was removed by filtration, washed with water, and dried to give 0.16 g (82%) of a product with mp 174°C. No melting-point depression was observed for a mixture of this product with a genuine sample.

Dehydrobis(1-phenyl-3-methyl-5-pyrazolon-4-yl)methane (VI). A solution of 0.23 g (1 mmole) of 1-phenyl-3-methyl-4-dimethylaminomethylene-5-pyrazolone in 20 ml of benzene was added to a solution of 0.196 g (2 mmole) of maleic anhydride in 10 ml of benzene, and the mixture was refluxed for 2 h. The excess benzene was then removed by distillation, and the residue was treated with petroleum ether. The precipitate was removed by filtration and dried to give 0.24 g (72%) of a product with mp 179-180°C. No melting-point depression was observed for a mixture of this product with a genuine sample.

LITERATURE CITED

1. I. Ya. Kvitko and A. A. Tarasenko, Zh. Org. Khim., 7, 1253 (1971).
2. A. I. Grigor'eva, L. P. Snegireva, G. K. Lebedeva, and I. Ya. Kvitko, Zh. Org. Khim., 14, 637 (1978).
3. B. A. Porai-Koshits and I. Ya. Kvitko, Zh. Obshch. Khim., 32, 4050 (1962).
4. A. Felix and P. Friedländer, Monatsh., 31, 55 (1910).
5. L. N. Kurkovskaya, N. N. Shapet'ko, I. Ya. Kvitko, Yu. N. Koshelev, and É. M. Sof'ina, Zh. Org. Khim., 9, 821 (1973).
6. I. Ya. Kvitko and B. A. Porai-Koshits, Zh. Org. Khim., 5, 1685 (1969).