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6,6-DIMETHYL-4,8-DIOXOSPIRO[2.5]OCTANE-1,1,2,2-TETRACARBONITRILE IN THE SYNTHESIS OF HETEROCYCLIC COMPOUNDS OF THE 2,3-DIHYDROFURAN AND 5,6,7,8-TETRAHYDRO-4H-CHROMENE SERIES

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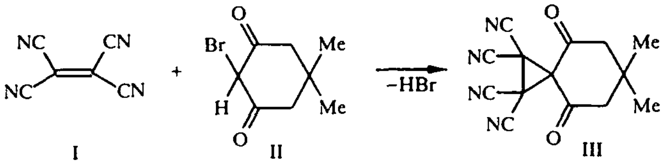
6,6-Dimethyl-4,8-dioxospiro[2.5]octane-1,1,2,2-tetracarbonitrile (III), synthesized by the interaction of tetracyanoethylene with 2-bromo-5,5-dimethyl-1,3-cyclohexanedione, reacts with alcohols and ketoximes to form 2-alkoxy-2-(3-alkoxycarbonyl-2,2-dimethylpropyl)-5-amino-3-dicyanomethylene-4-cyano-2,3-dihydrofurans and 2-alkylidenaminoxy-2-(3-alkylidenaminoxycarbonyl-2,2-dimethylpropyl)-5-amino-3-dicyanomethylene-4-cyano-2,3-dihydrofurans. Compound III with triarylphosphines forms 2-(triarylphosphoranilidenamino)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3,4,4-tricarbonitriles.

It was discovered rather recently that the interaction of tetracyanoethylene (I) with monobromomalononitrile produces hexacyanocyclopropane [1]. Continuing these studies, we have used 2-bromo-5,5-dimethyl-1,3-cyclohexanedione (II) as a monohalogen methylene-active compound. Upon interaction of the cyanide I with compound II in aqueous dioxane, we obtained 6,6-dimethyl-4,8-dioxospiro[2.5]octane-1,1,2,2-tetracarbonitrile (III). The molecular structure of compound III (Fig. 1) was proven by x-ray structure analysis of a single crystal.



Compound III does not react with methanol in the presence of catalytic quantities of sodium methylate, whereas hexacyanocyclopropane under these conditions reacts vigorously with methanol to form a pyrroline ring [2]. The reaction of compound III with methanol can be effected only by the use of a fourfold quantity of sodium methylate. The result of this interaction proved to be 2-methoxy-5-amino-3-dicyanomethylene-2-(3-methoxycarbonyl-2,2-dimethylpropyl)-4-cyano-2,3-dihydrofuran (Va). The molecular structure of Va was established by x-ray structure analysis of a single crystal (Fig. 2). The spirane III reacts analogously with ethanol and ketoximes. The structure of the dihydrofurans Vc-f was established by comparing their IR spectra with those of compound Va (Table 1). In view of the structures that have been established for compounds Va-f, we can conclude tentatively that the reaction of compound III with alcohols and oximes proceeds in accordance with the following scheme:

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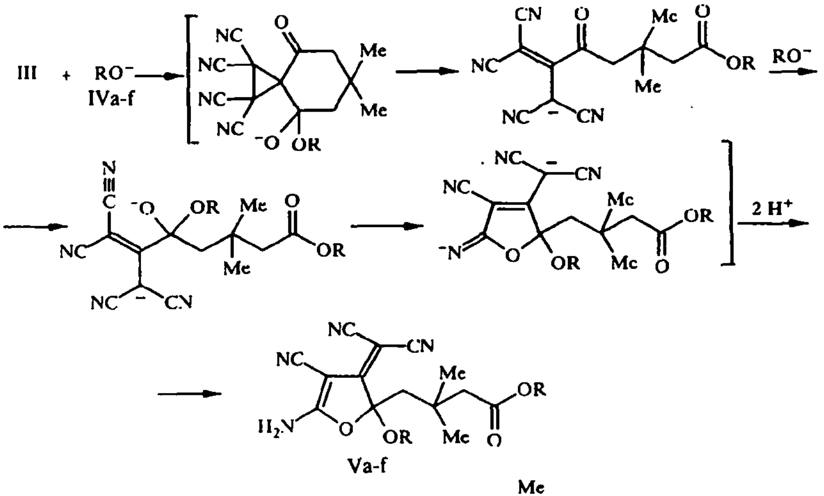
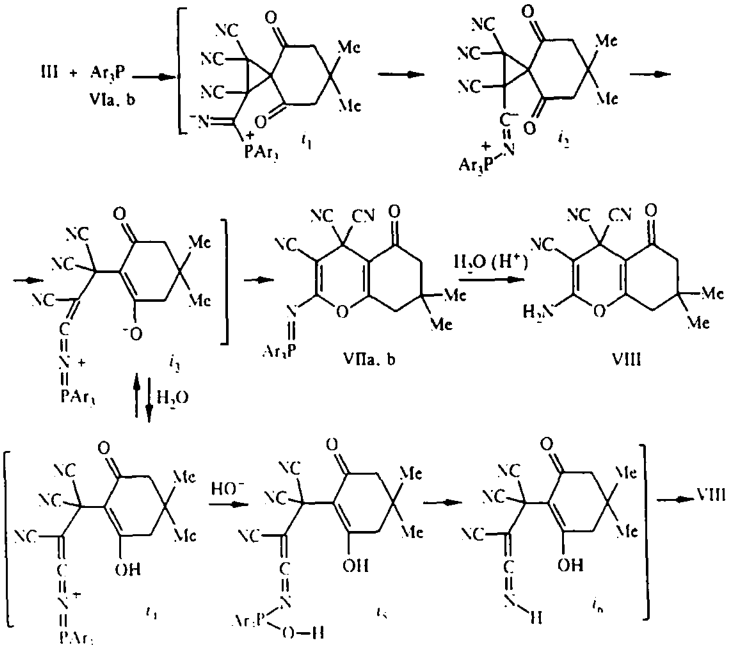
Scheme 1



IV, V a) R = Me, b) R = Et, c) R = $Me_2C{=}N$, d) R = $\begin{matrix}Me\\ Et\end{matrix}\!\!>C{=}N$, e) R = $(CH_2)_4C{=}N$,
f) R = $(CH_2)_5C{=}N$

The difference between hexacyanocyclopropane and compound III in their reactivities toward O-nucleophiles can most likely be attributed to a lowering of electrophilicity of the carbon atoms of the cyano groups in compound III at the expense of the oxygen atoms of the carbonyl groups (Fig. 1) [distances $O_{(1)}\ldots C_{(71)}$ 3.063(4), $O_{(1)}\ldots C_{(81)}$ 2.616(4), $O_{(2)}\ldots C_{(72)}$ 2.937(4), $O_{(2)}\ldots C_{(82)}$ 2.636(4) Å]. Nevertheless, in the case of the cyclopropane derivative III, nucleophilic attack through the cyano groups is possible. Original addition at the cyano group is the only possible explanation for the formation of 2-(triarylphosphoranylidenamino)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3,4,4-tricarbonitriles (VIIa, b) by the interaction of compound III with triarylphosphines (VIa,b). The structure of compound VIIb was established by x-ray structure analysis of a single crystal (Fig. 3). On the basis of the structure established for compounds VIIa,b, we can propose a sequence of stages in obtaining these compounds from the cyclopropane III and a triarylphosphine (Scheme 2). The presence of the keteneimino fragment in the betaine i_3 determines the formation of the pyran ring.

Scheme 2



VI, VII a) Ar = Ph, b) Ar = MeC_6H_4

TABLE 1. IR Spectra (cm^{-1}) of Compounds III, Va-f, VIIa, b, and VIII

Compound	ν_{NH2}	$\nu_{C\equiv N}$	$\nu_{C=X}$	ν_{O-C-O}
III	—	2270	1730, 1710	—
Va	3400, 3330, 3265, 3160	2230	1710, 1650	1200, 1130, 1045, 1030
Vb	3360, 3285, 3160	2240, 2220	1690, 1660	1200, 1130, 1070, 1030
Vc	3290, 3150	2230, 2225	1690, 1660	1160, 1110, 1075, 1010
Vd	3290, 3160	2240, 2225	1690, 1660	1160, 1110, 1075, 1010
Ve	3370, 3280, 3170	2240, 2225	1680, 1660	1180, 1110, 1070, 1035
Vf	3370, 3290, 3160	2240, 2220	1680, 1670	1180, 1110, 1070, 1035
VIIa	—	2210	1665, 1580	—
VIIb	—	2215	1645, 1580	—
VIII	3400, 3330, 3250, 3210	2225, 2205	1665, 1640	—

TABLE 2. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Coefficients of Equivalent Isotropic Displacement ($Å^2 \times 10^3$) of Compound III

Atom	*x*	*y*	*z*	$U_{(eq)}$
$O_{(1)}$	-7655(2)	6604(1)	7654(1)	39(1)
$O_{(2)}$	-3077(2)	6539(1)	10584(1)	65(1)
$O_{(3)}$	-2448(2)	5008(1)	7291(1)	37(1)
$O_{(4)}$	-1722(2)	3323(1)	7136(1)	35(1)
$N_{(71)}$	-5244(2)	6606(1)	6115(2)	41(1)
$N_{(72)}$	-796(3)	6650(1)	8853(2)	49(1)
$N_{(81)}$	-6828(3)	4758(1)	7408(2)	47(1)
$N_{(82)}$	-2800(3)	4723(1)	9985(2)	44(1)
$C_{(1)}$	-6683(3)	6979(1)	8347(1)	25(1)
$C_{(2)}$	-7007(3)	7818(1)	8695(2)	34(1)
$C_{(3)}$	-6159(3)	8009(1)	9860(2)	30(1)
$C_{(4)}$	-4325(3)	7845(1)	10102(2)	31(1)
$C_{(5)}$	-4000(3)	6965(1)	9942(2)	31(1)
$C_{(6)}$	-4978(3)	6617(1)	8868(1)	24(1)
$C_{(7)}$	-3938(2)	6418(1)	8126(1)	23(1)
$C_{(71)}$	-4658(3)	6532(1)	7002(2)	27(1)
$C_{(72)}$	-2177(3)	6546(1)	8521(2)	31(1)
$C_{(8)}$	-4672(2)	5724(1)	8635(1)	24(1)
$C_{(81)}$	-5959(3)	5223(1)	7931(2)	30(1)
$C_{(82)}$	-3560(3)	5206(1)	9430(2)	31(1)
$C_{(9)}$	-6428(4)	8907(2)	10074(2)	52(1)
$C_{(10)}$	-6861(4)	7469(2)	10557(2)	46(1)
$C_{(11)}$	-809(3)	4698(2)	7708(2)	40(1)
$C_{(12)}$	-833(3)	3813(2)	8018(2)	37(1)
$C_{(13)}$	-3349(3)	3639(1)	6711(2)	33(1)
$C_{(14)}$	-3310(3)	4524(1)	6406(2)	32(1)

It has been noted that when compound III interacts with triarylphosphines in solvents containing water, the formation of compound VIIa,b is accompanied by the formation of 2-amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3,4,4-tricarbonitrile (VIII). The structure of compound VIII was established by x-ray structure analysis of a single crystal (Fig. 4). In some cases, compound VIII can be obtained as the main product. We might assume that it is formed by hydrolysis of compounds VIIa,b. However, compounds VIIa,b are not hydrolyzed by heating to 40°C in the water-containing organic solvents that were used, either with the addition of either triarylphosphines or other compounds of a basic character. Compound VIII could be obtained from compounds VIIa,b only by acid hydrolysis with heating.

From the facts we have set forth, we can conclude tentatively that hydrolysis, when using solvents that are not water-free, proceeds to the formation of the pyran ring in the intermediate i_3.

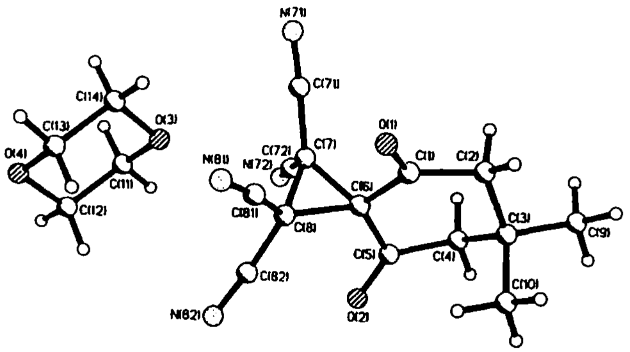


Fig. 1. Molecular structure of compound III.

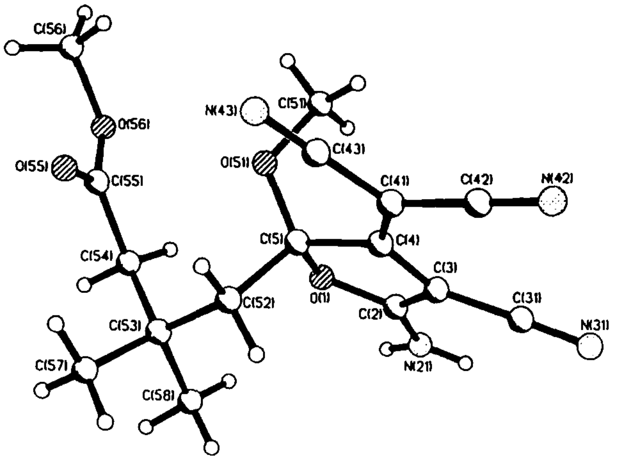


Fig. 2. Molecular structure of compound Va.

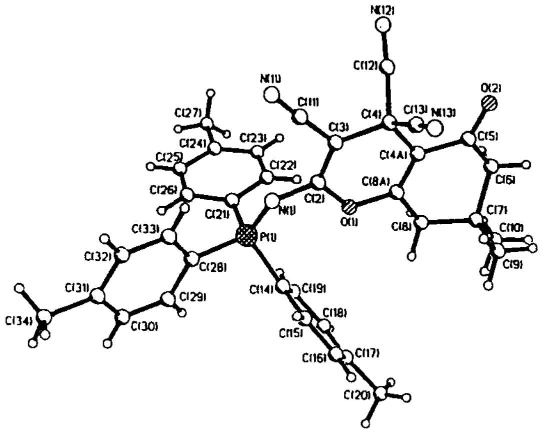


Fig. 3. Molecular structure of compound VIIb.

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument in white mineral oil. The elementary cell constants and the intensities of reflections for the x-ray structure analyses were measured on automatic four-circle diffractometers — Syntex $P2_1$ (for compound III) and Siemens P3/PC (for the other compounds) (λMoKα, graphite monochromator, $\theta/2\theta$ scanning). The structures of the compounds were deciphered by the direct method and refined by the full-matrix least squares method in

TABLE 3. Bond Lengths (Å) and Bond Angles in Molecule of Compound III

Atoms	Bond	Atoms	Angle, deg	Atoms	Angle, deg
$O_{(1)}$—$C_{(1)}$	1,201(2)	$C_{(14)}$—$O_{(3)}$—$C_{(11)}$	109,0(2)	$C_{(13)}$—$O_{(4)}$—$C_{(12)}$	109,6(2)
$O_{(2)}$—$C_{(5)}$	1,192(3)	$O_{(1)}$—$C_{(1)}$—$C_{(2)}$	123,5(2)	$O_{(1)}$—$C_{(1)}$—$C_{(6)}$	119,6(2)
$O_{(3)}$—$C_{(14)}$	1,421(3)	$C_{(2)}$—$C_{(1)}$—$C_{(6)}$	116,8(2)	$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	115,2(2)
$O_{(3)}$—$C_{(11)}$	1,430(3)	$C_{(9)}$—$C_{(3)}$—$C_{(4)}$	109,5(2)	$C_{(9)}$—$C_{(3)}$—$C_{(10)}$	109,4(2)
$O_{(4)}$—$C_{(13)}$	1,425(3)	$C_{(4)}$—$C_{(3)}$—$C_{(10)}$	109,7(2)	$C_{(9)}$—$C_{(3)}$—$C_{(2)}$	109,5(2)
$O_{(4)}$—$C_{(12)}$	1,430(3)	$C_{(4)}$—$C_{(3)}$—$C_{(2)}$	108,6(2)	$C_{(10)}$—$C_{(3)}$—$C_{(2)}$	110,2(2)
$N_{(71)}$—$C_{(71)}$	1,140(3)	$C_{(5)}$—$C_{(4)}$—$C_{(3)}$	111,3(2)	$O_{(2)}$—$C_{(5)}$—$C_{(4)}$	124,7(2)
$N_{(72)}$—$C_{(72)}$	1,137(3)	$O_{(2)}$—$C_{(5)}$—$C_{(6)}$	120,6(2)	$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	114,7(2)
$N_{(81)}$—$C_{(81)}$	1,136(3)	$C_{(1)}$—$C_{(6)}$—$C_{(8)}$	118,2(2)	$C_{(1)}$—$C_{(6)}$—$C_{(5)}$	117,2(2)
$N_{(82)}$—$C_{(82)}$	1,136(3)	$C_{(8)}$—$C_{(6)}$—$C_{(5)}$	117,7(2)	$C_{(1)}$—$C_{(6)}$—$C_{(7)}$	116,2(2)
$C_{(1)}$—$C_{(2)}$	1,493(3)	$C_{(8)}$—$C_{(6)}$—$C_{(7)}$	60,3(1)	$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	114,7(2)
$C_{(1)}$—$C_{(6)}$	1,525(3)	$C_{(71)}$—$C_{(7)}$—$C_{(72)}$	115,2(2)	$C_{(71)}$—$C_{(7)}$—$C_{(8)}$	116,4(2)
$C_{(2)}$—$C_{(3)}$	1,531(3)	$C_{(72)}$—$C_{(7)}$—$C_{(8)}$	117,4(2)	$C_{(71)}$—$C_{(7)}$—$C_{(6)}$	119,1(2)
$C_{(3)}$—$C_{(9)}$	1,518(3)	$C_{(72)}$—$C_{(7)}$—$C_{(6)}$	118,0(2)	$C_{(8)}$—$C_{(7)}$—$C_{(6)}$	59,2(1)
$C_{(3)}$—$C_{(4)}$	1,521(3)	$N_{(71)}$—$C_{(71)}$—$C_{(7)}$	178,5(2)	$N_{(72)}$—$C_{(72)}$—$C_{(7)}$	178,5(2)
$C_{(3)}$—$C_{(10)}$	1,524(3)	$C_{(81)}$—$C_{(8)}$—$C_{(82)}$	109,9(2)	$C_{(81)}$—$C_{(8)}$—$C_{(6)}$	121,5(2)
$C_{(4)}$—$C_{(5)}$	1,485(3)	$C_{(82)}$—$C_{(8)}$—$C_{(6)}$	121,2(2)	$C_{(81)}$—$C_{(8)}$—$C_{(7)}$	117,1(2)
$C_{(5)}$—$C_{(6)}$	1,528(3)	$C_{(82)}$—$C_{(8)}$—$C_{(7)}$	118,7(2)	$C_{(6)}$—$C_{(8)}$—$C_{(7)}$	60,6(1)
$C_{(6)}$—$C_{(8)}$	1,525(3)	$N_{(81)}$—$C_{(81)}$—$C_{(8)}$	171,8(2)	$N_{(82)}$—$C_{(82)}$—$C_{(8)}$	171,6(2)
$C_{(6)}$—$C_{(7)}$	1,547(3)	$O_{(3)}$—$C_{(11)}$—$C_{(12)}$	110,7(2)	$O_{(4)}$—$C_{(12)}$—$C_{(11)}$	110,9(2)
$C_{(7)}$—$C_{(71)}$	1,445(3)	$O_{(4)}$—$C_{(13)}$—$C_{(14)}$	110,8(2)	$O_{(3)}$—$C_{(14)}$—$C_{(13)}$	110,8(2)
$C_{(7)}$—$C_{(72)}$	1,447(3)				
$C_{(7)}$—$C_{(8)}$	1,542(3)				
$C_{(8)}$—$C_{(81)}$	1,456(3)				
$C_{(8)}$—$C_{(82)}$	1,456(3)				
$C_{(11)}$—$C_{(12)}$	1,499(4)				
$C_{(13)}$—$C_{(14)}$	1,499(3)				

the anisotropic approximation for the nonhydrogen atoms. The hydrogen atoms, localized objectively in a Fourier difference synthesis, were refined in the isotropic approximation. All calculations were performed by means of the programs SHELXTL PLUS and SHELXL-93. The coordinates of the atoms, the bond lengths, the bond angles, and the thermal parameters have been placed on file in the Cambridge Center of Crystallographic Data. The purities of the synthesized compounds and the degree of completion of the reaction were established by TLC (Silufol UV-254).

6,6-Dimethyl-4,8-dioxospiro[2.5]octane-1,1,2,2-tetracarbonitrile (III). In a mixture of 20 ml of absolute 1,4-dioxane and 50 ml of absolute acetonitrile, 6.4 g (50 mmoles) of tetracyanoethylene was dissolved with slight heating, then 13.14 g (60 mmoles) of 2-bromo-5,5-dimethyl-1,3-cyclohexanedione (II). The reaction mass was chilled to 5-10°C and stirred vigorously while adding 200 g of crushed ice in portions over a period of 30-40 min. The stirring was continued until the tetracyanoethylene had disappeared from the reaction mass. The precipitate was filtered off, washed with chilled 1,4-dioxane, and vacuum-dried to constant weight over P_2O_5. If necessary, the product was recrystallized from a 1:1 mixture of 1,4-dioxane and acetonitrile.

X-Ray Structure Study of Compound III. Transparent, colorless crystals in the form of prisms, classed in the monoclinic system. Basic crystallographic data: $C_{18}H_{18}N_4O_4$, M = 354.36; at 193 K, a = 8.520(2), b = 16.266(3), c = 13.294(3) Å, β = 107.60(2)°, V = 1756.0(6) $Å^3$, d_{calc} = 1.340 g/cm^3, space group $P2_1/n$, Z = 4, F(OOO) = 744. A total of 2954 reflections were measured, θ_{max} = 25°C. The final divergence factors R_f = 0.048 on the basis of 2728 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.139 for all 2734 independent reflections.

2-Alkoxy-5-amino-3-dicyanomethylene-2-(3-alkoxycarbonyl-2,2-dimethylpropyl)-2,3-dihydrofurans (Va,b). In 25 ml of absolute alcohol, 0.92 g (4 mmoles) of metallic sodium was dissolved, after which a suspension of 2.66 g (10 mmoles) of compound III and 15 ml of absolute alcohol was added in portions while stirring. After completion of the reaction (as determined by TLC), the reaction mass was neutralized with a 10% solution of sulfuric acid. Then the reaction solution was extracted with ethyl acetate. The organic layer was washed with sodium bicarbonate solution and then with a saturated sodium chloride solution, and dried over $MgSO_4$. Most of the ethyl acetate was distilled off, and the residue was dried. The resulting precipitate was filtered off and washed with chilled ethyl acetate. Compounds Va,b were purified by recrystallization from isopropyl alcohol. The purified compounds Va,b were vacuum-dried to constant weight over P_2O_5.

TABLE 4. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Coefficients of Equivalent Isotropic Displacement ($Å^2 \times 10^3$) of Compound Va

Atom	*x*	*y*	*z*	$U_{(eq)}$
$O_{(1)}$	980(2)	7355(1)	871(1)	36(1)
$O_{(51)}$	1075(2)	7610(1)	-662(1)	38(1)
$O_{(55)}$	3779(2)	9041(1)	-1288(1)	62(1)
$O_{(56)}$	653(2)	9397(1)	-1011(1)	62(1)
$N_{(21)}$	23(2)	6669(1)	2060(1)	48(1)
$N_{(31)}$	1650(3)	4654(1)	1379(1)	57(1)
$N_{(42)}$	3346(2)	4512(1)	-881(1)	49(1)
$N_{(43)}$	4247(3)	6806(1)	-2087(1)	56(1)
$C_{(2)}$	823(2)	6668(1)	1275(1)	34(1)
$C_{(3)}$	1582(2)	6053(1)	775(1)	32(1)
$C_{(31)}$	1623(2)	5271(1)	1089(1)	37(1)
$C_{(4)}$	2306(2)	6362(1)	-18(1)	29(1)
$C_{(41)}$	3104(2)	6005(1)	-744(1)	31(1)
$C_{(42)}$	3253(2)	5176(1)	-814(1)	34(1)
$C_{(43)}$	3740(2)	6447(1)	-1491(1)	38(1)
$C_{(5)}$	2128(2)	7253(1)	52(1)	31(1)
$C_{(51)}$	-858(3)	7286(1)	-934(1)	49(1)
$C_{(52)}$	4179(2)	7641(1)	211(1)	34(1)
$C_{(53)}$	4337(2)	8469(1)	636(1)	38(1)
$C_{(54)}$	2715(3)	9034(1)	246(1)	40(1)
$C_{(55)}$	2493(3)	9140(1)	-765(1)	43(1)
$C_{(56)}$	231(7)	9568(2)	-1961(2)	99(1)
$C_{(57)}$	6461(3)	8766(1)	481(2)	54(1)
$C_{(58)}$	4147(3)	8438(1)	1666(1)	52(1)

TABLE 5. Bond Lengths (d) and Bond Angles (φ) in Molecule of Compound Va

Bond	*d*, Å	Angle	φ, deg	Angle	φ, deg.
$O_{(1)}$—$C_{(2)}$	1,330(2)	$C_{(2)}$—$O_{(1)}$—$C_{(5)}$	108,8(1)	$C_{(5)}$—$O_{(51)}$—$C_{(51)}$	116,6(1)
$O_{(1)}$—$C_{(5)}$	1,484(2)	$C_{(55)}$—$O_{(56)}$—$C_{(56)}$	116,8(2)	$N_{(21)}$—$C_{(2)}$—$O_{(1)}$	116,5(1)
$O_{(51)}$—$C_{(5)}$	1,375(2)	$N_{(21)}$—$C_{(2)}$—$C_{(3)}$	130,7(1)	$O_{(1)}$—$C_{(2)}$—$C_{(3)}$	112,8(1)
$O_{(51)}$—$C_{(51)}$	1,435(2)	$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	108,2(1)	$C_{(2)}$—$C_{(3)}$—$C_{(31)}$	122,6(1)
$O_{(55)}$—$C_{(55)}$	1,202(2)	$C_{(4)}$—$C_{(3)}$—$C_{(31)}$	129,2(1)	$N_{(31)}$—$C_{(31)}$—$C_{(3)}$	177,0(2)
$O_{(56)}$—$C_{(55)}$	1,330(2)	$C_{(41)}$—$C_{(4)}$—$C_{(3)}$	131,1(1)	$C_{(41)}$—$C_{(4)}$—$C_{(5)}$	122,1(1)
$O_{(56)}$—$C_{(56)}$	1,447(3)	$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	106,8(1)	$C_{(4)}$—$C_{(41)}$—$C_{(43)}$	121,2(1)
$N_{(21)}$—$C_{(2)}$	1,308(2)	$C_{(4)}$—$C_{(41)}$—$C_{(42)}$	122,1(1)	$C_{(43)}$—$C_{(41)}$—$C_{(42)}$	116,6(1)
$N_{(31)}$—$C_{(31)}$	1,141(2)	$N_{(42)}$—$C_{(42)}$—$C_{(41)}$	178,8(2)	$N_{(43)}$—$C_{(43)}$—$C_{(41)}$	179,5(2)
$N_{(42)}$—$C_{(42)}$	1,145(2)	$O_{(51)}$—$C_{(5)}$—$O_{(1)}$	108,2(1)	$O_{(51)}$—$C_{(5)}$—$C_{(52)}$	109,3(1)
$N_{(43)}$—$C_{(43)}$	1,145(2)	$O_{(1)}$—$C_{(5)}$—$C_{(52)}$	108,9(1)	$O_{(51)}$—$C_{(5)}$—$C_{(4)}$	115,4(1)
$C_{(2)}$—$C_{(3)}$	1,401(2)	$O_{(1)}$—$C_{(5)}$—$C_{(4)}$	102,6(1)	$C_{(52)}$—$C_{(5)}$—$C_{(4)}$	112,0(1)
$C_{(3)}$—$C_{(4)}$	1,402(2)	$C_{(5)}$—$C_{(52)}$—$C_{(53)}$	120,0(1)	$C_{(57)}$—$C_{(53)}$—$C_{(54)}$	111,5(1)
$C_{(3)}$—$C_{(31)}$	1,419(2)	$C_{(57)}$—$C_{(53)}$—$C_{(58)}$	107,2(2)	$C_{(54)}$—$C_{(53)}$—$C_{(58)}$	107,2(1)
$C_{(4)}$—$C_{(41)}$	1,374(2)	$C_{(57)}$—$C_{(53)}$—$C_{(52)}$	106,4(1)	$C_{(54)}$—$C_{(53)}$—$C_{(52)}$	113,3(1)
$C_{(4)}$—$C_{(5)}$	1,536(2)	$C_{(58)}$—$C_{(53)}$—$C_{(52)}$	111,2(1)	$C_{(55)}$—$C_{(54)}$—$C_{(53)}$	118,2(1)
$C_{(41)}$—$C_{(43)}$	1,427(2)	$O_{(55)}$—$C_{(55)}$—$O_{(56)}$	123,4(2)	$O_{(55)}$—$C_{(55)}$—$O_{(54)}$	126,5(2)
$C_{(41)}$—$C_{(42)}$	1,430(2)	$O_{(56)}$—$C_{(55)}$—$C_{(54)}$	110,1(1)		
$C_{(5)}$—$C_{(52)}$	1,522(2)				
$C_{(52)}$—$C_{(53)}$	1,555(2)				
$C_{(53)}$—$C_{(57)}$	1,532(2)				
$C_{(53)}$—$C_{(54)}$	1,534(2)				
$C_{(53)}$—$C_{(58)}$	1,540(2)				
$C_{(54)}$—$C_{(55)}$	1,507(2)				

X-Ray Structure Study of Compound Va. Transparent, colorless crystals in the form of prisms, classed in the monoclinic system. Basic crystallographic data: $C_{16}H_{18}N_4O_4$, M = 330.34; at 293 K, *a* = 6.648(2), b = 17.153(4), c = 14.817(3) Å, β = 93.64(2)°, V = 1686.0(2) $Å^3$, d_{calc} = 1.301 g/cm^3, space group $P2_1/n$, Z = 4, F(000) = 696. A total of 3212 reflections were measured, θ_{max} = 25°C. Final divergence factors R_f = 0.039 based on 2483 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.107 based on all 2909 independent reflections.

2-Alkylidenaminoxy-5-amino-3-dicyanomethylene-2-(3-alkylidenaminoxycarbonyl-2,2-dimethylpropyl)-2,3-dihydrofurans (Vc-f). In 40 ml of absolute isopropyl alcohol, 0.92 g (40 mmoles) of metallic sodium was dissolved, after

TABLE 6. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Coefficients of Equivalent Isotropic Displacement ($Å^2 \times 10^3$) of Compound VIIb

Atom	*x*	*y*	*z*	$U_{(eq)}$
$P_{(1)}$	8106(1)	5890(1)	708(1)	36(1)
$O_{(1)}$	6701(1)	4609(1)	1374(1)	41(1)
$O_{(2)}$	4876(2)	3803(2)	3010(1)	63(1)
$N_{(1)}$	7384(2)	6343(2)	1178(1)	41(1)
$N_{(11)}$	6749(2)	8324(2)	2295(1)	57(1)
$N_{(12)}$	6822(3)	5739(3)	3638(1)	90(1)
$N_{(13)}$	3998(2)	6458(2)	2301(2)	86(1)
$C_{(2)}$	6866(2)	5751(2)	1535(1)	34(1)
$C_{(3)}$	6464(2)	6199(2)	2025(1)	35(1)
$C_{(4)}$	5856(2)	5515(2)	2430(1)	38(1)
$C_{(4A)}$	5758(2)	4288(2)	2206(1)	35(1)
$C_{(5)}$	5243(2)	3472(2)	2562(1)	43(1)
$C_{(6)}$	5248(2)	2245(2)	2368(1)	50(1)
$C_{(7)}$	5179(2)	2063(2)	1649(1)	47(1)
$C_{(8)}$	6061(2)	2748(2)	1450(1)	44(1)
$C_{(8A)}$	6152(2)	3930(2)	1709(1)	36(1)
$C_{(9)}$	4112(3)	2458(3)	1264(2)	73(1)
$C_{(10)}$	5328(3)	799(2)	1515(2)	74(1)
$C_{(11)}$	6631(2)	7377(2)	2165(1)	38(1)
$C_{(12)}$	6389(3)	5604(3)	3123(2)	55(1)
$C_{(13)}$	4787(2)	6019(2)	2370(2)	52(1)
$C_{(14)}$	7536(2)	4735(2)	191(1)	39(1)
$C_{(15)}$	6515(3)	4853(3)	-159(1)	62(1)
$C_{(16)}$	6007(3)	3952(3)	-504(2)	79(1)
$C_{(17)}$	6481(3)	2913(3)	-512(2)	72(1)
$C_{(18)}$	7493(3)	2809(3)	-175(2)	76(1)
$C_{(19)}$	8028(3)	3701(2)	174(2)	58(1)
$C_{(20)}$	5903(4)	1903(4)	-873(2)	123(1)
$C_{(21)}$	9356(2)	5421(2)	1159(1)	39(1)
$C_{(22)}$	9381(2)	4563(2)	1612(1)	50(1)
$C_{(23)}$	10316(2)	4194(3)	1982(1)	53(1)
$C_{(24)}$	11260(2)	4653(3)	1912(1)	53(1)
$C_{(25)}$	11239(2)	5524(3)	1473(1)	56(1)
$C_{(26)}$	10304(2)	5908(8)	1099(1)	49(1)
$C_{(27)}$	12282(3)	4198(3)	2308(2)	88(1)
$C_{(28)}$	8297(2)	7078(2)	221(1)	38(1)
$C_{(29)}$	8675(2)	6916(2)	-337(1)	52(1)
$C_{(30)}$	8870(2)	7838(3)	-695(1)	55(1)
$C_{(31)}$	8698(2)	8935(2)	-514(1)	53(1)
$C_{(32)}$	8310(3)	9086(2)	40(1)	62(1)
$C_{(33)}$	8117(2)	8176(2)	406(1)	50(1)
$C_{(34)}$	8912(3)	9946(3)	-908(2)	89(1)

which 80 mmoles of the appropriate oxime was added. Then, while the solution was stirred, 2.66 g (10 mmoles) of compound III was added in portions. After completion of the process (TLC), the reaction mass was neutralized with a 10% sulfuric acid solution and extracted with ethyl acetate. The organic layer was washed with sodium bicarbonate solution, then with saturated sodium chloride solution, and dried over $MgSO_4$. The ethyl acetate was distilled off, and aqueous isopropyl alcohol (1:1) was added to the residue. The precipitate was filtered off and washed with a chilled 1:1 mixture of isopropyl alcohol and water. Compounds Vc-f were purified by reprecipitation from isopropyl alcohol by the addition of water. These compounds were vacuum-dried over P_2O_5.

TABLE 7. Bond Lengths (d) and Bond Angles (φ) in Molecule of Compound VIIb

Bond	d, Å	Angle	φ, deg	Angle	φ, deg
$P_{(1)}-N_{(1)}$	1,601(2)	$N_{(1)}-P_{(1)}-C_{(28)}$	106,0(1)	$N_{(1)}-P_{(1)}-C_{(21)}$	110,9(1)
$P_{(1)}-C_{(28)}$	1,785(2)	$C_{(28)}-P_{(1)}-C_{(21)}$	109,1(1)	$N_{(1)}-P_{(1)}-C_{(14)}$	114,2(1)
$P_{(1)}-C_{(21)}$	1,791(3)	$C_{(28)}-P_{(1)}-C_{(14)}$	108,8(1)	$C_{(21)}-P_{(1)}-C_{(14)}$	107,8(1)
$P_{(1)}-C_{(14)}$	1,802(3)	$C_{(8A)}-O_{(1)}-C_{(2)}$	120,3(2)	$C_{(2)}-N_{(1)}-P_{(1)}$	128,7(2)
$O_{(1)}-C_{(8A)}$	1,367(3)	$N_{(1)}-C_{(2)}-C_{(3)}$	124,2(2)	$N_{(1)}-C_{(2)}-O_{(1)}$	116,0(2)
$O_{(1)}-C_{(2)}$	1,388(3)	$C_{(3)}-C_{(2)}-O_{(1)}$	119,7(2)	$C_{(2)}-C_{(3)}-C_{(11)}$	117,9(2)
$O_{(2)}-C_{(5)}$	1,217(3)	$C_{(2)}-C_{(3)}-C_{(4)}$	124,0(2)	$C_{(11)}-C_{(3)}-C_{(4)}$	118,1(2)
$N_{(1)}-C_{(2)}$	1,316(3)	$C_{(12)}-C_{(4)}-C_{(13)}$	106,0(2)	$C_{(12)}-C_{(4)}-C_{(4A)}$	111,6(2)
$N_{(11)}-C_{(11)}$	1,148(3)	$C_{(13)}-C_{(4)}-C_{(4A)}$	109,6(2)	$C_{(12)}-C_{(4)}-C_{(3)}$	109,4(2)
$N_{(12)}-C_{(12)}$	1,132(4)	$C_{(13)}-C_{(4)}-C_{(3)}$	109,4(2)	$C_{(4A)}-C_{(4)}-C_{(3)}$	110,1(2)
$N_{(13)}-C_{(13)}$	1,131(4)	$C_{(8A)}-C_{(4A)}-C_{(5)}$	119,8(2)	$C_{(8A)}-C_{(4A)}-C_{(4)}$	121,8(2)
$C_{(2)}-C_{(3)}$	1,365(3)	$C_{(5)}-C_{(4A)}-C_{(4)}$	118,4(2)	$O_{(2)}-C_{(5)}-C_{(4A)}$	119,6(2)
$C_{(3)}-C_{(11)}$	1,420(3)	$O_{(2)}-C_{(5)}-C_{(6)}$	123,2(2)	$C_{(4A)}-C_{(5)}-C_{(6)}$	117,1(2)
$C_{(3)}-C_{(4)}$	1,518(3)	$C_{(5)}-C_{(6)}-C_{(7)}$	114,1(2)	$C_{(9)}-C_{(7)}-C_{(6)}$	110,3(3)
$C_{(4)}-C_{(12)}$	1,492(4)	$C_{(9)}-C_{(7)}-C_{(10)}$	109,3(3)	$C_{(6)}-C_{(7)}-C_{(10)}$	109,8(2)
$C_{(4)}-C_{(13)}$	1,492(4)	$C_{(9)}-C_{(7)}-C_{(8)}$	110,1(2)	$C_{(6)}-C_{(7)}-C_{(8)}$	108,3(2)
$C_{(4)}-C_{(4A)}$	1,513(3)	$C(10)-C_{(7)}-C_{(8)}$	109,0(2)	$C_{(8A)}-C_{(8)}-C_{(7)}$	113,1(2)
$C_{(4A)}-C_{(8A)}$	1,336(3)	$C_{(4A)}-C_{(8A)}-O_{(1)}$	124,1(2)	$C_{(4A)}-C_{(8A)}-C_{(8)}$	124,8(2)
$C_{(4A)}-C_{(5)}$	1,468(3)	$O_{(1)}-C_{(8A)}-C_{(8)}$	111,1(2)	$N_{(11)}-C_{(11)}-C_{(3)}$	177,7(3)
$C_{(5)}-C_{(6)}$	1,497(4)	$N_{(12)}-C_{(12)}-C_{(4)}$	175,4(3)	$N_{(13)}-C_{(13)}-C_{(4)}$	175,4(3)
$C_{(6)}-C_{(7)}$	1,527(4)	$C_{(19)}-C_{(14)}-C_{(15)}$	118,2(3)	$C_{(19)}-C_{(14)}-P_{(1)}$	123,0(2)
$C_{(7)}-C_{(9)}$	1,527(4)	$C_{(15)}-C_{(14)}-P_{(1)}$	118,4(2)	$C_{(16)}-C_{(15)}-C_{(14)}$	120,5(3)
$C_{(7)}-C_{(10)}$	1,530(4)	$C_{(17)}-C_{(16)}-C_{(15)}$	121,7(3)	$C_{(18)}-C_{(17)}-C_{(16)}$	117,5(3)
$C_{(7)}-C_{(8)}$	1,532(4)	$C_{(18)}-C_{(17)}-C_{(20)}$	120,9(4)	$C_{(16)}-C_{(17)}-C_{(20)}$	121,6(4)
$C_{(8)}-C_{(8A)}$	1,488(3)	$C_{(17)}-C_{(18)}-C_{(19)}$	122,2(3)	$C_{(14)}-C_{(19)}-C_{(18)}$	119,8(3)
$C_{(14)}-C_{(19)}$	1,376(4)	$C_{(22)}-C_{(21)}-C_{(26)}$	118,1(3)	$C_{(22)}-C_{(21)}-P_{(1)}$	118,6(2)
$C_{(14)}-C_{(15)}$	1,385(4)	$C_{(26)}-C_{(21)}-P_{(1)}$	123,3(2)	$C_{(23)}-C_{(22)}-C_{(21)}$	120,9(3)
$C_{(15)}-C_{(16)}$	1,373(4)	$C_{(22)}-C_{(23)}-C_{(24)}$	121,2(3)	$C_{(23)}-C_{(24)}-C_{(25)}$	118,1(3)
$C_{(16)}-C_{(17)}$	1,367(5)	$C_{(23}-C_{(24)}-C_{(27)}$	120,1(3)	$C_{(25)}-C_{(24)}-C_{(27)}$	121,7(3)
$C_{(17)}-C_{(18)}$	1,365(5)	$C_{(24)}-C_{(25)}-C_{(26)}$	121,3(3)	$C_{(25)}-C_{(26)}-C_{(21)}$	120,3(3)
$C_{(17)}-C_{(20)}$	1,521(4)	$C_{(33)}-C_{(28)}-C_{(29)}$	118,9(2)	$C_{(33)}-C_{(28)}-P_{(1)}$	120,6(2)
$C_{(18)}-C_{(19)}$	1,382(4)	$C_{(29)}-C_{(28)}-P_{(1)}$	120,4(2)	$C_{(30)}-C_{(29)}-C_{(28)}$	120,3(3)
$C_{(21)}-C_{(22)}$	1,388(4)	$C_{(31)}-C_{(30)}-C_{(29)}$	121,4(2)	$C_{(30)}-C_{(31)}-C_{(32)}$	117,9(2)
$C_{(21)}-C_{(26)}$	1,391(4)	$C_{(30)}-C_{(31)}-C_{(34)}$	121,2(3)	$C_{(32)}-C_{(31)}-C_{(34)}$	120,9(3)
$C_{(22)}-C_{(23)}$	1,371(4)	$C_{(33)}-C_{(32)}-C_{(31)}$	121,6(3)	$C_{(32)}-C_{(33)}-C_{(28)}$	120,0(2)
$C_{(23)}-C_{(24)}$	1,379(4)				
$C_{(24)}-C_{(25)}$	1,380(4)				
$C_{(24)}-C_{(27)}$	1,512(4)				
$C_{(25)}-C_{(26)}$	1,380(4)				
$C_{(28)}-C_{(33)}$	1,382(4)				
$C_{(28)}-C_{(29)}$	1,390(3)				
$C_{(29)}-C_{(30)}$	1,377(4)				
$C_{(30)}-C_{(31)}$	1,375(4)				
$C_{(31)}-C_{(32)}$	1,387(4)				
$C_{(31)}-C_{(34)}$	1,512(4)				
$C_{(32)}-C_{(33)}$	1,375(4)				

2-(Triarylphosphoranilidenamino)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3,4,4-tricarbonitriles (VIIa,b). To a warm solution of 2.66 g (10 mmoles) of compound III in 5 ml of absolute acetonitrile, a warm solution of 10 mmoles of the triarylphosphine in 5 ml of absolute toluene was added while stirring. After completion of the reaction (TLC), the solvents were removed under vacuum, leaving an oily residue. Absolute isopropyl alcohol was added to this residue; the precipitate that formed was filtered off, washed with chilled isopropyl alcohol, and recrystallized from isopropyl alcohol. Compounds VIIa,b were vacuum-dried to constant weight.

X-Ray Structure Study of Compound VIIb. These crystals are classed in the monoclinic system. Basic crystallographic data: $C_{35}H_{31}N_4O_2P$, M = 570.61; at 293 K, a = 13.024(2), b = 11.730(2), c = 21.253(4) Å, β =

TABLE 8. Coordinates of Nonhydrogen Atoms (× 10^4) and Coefficients of Equivalent Isotropic Displacement (Å^2 × 10^3) of Compound VIII

Atom	*x*	*y*	*z*	$U_{(eq)}$
$O_{(1)}$	4518(1)	11282(1)	7972(1)	37(1)
$O_{(2)}$	7188(1)	11917(2)	5845(1)	59(1)
$N_{(1)}$	5573(2)	10757(2)	9087(1)	47(1)
$N_{(11)}$	9823(2)	10547(2)	8987(1)	79(1)
$N_{(12)}$	9556(2)	13294(2)	7320(1)	55(1)
$N_{(13)}$	9000(2)	9204(2)	6799(1)	67(1)
$C_{(2)}$	5877(2)	11006(2)	8404(1)	34(1)
$C_{(3)}$	7328(2)	10998(2)	8134(1)	35(1)
$C_{(4)}$	7557(2)	11275(2)	7334(1)	34(1)
$C_{(4A)}$	5963(2)	11535(2)	6916(1)	35(1)
$C_{(5)}$	5929(2)	11838(2)	6132(1)	43(1)
$C_{(6)}$	4349(2)	12081(3)	5711(1)	55(1)
$C_{(7)}$	2954(2)	11368(2)	6029(1)	49(1)
$C_{(8)}$	3003(2)	11707(2)	6849(1)	47(1)
$C_{(8A)}$	4605(2)	11504(2)	7240(1)	35(1)
$C_{(9)}$	3073(3)	9857(3)	5927(2)	70(1)
$C_{(10)}$	1391(3)	11885(4)	5640(1)	74(1)
$C_{(11)}$	8690(2)	10745(2)	8614(1)	48(1)
$C_{(12)}$	8666(2)	12435(2)	7294(1)	39(1)
$C_{(13)}$	8362(2)	10107(2)	7009(1)	41(1)
$O_{(1S)}$	7751(2)	14012(2)	4825(1)	53(1)

TABLE 9. Bond Lengths (d) and Bond Angles (φ) in Molecule of Compound VIII

Bond	*d*, Å	Angle	φ, deg	Angle	φ, deg
$O_{(1)}$—$C_{(8A)}$	1,361(2)	$C_{(8A)}$—$O_{(1)}$—$C_{(2)}$	119,0(1)	$N_{(1)}$—$C_{(2)}$—$C_{(3)}$	126,6(2)
$O_{(1)}$—$C_{(2)}$	1,363(2)	$N_{(1)}$—$C_{(2)}$—$O_{(1)}$	111,2(1)	$C_{(3)}$—$C_{(2)}$—$O_{(1)}$	122,2(1)
$O_{(2)}$—$C_{(5)}$	1,228(2)	$C_{(2)}$—$C_{(3)}$—$C_{(11)}$	119,4(1)	$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	122,8(1)
$N_{(1)}$—$C_{(2)}$	1,318(2)	$C_{(11)}$—$C_{(3)}$—$C_{(4)}$	117,8(1)	$C_{(12)}$—$C_{(4)}$—$C_{(13)}$	105,8(1)
$N_{(11)}$—$C_{(11)}$	1,143(2)	$C_{(12)}$—$C_{(4)}$—$C_{(4A)}$	112,2(1)	$C_{(13)}$—$C_{(4)}$—$C_{(4A)}$	110,4(1)
$N_{(12)}$—$C_{(12)}$	1,137(2)	$C_{(12)}$—$C_{(4)}$—$C_{(3)}$	108,8(1)	$C_{(13)}$—$C_{(4)}$—$C_{(3)}$	110,0(1)
$N_{(13)}$—$C_{(13)}$	1,132(2)	$C_{(4A)}$—$C_{(4)}$—$C_{(3)}$	109,6(1)	$C_{(8A)}$—$C_{(4A)}$—$C_{(5)}$	119,6(2)
$C_{(2)}$—$C_{(3)}$	1,361(2)	$C_{(8A)}$—$C_{(4A)}$—$C_{(4)}$	122,3(1)	$C_{(5)}$—$C_{(4A)}$—$C_{(4)}$	118,1(1)
$C_{(3)}$—$C_{(11)}$	1,407(2)	$O_{(2)}$—$C_{(5)}$—$C_{(4A)}$	119,1(2)	$O_{(2)}$—$C_{(5)}$—$C_{(6)}$	122,5(2)
$C_{(3)}$—$C_{(4)}$	1,514(2)	$C_{(4A)}$—$C_{(5)}$—$C_{(6)}$	118,4(2)	$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	114,3(2)
$C_{(4)}$—$C_{(12)}$	1,493(2)	$C_{(9)}$—$C_{(7)}$—$C_{(8)}$	109,9(2)	$C_{(9)}$—$C_{(7)}$—$C_{(6)}$	110,5(2)
$C_{(4)}$—$C_{(13)}$	1,496(2)	$C_{(8)}$—$C_{(7)}$—$C_{(6)}$	108,2(2)	$C_{(9)}$—$C_{(7)}$—$C_{(10)}$	109,8(2)
$C_{(4)}$—$C_{(4A)}$	1,512(2)	$C_{(8)}$—$C_{(7)}$—$C_{(10)}$	109,2(2)	$C_{(6)}$—$C_{(7)}$—$C_{(10)}$	109,3(2)
$C_{(4A)}$—$C_{(8A)}$	1,337(2)	$C_{(8A)}$—$C_{(8)}$—$C_{(7)}$	112,7(2)	$C_{(4A)}$—$C_{(8A)}$—$O_{(1)}$	124,0(1)
$C_{(4A)}$—$C_{(5)}$	1,460(2)	$C_{(4A)}$—$C_{(8A)}$—$C_{(8)}$	124,4(1)	$O_{(1)}$—$C_{(8A)}$—$C_{(8)}$	111,6(1)
$C_{(5)}$—$C_{(6)}$	1,502(3)	$N_{(11)}$—$C_{(11)}$—$C_{(3)}$	178,0(2)	$N_{(12)}$—$C_{(12)}$—$C_{(4)}$	174,4(2)
$C_{(6)}$—$C_{(7)}$	1,533(3)	$N_{(13)}$—$C_{(13)}$—$C_{(4)}$	176,4(2)		
$C_{(7)}$—$C_{(9)}$	1,520(3)				
$C_{(7)}$—$C_{(8)}$	1,530(3)				
$C_{(7)}$—$C_{(10)}$	1,534(3)				
$C_{(8)}$—$C_{(8A)}$	1,489(2)				

102.29(1)°, $V = 3172.2(9)$ Å^3, $d_{calc} = 1.195$ g/cm^3, space group $P2_1/n$, $Z = 4$, $F(000) = 1200$. A total of 5619 reflections were measured, $\theta_{max} = 25°$. The final divergence factors $R_f = 0.052$ on the basis of 3827 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.131$ based on all 5328 independent reflections.

2-Amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3,4,4-tricarbonitrile (VIII). *A*. To a warm solution of 2.66 g (10 mmoles) of compound III in 5 ml of acetonitrile, a warm solution of 10 mmoles of the triarylphosphine in 5 ml of toluene was added while stirring. After completion of the reaction, the solvents were removed under vacuum. The residue

TABLE 10. Characteristics of Compounds III, Va-f, VIIa, b, and VIII

Compound	Empirical formula	Found, % / Calculated, %			mp (decomp.), °C	Yield, %
		C	H	N		
III	$C_{14}H_{10}N_4O_2$	63,02 63,15	3,86 3,79	20,85 21,04	>112(decomp.)	85
Va	$C_{16}H_{18}N_4O_4$	58,07 58,18	5,36 5,49	16,74 16,96	201...203	44
Vb	$C_{18}H_{22}N_4O_4$	60,52 60,66	6,06 6,22	15,64 15,72	143...144	15
Vc	$C_{20}H_{24}N_6O_4$	58,11 58,24	5,73 5,86	15,38 15,52	177...179	19
Vd	$C_{22}H_{28}N_6O_4$	59,85 59,99	6,32 6,41	14,35 14,53	135...136	13
Ve	$C_{24}H_{28}N_6O_4$	61,13 61,26	5,88 6,00	17,74 17,86	174...175 (decomp.)	21
Vf	$C_{26}H_{32}N_6O_4$	63,27 63,40	6,43 6,55	16,95 17,06	179...180 (decomp.)	18
VIIa	$C_{32}H_{25}N_4O_2P$	72,55 72,72	4,61 4,77	10,47 10,60	168...170 (decomp.)	20
VIIb	$C_{35}H_{31}N_4O_2P$	73,56 73,67	4,33 5,48	9,71 9,82	180...181 (decomp.)	21
VIII	$C_{14}H_{12}N_4O_2$	62,55 62,68	4,41 4,51	20,76 20,88	174...175 (decomp.)	56

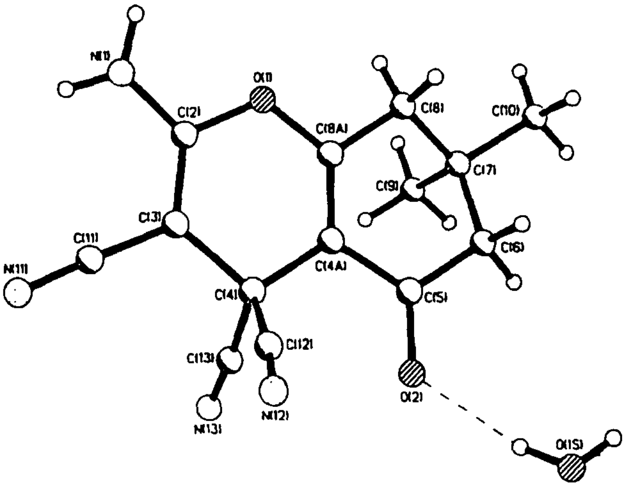


Fig. 4. Molecular structure of compound VIII.

was triturated with isopropyl alcohol. The precipitate that was formed was filtered off, washed with chilled isopropyl alcohol, and recrystallized from isopropyl alcohol. Compound VIII was vacuum-dried to constant weight over P_2O_5.

B. In a mixture of 4 ml of acetonitrile and 0.5 ml of a 5% hydrochloric acid solution, 2 mmoles of compound Va,b was dissolved while boiling over the course of 5 min. The solution was cooled and neutralized with a sodium bicarbonate solution. Then the product was extracted with ethyl acetate, and the organic layer was dried over $MgSO_4$. The ethyl acetate was driven off, and the residue was recrystallized from isopropyl alcohol.

X-Ray Structure Study of Compound VIII. The crystals are classed in the monoclinic system. Basic crystallographic data: $C_{14}H_{14}N_4O_3$, M = 286.29; at 293 K, a = 8.456(1), b = 9.951(1), c = 18.246(2) Å, β = 94.98(1)°, V = 1529.5(4) $Å^3$, d_{calc} = 1.243 g/cm^3, space group $P2_1/n$, Z = 4, F(000) = 1200. A total of 2901 reflections were measured, θ_{max} = 25°. The final divergence factors R_f = 0.040 based on 2022 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.105 based on all 2708 independent reflections.

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