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# REACTION OF 4-OXOALKANE-1,1,2,2-TETRACARBONITRILES WITH 1,3,5-TRIARYL-2,4-DIAZA-1,4-PENTADIENES

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*2-Aryl-1,2,3,4-tetrahydropyridine-3,3,4,4-tetracarbonitriles and 1,3,5-triaryl-9-oxo-1,2,3,4b,5,6,8a,9-octahydropyrido[3',4':3,4]pyrrolo[1,2-a][1,3,5]triazine-4b,8a-dicarbonitriles are formed by the reaction of 4-oxoalkane-1,1,2,2-tetracarbonitriles with 1,3,5-triaryl-2,4-diaza-1,4-pentadienes depending on the solvent used.*

We have shown recently that 1,5-diarylpyrrolidine-3,3,4,4-tetracarbonitriles are formed by the reaction of ethane-1,1,2,2-tetracarbonitrile with 1,3,5-triaryl-2,4-diaza-1,4-pentadienes (II)-(VII) [1]. The study of the reaction of compounds (II)-(VII) with 4-oxoalkane-1,1,2,2-tetracarbonitriles (Ia-f) is a continuation of these investigations. Compounds (I) react with the diazadienes (II)-(VII) in a wide range of solvents. It was discovered that products of different structure were formed depending on the solvent used. In glacial acetic acid 2-aryl-1,2,3,4-tetrahydropyridine-3,3,4,4-tetracarbonitriles (XI)-(XVI) are formed from cyanides (I) and diazadienes (II)-(VII) and reaction is complete at a reactant ratio of 2:1. The crystal structure of the (XIa) molecule was established by x-ray structural analysis (Fig. 1). The constitution of compounds (XIb-f), (XIIa), (XIIIa-d), (XIVa), (XVa) and (XVIa) was determined by comparison of their IR spectra with the IR spectrum of compound (XIa) and their composition from the data of elemental analysis (Table 1).

The reaction of compounds (II)-(VII) with cyanides (I) in alcohols or acetonitrile gave 1,3,5-triaryl-9-oxo-1,2,3,4b,5,6,8a,9-octahydropyrido[3',4':3,4]pyrrolo[1,2-*a*][1,3,5]triazine-4b,8a-dicarbonitriles (XXIII)-(XXV). The structure of compound (XXIIIa) was determined by x-ray structural investigation of a monocrystal (Fig. 2). The structure of compounds (XXIIIb-e), (XXIVa), (XXIVb), and (XXVa) were established on the basis of IR and $^{13}$C NMR spectra (Table 10). The intermediate compounds were isolated in order to explain the difference in reaction of diazadienes (II)-(VII) with compounds (I). These were 2-aryl-6-hydroxypiperidine-3,3,4,4-tetracarbonitriles (VIII)-(X), 2-aryl-3,3,4-tricyano-2,3,4,5-tetrahydropyridine-4-carboxamides (XVII)-(XIX), and 3-amino-4-aryl-1-oxo-3a,4,5,7a-tetrahydro-1H-pyrrolo[3,4-c]pyridine-3a,7a-dicarbonitriles (XX)-(XXII). In each specific case the concentration of reactants and the solvent were selected by the experimental route.

Like compounds (XVII)-(XIX), compounds (VIII)-(X) in isopropyl alcohol or acetonitrile containing an insignificant amount of water were practically completely converted into compounds (XX)-(XXII), which in turn may be obtained directly from diazadienes (II)-(VII) and cyanides (I). The tricyclic compounds (XXIII)-(XXV) may be obtained by the reaction of compounds (XX)-(XXII) with diazadienes (II)-(VII).

The cited facts of the conversions of compounds (VIII)-(X), (XVII)-(XIX), and (XX)-(XXII) suggest that they are intermediates in the reaction of diazadienes (II)-(VII) with cyanides (I) in the formation of the tricycles (XXIII)-(XXV). Regrettably we were unsuccessful in obtaining amides (XVII)-(XIX) directly from compounds (VIII)-(X), but their stereochemistry from x-ray structural data suggest the conversion. The hydroxyl group in compound (VIIIa) (Fig. 3) is in a trans position relative to the aryl substituent and occupies an axial position which suggests a 1,3 interaction with the carbon of the cyano group. The carbamoyl group in compound (XVIIIa) is also found in the trans position (Fig. 4). These data suggest

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TABLE 1. Characteristics of the Compounds Synthesized

| Compound | $R^1$ | $R^2$ | mp (decomp.), °C | Found, % |  |  | Empirical formula | Calculated, % |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | C | H | N |  | C | H | N |  |
| XIa | $(CH_2)_4$ |  | 126...128 | 72,87 | 4,85 | 22,28 | $C_{19}H_{15}N_5$ | 72,83 | 4,88 | 22,35 | 92 |
| XIb | $CH_3$ | $CH_3$ | 113...114 | 71,12 | 4,62 | 24,26 | $C_{17}H_{13}N_5$ | 71,06 | 4,56 | 24,37 | 61 |
| XIc | H | $CH_3$ | 143...144 | 70,42 | 4,10 | 25,48 | $C_{16}H_{11}N_5$ | 70,31 | 4,06 | 25,63 | 64 |
| XId | $(CH_2)_3$ |  | >140 | 72,25 | 4,40 | 23,35 | $C_{18}H_{13}N_5$ | 72,22 | 4,38 | 23,39 | 67 |
| XIe | $C_3H_7$ | $CH_3$ | 123...124 | 72,37 | 5,48 | 22,15 | $C_{19}H_{17}N_5$ | 72,36 | 5,43 | 22,20 | 57 |
| XIf | $i$-$C_3H_7$ | $CH_3$ | 141...142 | 72,42 | 5,51 | 22,07 | $C_{19}H_{17}N_5$ | 72,36 | 5,43 | 22,20 | 52 |
| XIIa | $(CH_2)_4$ |  | 91...95 | 67,25 | 4,31 | 23,17 | $C_{17}H_{13}N_5O$ | 67,31 | 4,31 | 23,09 | 71 |
| XIIIa | $(CH_2)_4$ |  | 127...130 | 69,92 | 4,99 | 20,31 | $C_{20}H_{17}N_5O$ | 69,96 | 4,95 | 20,39 | 84 |
| XIIIb | $CH_3$ | $CH_3$ | 106...107 | 68,15 | 4,81 | 22,01 | $C_{18}H_{15}N_5O$ | 68,13 | 4,76 | 22,07 | 51 |
| XIIIc | H | $CH_3$ | 130...131 | 67,36 | 4,33 | 23,04 | $C_{17}H_{13}N_5O$ | 67,31 | 4,32 | 23,09 | 62 |
| XIIId | $(CH_2)_3$ |  | 128...130 | 69,31 | 4,62 | 21,19 | $C_{19}H_{15}N_5O$ | 69,29 | 4,59 | 21,26 | 58 |
| XIVa | $(CH_2)_4$ |  | 126...127 | 69,88 | 5,01 | 20,16 | $C_{20}H_{17}N_5O$ | 69,96 | 4,99 | 20,39 | 84 |
| XVa | $(CH_2)_4$ |  | 125...126 | 63,71 | 3,99 | 23,35 | $C_{19}H_{14}N_6O_2$ | 63,68 | 3,94 | 23,45 | 70 |
| XVIa | $(CH_2)_4$ |  | 128...130 | 58,21 | 3,63 | 17,81 | $C_{19}H_{14}BrN_5$ | 58,18 | 3,60 | 17,85 | 65 |
| XXIIIa | $(CH_2)_4$ |  | >210 | 75,51 | 5,36 | 16,05 | $C_{33}H_{28}N_6O$ | 75,55 | 5,37 | 16,02 | 38 |
| XXIIIb | $CH_3$ | $CH_3$ | >140 | 74,53 | 5,17 | 16,69 | $C_{31}H_{26}N_6O$ | 74,68 | 5,26 | 16,87 | 34 |
| XXIIIc | H | $CH_3$ | 171...172 | 74,40 | 5,01 | 17,30 | $C_{30}H_{24}N_6O$ | 74,36 | 4,99 | 17,34 | 40 |
| XXIIId | $(CH_2)_3$ |  | 187...188 | 75,33 | 5,15 | 16,37 | $C_{32}H_{26}N_6O$ | 75,28 | 5,13 | 16,46 | 47 |
| XXIIIe | $C_3H_7$ | $CH_3$ | >155 | 75,29 | 5,71 | 16,03 | $C_{33}H_{30}N_6O$ | 75,26 | 5,74 | 15,96 | 31 |
| XXIVa | $(CH_2)_4$ |  | 148..150 | 65,60 | 4,52 | 17,02 | $C_{27}H_{22}N_6O_4$ | 65,58 | 4,48 | 16,99 | 40 |
| XXIVb | $CH_3$ | $CH_3$ | 141..142 | 64,12 | 4,32 | 17,82 | $C_{25}H_{20}N_6O_4$ | 64,09 | 4,30 | 17,94 | 42 |
| XXVa | $(CH_2)_4$ |  | 175..176 | 70,42 | 5,41 | 13,80 | $C_{36}H_{33}N_6O_4$ | 70,46 | 5,42 | 13,69 | 41 |

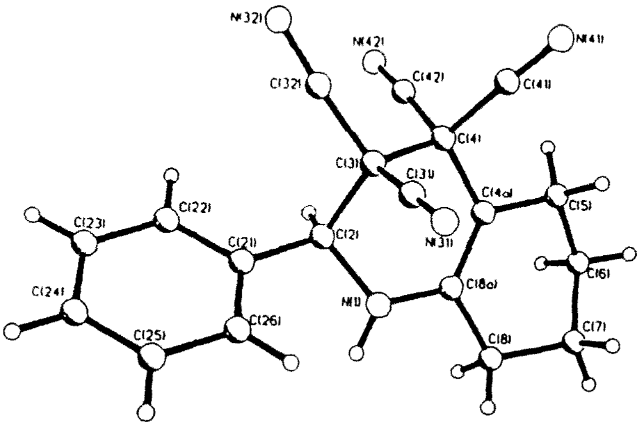


Fig. 1. Molecular structure of 5,6-tetramethylene-2-phenyl-1,2,3,4-tetrahydropyridine-3,3,4,4-tetracarbonitrile (XIa).

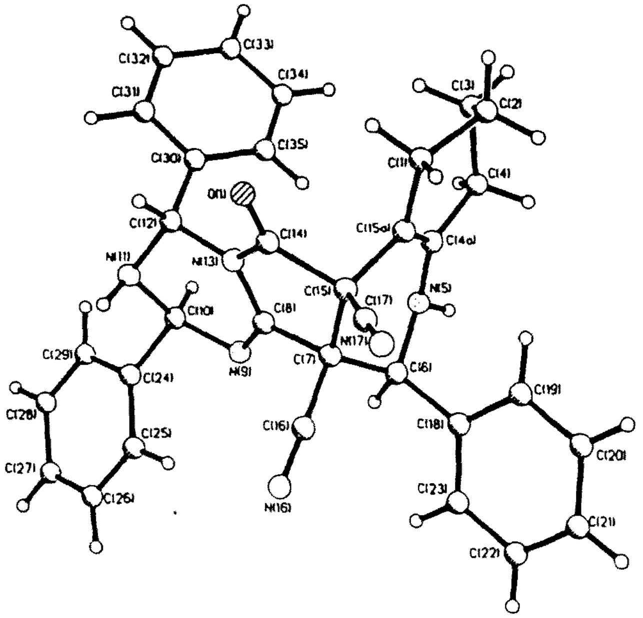


Fig. 2. Molecular structure of 9-oxo-1,3,5-triphenyl-1,2,3,4b,5,6,8*a*,9-octahydropyrido[3',4':3,4]pyrrolo[1,2-*a*][1,3,5]-triazine-4b,8a-dicarbonitrile (XXIIIa).

that the addition of the hydroxyl group to the cyano group, possibly through the formation of the bicyclic imidate (A), is the rate-determining step of the process. The observation that the conversion of compounds (VIII)-(X) into the bicycles (XX)-(XXII) is accelerated in the presence of basic compounds is in agreement with this.

It is possible that compounds (VIII)-(X) are also intermediates in the synthesis of the tetrahydropyridines (XI)-(XVI). This is indicated by the quantitative conversion of piperidines (VIII)-(X) into the tetrahydropyridines (XI)-(XVI) in glacial acetic acid. In this case the nucleophilicity of the hydroxyl group of compounds (VIII)-(X) is reduced due to the acid character of the solvent (most of all by protonation), consequently they are stabilized by elimination of water and the formation of the tetrahydropyridines (XI)-(XVI).

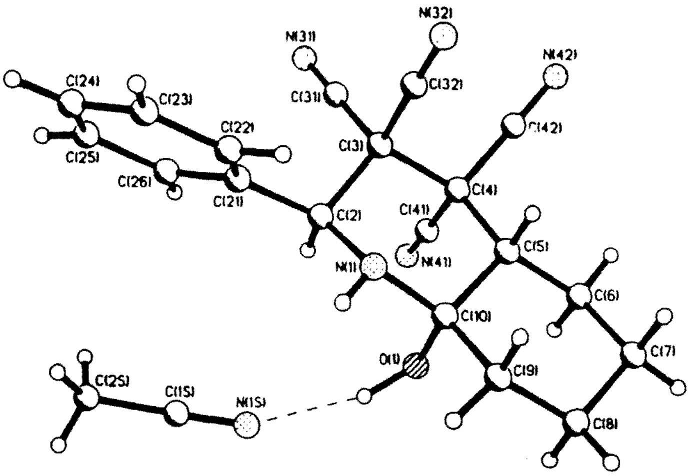
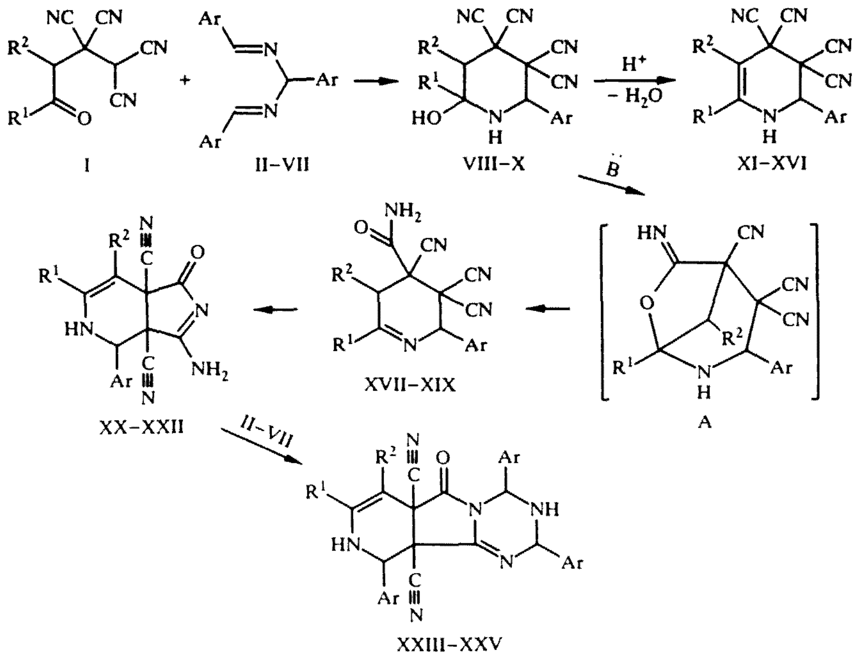


Fig. 3. Molecular structure of 6-hydroxy-5,6-tetramethylene-2-phenylpiperidine-3,3,4,4-tetracarbonitrile (VIIIa).



II, VIII, XI, XVII, XX, XXIII Ar = Ph; III, IX, XII, XVIII, XXI, XXIV Ar = 2-Fu;
IV, XIII, XIX, XXII, XXV Ar = $p$-$MeOC_6H_4$; V, XIV Ar = $o$-$MeOC_6H_4$; VI, XV Ar = $m$-$O_2NC_6$
VII, XVI Ar = $p$-$BrC_6H_4$

We were unsuccessful in isolating the intermediate precursors of compounds (VIII)-(X) but on the basis of some indirect data it was possible to judge the routes forming alcohols (VIII)-(X). It may be proposed that the first step in the reaction of 4-oxoalkane-1,1,2,2,-tetracarbonitriles (I) with 2,4-diazapenta-1,4-dienes (II)-(VII) is the addition of a strong CH acid at the C=N double bond with the formation of intermediate B. This is analogous to the hypothesis given by us previously in [1] regarding the reaction of ethane-1,1,2,2-tetracarbonitrile with the diazadienes (II)-(VII). Several routes are possible for the conversion of intermediate B. The first of these is an intramolecular nucleophilic addition at the C=O double bond with the formation of intermediate C. Another possible direction is the elimination of aldimine (analogous to the breakdown of hydrobenzamide on reduction [2]) with the formation of a compound with linear structure D. The problem of how the alcohols (VIII)-(X) are formed [from intermediates C by nucleophilic substitution or by addition of cyanide (I) to aldimine] remains open. On carrying out the reaction in an absolute aprotic solvent (such as acetonitrile) and a reactant ratio of cyanide (Ia) to

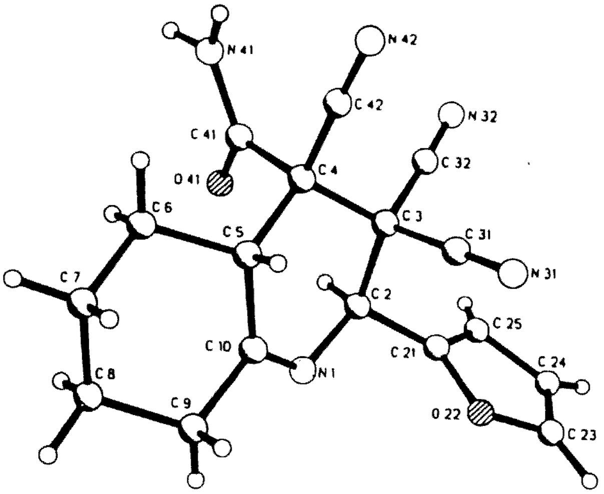
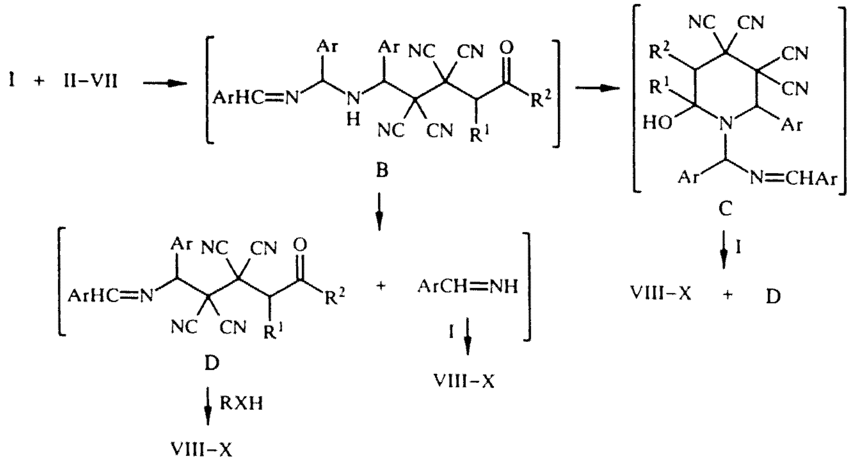


Fig. 4. Molecular structure of 5,6-tetramethylene-2-(2-furyl)-3,3,4-tricyano-2,3,4,5-tetrahydropyridine-4-carboxamide (XVIIIa).

diazadiene (II) of 2:1, compound (VIIIa) is formed in ~50% yield (calculated on cyanide taken), which indicates the possibility of forming a compound of linear structure D. An increase in the yield of compounds (VIII)-(X) to 60-70% on carrying out the reaction in a protic solvent suggests that the addition of the protic solvent at the C=N bond of intermediate D may also lead to the preparation of compounds (VIII)-(X).



## EXPERIMENTAL

The IR spectra were taken on a UR 20 instrument for samples in Nujol, the $^1H$ and $^{13}C$ NMR spectra on a Gemini 300 (Varian) spectrometer at frequencies of 300 and 75 MHz respectively, hexamethyldisiloxane being the internal standard. The unit cell parameters and the intensities of reflections for the x-ray structural analysis were measured with a Siemens automatic four-circle diffractometer P3/PC ($\lambda MoK\alpha$, graphite monochromator, $\theta/2\theta$ scanning). The structures of the compounds investigated were solved by the direct method and refined by the full-matrix least squares method in an anisotropic approach for the nonhydrogen atoms. The hydrogen atoms were located objectively with a Fourier difference synthesis and refined in an isotropic approach. All calculations were carried out on an IBM PC/AT-486 with the SHELXTLPLUS and SHELXL-93 programs. The coordinates of atoms, bond lengths, valence angles, and temperature parameters have been deposited with the Cambridge Center for Crystallographic Data. The purity of the synthesized compounds and the degree of completeness of reactions were established by TLC (Silufol UV 254).

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

| Atom | $x$ | $y$ | $z$ | $U_{(eq)}$ |
|---|---|---|---|---|
| $O_{(1)}$ | 1521(2) | 3597(1) | 6669(2) | 27(1) |
| $N_{(1)}$ | 515(3) | 4091(1) | 4506(2) | 22(1) |
| $N_{(31)}$ | 4079(3) | 3348(1) | 1438(3) | 54(1) |
| $N_{(32)}$ | 2658(3) | 4845(1) | 2231(2) | 34(1) |
| $N_{(41)}$ | 4613(3) | 3023(1) | 5731(3) | 40(1) |
| $N_{(42)}$ | 6673(3) | 4346(1) | 4508(3) | 39(1) |
| $C_{(2)}$ | 1076(3) | 3739(1) | 3485(3) | 22(1) |
| $C_{(21)}$ | -60(3) | 3698(1) | 2022(3) | 23(1) |
| $C_{(22)}$ | -969(3) | 4101(1) | 1423(3) | 28(1) |
| $C_{(23)}$ | -1994(3) | 4059(1) | 74(3) | 34(1) |
| $C_{(24)}$ | -2125(3) | 3613(1) | -689(3) | 38(1) |
| $C_{(25)}$ | -1235(4) | 3206(1) | -94(3) | 40(1) |
| $C_{(26)}$ | -209(3) | 3247(1) | 1257(3) | 31(1) |
| $C_{(3)}$ | 2790(3) | 3931(1) | 3265(3) | 22(1) |
| $C_{(31)}$ | 3509(3) | 3606(1) | 2219(3) | 31(1) |
| $C_{(32)}$ | 2689(3) | 4449(1) | 2668(3) | 25(1) |
| $C_{(4)}$ | 3915(3) | 3941(1) | 4854(3) | 21(1) |
| $C_{(41)}$ | 4260(3) | 3421(1) | 5370(3) | 25(1) |
| $C_{(42)}$ | 5482(3) | 4167(1) | 4663(3) | 25(1) |
| $C_{(5)}$ | 3117(3) | 4260(1) | 5982(3) | 21(1) |
| $C_{(6)}$ | 4100(3) | 4276(1) | 7547(3) | 26(1) |
| $C_{(7)}$ | 3299(3) | 4625(1) | 8543(3) | 32(1) |
| $C_{(8)}$ | 1562(3) | 4479(1) | 8580(3) | 31(1) |
| $C_{(9)}$ | 593(3) | 4445(1) | 7003(3) | 27(1) |
| $C_{(10)}$ | 1388(3) | 4087(1) | 6023(3) | 22(1) |
| $N_{(1S)}$ | -1320(4) | 3048(1) | 5480(4) | 67(1) |
| $C_{(1S)}$ | -1932(4) | 2783(1) | 4593(4) | 46(1) |
| $C_{(2S)}$ | -2730(6) | 2448(2) | 3453(5) | 63(1) |

TABLE 3. Bond Lengths and Valence Angles in the Compound (VIIIa) Molecule

| Bond | λ, Å | Angle | ω, deg | Angle | ω, deg |
|---|---|---|---|---|---|
| $O_{(1)}$—$C_{(10)}$ | 1,431(3) | $C_{(2)}$—$N_{(1)}$—$C_{(10)}$ | 115,3(2) | $C_{(31)}$—$C_{(3)}$—$C_{(2)}$ | 111,1(2) |
| $N_{(1)}$—$C_{(10)}$ | 1,447(3) | $N_{(1)}$—$C_{(2)}$—$C_{(3)}$ | 105,2(2) | $C_{(31)}$—$C_{(3)}$—$C_{(4)}$ | 109,8(2) |
| $N_{(32)}$—$C_{(32)}$ | 1,130(3) | $C_{(22)}$—$C_{(21)}$—$C_{(26)}$ | 118,8(2) | $C_{(2)}$—$C_{(3)}$—$C_{(4)}$ | 108,8(2) |
| $N_{(42)}$—$C_{(42)}$ | 1,137(3) | $C_{(26)}$—$C_{(21)}$—$C_{(2)}$ | 119,7(2) | $N_{(32)}$—$C_{(32)}$—$C_{(3)}$ | 178,0(3) |
| $C_{(2)}$—$C_{(3)}$ | 1,570(3) | $C_{(24)}$—$C_{(23)}$—$C_{(22)}$ | 120,0(3) | $C_{(41)}$—$C_{(4)}$—$C_{(5)}$ | 113,2(2) |
| $C_{(21)}$—$C_{(26)}$ | 1,384(4) | $C_{(24)}$—$C_{(25)}$—$C_{(26)}$ | 120,4(3) | $C_{(41)}$—$C_{(4)}$—$C_{(3)}$ | 109,2(2) |
| $C_{(23)}$—$C_{(24)}$ | 1,374(4) | $C_{(31)}$—$C_{(3)}$—$C_{(32)}$ | 108,9(2) | $C_{(5)}$—$C_{(4)}$—$C_{(3)}$ | 109,9(2) |
| $C_{(25)}$—$C_{(26)}$ | 1,383(4) | $C_{(32)}$—$C_{(3)}$—$C_{(2)}$ | 110,4(2) | $N_{(42)}$—$C_{(42)}$—$C_{(4)}$ | 179,1(3) |
| $C_{(3)}$—$C_{(32)}$ | 1,482(4) | $C_{(32)}$—$C_{(3)}$—$C_{(4)}$ | 107,8(2) | $C_{(6)}$—$C_{(5)}$—$C_{(4)}$ | 113,2(2) |
| $C_{(4)}$—$C_{(41)}$ | 1,480(4) | $N_{(31)}$—$C_{(31)}$—$C_{(3)}$ | 178,4(3) | $C_{(7)}$—$C_{(6)}$—$C_{(5)}$ | 109,8(2) |
| $C_{(4)}$—$C_{(5)}$ | 1,555(3) | $C_{(41)}$—$C_{(4)}$—$C_{(42)}$ | 106,6(2) | $C_{(7)}$—$C_{(8)}$—$C_{(9)}$ | 111,9(2) |
| $C_{(5)}$—$C_{(10)}$ | 1,530(3) | $C_{(42)}$—$C_{(4)}$—$C_{(5)}$ | 109,3(2) | $O_{(1)}$—$C_{(10)}$—$N_{(1)}$ | 112,8(2) |
| $C_{(7)}$—$C_{(8)}$ | 1,516(4) | $C_{(42)}$—$C_{(4)}$—$C_{(3)}$ | 108,5(2) | $N_{(1)}$—$C_{(10)}$—$C_{(9)}$ | 109,8(2) |
| $C_{(9)}$—$C_{(10)}$ | 1,524(3) | $N_{(41)}$—$C_{(41)}$—$C_{(4)}$ | 175,8(3) | $N_{(1)}$—$C_{(10)}$—$C_{(5)}$ | 108,7(2) |
| $N_{(1)}$—$C_{(2)}$ | 1,444(3) | $C_{(6)}$—$C_{(5)}$—$C_{(10)}$ | 111,6(2) | | |
| $N_{(31)}$—$C_{(31)}$ | 1,141(3) | $C_{(10)}$—$C_{(5)}$—$C_{(4)}$ | 110,8(2) | | |
| $N_{(41)}$—$C_{(41)}$ | 1,140(3) | $C_{(8)}$—$C_{(7)}$—$C_{(6)}$ | 111,7(2) | | |
| $C_{(2)}$—$C_{(21)}$ | 1,508(3) | $C_{(10)}$—$C_{(9)}$—$C_{(8)}$ | 111,0(2) | | |
| $C_{(21)}$—$C_{(22)}$ | 1,382(3) | $O_{(1)}$—$C_{(10)}$—$C_{(9)}$ | 110,7(2) | | |
| $C_{(22)}$—$C_{(23)}$ | 1,382(4) | $O_{(1)}$—$C_{(10)}$—$C_{(5)}$ | 105,7(2) | | |
| $C_{(24)}$—$C_{(25)}$ | 1,379(4) | $C_{(9)}$—$C_{(10)}$—$C_{(5)}$ | 109,0(2) | | |
| $C_{(3)}$—$C_{(31)}$ | 1,478(4) | $N_{(1)}$—$C_{(2)}$—$C_{(21)}$ | 112,3(2) | | |
| $C_{(3)}$—$C_{(4)}$ | 1,589(3) | $C_{(21)}$—$C_{(2)}$—$C_{(3)}$ | 112,6(2) | | |
| $C_{(4)}$—$C_{(42)}$ | 1,482(4) | $C_{(22)}$—$C_{(21)}$—$C_{(2)}$ | 121,5(2) | | |
| $C_{(5)}$—$C_{(6)}$ | 1,521(3) | $C_{(23)}$—$C_{(22)}$—$C_{(21)}$ | 120,9(3) | | |
| $C_{(6)}$—$C_{(7)}$ | 1,520(4) | $C_{(23)}$—$C_{(24)}$—$C_{(25)}$ | 119,6(3) | | |
| $C_{(8)}$—$C_{(9)}$ | 1,527(4) | $C_{(26)}$—$C_{(25)}$—$C_{(21)}$ | 120,2(3) | | |

TABLE 4. Bond Lengths and Valence Angles in the Molecule of Compound (XVIIa)

| Bond | λ. Å | Angle | ω. deg | Angle | ω. deg |
|---|---|---|---|---|---|
| $O_{(22)}$—$C_{(21)}$ | 1,355(2) | $C_{(21)}$—$O_{(22)}$—$C_{(23)}$ | 106,0(2) | $C_{(10)}$—$N_{(1)}$—$C_{(2)}$ | 121,5(2) |
| $O_{(41)}$—$C_{(41)}$ | 1,222(2) | $N_{(1)}$—$C_{(2)}$—$C_{(21)}$ | 110,7(2) | $N_{(1)}$—$C_{(2)}$—$C_{(3)}$ | 113,2(1) |
| $N_{(1)}$—$C_{(2)}$ | 1,453(2) | $C_{(21)}$—$C_{(2)}$—$C_{(3)}$ | 109,0(1) | $C_{(25)}$—$C_{(21)}$—$O_{(22)}$ | 110,6(2) |
| $N_{(32)}$—$C_{(32)}$ | 1,139(2) | $C_{(25)}$—$C_{(21)}$—$C_{(2)}$ | 129,9(2) | $O_{(22)}$—$C_{(21)}$—$C_{(2)}$ | 119,3(2) |
| $N_{(42)}$—$C_{(42)}$ | 1,138(2) | $C_{(24)}$—$C_{(23)}$—$O_{(22)}$ | 110,0(2) | $C_{(23)}$—$C_{(24)}$—$C_{(25)}$ | 107,1(2) |
| $C_{(2)}$—$C_{(3)}$ | 1,581(2) | $C_{(21)}$—$C_{(25)}$—$C_{(24)}$ | 106,2(2) | $C_{(32)}$—$C_{(3)}$—$C_{(31)}$ | 109,3(2) |
| $C_{(23)}$—$C_{(24)}$ | 1,312(4) | $C_{(32)}$—$C_{(3)}$—$C_{(4)}$ | 110,4(1) | $C_{(31)}$—$C_{(3)}$—$C_{(4)}$ | 107,6(1) |
| $C_{(3)}$—$C_{(32)}$ | 1,473(3) | $C_{(32)}$—$C_{(3)}$—$C_{(2)}$ | 108,2(2) | $C_{(31)}$—$C_{(3)}$—$C_{(2)}$ | 109,3(1) |
| $C_{(3)}$—$C_{(4)}$ | 1,571(2) | $C_{(4)}$—$C_{(3)}$—$C_{(2)}$ | 112,0(1) | $N_{(31)}$—$C_{(31)}$—$C_{(3)}$ | 177,5(2) |
| $C_{(4)}$—$C_{(41)}$ | 1,554(2) | $N_{(32)}$—$C_{(32)}$—$C_{(3)}$ | 177,8(2) | $C_{(42)}$—$C_{(4)}$—$C_{(41)}$ | 110,5(1) |
| $C_{(5)}$—$C_{(10)}$ | 1,521(2) | $C_{(42)}$—$C_{(4)}$—$C_{(5)}$ | 108,9(1) | $C_{(41)}$—$C_{(4)}$—$C_{(5)}$ | 111,0(1) |
| $C_{(6)}$—$C_{(7)}$ | 1,521(3) | $C_{(42)}$—$C_{(4)}$—$C_{(3)}$ | 107,1(1) | $C_{(41)}$—$C_{(4)}$—$C_{(3)}$ | 110,5(1) |
| $C_{(8)}$—$C_{(9)}$ | 1,526(3) | $C_{(5)}$—$C_{(4)}$—$C_{(3)}$ | 108,8(1) | $O_{(41)}$—$C_{(41)}$—$N_{(41)}$ | 124,8(2) |
| $O_{(22)}$—$O_{(23)}$ | 1,378(3) | $O_{(41)}$—$C_{(41)}$—$C_{(4)}$ | 117,8(2) | $N_{(41)}$—$C_{(41)}$—$C_{(4)}$ | 117,3(2) |
| $N_{(1)}$—$C_{(10)}$ | 1,272(2) | $N_{(42)}$—$C_{(42)}$—$C_{(4)}$ | 177,9(2) | $C_{(10)}$—$C_{(5)}$—$C_{(6)}$ | 112,2(1) |
| $N_{(31)}$—$C_{(31)}$ | 1,138(2) | $C_{(10)}$—$C_{(5)}$—$C_{(4)}$ | 113,9(2) | $C_{(6)}$—$C_{(5)}$—$C_{(4)}$ | 111,5(2) |
| $N_{(41)}$—$C_{(41)}$ | 1,317(2) | $C_{(7)}$—$C_{(6)}$—$C_{(5)}$ | 111,1(2) | $C_{(8)}$—$C_{(7)}$—$C_{(6)}$ | 110,0(2) |
| $C_{(2)}$—$C_{(21)}$ | 1,494(2) | $C_{(7)}$—$C_{(8)}$—$C_{(9)}$ | 110,2(2) | $C_{(10)}$—$C_{(9)}$—$C_{(8)}$ | 113,1(2) |
| $C_{(21)}$—$C_{(25)}$ | 1,326(3) | $N_{(1)}$—$C_{(10)}$—$C_{(9)}$ | 118,2(2) | $N_{(1)}$—$C_{(10)}$—$C_{(5)}$ | 127,9(2) |
| $C_{(24)}$—$C_{(25)}$ | 1,425(4) | $C_{(9)}$—$C_{(10)}$—$C_{(5)}$ | 113,8(2) | | |
| $C_{(3)}$—$C_{(31)}$ | 1,477(2) | | | | |
| $C_{(4)}$—$C_{(42)}$ | 1,479(2) | | | | |
| $C_{(4)}$—$C_{(5)}$ | 1,557(2) | | | | |
| $C_{(5)}$—$C_{(6)}$ | 1,536(2) | | | | |
| $C_{(7)}$—$C_{(8)}$ | 1,514(3) | | | | |
| $C_{(9)}$—$C_{(10)}$ | 1,505(3) | | | | |

**6-Hydroxy-5,6-tetramethylene-2-phenylpiperidine-3,3,4,4-tetracarbonitrile (VIIIa) $C_{19}H_{17}N_5O$.** A. Ketone (Ia) (0.45 g: 2 mmole) and diene (II) (0.3 g: 1 mmole) were dissolved with stirring in acetonitrile (5 ml). After 15-20 min a precipitate began to form. At the end of the reaction (TLC) the solid was filtered off, washed with cold isopropyl alcohol, and dried in vacuum to constant weight. A colorless crystalline substance (0.3 g: 45%) of mp >150°C (decomp.) was obtained. IR spectrum (thin film): 2265 ($\nu$ C≡N), 3345 ($\nu$N–H), 3535 cm$^{-1}$ ($\nu$O–H).

B. Ketone (Ia) (0.45 g: 2 mmole) and diene (II) (0.3 g: 1 mmole) were dissolved with stirring in isopropyl alcohol (5 ml) at 15°C. At the end of the reaction (TLC) the resulting solid was filtered off, washed with cold isopropyl alcohol, and dried in vacuum. The yield of compound (VIIIa) was 0.3 g (60%).

**X-Ray Structural Investigation of Compound (VIIIa).** Transparent colorless crystals of compound (VIIIa) were removed from the reaction mixture (method A). Principal crystallographic data: monoclinic crystals ($C_{19}H_{17}N_5O \cdot C_2H_3N$); at 153°K $a$ = 8.399(3), b = 26.741(8), c = 9.005(2) Å, $\beta$ = 98.81(2)°, $\alpha$ = 90.00(2)°, $\gamma$ = 90.00(2)°, V = 1998.6(10) Å$^3$, d = 1.238 g/cm$^3$, space group P2$_1$/n, Z = 4, F(000) = 784. Total reflections measured 3786, $\theta_{max}$ = 25.05°. Final divergence factors were $R_1$ = 0.0580 for 3524 independent reflections with I > 2$\sigma$ (I) and w$R_2$ = 0.1392 at each of 3538 independent reflections.

**2-(p-Bromophenyl-6-hydroxy-5,6-tetramethylenepiperidine-3,3,4,4-tetracarbonitrile (Xa) $C_{19}H_{16}BrN_5O$.** Ketone (Ia) (0.45 g: 2 mmole) and diene (VIIc) (0.53 g: 1 mmole) were dissolved with stirring in acetonitrile (5 ml), the solid which precipitated after 20-30 min was filtered off, washed with cold isopropyl alcohol, and dried in the air. A white crystalline substance (0.36 g: 40%) of mp 65°C was obtained. Found, %: C 55.34; H 4.21; N 19.04. $C_{19}H_{16}BrN_5O \cdot C_2H_3N$. Calculated, %: C 55.81; H 4.24; N 18.62. IR spectrum: 2270 ($\nu$C≡N), 3330 ($\nu$N–H), 3340 cm$^{-1}$ ($\nu$O–H).

**6-Hydroxy-5,6-tetramethylene-2-(2-furyl)piperidine-3,3,4,4-tetracarbonitrile (IXa) $C_{17}H_{15}N_5O_2$.** Ketone (Ia) (0.45 g: 2 mmole) and diene (III) (0.27 g: 1 mmole) were suspended in isopropyl alcohol (5 ml) at 15°C. The new crystalline substance formed as the reactants dissolved. At the end of the reaction (TLC) the precipitate was filtered off, washed, and dried in vacuum to constant weight. A white crystalline substance (0.45 g: 70%) of mp 83°C (decomp.) was obtained. Found, %: C 63.41; H 4.78; N 21.22. $C_{17}H_{15}N_5O_2$. Calculated, %: C 63.54; H 4.71; N 21.79. IR spectrum: 2270 ($\nu$C≡N), 3330 ($\nu$N–H), 3500 cm$^{-1}$ ($\nu$O–H).

**5,6-Tetramethylene-3,3,4-tricyano-2-phenyl-2,3,4,5-tetrahydropyridine-4-carboxamide (XVIIa) $C_{19}H_{17}N_5O$.** Diene (II) (0.3 g: 1 mmole) was added to a suspension of ketone (Ia) (0.45 g: 2 mmole) in isopropyl alcohol (5 ml) at 25°C and the mixture stirred until a clear solution was formed, keeping the temperature of the reaction mixture at 25-30°C. After 10-15 min

TABLE 5. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Coefficients of Equivalent Isotropic Displacement ($Å^2 \times 10^3$) for Compound (XVIIa)

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| $O_{(22)}$ | 7498(2) | 3235(1) | 3539(1) | 38(1) |
| $O_{(41)}$ | 9623(2) | 931(1) | 902(1) | 31(1) |
| $N_{(1)}$ | 9997(2) | 2478(1) | 2928(1) | 23(1) |
| $N_{(31)}$ | 7735(2) | 1233(1) | 4755(2) | 39(1) |
| $N_{(32)}$ | 5685(2) | 655(1) | 1324(2) | 42(1) |
| $N_{(41)}$ | 9622(2) | -588(1) | 1220(1) | 26(1) |
| $N_{(42)}$ | 8707(2) | -1007(1) | 3671(1) | 31(1) |
| $C_{(2)}$ | 8520(2) | 2171(1) | 2353(2) | 19(1) |
| $C_{(21)}$ | 7352(2) | 2830(1) | 2532(2) | 23(1) |
| $C_{(23)}$ | 6226(3) | 3751(2) | 3471(2) | 44(1) |
| $C_{(24)}$ | 5344(3) | 3664(2) | 2479(3) | 46(1) |
| $C_{(25)}$ | 6068(3) | 3064(2) | 1857(2) | 31(1) |
| $C_{(3)}$ | 8120(2) | 1182(1) | 2718(1) | 18(1) |
| $C_{(31)}$ | 7876(2) | 1221(1) | 3861(2) | 23(1) |
| $C_{(32)}$ | 6736(2) | 881(1) | 1948(2) | 25(1) |
| $C_{(4)}$ | 9412(2) | 478(1) | 2719(1) | 18(1) |
| $C_{(41)}$ | 9556(2) | 277(1) | 1509(1) | 20(1) |
| $C_{(42)}$ | 9036(2) | -368(1) | 3254(1) | 21(1) |
| $C_{(5)}$ | 10895(2) | 876(1) | 3430(1) | 19(1) |
| $C_{(6)}$ | 12263(2) | 390(1) | 3177(2) | 26(1) |
| $C_{(7)}$ | 13704(2) | 766(2) | 3896(2) | 32(1) |
| $C_{(8)}$ | 13821(2) | 1783(2) | 3692(2) | 33(1) |
| $C_{(9)}$ | 12498(2) | 2287(1) | 3973(2) | 32(1) |
| $C_{(10)}$ | 11013(2) | 1912(1) | 3366(1) | 22(1) |

the solid formed was filtered off, washed with cold isopropyl alcohol, and dried to constant weight in vacuum. The yield of compound (XVIIa) was 0.45 g (68%) of mp 125-130°C (decomp.). Found, %: C 68.52; H 5.29; N 21.06. $C_{19}H_{17}N_5O$. Calculated, %: C 68.74; H 5.24; N 21.19. IR spectrum: 1615, 1645 ($\nu$C=N, $\delta NH_2$); 1690 ($\nu$C=O); 2260 ($\nu C\equiv N$); 3170, 3330 $cm^{-1}$ ($\nu_s NH_2$, $\nu_{as} NH_2$). $^{13}C$ NMR spectrum (acetone-$D_6$): $C_{(2)}$ $\delta$ 61.73; $C_{(3)}$ 44.97; $C_{(4)}$ 52.77; $C_{(5)}$ 41.28; $C_{(CN)}$ 117.42; 113.24; 112.03; $C_{(CONH_2)}$ 163.11; $C_{(CH_2)}$ 28.45; 25.10; 26.15; 38.73; $C_{(C_6H_5)}$ 129.01; 131.03; 114.41; 142.18; 161.16 ppm.

**5,6-Tetramethylene-2-(p-methoxyphenyl)-3,3,4-tricyano-2,3,4,5-tetrahydropyridine-4-carboxamide (XIXa) $C_{20}H_{19}N_5O_2$** was obtained analogously to compound (XVIIa) using diene (IV) (0.39 g: 1 mmole) at a reaction temperature of 15-20°C. Yield was 0.43 g (60%) of mp 77-78°C (decomp.). Found, %: C 66.47; H 5.25; N 19.28. $C_{20}H_{19}N_5O_2$. Calculated, %: C 66.47; H 5.30; N 19.38. IR spectrum: 1660 ($\nu$C=N, $\delta$ $NH_2$); 1700 ($\nu$C=O); 2260 ($\nu C\equiv N$); 3130, 3220 $cm^{-1}$ ($\nu_s NH_2$, $\nu_{as} NH_2$).

**5,6-Tetramethylene-2-(2-furyl)-3,3,4-tricyano-2,3,4,5-tetrahydropyridine-4-carboxamide (XVIIIa) $C_{17}H_{15}N_5O_2$.** Ketone (Ia) (0.45 g: 2 mmole) and diene (III) (0.268 g: 1 mmole) were dissolved in acetonitrile (5 ml). The reaction mixture was maintained at room temperature for 2 h, the precipitate formed was filtered off, washed with cold isopropyl alcohol, and dried in vacuum to constant weight. A white crystalline substance (0.49 g: 75%) was obtained having mp > 130°C (decomp.). Found, %: C 63.51; H 4.70; N 21.85. $C_{17}H_{15}N_5O_2$. Calculated, %: C 63.54; H 4.71; N 21.79. IR spectrum: 1650 ($\nu$C=N, $\nu NH_2$); 1690 ($\nu$C=O); 2260 ($\nu C\equiv N$); 3150, 3270 $cm^{-1}$ ($\nu_s NH_2$, $\nu_{as} NH_2$).

**X-Ray Structural Investigation of Compound (XVIIIa).** Clear colorless crystals were selected from the reaction mixture. Principal crystallographic data: the crystals of compound (XVIIIa) were monoclinic, at 153°K $a$ = 9.193(2), b = 14.605(3), c = 12.323(2) Å, $\beta$ = 103.01(2)°, V = 1612.1(5) $Å^3$, $d_{calc}$ = 1.324 $g/cm^3$, space group $P2_1/c$, Z = 4, F(000) = 672. Reflections measured were 5563, $\theta_{max}$ = 27°. Final divergence factors were $R_1$ = 0.058 for 5235 independent reflections with $I > 2\sigma(I)$ and $wR_2$ = 0.129 at each of 5271 independent reflections.

**3-Amino-6,7-tetramethylene-1-oxo-4-phenyl-3*a*,4,5,7*a*-tetrahydro-1H-pyrrolo[3,4-c]pyridine-3*a*,7*a*-dicarbonitrile (XXa) $C_{19}H_{17}N_5O$.** A. Compound (VIIIa) (0.33 g: 1 mmole) was dissolved with heating in isopropyl alcohol (3 ml), the solution was cooled, and the resulting solid was filtered off. The solid was washed with cold isopropyl alcohol, and dried in vacuum to constant weight. A colorless crystalline substance (0.31 g: 94%) of mp 208-210°C (decomp.) was obtained. Found, %: C 68.31; H 5.15; N 21.10. $C_{19}H_{17}N_5O$. Calculated, %: C 68.87; H 5.15; N 21.13. IR spectrum: 1566, 1650 ($\nu$C=N, $\nu NH_2$); 1730 ($\nu$C=O); 2265 ($\nu C\equiv N$); 3325 $cm^{-1}$ ($\nu$N-H). $^{13}C$ NMR spectrum (DMSO-$D_6$): $C_{(1)}$ $\delta$ 179.37; $C_{(3)}$ 178.14;

TABLE 6. Bond Lengths and Valence Angles in the Compound (XIa) Molecule

| Bond | λ. Å | Angle | ω. deg | Angle | ω. deg |
|---|---|---|---|---|---|
| $N_{(1)}$—$C_{(8A)}$ | 1,386(1) | $C_{(8A)}$—$N_{(1)}$—$C_{(2)}$ | 118,04(7) | $N_{(1)}$—$C_{(2)}$—$C_{(21)}$ | 112,76(7) |
| $N_{(31)}$—$C_{(31)}$ | 1,143(1) | $N_{(1)}$—$C_{(2)}$—$C_{(3)}$ | 105,79(7) | $C_{(21)}$—$C_{(2)}$—$C_{(3)}$ | 113,10(7) |
| $N_{(41)}$—$C_{(41)}$ | 1,140(1) | $C_{(26)}$—$C_{(21)}$—$C_{(22)}$ | 119,45(9) | $C_{(26)}$—$C_{(21)}$—$C_{(2)}$ | 121,96(8) |
| $C_{(2)}$—$C_{(21)}$ | 1,509(1) | $C_{(22)}$—$C_{(21)}$—$C_{(2)}$ | 118,58(8) | $C_{(23)}$—$C_{(22)}$—$C_{(21)}$ | 120,23(9) |
| $C_{(21)}$—$C_{(26)}$ | 1,392(1) | $C_{(22)}$—$C_{(23)}$—$C_{(24)}$ | 120,0(1) | $C_{(25)}$—$C_{(24)}$—$C_{(23)}$ | 120,17(9) |
| $C_{(22)}$—$C_{(23)}$ | 1,386(1) | $C_{(24)}$—$C_{(25)}$—$C_{(26)}$ | 119,9(1) | $C_{(25)}$—$C_{(26)}$—$C_{(21)}$ | 120,22(9) |
| $C_{(24)}$—$C_{(25)}$ | 1,385(2) | $C_{(31)}$—$C_{(3)}$—$C_{(32)}$ | 109,34(7) | $C_{(31)}$—$C_{(3)}$—$C_{(2)}$ | 110,29(7) |
| $C_{(25)}$—$C_{(26)}$ | 1,392(1) | $C_{(32)}$—$C_{(3)}$—$C_{(2)}$ | 111,79(7) | $C_{(31)}$—$C_{(3)}$—$C_{(4)}$ | 109,90(7) |
| $C_{(3)}$—$C_{(31)}$ | 1,477(1) | $C_{(32)}$—$C_{(3)}$—$C_{(4)}$ | 108,63(7) | $C_{(2)}$—$C_{(3)}$—$C_{(4)}$ | 106,85(7) |
| $C_{(3)}$—$C_{(32)}$ | 1,480(1) | $N_{(31)}$—$C_{(31)}$—$C_{(3)}$ | 178,9(1) | $N_{(32)}$—$C_{(32)}$—$C_{(3)}$ | 175,5(1) |
| $C_{(3)}$—$C_{(4)}$ | 1,583(1) | $C_{(41)}$—$C_{(4)}$—$C_{(42)}$ | 108,61(7) | $C_{(41)}$—$C_{(4)}$—$C_{(4A)}$ | 109,37(7) |
| $C_{(4)}$—$C_{(41)}$ | 1,487(1) | $C_{(42)}$—$C_{(4)}$—$C_{(4A)}$ | 109,28(7) | $C_{(41)}$—$C_{(4)}$—$C_{(3)}$ | 109,41(7) |
| $C_{(4)}$—$C_{(42)}$ | 1,488(1) | $C_{(42)}$—$C_{(4)}$—$C_{(3)}$ | 108,25(7) | $C_{(4A)}$—$C_{(4)}$—$C_{(3)}$ | 111,86(7) |
| $C_{(4)}$—$C_{(4A)}$ | 1,523(1) | $N_{(41)}$—$C_{(41)}$—$C_{(4)}$ | 176,8(1) | $N_{(42)}$—$C_{(42)}$—$C_{(4)}$ | 176,93(9) |
| $C_{(4A)}$—$C_{(8A)}$ | 1,346(1) | $C_{(8A)}$—$C_{(4A)}$—$C_{(5)}$ | 124,29(8) | $C_{(8A)}$—$C_{(4A)}$—$C_{(4)}$ | 120,19(8) |
| $C_{(4A)}$—$C_{(5)}$ | 1,509(1) | $C_{(5)}$—$C_{(4A)}$—$C_{(4)}$ | 115,53(7) | $C_{(4A)}$—$C_{(5)}$—$C_{(6)}$ | 112,20(8) |
| $C_{(5)}$—$C_{(6)}$ | 1,525(1) | $C_{(7)}$—$C_{(6)}$—$C_{(5)}$ | 110,45(8) | $C_{(6)}$—$C_{(7)}$—$C_{(8)}$ | 111,40(8) |
| $C_{(6)}$—$C_{(7)}$ | 1,524(1) | $C_{(8A)}$—$C_{(8)}$—$C_{(7)}$ | 113,13(8) | $C_{(4A)}$—$C_{(8A)}$—$N_{(1)}$ | 123,21(8) |
| $C_{(7)}$—$C_{(8)}$ | 1,525(1) | $C_{(4A)}$—$C_{(8A)}$—$C_{(8)}$ | 121,50(8) | $N_{(1)}$—$C_{(8A)}$—$C_{(8)}$ | 115,28(8) |
| $C_{(8)}$—$C_{(8A)}$ | 1,504(1) | | | | |
| $N_{(1)}$—$C_{(2)}$ | 1,443(1) | | | | |
| $N_{(32)}$—$C_{(32)}$ | 1,142(1) | | | | |
| $N_{(42)}$—$C_{(42)}$ | 1,143(1) | | | | |
| $C_{(2)}$—$C_{(3)}$ | 1,573(1) | | | | |
| $C_{(21)}$—$C_{(22)}$ | 1,395(1) | | | | |
| $C_{(23)}$—$C_{(24)}$ | 1,391(2) | | | | |

TABLE 7. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Coefficients of Equivalent Isotropic Displacement ($Å^2 \times 10^3$) for Compound (XIa)

| ATOM | *x* | *y* | *z* | *U(eq)* |
|---|---|---|---|---|
| $N_{(1)}$ | 4410(1) | -863(1) | 7494(1) | 17(1) |
| $N_{(31)}$ | 4135(2) | 2428(2) | 8878(1) | 34(1) |
| $N_{(32)}$ | -1944(1) | 4427(1) | 7997(1) | 29(1) |
| $N_{(41)}$ | 2531(1) | 6467(1) | 6900(1) | 28(1) |
| $N_{(42)}$ | -605(1) | 3757(1) | 5739(1) | 25(1) |
| $C_{(2)}$ | 2283(1) | 115(1) | 7644(1) | 15(1) |
| $C_{(21)}$ | 1632(1) | -850(1) | 8422(1) | 16(1) |
| $C_{(22)}$ | -292(2) | -783(2) | 8424(1) | 23(1) |
| $C_{(23)}$ | -921(2) | -170(2) | 9118(1) | 28(1) |
| $C_{(24)}$ | 370(2) | -2701(2) | 9813(1) | 27(1) |
| $C_{(25)}$ | 2269(2) | -2746(2) | 9823(1) | 27(1) |
| $C_{(26)}$ | 2903(2) | -1821(2) | 9128(1) | 23(1) |
| $C_{(3)}$ | 1841(1) | 2291(1) | 7701(1) | 15(1) |
| $C_{(31)}$ | 3147(1) | 2368(1) | 8359(1) | 19(1) |
| $C_{(32)}$ | -289(2) | 3458(1) | 7897(1) | 19(1) |
| $C_{(4)}$ | 2309(1) | 3179(1) | 6795(1) | 15(1) |
| $C_{(41)}$ | 2383(1) | 5061(1) | 6861(1) | 19(1) |
| $C_{(42)}$ | 645(1) | 3556(1) | 6196(1) | 17(1) |
| $C_{(4A)}$ | 4292(1) | 1802(1) | 6451(1) | 15(1) |
| $C_{(5)}$ | 5106(1) | 2691(1) | 5702(1) | 21(1) |
| $C_{(6)}$ | 6771(1) | 1149(2) | 5255(1) | 22(1) |
| $C_{(7)}$ | 8230(1) | -440(1) | 5907(1) | 22(1) |
| $C_{(8)}$ | 7172(1) | -1464(1) | 6494(1) | 20(1) |
| $C_{(8A)}$ | 5196(1) | -75(1) | 6809(1) | 15(1) |

$C_{(4)}$ 63.13; $C_{(6)}$ 95.51; $C_{(7)}$ 141.67; $C_{(3a)}$, $C_{(7a)}$ 56.40; 56.88; $C_{(CN)}$ 117.13; 114.70; $C_{(CH_2)}$ 22.86; 23.64; 25.85; 27.97; $C_{(C_6H_5)}$ 129.03; 129.40; 130.57; 136.27 ppm.

TABLE 8. Bond Lengths and Valence Angles in the Compound (XXIIIa) Molecule

| Bond | λ, Å | Angle | ω, deg | Angle | ω, deg |
|---|---|---|---|---|---|
| O$_{(1)}$—C$_{(14)}$ | 1,206(2) | C$_{(4A)}$—N$_{(5)}$—C$_{(6)}$ | 119,7(1) | C$_{(8)}$—N$_{(9)}$—C$_{(10)}$ | 115,9(1) |
| N$_{(5)}$—C$_{(4A)}$ | 1,390(2) | C$_{(12)}$—N$_{(11)}$—C$_{(10)}$ | 113,0(1) | C$_{(14)}$—N$_{(13)}$—C$_{(8)}$ | 114,5(1) |
| N$_{(5)}$—C$_{(6)}$ | 1,448(2) | C$_{(14)}$—N$_{(13)}$—C$_{(12)}$ | 126,2(1) | C$_{(8)}$—N$_{(13)}$—C$_{(12)}$ | 119,0(1) |
| N$_{(9)}$—C$_{(8)}$ | 1,265(2) | C$_{(15A)}$—C$_{(1)}$—C$_{(2)}$ | 112,0(2) | C$_{(3)}$—C$_{(2)}$—C$_{(1)}$ | 110,3(2) |
| N$_{(9)}$—C$_{(10)}$ | 1,489(2) | C$_{(4)}$—C$_{(3)}$—C$_{(2)}$ | 109,1(2) | C$_{(4A)}$—C$_{(4)}$—C$_{(3)}$ | 112,3(2) |
| N$_{(11)}$—C$_{(12)}$ | 1,446(2) | C$_{(15A)}$—C$_{(4A)}$—N$_{(5)}$ | 123,5(2) | C$_{(15A)}$—C$_{(4A)}$—C$_{(4)}$ | 122,1(2) |
| N$_{(11)}$—C$_{(10)}$ | 1,464(2) | N$_{(5)}$—C$_{(4A)}$—C$_{(4)}$ | 114,3(1) | N$_{(5)}$—C$_{(6)}$—C$_{(18)}$ | 115,8(1) |
| N$_{(13)}$—C$_{(14)}$ | 1,371(2) | N$_{(5)}$—C$_{(6)}$—C$_{(7)}$ | 107,0(1) | C$_{(18)}$—C$_{(6)}$—C$_{(7)}$ | 113,2(1) |
| N$_{(13)}$—C$_{(8)}$ | 1,384(2) | C$_{(16)}$—C$_{(7)}$—C$_{(8)}$ | 105,8(1) | C$_{(16)}$—C$_{(7)}$—C$_{(6)}$ | 110,7(1) |
| N$_{(13)}$—C$_{(12)}$ | 1,476(2) | C$_{(8)}$—C$_{(7)}$—C$_{(6)}$ | 111,3(1) | C$_{(16)}$—C$_{(7)}$—C$_{(15)}$ | 111,5(1) |
| N$_{(16)}$—C$_{(16)}$ | 1,145(2) | C$_{(8)}$—C$_{(7)}$—C$_{(15)}$ | 102,9(1) | C$_{(6)}$—C$_{(7)}$—C$_{(15)}$ | 114,3(1) |
| N$_{(17)}$—C$_{(17)}$ | 1,144(2) | N$_{(9)}$—C$_{(8)}$—N$_{(13)}$ | 127,0(1) | N$_{(9)}$—C$_{(8)}$—C$_{(7)}$ | 124,6(1) |
| C$_{(1)}$—C$_{(15A)}$ | 1,511(2) | N$_{(13)}$—C$_{(8)}$—C$_{(7)}$ | 108,0(1) | N$_{(11)}$—C$_{(10)}$—N$_{(9)}$ | 114,6(1) |
| C$_{(1)}$—C$_{(2)}$ | 1,530(3) | N$_{(11)}$—C$_{(10)}$—C$_{(24)}$ | 108,5(1) | N$_{(9)}$—C$_{(10)}$—C$_{(24)}$ | 110,2(1) |
| C$_{(2)}$—C$_{(3)}$ | 1,517(3) | N$_{(11)}$—C$_{(12)}$—N$_{(13)}$ | 108,9(1) | N$_{(11)}$—C$_{(12)}$—C$_{(30)}$ | 112,4(1) |
| C$_{(3)}$—C$_{(4)}$ | 1,516(2) | N$_{(13)}$—C$_{(12)}$—C$_{(30)}$ | 110,9(1) | O$_{(1)}$—C$_{(14)}$—N$_{(13)}$ | 126,1(1) |
| C$_{(4)}$—C$_{(4A)}$ | 1,504(2) | O$_{(1)}$—C$_{(14)}$—C$_{(15)}$ | 126,9(1) | N$_{(13)}$—C$_{(14)}$—C$_{(15)}$ | 106,8(1) |
| C$_{(4A)}$—C$_{(15A)}$ | 1,348(2) | C$_{(17)}$—C$_{(15)}$—C$_{(15A)}$ | 112,2(1) | C$_{(17)}$—C$_{(15)}$—C$_{(14)}$ | 110,4(1) |
| C$_{(6)}$—C$_{(18)}$ | 1,527(2) | C$_{(15A)}$—C$_{(15)}$—C$_{(14)}$ | 104,1(1) | C$_{(17)}$—C$_{(15)}$—C$_{(7)}$ | 113,3(1) |
| C$_{(6)}$—C$_{(7)}$ | 1,553(2) | C$_{(15A)}$—C$_{(15)}$—C$_{(7)}$ | 112,9(1) | C$_{(14)}$—C$_{(15)}$—C$_{(7)}$ | 102,8(1) |
| C$_{(7)}$—C$_{(16)}$ | 1,475(2) | C$_{(4A)}$—C$_{(15A)}$—C$_{(1)}$ | 122,9(2) | C$_{(4A)}$—C$_{(15A)}$—C$_{(15)}$ | 120,2(1) |
| C$_{(7)}$—C$_{(8)}$ | 1,546(2) | C$_{(1)}$—C$_{(15A)}$—C$_{(15)}$ | 116,7(1) | N$_{(16)}$—C$_{(16)}$—C$_{(7)}$ | 177,5(2) |
| C$_{(7)}$—C$_{(15)}$ | 1,569(2) | N$_{(17)}$—C$_{(17)}$—C$_{(15)}$ | 178,7(2) | C$_{(23)}$—C$_{(18)}$—C$_{(19)}$ | 118,7(2) |
| C$_{(10)}$—C$_{(24)}$ | 1,516(2) | C$_{(23)}$—C$_{(18)}$—C$_{(6)}$ | 117,9(1) | C$_{(19)}$—C$_{(18)}$—C$_{(6)}$ | 123,3(2) |
| C$_{(12)}$—C$_{(30)}$ | 1,518(2) | C$_{(18)}$—C$_{(19)}$—C$_{(20)}$ | 120,3(2) | C$_{(21)}$—C$_{(20)}$—C$_{(19)}$ | 120,5(2) |
| C$_{(14)}$—C$_{(15)}$ | 1,557(2) | C$_{(22)}$—C$_{(21)}$—C$_{(20)}$ | 119,8(2) | C$_{(21)}$—C$_{(22)}$—C$_{(23)}$ | 119,9(2) |
| C$_{(15)}$—C$_{(17)}$ | 1,476(2) | C$_{(18)}$—C$_{(23)}$—C$_{(22)}$ | 120,8(2) | C$_{(25)}$—C$_{(24)}$—C$_{(29)}$ | 118,7(2) |
| C$_{(15)}$—C$_{(15A)}$ | 1,529(2) | C$_{(25)}$—C$_{(24)}$—C$_{(10)}$ | 122,4(1) | C$_{(29)}$—C$_{(24)}$—C$_{(10)}$ | 118,9(2) |
| C$_{(18)}$—C$_{(23)}$ | 1,386(2) | C$_{(24)}$—C$_{(25)}$—C$_{(26)}$ | 120,1(2) | C$_{(27)}$—C$_{(26)}$—C$_{(25)}$ | 120,8(1) |
| C$_{(18)}$—C$_{(19)}$ | 1,387(2) | C$_{(26)}$—C$_{(27)}$—C$_{(28)}$ | 119,4(2) | C$_{(27)}$—C$_{(28)}$—C$_{(29)}$ | 120,3(2) |
| C$_{(19)}$—C$_{(20)}$ | 1,389(3) | C$_{(28)}$—C$_{(29)}$—C$_{(24)}$ | 120,7(2) | C$_{(35)}$—C$_{(30)}$—C$_{(31)}$ | 118,8(2) |
| C$_{(20)}$—C$_{(21)}$ | 1,377(3) | C$_{(35)}$—C$_{(30)}$—C$_{(12)}$ | 123,9(1) | C$_{(31)}$—C$_{(30)}$—C$_{(12)}$ | 117,2(2) |
| C$_{(21)}$—C$_{(22)}$ | 1,377(3) | C$_{(32)}$—C$_{(31)}$—C$_{(30)}$ | 120,2(2) | C$_{(31)}$—C$_{(32)}$—C$_{(33)}$ | 120,9(2) |
| C$_{(22)}$—C$_{(23)}$ | 1,392(3) | C$_{(32)}$—C$_{(33)}$—C$_{(34)}$ | 119,2(2) | C$_{(33)}$—C$_{(34)}$—C$_{(35)}$ | 120,2(2) |
| C$_{(24)}$—C$_{(25)}$ | 1,382(2) | C$_{(30)}$—C$_{(35)}$—C$_{(34)}$ | 120,7(2) | | |
| C$_{(24)}$—C$_{(29)}$ | 1,389(2) | | | | |
| C$_{(25)}$—C$_{(26)}$ | 1,391(3) | | | | |
| C$_{(26)}$—C$_{(27)}$ | 1,372(3) | | | | |
| C$_{(27)}$—C$_{(28)}$ | 1,376(3) | | | | |
| C$_{(28)}$—C$_{(29)}$ | 1,385(3) | | | | |
| C$_{(30)}$—C$_{(35)}$ | 1,384(2) | | | | |
| C$_{(30)}$—C$_{(31)}$ | 1,392(2) | | | | |
| C$_{(31)}$—C$_{(32)}$ | 1,376(3) | | | | |
| C$_{(32)}$—C$_{(33)}$ | 1,382(3) | | | | |
| C$_{(33)}$—C$_{(34)}$ | 1,383(3) | | | | |
| C$_{(34)}$—C$_{(35)}$ | 1,385(3) | | | | |

B. The compound (0.33 g: 1 mmole) was dissolved with heating in isopropyl alcohol (5 ml), the solution cooled, the solvent removed in vacuum, the residue triturated with hexane, and the solid was filtered off and dried in vacuum. The yield of compound (XXa) was 0.33 g (100%).

C. Ketone (Ia) (0.45 g: 2 mmole) and diene (II) (0.3 g: 1 mmole) were stirred in isopropyl alcohol (5 ml) until a clear solution was formed. Triethylamine (1 drop) was added and the solution kept in a closed vessel for 8 h. The resulting solid was filtered off, washed with cold isopropyl alcohol, and dried in vacuum. The yield of compound (XXa) was 0.46 g (70%).

**3-Amino-6,7-tetramethylene-1-oxo-4-(2-furyl)-3*a*,4,5,7*a*-tetrahydro-1H-pyrrolo[3,4-c]pyridine-3*a*,7*a*-dicarbonitrile (XXIa) $C_{17}H_{15}N_5O_2$.** A. This method was analogous to method A for compound (XXa) using alcohol (IXa) (0.32 g: 1 mmole).

TABLE 9. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Coefficients of Equivalent Isotropic Displacement ($Å^2 \times 10^3$) for Compound (XXIIIa)

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| $O_{(1)}$ | 1775(1) | 19(1) | 4558(1) | 25(1) |
| $N_{(5)}$ | 1908(1) | 4127(1) | 4180(1) | 22(1) |
| $N_{(9)}$ | -1242(1) | 3198(1) | 5856(1) | 21(1) |
| $N_{(11)}$ | -1519(1) | 1200(1) | 7216(1) | 23(1) |
| $N_{(13)}$ | 364(1) | 1445(1) | 5484(1) | 20(1) |
| $N_{(16)}$ | -1703(2) | 3454(1) | 2887(1) | 35(1) |
| $N_{(17)}$ | 1846(2) | 1820(1) | 1515(1) | 37(1) |
| $C_{(1)}$ | 4313(2) | 1333(2) | 3384(2) | 36(1) |
| $C_{(2)}$ | 5679(2) | 1629(2) | 3380(2) | 43(1) |
| $C_{(3)}$ | 5430(2) | 2118(2) | 4410(2) | 39(1) |
| $C_{(4)}$ | 4373(2) | 3293(2) | 4255(2) | 32(1) |
| $C_{(4A)}$ | 3070(2) | 3215(1) | 3981(1) | 22(1) |
| $C_{(6)}$ | 758(2) | 4378(1) | 3628(1) | 19(1) |
| $C_{(7)}$ | 344(2) | 3174(1) | 3865(1) | 20(1) |
| $C_{(8)}$ | -263(1) | 2640(1) | 5193(1) | 19(1) |
| $C_{(10)}$ | -1782(2) | 2479(1) | 7075(1) | 21(1) |
| $C_{(12)}$ | -63(2) | 712(1) | 6704(1) | 22(1) |
| $C_{(14)}$ | 1277(2) | 1044(1) | 4553(1) | 20(1) |
| $C_{(15)}$ | 1627(2) | 2164(1) | 3531(1) | 21(1) |
| $C_{(15A)}$ | 3031(2) | 2303(1) | 3625(1) | 23(1) |
| $C_{(16)}$ | -791(2) | 3341(1) | 3292(1) | 23(1) |
| $C_{(17)}$ | 1749(2) | 1983(1) | 2389(1) | 25(1) |
| $C_{(18)}$ | 1029(2) | 5082(1) | 2332(1) | 23(1) |
| $C_{(19)}$ | 2332(2) | 4916(2) | 1530(2) | 37(1) |
| $C_{(20)}$ | 2506(2) | 5590(2) | 363(2) | 46(1) |
| $C_{(21)}$ | 1390(2) | 6433(2) | -11(2) | 41(1) |
| $C_{(22)}$ | 99(2) | 6623(2) | 780(2) | 40(1) |
| $C_{(23)}$ | -80(2) | 5946(2) | 1949(2) | 30(1) |
| $C_{(24)}$ | -3364(2) | 2922(1) | 7501(1) | 23(1) |
| $C_{(25)}$ | -4226(2) | 3547(2) | 6736(2) | 28(1) |
| $C_{(26)}$ | -5670(2) | 3942(2) | 7173(2) | 35(1) |
| $C_{(27)}$ | -6264(2) | 3709(2) | 8362(2) | 38(1) |
| $C_{(28)}$ | -5419(2) | 3064(2) | 9128(2) | 49(1) |
| $C_{(29)}$ | -3977(2) | 2677(2) | 8703(2) | 42(1) |
| $C_{(30)}$ | 944(2) | 628(1) | 7416(1) | 24(1) |
| $C_{(31)}$ | 856(2) | -226(2) | 8500(2) | 38(1) |
| $C_{(32)}$ | 1737(2) | -351(2) | 9190(2) | 49(1) |
| $C_{(33)}$ | 2729(2) | 357(2) | 8820(2) | 46(1) |
| $C_{(34)}$ | 2829(2) | 1201(2) | 7740(2) | 40(1) |
| $C_{(35)}$ | 1939(2) | 1336(2) | 7045(2) | 31(1) |

The yield of compound (XXIa) was 0.22 g (70%) of mp >210°C (decomp.). Found, %: 63.50; H 4.18; N 21.75. $C_{17}H_{15}N_5O_2$. Calculated, %: C 63.54; H 4.71; N 21.79. IR spectrum: 1570, 1680 ($\nu$C=N, $\nu$C=C, $\nu NH_2$); 1750 ($\nu$C=O); 2250 ($\nu C\equiv N$); 3320, 3360 $cm^{-1}$ ($\nu$N−H). $^{13}C$ NMR spectrum (acetone-$D_6$): $C_{(1)}$ $\delta$ 179.26; $C_{(3)}$ 178.44; $C_{(4)}$ 53.70; $C_{(6)}$ 96.14; $C_{(7)}$ 139.87; $C_{(3a)}$, $C_{(7a)}$ 53.56; 55.30; $C_{(CN)}$ 115.00; 116.59; $C_{(CH_2)}$ 22.71; 23.53; 24.98; 28.38; $C_{(C_4H_3O)}$ 111.54; 110.40; 143.97 ppm.

B. Similarly to compound (XXa) (by method C) using amide (XVIIIa) (0.32 g: 1 mmole). The yield of compound (XXIa) was 0.29 g (91%).

**3-Amino-4-(p-methoxyphenyl)-6,7-tetramethylene-1-oxo-3*a*,4,5,7*a*-tetrahydro-1H-pyrrolo[3,4-c]pyridine-3*a*,7*a*-dicarbonitrile (XXIIa), $C_{20}H_{19}N_5O_2$** was obtained analogously to compound (XXa) (by method B) using amide (XIXa) (0.36 g: 1 mmole). The yield of compound (XXIIa) was 0.34 g (95%) of mp 161-163°C (decomp.). Found, %: C 66.45; H 5.29; N 19.32. $C_{20}H_{19}N_5O_2$. Calculated, %: C 66.47; H 5.30; N 19.38. IR spectrum: 1560, 1670 ($\nu$C=N, $\nu$C=C, $\nu NH_2$); 1730 ($\nu$C=O); 2240 ($\nu C\equiv N$); 3280, 3340 $cm^{-1}$ ($\nu$N−H).

**3-Amino-6-methyl-7-propyl-1-oxo-3*a*,4,5,7*a*-tetrahydro-1H-pyrrolo[3,4-c]pyridine-3*a*,7*a*-dicarbonitrile (XXe) $C_{19}H_{19}N_5O$.** Ketone (Ie) (0.45 g: 2 mmole) and diene (II) (0.3 g: 1 mmole) were dissolved in acetonitrile (5 ml) at room

TABLE 10. IR Spectra (cm$^{-1}$) of the Synthesized Compounds

| Compound | $\nu_{C=C}$, $\nu_{C=N}$ | $\nu_{C=O}$ | $\nu_{C\equiv N}$ | $\nu_{N-H}$ |
|---|---|---|---|---|
| XIa | 1640 | — | 2250 | 3345 |
| XIб | 1660 | — | 2260 | 3400 |
| XIв | 1645 | — | 2265 | 3410 |
| XIг | 1650 | — | 2250 | 3400 |
| XIд | 1635 | — | 2270 | 3380 |
| XIe | 1630 | — | 2270 | 3375 |
| XIIa | 1655 | — | 2260 | 3380 |
| XIIIa | 1595, 1640 | — | 2270 | 3370 |
| XIIIб | 1600, 1660 | — | 2260 | 3400 |
| XIIIв | 1600, 1650 | — | 2260 | 3415 |
| XIIIг | 1600, 1670 | — | 2265 | 3400 |
| XIVa | 1590, 1645 | — | 2270 | 3365 |
| XVa | 1660 | — | 2270 | 3370 |
| XVIa | 1640 | — | 2265 | 3370 |
| XXIIIa | 1658 | 1730 | 2260 | 3320 |
| XXIIIб | 1670 | 1750 | 2250 | 3320 |
| XXIIIв | 1660 | 1740 | 2260 | 3330 |
| XXIIIг | 1670 | 1740 | 2260 | 3320, 3340 |
| XXIIIд | 1660 | 1735 | 2260 | 3305 |
| XXIVa | 1655 | 1730 | 2260 | 3280 |
| XXIVб | 1645 | 1745 | 2270 | 3305, 3285 |
| XXVa | 1660 | 1735 | 2260 | 3305 |

temperature, triethylamine (a drop) was added, and the mixture set aside for a day. The reaction mixture was diluted with isopropyl alcohol, and dried in vacuum to constant weight. A white powder (0.39 g: 61%) of mp 150-152°C (decomp.) was obtained. Found, %: C 68.51; H 5.78; N 20.96. $C_{19}H_{19}N_5O$. Calculated, %: C 68.45; H 5.74; N 21.01. IR spectrum: 1560, 1660 ($\nu$C=N, $\nu$C=C, $\nu NH_2$); 1725 ($\nu$C=O); 2250 ($\nu C\equiv N$); 3260, 3360 cm$^{-1}$ ($\nu$N–H).

**2-Aryl-1,2,3,4-tetrahydropyridine-3,3,4,4-tetracarbonitriles (XIa-f), (XIIIa-d), (XIVa), (XVa), (XVIa). General Procedure.** The appropriate diene (II)-(VII) (5 mmole) was added to a suspension of ketone (Ia-f) (10 mmole) in glacial acetic acid (5 ml). The reactants dissolved completely on stirring for 5-10 min and the resulting viscous solution crystallized shortly afterwards. The solid was filtered off, and washed with a cold mixture of isopropyl alcohol and hexane (1:1). Recrystallization was from isopropyl alcohol. The constants and data of elemental analysis are given in Table 1 and the IR spectral data in Table 10.

**5,6-Tetramethylene-2-furyl-1,2,3,4-tetrahydropyridine-3,3,4,4-tetracarbonitrile(XIIa) $C_{17}H_{13}N_5O$.** Alcohol (IXa) (3.21 g: 10 mmole) was dissolved in glacial acetic acid (5 ml) by heating to 50°C. The solution was cooled, and water (5 ml) added. The resulting precipitate was filtered off, washed with isopropyl alcohol, and then recrystallized from 1,4-dioxan. Compound (IXa) (2.15 g: 71%) was obtained.

**5,6-Tetramethylene-2-phenyl-1,2,3,4-tetrahydropyridine-3,3,4,4-tetracarbonitrile (XIa) $C_{19}H_{15}N_5$** was obtained analogously in 96% yield using alcohol (VIIIa). $^{13}$C NMR spectrum of compound (XIa) (acetone-$D_6$): $C_{(2)}$ 60.30; $C_{(3)}$, $C_{(4)}$ 47.10; 46.27; $C_{(5)}$ 144.81; $C_{(6)}$ 87.16; $C_{(C_6H_5)}$ 129.27; 130.00; 131.84, 133.61; $C_{(CN)}$ 112.50; 111.76 (double); 110.44; $C_{(CH_2)}$ 22.33; 23.41; 26.06; 28.27 ppm.

**X-Ray Structural Investigation of Compound (XIa).** Clear colorless crystals were obtained from methanol and were triclinic. At 173 K $a$ = 7.363(1), b = 7.671(2), c = 15.865(3) Å, $\alpha$ = 81.46(1)°, $\beta$ = 87.23(1)°, $\gamma$ = 64.66(1)°, V = 800.8(3) Å$^3$, d = 1.300 g/cm$^3$, space group $P_1$, Z = 2, F(000) = 328. Reflections measured were 4256, $\theta_{max}$ = 29.06°. Final divergence factors were $R_1$ = 0.0335 for 3876 independent reflections with $I > 2\sigma$ (I) and $wR_2$ = 0.1067 at each of 3940 independent reflections.

**9-Oxo-1,3,5-triphenyl-1,2,3,4b,5,6,8*a*,9-octahydropyrido[3′,4′:3,4]pyrrolo[1,2-*a*][1,3,5]triazine-4b,8*a*-dicarbonitrile (XXIIIa) $C_{33}H_{28}N_6O$.** A. Ketone (Ia) (0.23 g: 1 mmole) and diene (II) (0.3 g: 1 mmole) were dissolved in isopropyl alcohol (5 ml) with stirring until a clear solution was formed. A copious precipitate formed straight away in the reaction mixture and was dissolved by heating to boiling. After 2 h the precipitate was filtered off, washed, and dried to constant weight in vacuum. Compound (XXIIIa) (0.45 g: 86%) was obtained.

B. Compound (XXa) (0.33 g: 1 mmole) and diene (II) (0.3 g: 1 mmole) were dissolved by heating in isopropyl alcohol (5 ml). Crystallization began even in the hot solution. The reaction mixture was cooled, the solid filtered off, washed with isopropyl alcohol, and dried in vacuum. The yield of compound (XXIIIa) was 0.53 g (98%).

C. Alcohol (VIIIa) (0.33 g: 1 mmole) and diene (II) (0.3 g) were dissolved by heating in isopropyl alcohol (5 ml). The reaction mixture was then cooled, the solid filtered off, washed with isopropyl alcohol, and dried in vacuum. The yield of compound (XXIIIa) was 0.47 g (90%).

D. Compound (XXIIIa) was obtained similarly using amide (XVIIa). The yield was 99%. The constants and data of elemental analysis are given in Table 1, and the IR spectra in Table 10.

**1,3,5-Triaryl-9-oxo-1,2,3,4b,5,6,8*a*,9-octahydropyrido[3′,4′:3,4]pyrrolo[1,2-*a*][1,3,5]triazine-4b,8*a*-dicarbonitriles (XXIIIa-e), (XXIVa, b), (XXVa). General Method.** Ketone (Ia-e) (1 mmole) and the appropriate diene (II)-(VII) (1 mmole) were mixed in acetonitrile (3 ml). The reagents dissolved after 2-3 min and the reaction mixture was set aside for 1 day. The solid was filtered off, washed with isopropyl alcohol, and dried in vacuum to constant weight. Yield, constants, and data of elemental analysis are given in Table 1 and IR spectra in Table 10. $^{13}$C NMR spectrum of compound (XXIIIb) (acetone-$D_6$): $C_{(1)}$, $C_{(3)}$ $\delta$ 67.80; 67.09; $C_{(4a)}$ 148.28; $C_{(4b)}$, $C_{(8a)}$ 52.33; 53.53; $C_{(5)}$ 60.10; $C_{(7)}$ 87.70; $C_{(8)}$ 141.98; $C_{(9)}$ 165.63; $C_{(CN)}$ 116.40; 115.33; $C_{(CH_3)}$ 14.63; 17.34 ppm.

$^{13}$C NMR spectrum of compound (XXIVb) (acetone-$D_6$): $C_{(1)}$, $C_{(3)}$ $\delta$ 64.14; 64.06; 63.99; 62.40; 62.34; 62.27; $C_{(4a)}$ 153.61; $C_{(4b)}$, $C_{(8a)}$ 50.27; 52.99; $C_{(5)}$ 52.02; $C_{(7)}$ 89.18; $C_{(8)}$ 140.16; $C_{(9)}$ 164.29; $C_{(CN)}$ 115.32; 115.27; $C_{(CH_3)}$ 14.99; 18.01 ppm.

**X-Ray Structural Investigation of Compound (XXIIIa).** Crystals of compound (XXIIIa) were selected from the reaction mixture on carrying out the reaction in acetonitrile. The colorless crystals were triclinic, at 173 K $a$ = 10.155(4), b = 12.217(5), c = 12.481(5) Å, $\alpha$ = 70.02(1)°, $\beta$ = 71.23(1)°, $\gamma$ = 73.09(1)°, V = 1349.1(9) Å$^3$, d = 1.291 g/cm$^3$, space group $P_1$, Z = 2, F(000) = 552. Reflections measured were 5554, $\theta_{max}$ = 29.06°. Final divergence factors were $R_1$ = 0.0423 for 5166 independent reflections with I > 2$\sigma$ (I) and $wR_2$ = 0.1059 at each of 5215 independent reflections.

## REFERENCES

1. O. E. Nasakin, A. N. Lyshchikov, P. M. Lukin, and A. Kh. Bulai, Khim. Geterotsikl. Soedin., No. 3, 353 (1994).
2. A. Galffe, Chem. Ind., **93**, No. 3, 259 (1965).