7,7-Dimethyl-2,4-diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline Oxime (Vf, $C_{23}H_{22}N_2O$). A mixture of 4 g (10 mmole) of the hexahydroquinoline (IIIf) and 0.91 g (13 mmole) of hydroxylamine hydrochloride in 40 ml of absolute ethanol was boiled for 10 h. The mixture was then cooled, poured into 100 ml of 2% aqueous sodium hydroxide, and the solid which separated was filtered off, washed with water, dried, and recrystallized from ethanol. Yield 4.1 g (95%).

Oximes (Va-c, e, g, h) were obtained similarly, and identified by mixed melting points with samples obtained as described in [6].

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DIAZOCARBONYL DERIVATIVES OF HETEROCYCLES.

7.* SYNTHESIS, PROPERTIES, AND STRUCTURE OF 2,4-DIAZIDO-6-DIAZOACETYLPYRIMIDINE

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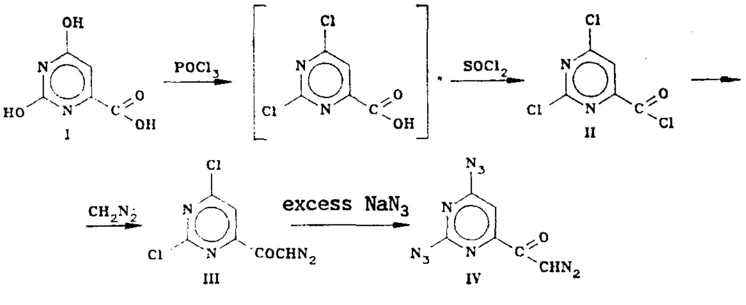
The reaction of 2,4-dichloro-6-diazoacetylpyrimidine with sodium azide to give 2,4-diazido-6-diazoacetylpyrimidine has been examined, and the crystal structure of the latter, and its 1,3-dipolar cycloadditions at the carbonyl group, studied.

In order to obtain novel heterocyclic derivatives of diazoketones, and to study their reactions in which the diazo-group is conserved, we have now synthesized 2,4-dichloro-6-diazoacetylpyrimidine, and examined its reaction with sodium azide.

We have previously reported the nucleophilic replacement of chlorine in some aliphatic diketones [2]. Reactions resulting in the replacement of chlorine by the azide function in chloropyrimidines are well known [3]. This reaction has been carried out for the first time with a diazocarbonyl derivative of dichloropyrimidine.



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*For Communication 6, see [1].

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TABLE 1. Properties of Pyrimidines (II)-(IV)

Compound	M*	mp, °C	R_f**	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max} (log ε)	PMR spectrum, δ, ppm		Yield, %
						5-H	CHN$_2$	
II	210	28...30	0,90	1740 (C=O)	208 (4,29), 268 (3,76)	7,80	—	40
III	217	145	0,55	2130 (N=N)	206 (4,26), 218 (4,12), 284 (3,82), 322 (3,95)	7,93	6,66	70
IV	230	98...100	0,65	2225, 2250 (N$_3$); 2140; 2120 (N=N); 1635 (C=O); 1590	211 (4,17), 242 (4,32), 254 (4,33), 334 (4,23)	7,16	6,60	80

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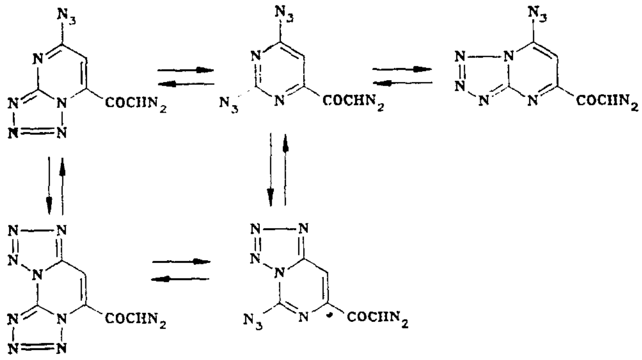
*Found by mass spectrometry.

**In the system benzene—ethyl acetate (7:1).

The acid chloride (II) was obtained by successive treatment of orotic acid with an excess of POCl$_3$ and SOCl$_2$. Reaction of (II) with ethereal diazomethane at −15°C gave the 2,4-dichloro-6-diazoacetylpyrimidine (III). Nucleophilic replacement of the chlorines in (III) was extremely facile (room temperature, aqueous acetone), giving the replacement product (IV) after two hours. The properties of the compounds obtained are shown in Table 1. It will be seen from this Table that (IV) is the nucleophilic replacement product of the two chlorines in the diazoketone (III) by azido-groups. The presence of strong absorption in the IR spectrum of (IV) at 2120-2140 cm^{-1} shows that the diazoacetyl grouping has been retained, and that at 2225 and 2250 cm^{-1} shows the presence of azide groups. However, in examining the structure of the diazoketone (IV), the possibility must be borne in mind of azide-tetrazole tautomerism, which is well known in aziodpyridines [4], azidopyrazines [5], azidopyrimidines [6], and other azines. In some cases, it has been possible to isolate the mutually interconvertible forms [7].

Possible tautomeric reactions of 2,4-diazido-6-diazoacetylpyrimidine (IV) are shown below:



The structure of (IV) in the crystal was established unambiguously by x-ray diffraction examination (see Experimental).

The structure of the molecule is shown in Fig. 1. The X-ray structural studies showed that in the crystal (IV) exists in the diazide form. The pyrimidine heterocycle is planar to within 0.01 Å, and the azide groups lie in this plane, the departure of the nitrogen atoms from the plane being no greater than 0.05 Å. The planar diazocarbonyl group forms an angle of 14° with the plane of the heterocycle. The bond lengths and valence angles in the diazocarbonyl fragment (r $C_{(13)}$–$C_{(1)}$ = 1.222 Å, r $C_{(12)}$–$C_{(13)}$ = 1.427 Å, r $C_{(12)}$–$N_{(3)}$ = 1.320 Å, angle $C_{(12)}N_{(3)}N_{(2)}$ = 177.8°) are closely similar to those in other diazocarbonyl compounds which have been structurally studied [8-10], showing the conservative nature of its structure, which is independent of the substituent at $C_{(13)}$. Taken together with the $C_{(13)}$–$C_{(14)}$ bond length of 1.490 Å, which is significantly greater than that for sp^2-hybridized carbons, these findings show that the π-system of the diazocarbonyl moiety is not prone

TABLE 2. Atom Coordinates (×10^4) for (IV)*

Atom	x	y	z	Atom	x	y	z
$O_{(1)}$	1163(2)	556(2)	493(5)	$N_{(11)}$	−2524(3)	1621(3)	−9619(8)
$N_{(2)}$	3420(3)	595(3)	1793(9)	$C_{(12)}$	2303(2)	1374(3)	−1484(8)
$N_{(3)}$	2917(2)	965(2)	290(7)	$C_{(13)}$	1384(2)	1101(2)	−1244(7)
$N_{(4)}$	899(2)	2238(2)	−4884(6)	$C_{(14)}$	683(2)	1508(2)	−3293(7)
$N_{(5)}$	−568(2)	2225(2)	−7176(6)	$C_{(15)}$	253(2)	2552(2)	−6657(7)
$N_{(6)}$	480(2)	3338(2)	−8274(7)	$C_{(16)}$	−739(2)	1499(2)	−5537(7)
$N_{(7)}$	−134(2)	3661(2)	−9916(7)	$C_{(17)}$	−151(2)	1120(2)	−3519(7)
$N_{(8)}$	−618(3)	4013(3)	−11494(8)	$H_{(18)}$	2560	1780	−3100
$N_{(9)}$	−1574(2)	1085(2)	−5914(6)	$H_{(19)}$	−330	580	−2330
$N_{(10)}$	−2045(2)	1410(2)	−7901(7)				

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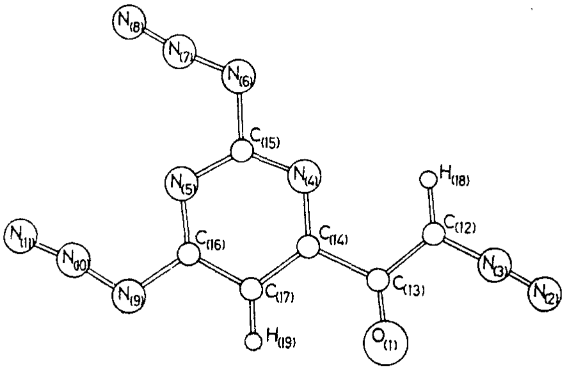
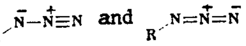
*The anisotropic thermal vibration coefficients may be obtained from the authors.



Molecular structure of (IV)

to π–π conjugation with its closest neighbors. The orientation of the diazomethine grouping relative to the pyrimidine ring is probably stabilized by the intramolecular $N_{(4)}\cdots H_{(18)}$ contact of 2.53 Å. Both azide groups are trans- to the diazomethine fragment.

Of the two possible canonical forms for organic azides:



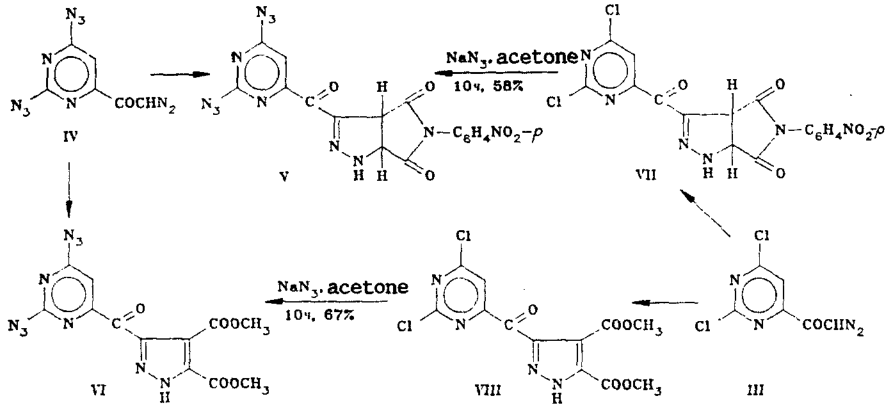
$$R-\overset{-}{N}-\overset{+}{N}\equiv N \quad \text{and} \quad R-N=\overset{+}{N}=\overset{-}{N}$$

the contribution of the first is greater in the present case. This is shown by the bond lengths: $N_{(6)}-N_{(7)}$ 1.241; $N_{(9)}-N_{(10)}$ 1.254 Å, and $N_{(7)}-N_{(8)}$ 1.117; $N_{(10)}-N_{(11)}$ 1.118 Å. The identity of the geometrical parameters in the two independent azide groups is evidence of the clear reflection of the electronic structure of the molecule in its bond lengths and valence angles. Interaction of the lone pair at $N_{(5)}$ with the positively charged central nitrogen atoms could be the reason for the significant departure of the latter from linearity. Angles $N_{(6)}N_{(7)}N_{(8)}$ and $N_{(9)}N_{(10)}N_{(11)}$ are 172.5 and 172.3° respectively.

There are three dipole fragments in (IV) (the two azide groups, and one diazomethine group) which are able to interact with activated dipolarophiles to give triazole or pyrazole systems respectively. Azidopyrimidines are known to react with dimethyl acetylenedicarboxylate (DMAD) [3] and other dipolarophiles [11] to give triazoles.

Our studies of the reactions of (IV) with DMAD and with N-(p-nitrophenyl)maleimide have shown that the azide groups in the 2- and 4-positions of the pyrimidine ring are unable to compete in reactivity with the diazomethine fragment. Using a reactant ratio of 1:1, under a range of conditions (from room temperature to 80°C), only the products of the dipolar addition at the CHN_2 group were obtained (compounds (V) and (VI)).

Structures (V) and (VI) are supported by their IR spectra, viz., the absence of N≡N absorption at ~2100 cm^{-1}, the presence of strong absorption at 2220-2260 cm^{-1} (N_3), and a broad band at 3280-3300 cm^{-1} (NH). In addition, the PMR spectrum does not show a singlet for the $COCHN_2$ proton. The structures of (V) and (VI) were also confirmed by direct synthesis from (VII) and (VIII).



These findings are in accordance with the high 1,3-dipolar reactivity of the diazocarbonyl group in alternative cycloaddition reactions [12, 13].

EXPERIMENTAL

UV spectra were obtained on a Specord UV-Vis in methanol, and IR spectra on a Specord IR-75 in vaseline grease. PMR spectra were recorded on a Bruker WM-250 spectrometer in $CDCl_3$ relative to TMS. Mass spectra were obtained on a Finnigan-4021 with direct sample introduction into the ion source, ionizing electron energy 70 eV, emission current 150 μA.

X-Ray Structural Examination of (IV). The yellow, prismatic crystals of (IV) were monoclinic. Crystallographic data: a = 14.324(5), b = 13.600(5), c = 5.066(4) Å; γ = 81.15(5)°; V = 975.1 Å, M = 230.14, $d_{X\text{-ray}}$ = 1.577 g/cm³, Z = 4, space group $P2_1/n$. The elementary cell parameters were found from the X-ray oscillation diagrams, and refined on a DRON-2 diffractometer. The experimental data consisting of 1198 independent nonzero reflections were obtained on a DAR-UM automatic diffractometer with monochromatized CuK_α-irradiation. Maximum $\sin\theta/\lambda$ = 0.55. Absorption was ignored. The structure was determined by the direct statistical method using the Rentgen-75 programs [14]. The hydrogen atoms were located from the difference synthesis. Refinement was carried out in anisotropic (for the nonhydrogen atoms) full-matrix approximation. The final value of the R factor was 0.055. The atom coordinates are given in Table 2.

2,4-Dichloropyrimidine-6-carbonyl Chloride (II). A mixture of 15.6 g (0.1 mole) of orotic acid with a threefold excess of $POCl_3$ was boiled for 8 h, the $POCl_3$ distilled off, 24 g of $SOCl_2$ added, boiled for 6 h, the thionyl chloride distilled off, and the residue recrystallized from hexane.

2,4-Dichloro-6-diazoacetylpyrimidine (III, $C_6H_2Cl_2N_4O$). A solution of 2.1 g (0.01 mole) of (II) in 30 ml of dry ether was added dropwise over 30 min with stirring at −15°C to a fourfold excess of ethereal diazomethane (200 ml). The solid which separated was filtered off, washed with cold ether, and dried.

2,4-Diazido-6-diazoacetylpyrimidine (IV, $C_6H_2N_{10}O$). To a solution of 1.1 g (~0.005 mole) of (III) in 10 ml of acetone was added dropwise a threefold excess of NaN_3 as the 20% aqueous solution. The mixture was stirred for five hours at room temperature, then the solvents were removed under reduced pressure, and the residue chromatographed in the system benzene—ethyl acetate (7:1) on a column of $L_{100}/_{100}$ silica gel, the fraction with R_f 0.55-0.70 being collected.

Adducts of Cycloaddition to (III) and (IV) (V-VIII). The reactions were carried out by boiling the diazoketones (III) and (IV) with equimolar amounts of N-(p-nitrophenyl)maleimide or dimethyl acetylenedicarboxylate in chloroform for 12 h. The solvent was distilled off, and the residue chromatographed on a column of $L_{40}/_{100}$ silica gel, the fraction with the appropriate R_f value being collected.

(V), $C_{16}H_8N_{12}O_5$. Yield 58%, mp 255-260°C (decomp.), R_f 0.38 (benzene—ethyl acetate, 1:1). UV spectrum, λ_{max} (log ε): 212 (4.21), 248 (3.98, 340 (4.27).

(VI), $C_{12}H_8N_{10}O_5$. Yield 70%, mp 174-176°C (decomp.), R_f 0.23 (benzene—ethyl acetate, 6:1). UV spectrum: 212 (4.43), 263 (4.02).

(VII), $C_{16}H_8CL_2N_6O_5$. Yield 64%, mp 246-248°C, R_f 0.32 (benzene—ethyl acetate), 1:1). UV spectrum: 274 (4.23, 336 (4.06).

(VIII). $C_{12}H_8Cl_2N_4O_5$. Yield 78%, mp 73-75°C. R_f 0.20 (benzene—ethyl acetate, 6:1). UV spectrum: 209 (4.29), 264 (3.76).

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