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STRUCTURE OF THE PRODUCTS OF THE REACTION OF 5,6-DIAMINO-1,3-DIMETHYLURACIL WITH 1,3-DIARYL-2,3-DIHALOPROPANONES

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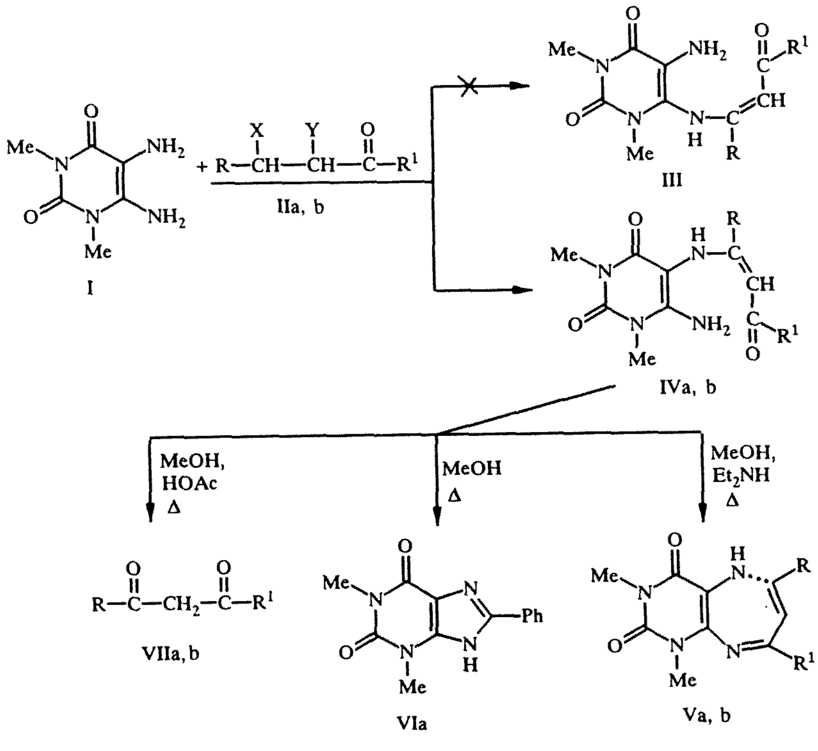
The reaction of 5,6-diamino-1,3-dimethyluracil with α,β-dihalopropanones gives only β-(5-imino-6-amino-1,3-uracil)chalcones. An x-ray diffraction structural analysis was carried out for one of these products.

In previous work [1], we reported that the reaction of 5,6-diamino-1,3-dimethyluracil (I) with 1,3-diaryl-2,3-dihalopropanones may lead to either β-(5-amino-6-imino-1,3-dimethyluracil)chalcones III or β-(5-imino-6-amino-1,3-dimethyluracil)chalcone IV as the major product. Product IVa was also obtained in the reaction of diamine I with dibenzoylmethane [1] and α-bromochalcone [1]. The structure of the products of these reactions was demonstrated only indirectly [1, 2]. Thus, in the present work, we attempted to establish the course of this reaction by x-ray diffraction structural analysis of one of the products isolated in the reaction of dihalochalcone IIb with diamine I.



II, IV—VII a R = R^1 = C_6H_5, b R = p-$NO_2C_6H_4$, R^1 = C_6H_5;
IIa X = Cl, Y = Br, b X = Y = Br

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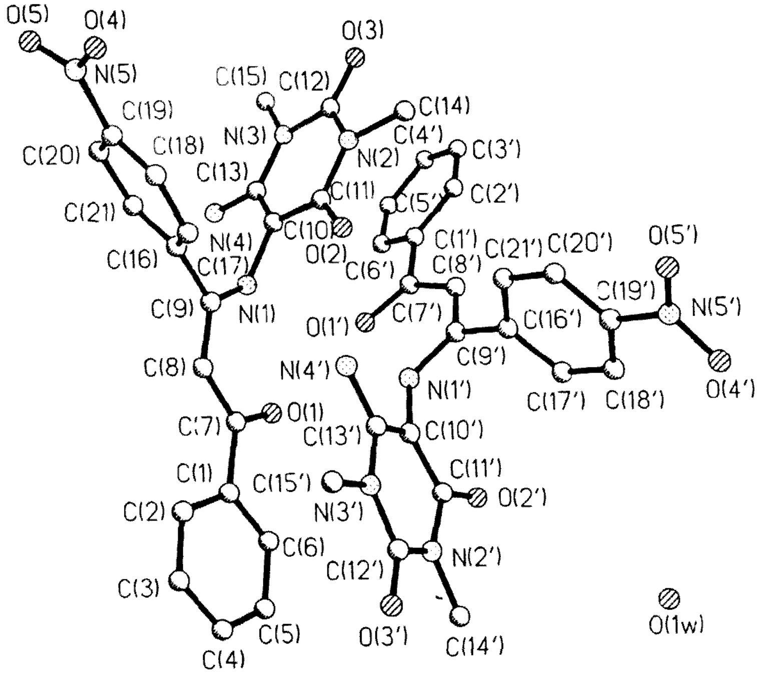

Fig. 1. General view of symmetrically independent molecules of IVb with numbering of the atoms.

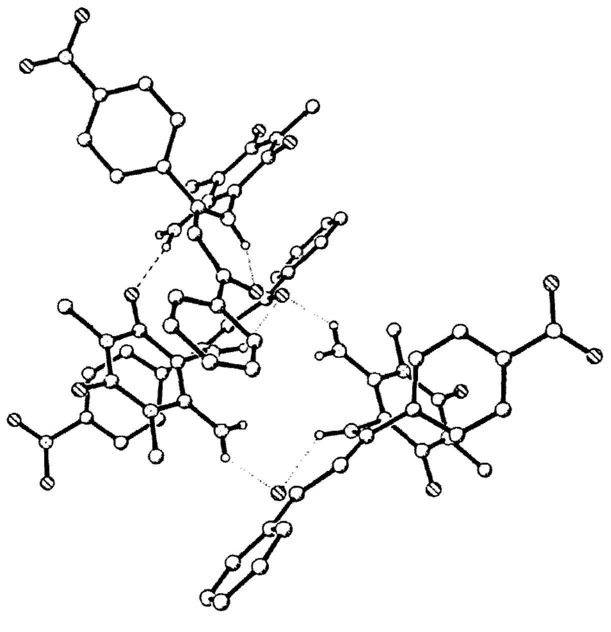

Fig. 2. Hydrogen bond system in crystalline IVb.

β-Aminochalcones IVa and IVb were obtained according to our previous procedure [1]. A careful study of the conversion of these compounds into pyrimido[4,5-*b*]-1,5-diazepins Va and Vb showed that prolonged heating of IVa in methanol with a catalytic amount of triethylamine leads to 8-phenyltheophylline IVa due to the greater thermodynamic stability of the five-membered ring. The yield of cyclization product Va under these conditions does not exceed 10%. A significant increase

TABLE 1. Bond Lengths (Å) in IVb

Bond	*l*	Bond	*l*
$N_{(1)}-C_{(9)}$	1,363(6)	$N_{(1)}-C_{(10)}$	1,428(6)
$N_{(2)}-C_{(11)}$	1,415(6)	$N_{(2)}-C_{(12)}$	1,372(6)
$N_{(2)}-C_{(14)}$	-1,47(1)	$N_{(3)}-C_{(12)}$	1,372(8)
$N_{(3)}-C_{(13)}$	1,378(6)	$N_{(3)}-C_{(15)}$	1,484(6)
$N_{(4)}-C_{(13)}$	1,319(8)	$N_{(5)}-O_{(4)}$	1,219(8)
$N_{(5)}-O_{(5)}$	1,220(8)	$N_{(5)}-C_{(19)}$	1,495(7)
$O_{(1)}-C_{(7)}$	1,259(5)	$O_{(2)}-C_{(11)}$	1,234(6)
$O_{(3)}-C_{(12)}$	1,231(7)	$C_{(1)}-C_{(2)}$	1,384(8)
$C_{(1)}-C_{(6)}$	1,383(7)	$C_{(1)}-C_{(7)}$	1,492(6)
$C_{(2)}-C_{(3)}$	1,373(8)	$C_{(3)}-C_{(4)}$	1,382(9)
$C_{(4)}-C_{(5)}$	1,360(9)	$C_{(5)}-C_{(6)}$	1,385(7)
$C_{(7)}-C_{(8)}$	1,418(6)	$C_{(8)}-C_{(9)}$	1,374(6)
$C_{(9)}-C_{(16)}$	1,474(6)	$C_{(10)}-C_{(11)}$	1,383(9)
$C_{(10)}-C_{(13)}$	1,385(6)	$C_{(16)}-C_{(17)}$	1,389(7)
$C_{(16)}-C_{(21)}$	1,389(8)	$C_{(17)}-C_{(18)}$	1,387(7)
$C_{(18)}-C_{(19)}$	1,359(8)	$C_{(19)}-C_{(20)}$	1,377(8)
$C_{(20)}-C_{(21)}$	1,382(7)	$N_{(1')}-C_{(9')}$	1,338(8)
$N_{(1')}-C_{(10')}$	1,441(5)	$N_{(2')}-C_{(11')}$	1,416(6)
$N_{(2')}-C_{(12')}$	1,350(6)	$N_{(2')}-C_{(14')}$	1,449(6)
$N_{(3')}-C_{(12')}$	1,379(6)	$N_{(3')}-C_{(13')}$	1,382(5)
$N_{(3')}-C_{(15')}$	1,476(6)	$N_{(4')}-C_{(13')}$	1,345(6)
$N_{(5')}-O_{(4')}$	1,25(1)	$N_{(5')}-O_{(5')}$	1,17(1)
$N_{(5')}-C_{(19')}$	1,48(1)	$O_{(1')}-C_{(7')}$	1,259(8)
$O_{(2')}-C_{(11')}$	1,223(7)	$O_{(3')}-C_{(12')}$	1,235(6)
$C_{(1')}-C_{(2')}$	1,367(9)	$C_{(1')}-C_{(6')}$	1,374(9)
$C_{(1')}-C_{(7')}$	1,516(6)	$C_{(2')}-C_{(3')}$	1,395(6)
$C_{(3')}-C_{(4')}$	1,36(1)	$C_{(4')}-C_{(5')}$	1,35(1)
$C_{(5')}-C_{(6')}$	1,392(7)	$C_{(7')}-C_{(8')}$	1,415(9)
$C_{(8')}-C_{(9')}$	1,382(6)	$C_{(9')}-C_{(16')}$	1,492(9)
$C_{(10')}-C_{(11')}$	1,409(7)	$C_{(10')}-C_{(13')}$	1,346(6)
$C_{(16')}-C_{(17')}$	1,38(1)	$C_{(16')}-C_{(21')}$	1,371(7)
$C_{(17')}-C_{(18')}$	1,37(1)	$C_{(18')}-C_{(19')}$	1,34(1)
$C_{(19')}-C_{(20')}$	1,35(1)	$C_{(20')}-C_{(21')}$	1,38(1)

in the yield of Va was observed upon heating enamine IVa in 2:1 methanol–diethylamine. Under analogous conditions, chalcone IVb is cyclized to diazepin Vb in good yield. Attempts to cyclize enamines IVa and IVb in a weakly acidic medium (acetic acid in methanol) led exclusively to β-diketones VIIa and VIIb. Diazepin Va does not differ in its indices from a sample obtained in our previous work [1] in the reaction of I with 1,3-diphenyl-2,3-dibromopropanone. Thus, independently of the electronic nature of substituent R and the halogen in the starting α,β-dihalochalcones, the β-enaminoketones isolated, IVa and IVb, belong to the same series. This question was solved unequivocally by an x-ray diffraction structural analysis of IVb (Fig. 1, Tables 1 and 2).

The unit cell of the crystal consists of two symmetrically independent molecules of IVb (A and B) and one water molecule. The bond lengths and bond angles of molecules A and B hardly differ. The $C{=}C-C{=}C$ fragment has *s-cis* configuration: $C_{(1)}$, $C_{(7)}$, $O_{(1)}$, $C_{(8)}$, $C_{(9)}$, and $N_{(1)}$ lie within a single plane to $\pm 3\sigma$. The bond lengths in this fragment are significantly equalized, indicating strong delocalization of the π-conjugated system. $N_{(1)}$ and $N_{(4)}$ have plane trigonal coordination.

Molecules A and B differ in the conformation of the substituents at $C_{(9)}$. The nitrophenyl fragment is twisted relative to the plane of the $C_{(8)}{=}C_{(9)}$ double bond by 58.9(9)° in A and −103.1(6)° in B. The conjugation between the uracil ring and C=C double bond is also significantly violated but differently in the two molecules. Twisting is found in molecule A about the $N_{(1)}-C_{(9)}$ (the $C_{(8)}-C_{(9)}-N_{(1)}-C_{(10)}$ torsion angle is −156.5(8)°) and $N_{(1)}-C_{(10)}$ bonds (the $C_{(9)}-N_{(1)}-C_{(10)}-C_{(11)}$ torsion angle is 63.6(7)°). The breakdown in conjugation in molecule B occurs only due to twisting about the $N_{(1')}-C_{(10')}$ bond (the corresponding torsion angles are 174.5(5) and −88.8(7)°) Such a conformation for the substituents at $C_{(9)}$ is largely a consequence of short intramolecular contacts: $O_{(1)}\cdots N_{(1)}$, 2.69(1) Å in A and 2.71(1) Å in B (the sum of the van der Waals radii is 2.76 Å [3]), $C_{(21)}\cdots C_{(10)}$, 3.16(1) Å in A (the sum of the van der Waals radii is 3.42 Å), and $C_{(11)}\cdots C_{(16)}$, 3.26(1) Å in B. The phenyl substituent at $C_{(7)}$ is somewhat extruded from the plane of the carbonyl group. The $C_{(6)}-C_{(1)}-C_{(7)}-O_{(1)}$

TABLE 2. Bond Angles in the Structure of IVb

Bond angle	ω	Bond angle	ω
$C_{(9)}$—$N_{(1)}$—$C_{(10)}$	121,8(3)	$C_{(11)}$—$N_{(2)}$—$C_{(12)}$	124,3(5)
$C_{(11)}$—$N_{(2)}$—$C_{(14)}$	119,4(4)	$C_{(12)}$—$N_{(2)}$—$C_{(14)}$	116,3(5)
$C_{(12)}$—$N_{(3)}$—$C_{(13)}$	123,0(4)	$C_{(12)}$—$N_{(3)}$—$C_{(15)}$	116,8(4)
$C_{(13)}$—$N_{(3)}$—$C_{(15)}$	120,2(5)	$O_{(4)}$—$N_{(5)}$—$O_{(5)}$	125,5(5)
$O_{(4)}$—$N_{(5)}$—$C_{(19)}$	116,2(5)	$O_{(5)}$—$N_{(5)}$—$C_{(19)}$	118,3(5)
$C_{(2)}$—$C_{(1)}$—$C_{(6)}$	118,9(4)	$C_{(2)}$—$C_{(1)}$—$C_{(7)}$	122,3(4)
$C_{(6)}$—$C_{(1)}$—$C_{(7)}$	118,8(4)	$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	120,3(6)
$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	120,6(6)	$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	119,2(5)
$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	120,9(6)	$C_{(1)}$—$C_{(6)}$—$C_{(5)}$	120,0(5)
$O_{(1)}$—$C_{(7)}$—$C_{(1)}$	117,5(4)	$O_{(1)}$—$C_{(7)}$—$C_{(8)}$	122,0(4)
$C_{(1)}$—$C_{(7)}$—$C_{(8)}$	120,5(4)	$C_{(7)}$—$C_{(8)}$—$C_{(9)}$	124,5(4)
$N_{(1)}$—$C_{(9)}$—$C_{(8)}$	122,7(4)	$N_{(1)}$—$C_{(9)}$—$C_{(16)}$	116,6(4)
$C_{(8)}$—$C_{(9)}$—$C_{(16)}$	120,7(4)	$N_{(1)}$—$C_{(10)}$—$C_{(11)}$	119,8(4)
$N_{(1)}$—$C_{(10)}$—$C_{(13)}$	117,5(5)	$C_{(11)}$—$C_{(10)}$—$C_{(13)}$	122,4(5)
$N_{(2)}$—$C_{(11)}$—$O_{(2)}$	118,5(5)	$N_{(2)}$—$C_{(11)}$—$C_{(10)}$	115,4(4)
$O_{(2)}$—$C_{(11)}$—$C_{(10)}$	126,0(5)	$N_{(2)}$—$C_{(12)}$—$N_{(3)}$	116,5(5)
$N_{(2)}$—$C_{(12)}$—$O_{(3)}$	121,8(6)	$N_{(3)}$—$C_{(12)}$—$O_{(3)}$	121,7(4)
$N_{(3)}$—$C_{(13)}$—$N_{(4)}$	118,7(4)	$N_{(3)}$—$C_{(13)}$—$C_{(10)}$	118,3(5)
$N_{(4)}$—$C_{(13)}$—$C_{(10)}$	123,0(5)	$C_{(9)}$—$C_{(16)}$—$C_{(17)}$	120,7(5)
$C_{(9)}$—$C_{(16)}$—$C_{(21)}$	120,4(4)	$C_{(17)}$—$C_{(16)}$—$C_{(21)}$	118,9(4)
$C_{(16)}$—$C_{(17)}$—$C_{(18)}$	120,6(5)	$C_{(17)}$—$C_{(18)}$—$C_{(19)}$	118,1(5)
$N_{(5)}$—$C_{(19)}$—$C_{(18)}$	119,0(5)	$N_{(5)}$—$C_{(19)}$—$C_{(20)}$	117,3(5)
$C_{(18)}$—$C_{(19)}$—$C_{(20)}$	123,7(5)	$C_{(19)}$—$C_{(20)}$—$C_{(21)}$	117,3(5)
$C_{(16)}$—$C_{(21)}$—$C_{(20)}$	121,3(5)	$C_{(9')}$—$N_{(1')}$—$C_{(10')}$	124,9(5)
$C_{(11')}$—$N_{(2')}$—$C_{(12')}$	124,3(4)	$C_{(11')}$—$N_{(2')}$—$C_{(14')}$	118,5(4)
$C_{(12')}$—$N_{(2')}$—$C_{(14')}$	117,2(4)	$C_{(12')}$—$N_{(3')}$—$C_{(13')}$	122,5(4)
$C_{(12')}$—$N_{(3')}$—$C_{(15')}$	116,9(4)	$C_{(13')}$—$N_{(3')}$—$C_{(15')}$	120,6(4)
$O_{(4')}$—$N_{(5')}$—$O_{(5')}$	124,8(10)	$O_{(4')}$—$N_{(5')}$—$C_{(19')}$	113,6(7)
$O_{(5')}$—$N_{(5')}$—$C_{(19')}$	121,5(8)	$C_{(2')}$—$C_{(1')}$—$C_{(6')}$	118,7(4)
$C_{(2')}$—$C_{(1')}$—$C_{(7')}$	122,3(5)	$C_{(6')}$—$C_{(1')}$—$C_{(7')}$	119,0(5)
$C_{(1')}$—$C_{(2')}$—$C_{(3')}$	120,5(6)	$C_{(2')}$—$C_{(3')}$—$C_{(4')}$	119,9(6)
$C_{(3')}$—$C_{(4')}$—$C_{(5')}$	120,3(5)	$C_{(4')}$—$C_{(5')}$—$C_{(6')}$	119,9(6)
$C_{(1')}$—$C_{(6')}$—$C_{(5')}$	120,6(6)	$O_{(1')}$—$C_{(7')}$—$C_{(1')}$	117,3(5)
$O_{(1')}$—$C_{(7')}$—$C_{(8')}$	123,4(4)	$C_{(1')}$—$C_{(7')}$—$C_{(8')}$	119,3(6)
$C_{(7')}$—$C_{(8')}$—$C_{(9')}$	123,7(6)	$N_{(1')}$—$C_{(9')}$—$C_{(8')}$	123,5(6)
$N_{(1')}$—$C_{(9')}$—$C_{(16')}$	117,5(4)	$C_{(8')}$—$C_{(9')}$—$C_{(16')}$	119,0(6)
$N_{(1')}$—$C_{(10')}$—$C_{(11')}$	117,7(4)	$N_{(1')}$—$C_{(10')}$—$C_{(13')}$	119,5(4)
$C_{(11')}$—$C_{(10')}$—$C_{(13')}$	122,8(4)	$N_{(2')}$—$C_{(11')}$—$O_{(2')}$	119,9(4)
$N_{(2')}$—$C_{(11')}$—$C_{(10')}$	114,4(4)	$O_{(2')}$—$C_{(11')}$—$C_{(10')}$	125,7(4)
$N_{(2')}$—$C_{(12')}$—$N_{(3')}$	116,9(4)	$N_{(2')}$—$C_{(12')}$—$O_{(3')}$	122,1(4)
$N_{(3')}$—$C_{(12')}$—$O_{(3')}$	121,0(4)	$N_{(3')}$—$C_{(13')}$—$N_{(4')}$	117,2(4)
$N_{(3')}$—$C_{(13')}$—$C_{(10')}$	118,7(4)	$N_{(4')}$—$C_{(13')}$—$C_{(10')}$	124,2(4)
$C_{(9')}$—$C_{(16')}$—$C_{(17')}$	121,9(5)	$C_{(9')}$—$C_{(16')}$—$C_{(21')}$	119,4(6)
$C_{(17')}$—$C_{(16')}$—$C_{(21')}$	118,7(7)	$C_{(16')}$—$C_{(17')}$—$C_{(18')}$	120,5(6)
$C_{(17')}$—$C_{(18')}$—$C_{(19')}$	119,1(7)	$N_{(5')}$—$C_{(19')}$—$C_{(18')}$	121,0(8)
$N_{(5')}$—$C_{(19')}$—$C_{(20')}$	116,2(6)	$C_{(18')}$—$C_{(19')}$—$C_{(20')}$	122,8(8)
$C_{(19')}$—$C_{(20')}$—$C_{(21')}$	118,2(6)	$C_{(16')}$—$C_{(21')}$—$C_{(20')}$	120,7(7)

torsion angle is 8.4(9)° in A and −12.9(7)° in B. The nitro group is virtually coplanar to the plane of the $C_{(16)}\cdots C_{(21)}$ benzene ring. The $O_{(5)}-N_{(5)}-C_{(19)}-C_{(20)}$ torsion angle is 8.9(8)° in A and −2.1(1)° in B.

A complex hydrogen bond system exists in this crystal structure (Fig. 2). Both molecules in IVb display an intramolecular $O_{(1)}\cdots H_{(1A)}$ hydrogen bond. The parameters of this bond are different in A and B: the O···H distance is 2.14(1) Å in and 2.03(1) Å in B; the $O\cdots H-N_{(1)}$ angle is 118(1)° in A and 131(1)° in B. A hydrogen bond is also found between the two independent molecules: $O_{(2)}\cdots H_{(4'B)}$ (O···H, 2.17(1) Å, $O\cdots H-N_{(4')}$, 166(1)°). Furthermore, $O_{(1)}$ in molecule

TABLE 3. Coordinates of the Nonhydrogen Atoms (Å×10^4) in IVb

Atom	*x*	*y*	*z*
1	2	3	4
$N_{(1)}$	1042(4)	4464(3)	3144(3)
$N_{(2)}$	-1067(4)	5924(3)	1790(3)
$N_{(3)}$	-1265(4)	6946(3)	3055(3)
$N_{(4)}$	-101(4)	6343(3)	4099(3)
$N_{(5)}$	3993(4)	6900(4)	-808(4)
$O_{(1)}$	1458(3)	2549(2)	4102(2)
$O_{(2)}$	318(3)	4318(2)	1512(2)
$O_{(3)}$	-2462(4)	7521(3)	2078(3)
$O_{(4)}$	4180(4)	6674(4)	-1670(3)
$O_{(5)}$	4128(5)	7683(3)	-602(4)
$C_{(1)}$	3338(5)	1275(3)	3518(4)
$C_{(2)}$	4557(6)	1008(4)	2925(5)
$C_{(3)}$	5264(6)	-6(5)	2967(6)
$C_{(4)}$	4779(6)	-765(5)	3624(6)
$C_{(5)}$	3595(6)	-494(4)	4241(5)
$C_{(6)}$	2859(5)	515(3)	4180(4)
$C_{(7)}$	2519(5)	2351(3)	3456(3)
$C_{(8)}$	2925(5)	3104(3)	2675(3)
$C_{(9)}$	2212(5)	4088(3)	2517(3)
$C_{(10)}$	190(5)	5280(3)	2795(3)
$C_{(11)}$	-125(5)	5111(3)	2008(3)
$C_{(12)}$	-1647(5)	6835(4)	2297(4)
$C_{(13)}$	-379(5)	6181(3)	3336(3)
$C_{(14)}$	-1522(6)	5784(5)	1019(4)
$C_{(15)}$	-1878(6)	7936(4)	3598(4)
$C_{(16)}$	2700(5)	4801(3)	1656(4)
$C_{(17)}$	3157(5)	4511(4)	647(4)
$C_{(18)}$	3579(5)	5196(4)	-166(4)
$C_{(19)}$	3554(5)	6145(4)	56(4)
$C_{(20)}$	3166(5)	6453(4)	1043(4)
$C_{(21)}$	2713(5)	5773(3)	1841(4)
$N_{(1')}$	-218(4)	2164(3)	3179(3)
$N_{(2')}$	1441(4)	-652(3)	3151(3)
$N_{(3')}$	2584(4)	247(3)	1782(3)
$N_{(4')}$	1889(4)	2041(3)	1424(3)
$N_{(5')}$	-1253(6)	807(6)	-459(6)
$O_{(1')}$	-1270(4)	3770(3)	4446(3)
$O_{(2')}$	-508(4)	192(3)	4087(3)
$O_{(3')}$	3304(4)	-1505(3)	2115(3)
$O_{(4')}$	-1584(6)	-11(5)	-231(6)
$O_{(5')}$	-952(7)	1200(6)	-1291(5)
$C_{(1')}$	-3086(5)	5042(4)	4404(4)
$C_{(2')}$	-3870(5)	5535(4)	3892(4)
$C_{(3')}$	-4819(5)	6422(4)	4273(5)
$C_{(4')}$	-4972(6)	6800(4)	5166(5)
$C_{(5')}$	-4205(6)	6317(4)	5685(5)
$C_{(6')}$	-3240(5)	5448(4)	5292(4)

TABLE 3 (continued)

1	2	3	4
$C_{(7')}$	-2065(5)	4059(4)	4032(4)
$C_{(8')}$	-2063(5)	3501(4)	3270(4)
$C_{(9')}$	-1169(5)	2604(4)	2874(4)
$C_{(10')}$	674(5)	1183(3)	2848(3)
$C_{(11')}$	449(5)	258(4)	3419(4)
$C_{(12')}$	2479(5)	-684(4)	2345(4)
$C_{(13')}$	1687(5)	1183(3)	2029(4)
$C_{(14')}$	1333(6)	-1625(4)	3753(5)
$C_{(15')}$	3704(5)	205(4)	883(4)
$C_{(16')}$	-1219(5)	2123(4)	2021(4)
$C_{(17')}$	-1607(6)	1234(5)	2190(5)
$C_{(18')}$	-1625(7)	803(5)	1388(6)
$C_{(19')}$	-1270(6)	1258(5)	436(6)
$C_{(20')}$	-891(6)	2131(6)	230(5)
$C_{(21')}$	-873(6)	2570(5)	1040(4)
$O_{(1)}$	5997(4)	7696(3)	874(4)

A forms an intermolecular hydrogen bond with $H_{(4B)}$ of the molecule related to the base molecule by symmetry transformations $1 - x$, $1 - y$, $1 - z$ (O···H, 2.06(1) Å; O···H–N, 140(1)°).

The $C_{(1)}\cdots C_{(6)}$ phenyl ring in molecule A is located almost parallel to the uracil ring of molecule B (Fig. 2) (the angle between them is only 8(1)°). The distance between the centers of these rings (3.54(1) Å) provides the possibility for overlap of their π-electron systems. Such stacking interactions are unlikely for the other pair of such rings, which are arranged analogously, since the distance between their centers is 4.14(1) Å. There is also a short contact in the crystal between $C_{(3')}$ of molecule B and $H_{(4'A)}$ (2.83(1) Å) related to the base molecule by symmetry transformation $1 - x$, $1 + y$, z.

Thus, the product of the reaction of diamine I with dibromide IIb is β-(5-imino-6-amino-1,3-dimethyluracilo)-4-nitrochalcone IVb, which is in good accord with our previous conclusions on the participation of the more nucleophilic amino group of the heterocyclic diamine in the nucleophilic substitution step under base catalysis conditions [4].

EXPERIMENTAL

6,8-Dimethyl-7,9-dioxo-2,4-diphenylpyrimido[4,5-*b*]-1,5-diazepin (Va). A solution containing 0.38 g (1 mmole) enaminoketone IVa in 40 ml 2:1 methanol–diethylamine was heated at reflux for 4 h. After cooling, water was added to the solution until a precipitate appeared. Yellow crystalline diazepin Va was filtered off. The yield of Va was 0.16 g (45%), mp 232-234°C (from methanol), R_f ($CHCl_3$) [1].

Diazepin Vb was obtained analogously in 62% yield, mp 254°C (from methanol).

1-(4-Nitrophenyl)-3-phenyl-1,3-propanedione (VIIb). A sample of 0.42 g (1 mmole) IVb in 20 ml 3:1 methanol–acetic acid was heated at reflux for 0.5 h. Upon cooling, water was added until a precipitate appeared. The yield of diketone VIIb was 0.19 g (70%), mp 156-157°C (156-157°C [5]).

Dibenzoylmethane (VIIa) is formed in 80% yield under these conditions.

X-Ray Diffraction Structural Analysis. The unit cell parameters for triclinic crystals of IVb at 20°C: $a = 12.465(8)$, $b = 13.497(5)$, $c = 14.085(5)$ Å, $\alpha = 79.90(1)°$, $\beta = 67.51(2)°$, $\gamma = 71.16(1)°$, $V = 2068$ Å^3, $d_{calc} = 1.379$ g/cm^3, space group P1, Z = 2. The unit cell parameters and intensities of 2589 reflections with $F > 6\sigma(F)$ were measured on a Siemens P3/PC automatic four-circle diffractometer using αMoK_α radiation, graphite monochromator, and $\theta/2\theta$ scanning; $2\theta_{max} = 60°$.

The structure was solved by the direct method using the SHELXTL PLUS program package [6]. The positions of the hydrogen atoms were found from the electron density difference map and were further refined using the "rider" model with fixed $U_{iso} = 0.08$ Å^2. The least squares refinement by the block diagonal method was carried out to R = 0.070 (R_w = 0.066, S = 2.67). The coordinates of the nonhydrogen atoms are given in Table 3.

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