B. A solution of 2.0 g (10 mmole) of (III) and 1.53 g (10 mmole) of $POCl_3$ in 20 ml of DMF was flushed through with argon, saturated with dry HCl for 20 min, the temperature rising to 115°C. When the reaction was complete, the mixture was poured into 100 ml of ice water, and the crystals which separated were filtered off and dried to give 1.45 g (79%) of product, mp 50°C.

C. A solution of 2.0 g (10 mmole) of (III) and 1.53 g (10 mmole) of $POCl_3$ in 20 ml of dry benzene was heated in a stainless-steel autoclave for 1 h at 190°C. The benzene was removed, and the residue treated with 20 ml of water, extracted with ether (2 × 10 ml), the ether layer dried over $CaCl_2$, and the ether evaporated to give 1 g (76%) of product, mp 50°C.

D. A mixture of 6.48 g (45 mmole) of the nitrile (I), 1.68 g (30 mmole) of acrolein, and 0.3 g (1.5 mmole) of Cu_2Cl_2 in 25 ml of dry benzene was heated in a stainless-steel autoclave for 5 h at 90°C, then 4.6 g (30 mmole) of $POCl_3$ was added and heating continued for 30 min at 180°C. The benzene was removed, and the residue treated with water, extracted with ether (4 × 40 ml), the ether layer dried over $CaCl_2$, and the ether evaporated to give 3.8 g (70%) of product, mp 50°C.

Hydrolysis of (IV) under the Experimental Conditions. A stream of dry HCl was passed through a solution of 1.46 g (8 mmole) of the pyridine (IV) and 0.144 g (8 mmole) of water in 15 ml of DMF for 1 h, maintaining the temperature at 110-115°C. When the reaction was complete, the mixture was poured into ice water, and the solid filtered off to give 1.4 g (96%) of the pyridine (IV), mp 50°C.

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CRYSTAL AND MOLECULAR STRUCTURE OF 7,7-DIMETHYL-2,3-DI(4-METHOXYPHENYL)-5-OXO-5,6,7,8-TETRAHYDROQUINOLINE

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An x-ray crystallographic investigation of 7,7-dimethyl-2,3-di(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydroquinoline, obtained by the hydrolysis of its oxime, was undertaken. The oxime, together with the isomeric oxime of 7,7-dimethyl-2,4-di(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydroquinoline, is formed in the reaction of 5,5-dimethyl-2-[1,3-di(4-methoxyphenyl)-3-oxopropyl]cyclohexane-1,3-dione with hydroxylamine hydrochloride.

2,4-Diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline oxime is formed in the reaction of 2-(1,3-diphenyl-3-oxopropyl)cyclohexane-1,3-dione with hydroxylamine hydrochloride [1]. We found that, in addition to the expected 2,4-diaryl-5-oxohydroquinoline oxime (II), 5,5-dimethyl-2-[1,3-(4-methoxyphenyl)-3-oxopropyl]cyclohexane-1,3-dione (I) under analogous conditions forms a compound to which the structure of the isomeric 2,3-diaryl-5-oxohydroquinoline oxime (III) was assigned on the basis of the data from IR and PMR spectroscopy [2].

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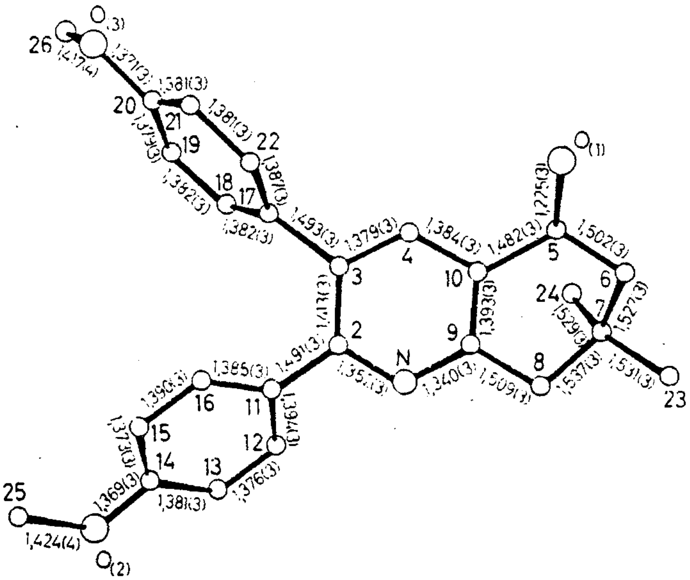


Fig. 1. Molecular structure of compound (IV).

TABLE 1. Bond Angles ω in the Molecule

Angle	ω°	Angle	ω°	Angle	ω°
$C_{(2)}NC_{(9)}$	119,6(2)	$C_{(2)}C_{(11)}C_{(16)}$	123,4(2)	$C_{(23)}C_{(7)}C_{(24)}$	108,7(2)
$NC_{(2)}C_{(3)}$	122,0(2)	$C_{(16)}C_{(11)}C_{(12)}$	117,1(2)	$C_{(7)}C_{(8)}C_{(9)}$	112,4(2)
$NC_{(2)}C_{(11)}$	114,2(2)	$C_{(11)}C_{(12)}C_{(13)}$	121,6(2)	$NC_{(9)}C_{(8)}$	117,7(2)
$C_{(3)}C_{(2)}C_{(11)}$	123.8(2)	$C_{(12)}C_{(13)}C_{(14)}$	120,2(2)	$NC_{(9)}C_{(10)}$	121,9(2)
$C_{(2)}C_{(3)}C_{(4)}$	116.5(2)	$O_{(2)}C_{(14)}C_{(13)}$	115,3(2)	$C_{(10)}C_{(9)}C_{(8)}$	120,4(2)
$C_{(2)}C_{(3)}C_{(17)}$	126,0(2)	$O_{(2)}C_{(14)}C_{(15)}$	125,2(2)	$C_{(3)}C_{(17)}C_{(18)}$	121,4(2)
$C_{(4)}C_{(3)}C_{(17)}$	117,4(2)	$C_{(13)}C_{(14)}C_{(15)}$	119,5(2)	$C_{(3)}C_{(17)}C_{(22)}$	120,4(2)
$C_{(3)}C_{(4)}C_{(10)}$	122.0(2)	$C_{(14)}C_{(15)}C_{(16)}$	120,0(2)	$C_{(22)}C_{(17)}C_{(18)}$	117,8(2)
$C_{(4)}C_{(10)}C_{(5)}$	120,7(2)	$C_{(11)}C_{(16)}C_{(15)}$	121,6(2)	$C_{(17)}C_{(18)}C_{(19)}$	121,9(2)
$C_{(4)}C_{(10)}C_{(9)}$	117,7(2)	$C_{(5)}C_{(6)}C_{(7)}$	114,3(2)	$C_{(18)}C_{(19)}C_{(20)}$	119,4(2)
$C_{(5)}C_{(10)}C_{(9)}$	121,4(2)	$C_{(6)}C_{(7)}C_{(8)}$	108,7(2)	$O_{(3)}C_{(20)}C_{(19)}$	124,6(2)
$O_{(1)}C_{(5)}C_{(6)}$	121,9(2)	$C_{(6)}C_{(7)}C_{(23)}$	109,7(2)	$O_{(3)}C_{(20)}C_{(21)}$	115.6(2)
$O_{(1)}C_{(5)}C_{(10)}$	120,6(2)	$C_{(6)}C_{(7)}C_{(24)}$	110,0(2)	$C_{(19)}C_{(20)}C_{(21)}$	119,9(2)
$C_{(10)}C_{(5)}C_{(6)}$	117,5(2)	$C_{(8)}C_{(7)}C_{(23)}$	109,7(2)	$C_{(20)}C_{(21)}C_{(22)}$	120.0(2)
$C_{(2)}C_{(11)}C_{(12)}$	109,5(2)	$C_{(8)}C_{(7)}C_{(24)}$	110,0(2)	$C_{(17)}C_{(22)}C_{(21)}$	121,0(2)

TABLE 2. Principal Torsion Angles τ in the Molecule of (IV)

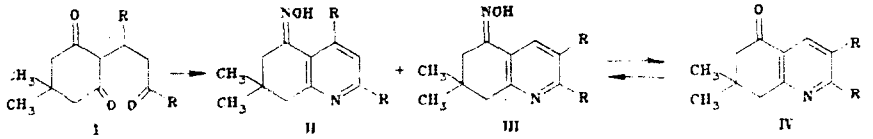
Angle	τ°	Angle	τ°	Angle	τ°	Ideal sofa [5]
$NC_{(2)}C_{(3)}C_{(4)}$	−6.0(9)	$NC_{(2)}C_{(11)}C_{(16)}$	151,5(4)	$C_{(10)}C_{(5)}C_{(6)}C_{(7)}$	26,7(3)	20
$C_{(2)}C_{(3)}C_{(4)}C_{(10)}$	4,5(8)	$C_{(2)}C_{(3)}C_{(17)}C_{(18)}$	−54,5(4)	$C_{(5)}C_{(6)}C_{(7)}C_{(8)}$	−53,3(3)	−51
$C_{(3)}C_{(4)}C_{(10)}C_{(9)}$	0,4(8)	$C_{(11)}C_{(2)}C_{(3)}C_{(17)}$	−10,7(8)	$C_{(6)}C_{(7)}C_{(8)}C_{(9)}$	54,1(3)	58
$C_{(4)}C_{(10)}C_{(9)}N$	−4,4(9)	$C_{(13)}C_{(14)}O_{(2)}C_{(25)}$	−176,9(5)	$C_{(7)}C_{(8)}C_{(9)}C_{(10)}$	−29.1(3)	−32
$C_{(10)}C_{(9)}NC_{(2)}$	3,1(9)	$C_{(21)}C_{(20)}O_{(3)}C_{(26)}$	173,0(4)	$C_{(8)}C_{(9)}C_{(10)}C_{(5)}$	0,3(3)	0
$C_{(9)}NC_{(2)}C_{(3)}$	2,3(9)			$C_{(9)}C_{(10)}C_{(5)}C_{(6)}$	1,2(3)	−5,7

The formation of the sterically more hindred structure of the oxime (III) under the conditions of this reaction is unexpected and probably results from a rearrangement which has not been observed before for such systems. We tried to undertake an x-ray crystallographic analysis of the oxime (III) but were unable to obtain its crystals. For this reason an x-ray crystallographic investigation was undertaken for the product from the hydrolysis of the oxime (III), i.e., 2,3-diaryl-5-oxohydroquinoline (IV). The latter is converted into the oxime (III) with a quantitative yield in reaction with hydroxylamine hydrochloride.

The x-ray crystallographic investigation showed that compound (IV) is 7,7-dimethyl-2,3-di(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydroquinoline, in the molecule of which the 4-methoxyphenol substituents are situated at neighboring carbon atoms. The molecular structure of

TABLE 3. Atomic Coordinates of (IV) (× 10^4, for the H Atoms × 10^3) and Their Equivalent Isotropic Temperature Factors (isotropic for the H atoms)

Atom	x	y	z	B_{iso}^{eq}/B_{iso}, Å^2
$O_{(1)}$	1141(2)	5287(1)	5935(2)	5,20(6)
$O_{(2)}$	−9347(2)	1873(3)	11564(2)	5,61(1)
$O_{(3)}$	−6642(2)	8929(2)	4994(2)	5,36(7)
N	−2678(2)	2503(2)	8847(2)	3.63(6)
$C_{(2)}$	−3682(2)	3484(2)	8555(2)	3,28(7)
$C_{(3)}$	−3299(2)	4732(2)	7585(2)	3,07(7)
$C_{(4)}$	−1846(2)	4943(2)	7045(2)	3,33(7)
$C_{(5)}$	749(2)	4192(2)	6696(2)	3,72(8)
$C_{(6)}$	1808(2)	3038(2)	6984(2)	4,18(8)
$C_{(7)}$	1214(2)	1702(2)	7367(2)	3,69(7)
$C_{(8)}$	−193(2)	1586(2)	8554(2)	4,00(7)
$C_{(9)}$	−1273(2)	2727(2)	8249(2)	3,39(7)
$C_{(10)}$	−807(2)	3961(2)	7365(2)	3,31(7)
$C_{(11)}$	−5199(2)	3127(2)	9334(2)	3.31(7)
$C_{(12)}$	−5529(2)	1810(2)	9823(2)	4.36(8)
$C_{(13)}$	−6911(2)	1430(2)	10562(3)	4,62(8)
$C_{(14)}$	−8013(2)	2356(2)	10843(2)	3,90(7)
$C_{(15)}$	−7714(2)	3657(2)	10400(2)	3,76(7)
$C_{(16)}$	−6315(2)	4033(2)	9657(2)	3,58(7)
$C_{(17)}$	−4310(2)	5795(2)	7022(2)	3,03(6)
$C_{(18)}$	−5215(2)	5563(2)	6423(2)	3,48(7)
$C_{(19)}$	−6014(2)	6573(2)	5741(2)	3,70(7)
$C_{(20)}$	−5919(2)	7849(2)	5659(2)	3,66(7)
$C_{(21)}$	−5050(2)	8102(2)	6278(2)	3,83(7)
$C_{(22)}$	−4257(2)	7081(2)	6955(2)	3,42(7)
$C_{(23)}$	2318(2)	599(2)	7795(3)	5,33(9)
$C_{(24)}$	923(2)	1579(2)	6146(2)	4,72(9)
$C_{(25)}$	−10533(3)	2797(3)	11821(4)	8,38(15)
$C_{(26)}$	−7418(4)	8742(3)	4217(4)	8,50(16)
$H_{(3)}$	−153(2)	573(2)	641(2)	3,2(4)
$H_{(6.1)}$	210(2)	307(2)	775(2)	5,4(5)
$H_{(6.2)}$	267(2)	318(2)	622(2)	4,7(5)
$H_{(8.1)}$	−66(2)	75(2)	877(2)	5,1(5)
$H_{(8.2)}$	6(2)	159(2)	935(2)	6,1(6)
$H_{(12)}$	−475(2)	117(2)	962(2)	5,3(5)
$H_{(13)}$	−709(2)	50(2)	1085(2)	5,8(5)
$H_{(15)}$	−843(2)	428(2)	1057(2)	3,6(4)
$H_{(16)}$	−614(2)	493(2)	940(2)	4,0(4)
$H_{(18)}$	−527(2)	468(2)	646(2)	4,1(4)
$H_{(19)}$	−661(2)	636(2)	536(2)	4,1(4)
$H_{(21)}$	−498(2)	897(2)	619(2)	5.5(2)
$H_{(22)}$	−362(2)	727(2)	735(2)	3,9(4)
$H_{(23.1)}$	195(2)	−30(2)	810(2)	7,1(6)
$H_{(23.2)}$	325(2)	70(2)	707(2)	7,0(6)
$H_{(23.3)}$	257(2)	65(2)	855(2)	7,3(6)
$H_{(24.1)}$	182(2)	162(2)	540(2)	7,7(7)
$H_{(24.2)}$	47(2)	71(2)	645(2)	6,4(6)
$H_{(24.3)}$	23(2)	229(2)	583(2)	4,8(5)
$H_{(25.1)}$	−1132(3)	226(2)	1231(3)	8,0(7)
$H_{(25.2)}$	−1040(3)	324(3)	1235(3)	10,8(8)
$H_{(25.3)}$	−1058(4)	358(3)	1090(4)	14,0(1)
$H_{(26.1)}$	−778(3)	961(3)	382(3)	10,1(8)
$H_{(26.2)}$	−818(3)	813(3)	488(3)	12,1(9)
$H_{(26.3)}$	−682(3)	830(3)	354(4)	13,0(1)



R = p-$CH_3OC_6H_4$

(IV) with the bond lengths is shown in Fig. 1, and the bond and torsion angles are given in Tables 1 and 2.

The position of the 4-methoxyphenyl substituents at neighboring carbon atoms of the pyridine ring gives rise to significant steric hindrances, which are resolved to some degree not only by rotation of these substituents in relation to the plane of the heterocycle (angles of rotation about the $C_{(2)}$-$C_{(11)}$ and $C_{(3)}$-$C_{(17)}$ bonds 26.5 and 55.5°, respectively) but also by the projection of the C_{11} atom by −0.123(6) Å and of the $C_{(17)}$ atom by 0.228(6) Å on opposite sides of the plane of the heterocycle. As a result the torsion angle $C_{(11)}C_{(2)}$·

$C_{(3)}C_{(17)}$ amounts to 10.7(8)°. The pyridine ring was found to be not completely planar (see the torsion angles in Table 2); for example, the departures of the $C_{(3)}$ and $C_{(9)}$ atoms from the mean-square plane drawn through all the ring atoms are 0.031(6) and 0.030(6) Å, respectively. The benzene rings are planar, and the bond lengths and the bond angles [1.376(3)-1.394(3) Å and 117.8(2)-121.6(2)°] are normal [3]. The methoxy groups lie in the planes of the benzene rings (Table 2); the corresponding bond lengths and bond angles in these groups agree and have the normal values [3, 4].

The conformation of the cyclohexene ring is a sofa, where the C_7 atom projects by 0.651(6) Å from the $C_{(10)}C_{(5)}C_{(6)}C_{(8)}C_{(9)}$ plane, which is fulfilled with an accuracy of 0.007(7) Å, and the torsion angles (Table 2) in this ring of the (IV) molecule only differ little from the values calculated by molecular mechanics for the cyclohexene molecule in the sofa conformation [5]. The realization of this conformation in the molecule of the oxohydroquinoline (IV) instead of the half-chair conformation more usual for cyclohexane and its derivatives is due to the conjugation between the carbonyl group and the π-electron system of the pyridine ring, which leads to its coplanarity and, consequently, to the coplanarity of the $C_{(6)}$ atom with this ring. The molecule of 8-oxo-2-phenyl-5,6,7,8-tetrahydroquinoline (V) [6], where dine ring, also conjugation between the carbonyl group and the π-electron system of the pyriine ring, also has a conformation similar to that found in the molecule of (IV).

The bond lengths and bond angles in the molecule of (IV) are close both to the standard values [3] and to the values found in the molecules of pyridine [7] and of compound (V) [6]. The intermolecular contacts in the crystal of (IV) are made at the van der Waals separations.

EXPERIMENTAL

The reactions were monitored by TLC on Silufol-254 plates in a 2:1:1 mixture of hexane, ether, and chloroform with iodine vapor as developer.

7,7-Dimethyl-2,3-di(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydroquinoline Oxime (III). A. A mixture of 5 g (0.012 mole) of (I), 5 g (0.072 mole) of hydroxylamine hydrochloride, and 50 ml of absolute ethanol was boiled for 20 h, cooled, and poured into 200 ml of a 2% aqueous solution of potassium hydroxide. The precipitate was separated, washed to pH 7.0 with water, and then with 30 ml of ethanol, and dried. We obtained 4.85 g (97%) of a mixture of the oximes (II) and (III). By fractional crystallization from ethanol we obtained 2.1 g (42%) of the oxime (III); mp 233-235°C (from ethanol). Found, %: C 74.7, H 6.4, N 6.6. $C_{25}H_{26}N_2O_3$. Calculated, %: C 74.8, H 6.2, N 6.9.

B. A mixture of 0.7 g (18 mmole) of 5-oxohydroquinoline (IV), 0.38 g (54 mmole) of hydroxylamine hydrochloride, and 15 ml of absolute ethanol was boiled for 8 h and cooled. The precipitate was separated, washed to pH 7.0 with water, dried, and recrystallized from ethanol. We obtained 0.68 g (94%) of the oxime (III); mp 233-235°.

7,7-Dimethyl-2,3-di(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydroquinoline (IV). A mixture of 2 g (5 mmole) of the oxime (III) and 50 ml of 25% sulfuric acid was heated in a boiling water bath for 48 h and cooled. The precvipitate was separated, washed to pH 7.0 with water, dried, and recrystallized from ethanol. We obtained 1.67 g (87%) of 5-oxohydroquinoline (IV); mp 149-149.5°. Found, %: C 77.5, H 6.8, N 4.0. $C_{25}H_{25}NO_3$. Calculated, %: C 77.6, H 6.5, N 3.6.

The crystals of (IV) are triclinic; at 20°C a = 9.8848(9), b = 10.904(2), c = 11.067(1) Å, α = 68.885(9), β = 69.878(7), γ = 79.797(9)°, V = 1042.9(2) Å^3, d_{calc} = 1.237 g/cm^3, space group $P\bar{1}$. The unit cell parameters and the intensities of 2330 reflections with $F^2 \geq 3.5\sigma$ were measured on a Hilger–Watts four-circle automatic diffractometer (λ_{MoK_α}, graphite monochromator, θ/2θ scan, θ ≤ 30°). The structure was interpreted by the direct method using the MULTAN program and was refined by full-matrix least-squares treatment first in isotropic and then in anisotropic approximation. All the hydrogen atoms were revealed in the difference synthesis and were included in the refinement in isotropic approximation. The final R value was 0.037 (R_w = 0.039). The calculations were made on an Eclipse S/200 computer by means of the INEXTL program [8]. The atomic coordinates and the isotropic equivalent temperature factors are given in Table 3.

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REDUCTION OF ENAMINES OF THE 3,3-DIALKYL-3,4-DIHYDROISOQUINOLINE SERIES

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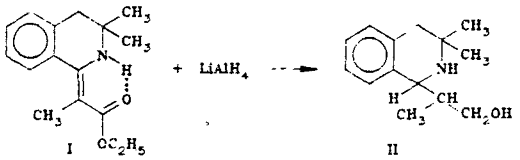
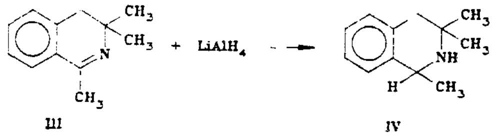
Lithium aluminum hydride reduced enamines of the 3,3-dialkyl-3,4-dihydroisoquinoline series to the corresponding tetrahydroisoquinolines. In the presence of a hydrogen atom at the β-carbon atom of the enamino ester the action of lithium aluminum hydride and alkylmagnesium bromide leads to the products from the condensation of two molecules of the initial compound.

Lithium aluminum hydride effectively reduces enamines, but various reaction products are formed, depending on the presence and the nature of the substituents [1]. This reaction has been studied in the series of α-(1,2,3,4-tetrahydro-1-isoquinolylidene) carboxylic esters [2]. We reproduced it as applied to enamines of the 3,3-dialkyl-3,4-dihydroisoquinoline series. Here it was found that ethyl α-(3,3-dimethyl-1,2,3,4-tetrahydro-1-isoquinolylidene)-propionate (I) is reduced by an excess of the reagent to 2-(3,3-dimethyl-1,2,3,4-tetrahydro-1-isoquinolyl)propanol (II):



Similarly, 1,3,3-trimethyl-3,4-dihydroisoquinoline (III), which exhibits the characteristics of an enamine, is converted by the action of lithium aluminum hydride into 1,3,3-trimethyl-1,2,3,4-tetrahydroisoquinoline (IV):



The structures of compounds (II) and (IV) are confirmed by the data from IR and PMR spectroscopy. The IR spectrum of (II) contains absorption bands due to the stretching vibrations of the O–H and N–H bonds at 3640 and 3340 cm^{-1}, respectively. The stretching vibrations of the N–H bond in the spectrum of (IV) are at 3210 cm^{-1}. In both cases there is no absorption characteristic of the initial compounds [3] in the region of 1800-1600 cm^{-1}. The PMR spectra are given in Table 1.

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