For the reliability of comparison, all the determinations of δ, ν, λ, R_f, and τ_R for the pairs (Ia)-(IIa), (Ib)-(IIb), (Ic)-(IIc), and (Id)-(IId) were carried out concurrently.

CONCLUSIONS

^1H and ^{13}C NMR spectroscopy was used for the reliable determination of the configurations of the E- and Z-isomers of 3-bromo-2-butenoic acids and their esters.

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REACTION OF 3-PHENYL-3-CHLORO-2-OXOPROPIONIC ACID DERIVATIVES WITH ORTHO-PHENYLENEDIAMINE

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UDC 542.91:547.484.2:547.553.1:547.863.19

α-Haloketones react with various bifunctional reagents to give the thiazoles [1], oxathiines and dithiines [2, 3], and thiadiazines [4], which possess a broad spectrum of biological activity. The formation of quinoxalines has been described in the reactions of α-chloroketones with o-phenylenediamine (PDA) [5, 6] but the effect of substituents in the chloroketones on the course of these reactions has not been studied sufficiently.

In the present work, we report on the reactions of esters and amides of 3-phenyl-3-chloro-2-oxopropionic acid with PDA.

Heating dialkylamides of 3-phenyl-3-chloro-2-oxopropionic acid (I)-(III) [7] with PDA in ethanol gives crystalline products (IV)-(VI) with IR bands for the carboxamide group (νC=O 1635-1650 cm^{-1}). These products were identified as 2-(N,N-dialkylcarbamoyl)-3-phenyl-1,4-dihydroquinoxalines

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1412-1414, June, 1989. Original article submitted July 4, 1988.

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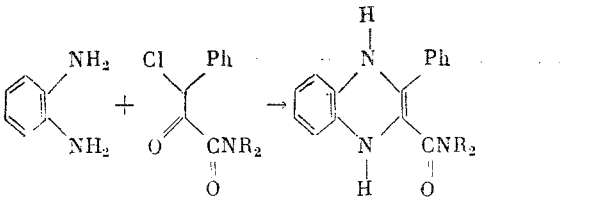
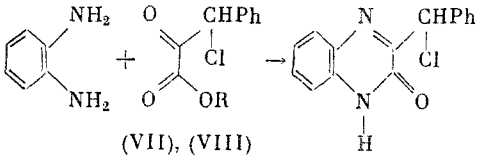


(I)—(III) (IV)—(VI)

R = Me (I), (IV), Et (II), (V), and i-Pr (III), (VI). The PMR spectra support the proposed structures for (IV)-(VI).

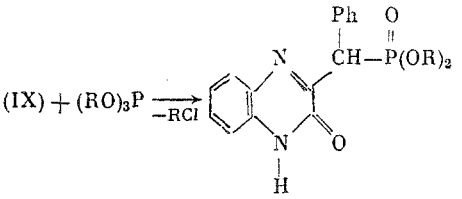
Esters of 3-phenyl-3-chloro-2-oxopropionic acid (VII) and (VIII) react with PDA in ethanol at 20°C to form 3-(α-chlorobenzyl)-2-oxo-1,2-dihydroquinoxaline (IX)



(VII), (VIII) (IX)

R=Me (VII), Et (VIII).

Heating (IX) with trialkyl phosphites at reflux leads to the formation of 3-(O,O-dialkylphosphonobenzyl)-2-oxo-1,2-dihydroquinoxalines (X) and (XI), whose structure was supported by ^{1}H and ^{31}P NMR spectroscopy.



(X), (XI)

R=Me (X), Et (XI).

The observed differences in the behavior of the amides and esters of 3-phenyl-3-chloro-2-oxopropionic acid in reactions with PDA may be attributed to the greater resonance stabilization of the amides relative to the esters due to the contribution of resonance forms.

EXPERIMENTAL

The IR spectra were taken in vaseline mull on a UR-20 spectrometer. The PMR spectra were taken on a Varian T-60 spectrometer with TMS as the internal standard. The ^{31}P NMR spectra were taken on a KGU-4 spectrometer at 10.2 MHz with 85% H_3PO_4 as the external standard.

2-(N,N-Dimethylcarbamoyl)-3-phenyl-1,4-dihydroquinoxaline (IV). A solution of equimolar amounts of PDA and (I) was heated at reflux in ethanol for ~6 h. After removal of ethanol in vacuum, the residue was recrystallized from hexane to give crystalline (IV) in 56% yield, mp 121-123°C. IR spectrum (ν, cm^{-1}): 1650 (C=O), 1600 (C=C). PMR spectrum in $CDCl_3$ (δ, ppm): 2.63 s and 3.00 s ($N(CH_3)_2$), 7.00-8.06 m (C_6H_4, C_6H_5), 2NH). Found, %: C 73.01; H 5.85; N 15.12. $C_{17}H_{17}N_3O$. Calculated, %: C 73.13; H 6.08; N 15.04.

Analogous procedures gave 2-(N,N-diethylcarbamoyl)-3-phenyl-1,4-dihydroquinoxaline (V) and 2-(N,N-diisopropylcarbamoyl)-3-phenyl-1,4-dihydroquinoxaline (VI). Quinoxaline (V) was obtained in 55% yield, mp 138-139°C (from hexane). IR spectrum (ν, cm^{-1}): 1650 (C=O), 1600 (C=C). PMR spectrum in $CDCl_3$ (δ, ppm): 0.90 s and 1.13 t ($2CH_3$), 2.93 q and 3.50 q ($2CH_2$), 7.16-8.16 m (C_6H_4, C_6H_5, 2NH). Found, %: C 74.2; H 6.57; N 13.71. $C_{19}H_{21}N_3O$. Calculated, %: C 74.28; H 6.83; N 13.67.

Quinoxaline (VI) was obtained in 71% yield, mp 208-208.5°C (from ethanol). IR spectrum (ν, cm^{-1}): 1635 (C=O). PMR spectrum in $CDCl_3$ (δ, ppm): 0.80 d and 1.53 d ($4CH_3$), 3.03-3.60 m (2CH), 7.16-8.16 m (C_6H_5, C_6H_4, 2NH). Found, %: C 75.21; H 7.32; N 12.71. $C_{21}N_{25}N_3O$. Calculated, %: C 75.23; H 7.45; N 12.52.

3-(α-Chlorobenzyl)-2-oxo-1,2-dihydroquinoxaline (IX). Equimolar amounts of the methyl or ether ester of 3-phenyl-3-chloro-2-oxopropionic acid and PDA in ethanol (or benzene) were maintained for 20 min. The crystalline precipitate was filtered off and recrystallized from 1:1 benzene–ethanol, mp 215-216°C. IR spectrum (ν, cm^{-1}): 1665 (C=O). PMR spectrum in DMF-d_7 (δ, ppm): 6.56 s (ClCH), 7.03-7.73 m (C_6H_5, C_6H_4, NH). Found, %: C 66.41; H 3.95; Cl 12.85; N 10.12. $C_{15}H_{11}ClN_2O$. Calculated, %: C 66.57; H 4.06; Cl 13.10; N 10.36.

3-(O,O-Dimethylphosphonobenzyl)-2-oxo-1,2-dihydroquinoxaline (X). A mixture of 1 g (0.0036 mole) (IX) and 5 ml $(MeO)_3P$ was heated in a flask equipped with a reflux condenser at 100°C until the singlet at 6.56 ppm in the PMR spectrum disappeared (~8 h). The excess phosphite was evaporated and the remaining oil was characterized. IR spectrum (ν, cm^{-1}): 1665 (C=O), 1600 (N=C), 1260 (P=O). PMR spectrum in $CDCl_3$ (δ, ppm, J, Hz): 3.73 d (CH_3O, J_{POCH} = 11.0), 5.53 d (CH, $^2J_{PCH}$ = 22), 6.96-7.83 m (C_6H_5, C_6H_4, NH). $\delta_{^{31}P}$ 22 ppm. Found, %: P 9.17; N 8.04. $C_{17}H_{17}N_2O_4P$. Calculated, %: P 8.99; N 8.13.

An analogous procedure gave 3-(O,O-diethylphosphonobenzyl)-2-oxo-1,2-dihydroquinoxaline (XI). IR spectrum (ν, cm^{-1}): 1670 (C=O), 1600 (C=N), 1260 (P=O). PMR spectrum in $CDCl_3$ (δ, ppm, J, Hz): 1.33 t ($2CH_3$), 4.10 q and 4.23 q (CH_2, $^3J_{POCH}$ = 10), 5.50 d (CH, $^2J_{PCH}$ = 22), 6.96-7.90 m (C_6H_5, C_6H_4, NH). $\delta_{^{31}P}$ 22 ppm. Found, %: P 8.47; N 7.36. $C_{19}N_{21}N_2O_4P$. Calculated, %: P 8.32; N 7.52.

CONCLUSIONS

The reaction of dialkylamides of 3-phenyl-3-chloro-2-oxopropionic acid with ortho-phenylenediamine gave 2-(N,N-dialkylcarbamoyl)-1,4-dihydroquinoxalines, while esters of this acid react with ortho-phenylenediamine to give 3-(α-chlorobenzyl)-2-oxo-1,2-dihydroquinoxalines, which react with phosphites to yield the corresponding 3-(O,O-dialkylphosphonobenzyl)-2-oxo-1,2-dihydroquinoxalines.

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