4-Azafluorenone 3-carboxylic acid chloride (XI) was obtained from acid (IX) and thionyl chloride in 90% yield as yellow crystals of mp 247-248°C (from a heptane–acetone mixture, 5:1). IR spectrum: 1775, 1730 cm^{-1} (CO). Found: N 5.5%; M^+ 243. $C_{13}H_6ClNO_2$. Calculated: N 5.7%.

4-Azafluorenone 3-carboxymorpholide (XII) was obtained from acid chloride (XI) and morpholine in dioxan in 79% yield as yellow crystals of mp 138-140°C (from a heptane–acetone mixture, 10:1). Found: N 9.1%; M^+ 294. $C_{17}H_{14}N_2O_3$. Calculated: N 9.5%.

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REACTION OF 1-METHYLURACIL WITH PHENYLBENZHYDRAZONOYL CHLORIDE

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The ambident anion of 1-methyluracil gives with phenylbenzyhydrazonoyl chloride, depending on the conditions, the N-acylation product (polar solvent, room temperature), or the O-acylation product (nonpolar solvent, heating), which rearranges to a cytosine derivative. Convenient methods have been developed for the preparation of 6-methyl-1,3-diphenyl-5,6-dihydro-5-oxopyrimido[4,3-c]triazolium chloride, a fluorescent derivative of 1-methyluracil, from the N-acylation product, and for the rapid base cleavage of the uracil ring under very mild conditions.

The search for new reactions of uracils suitable for the chemical modification of the uracil ring under mild conditions is of great importance and potential for the modification of nucleotides and RNA. In contrast to the well-known alkylation of uracils, acylation has been investigated only in isolated instances [1, 2]. The most suitable model compound for such studies is 1-methyluracil.

The aim of this investigation was to examine the reactions of 1-methyluracil (I) with phenylbenzyhydrazonoyl chloride (II) in the presence of bases. We have found that (II) functions as an acylating agent, and depending on the reaction conditions, gives with (I) the N-acylation products 1-methyl-3-($N_{(1)}$-phenylbenzhydrazonoyl)uracil (III) and 1-methyl-4-($N_{(1)}$-benzoyl-N-phenylhydrazino)-1H-pyrimidin-2-one (IV), which is apparently formed by rearrangement of an O-acylated product of the uracil (I), which we have been unable to isolate.

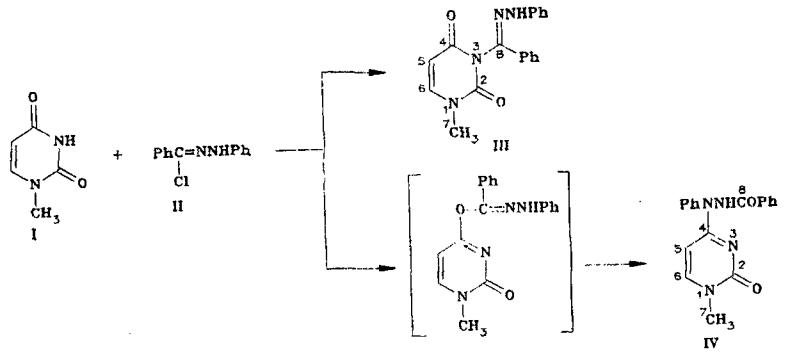

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TABLE 1. PMR Spectra of the Compounds Obtained (δ, ppm; J, Hz)

Compound *	5-H, d	6-H, d	J	CH_3, s	NH, s	Ar, m
I	5,74	7,74	8	3,45	9,0	—
III	5,79	7,82	8	3,35	10,0	6,88—7,6
IV	5,92	7,81	8	3,30	11,54	7,22—7,98
VII	7,30	8,46	8	3,9	—	7,18—8,18
X†	5,27	7,14	14	3,25	—	7,4—8,2

*Compounds (I), (III), and (IV) recorded in DMSO-D_6, (VII) in D_2O/CD_3O, and (X) in $(CD_3)_2CO$.
†Signals for the OEt group: 1.27 (3H, t); 4.2 ppm (2H, q).

When the sodium salt of (I) reacts with the chloride (II) in aqueous ethanol, (III) is the main product (70% yield), together with ~9% of (IV).

The IR spectrum of (III) is typical of 1,3-disubstituted uracils [3], showing absorption at 1720 (C_2=O), 1680 (C_4=O), and 3355 cm^{-1} (NH), the latter becoming more intense as the solution is diluted. The PMR spectrum of (III) contains signals for the 5-H and 6-H protons (AB system, characteristic of the pyrimidine ring [4]), and in the ^{13}C NMR spectrum the signals for $C_{(5)}$ and $C_{(6)}$ are clearly apparent (Tables 1 and 2) [5]. Comparison of the spectral region 140-165 ppm for (I) and (III) enables the singlet signals to be assigned to $C_{(2)}$, $C_{(4)}$, and $C_{(8)}$. The molecular ion peak in the mass spectrum of (III) (m/z 320) corresponds to the empirical formula of the structure given. The IR spectrum of (IV) is similar to those of cytosine derivatives [3], with absorption at 1740 ($C_{(2)}$= O), 1642 (hydrazide C=O), and 3225 cm^{-1} (NH). The UV spectrum of (IV) in ethanol (λ_{max} 289 nm) is similar to that of $N_{(4)}$-phenylcytosine (λ_{max} 293 nm [6]). The mass spectrum of (IV) contains the molecular ion peak (m/z 320) together with peaks with m/z 201 and 119 corresponding to fission of the N—N bond, which is typical of diaryl benzohydrazides [7]. The ion with m/z 201 corresponds in its mass to 1-methyl-$N_{(4)}$-phenylcytosine, and the spectrum also contains a peak for the corresponding doubly-charged ion with m/z 100.5. This peak is present also in the spectrum of 1-methyl-$N_{(4)}$-phenylcytosine, specially synthesized by us by the method given in [6]. From the PMR and ^{13}C NMR spectra (Tables 1 and 2), it may be concluded that the molecule contains the $C_{(5)}H$=$C_{(6)}H$— grouping, three carbon atoms doubly bonded to the heteroatoms ($C_{(2)}$, $C_{(4)}$, and $C_{(8)}$), aromatic rings, and the N-CH_3 group.

The formation of two reaction products (III) and (IV) when 1-methyluracil reacts with phenylbenzhydrazonoyl chloride prompted us to examine the reaction conditions favoring the formation of one or other of these products (Table 3).

When the sodium salt of (I) is reacted with (II) in DMF, the main product is (III). Similar behavior is observed when the reaction is carried out in aqueous alcoholic sodium hydroxide. However, when triethylamine is used as the base the proportion of (IV) in the reaction products increases, although the extent of reaction of the starting material (I) is small. On prolonged boiling in dry benzene, however, high yields of the pyrimidine (IV) were obtained, no N-acylated product being obtained under these conditions.

It is assumed that (III) is formed by electrophilic attack of the chloride (II) on the nitrogen atom of the ambident anion of 1-methyluracil, and the formation of (IV) results from rearrangement of the intermediate O-acylation product of the ambident anion. Similar O-acylation is well known in the reaction of (II) with phenols in the presence of triethylamine [7-11]. The initially formed hydrazonate (V) then rearranges to N'N'-diphenylbenzohydrazide (VI):

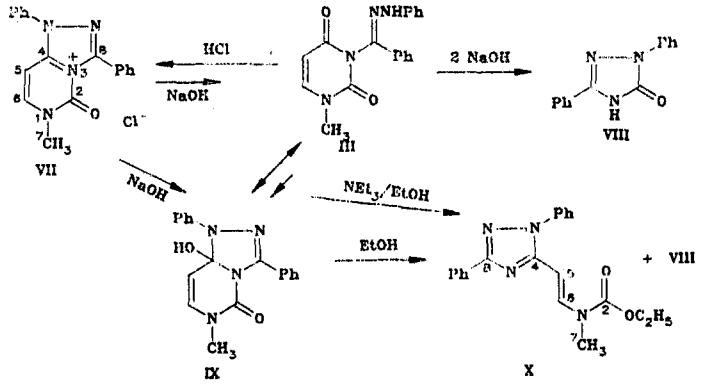
II + PhOH ⟶ PhOC(Ph)=NNHPh (V) ⟶ $PhCONHNPh_2$ (VI)

It is noteworthy that 1,3-dimethyluracil is recovered totally unchanged following heating for many hours with (II) in dry benzene with triethylamine, although it might be expected that the 1,3-dipole formed under these conditions would undergo cycloaddition to the $C_{(5)}$=$C_{(6)}$ double bond in the uracil. The structures of (III) and (IV) were also confirmed by their chemical reactions.

TABLE 2. ^{13}C NMR Spectra of Compounds Obtained, ppm

Compound	$C_{(2)}$, s	$C_{(4)}$, s	$C_{(5)}$, d	$C_{(6)}$, d	$C_{(7)}$, q	$C_{(8)}$, s	Ar
I	151,4	164,0	100,6	146,6	35,2	—	—
III	149,7	161,7	100,3	146,5	36,0	144,5	133,9; 128,9; 128,5; 127,75; 124,2; 119,8; 113,0
IV	155,5	164,5	91,2	148,7	37,0	165,3	142,1; 132,3; 131,3; 128,9; 128,6; 127,7; 126,3; 125,9
VII	151,05	148,8	90,4	149,5	39,5	144,6	134,85; 133,6; 132,6; 131,8; 129,65; 125,4; 123,95
X†	161,9	151,7	96,9	135,9	36,9	155,2	138,8; 132,2; 130,2; 130,05; 129,4; 127,1; 125,4

*The solvents used were the same as for the PMR spectra.
†Signals for the OEt group: 63.2 (t); 14.7 ppm (q).



On heating (III) with dilute hydrochloric acid in ethanol, it is converted almost quantitatively into crystalline 6-methyl-1,3-diphenyl-5,6-dihydro-5-oxopyrimido[4,3-c]triazolium chloride (VII). The (VII) cation on paper electrophoresis moves to the cathode, has a UV spectrum with characteristic long-wave absorption maxima (314 and 268 nm), has a deep blue fluorescence (excitation λ_{max} 320 nm, emission λf_{max} 414 nm, relative quantum fluorescence yield ~30%), and is similar in its properties to phenylimidazo[1,2-c]pyrimidines [12]. The IR spectrum differs markedly at 1680-1800 cm^{-1} from that of 1,3-disubstituted uracils, but is similar to that of $N_{(3)}O_{(4)}$-ethylene-1-methyluracilium sulfonate [4]: there is no absorption at ~1670 cm^{-1} corresponding to $C_{(4)}=O$, all the proton signals are shifted to lower field in comparison with the original (III), as would also be expected for a heteronuclear cation (see [4]). The ^{13}C NMR spectrum (Table 2) is similar to those pyrimidines.

Unlike (III), (IV) is stable towards mild acid hydrolysis (2 N HCl, 1 h, 80°C), and only under more severe conditions (2 N HCl, 24 h 100°C) does it decompose to (I), benzoic acid, and a phenylhydrazine, identified as 1,3,5-triphenylpyrazoline following reaction with benzalacetophenone.

Like 1,3-disubstituted uracils [13-15], on treatment with aqueous alkali (III) undergoes extremely facile cleavage of the pyrimidine nucleus with the formation of a single product, 1,3-diphenyl(4H)-1,2,4-triazol-5-one (VIII), an authentic sample of which was obtained by direct synthesis [16].

The mass spectrum of the triazoline (VIII) contains the molecular ion peak with m/z 237, the principal breakdown route being cleavage of a molecule of HNCO to give an ion with m/z 194, this reaction being accompanied by a metastable transition with m*/z 159. Partial formation of the triazoline (VIII) from the uracil (III) takes place on drying in an oil-pump vacuum at 60°C. The triazoline (VIII) is also formed under the conditions of recording of the mass spectrum, the ion with m/z 194 being the most intense peak in the spectrum, and a metastable ion is also present corresponding to the transition m/z 237 → 194.

On heating the uracil (III) with ethanol in the presence of triethylamine, in addition to (VIII) (33%) there was also isolated (X) (52%). It would appear that intramolecular nucleophilic attack of the hydrazine nitrogen on $C_{(4)}$ of the uracil nucleus leads to the formation of the intermediate (IX), which adds ethanol at the $C_{(2)}$—$N_{(3)}$ bond of the pyrimidine ring to

TABLE 3. Formation of Products of the Reaction of the Uracil (I) with Chloride (II) (as % of (I))

Compound	ETOH, 20°. 1 N NaOH, 1 - 1.5 h	DMF, NaH, 20°C, 1 - 1.5 h	EtOH+H_2O, Et_3N, 20°, 40 h	Benzene, Et_3N, boiled for 30 h
I	16,0	17,7	66,4	12,5
III	70,0	65,7	28,1	—
IV	8,8	4,5	10,6	78,6

give (X). This compound was also formed in 79% yield on treatment of the salt (VII) with an equimolar amount of alkali in aqueous alcohol, in addition to 5% of the starting material (III). The hydroxyl ion attacks the (VII) cation at $C_{(4)}$ of the pyrimidine nucleus [4] to give the same intermediate (IX), which adds a molecule of ethanol, or recyclizes to the starting material (III).

The IR spectrum of (X) shows strong absorption at 1642 cm^{-1} (characteristic of enamine C=C [17]) and 1700 cm^{-1} (ester carbonyl), but no absorption is seen in the NH or OH regions. The PMR spectrum (Table 1) shows signals for the NCH_3 and EtO protons, aromatic protons, and an AB system for the protons of the —CH=CH—N— fragment. The chemical shifts of the latter (7.14 and 5.27 ppm, respectively) are similar to those of enamine protons [18-20], and the coupling constant corresponds to the trans-configuration of the double bond, and hence indicates opening of the pyrimidine ring. The ^{13}C NMR spectrum (Table 2) also corresponds to structure (X). The most intense ion in the mass spectrum has m/z 91, typical of N-phenyl compounds, the molecular ion (m/z 348, being 98% of the maximum. The main course of breakdown is cleavage of the ethoxycarbonyl group, accompanied by the metastable transition m*/z 217 (calculated, 217.3) and loss of the ethoxy-group [21-23]. Cleavage of the heterocyclic substituent from the molecular ion or from the fragment ion with m/z 276 gives an ion with m/z 221, the mass of which is equal to the molecular mass of 3,5-diphenyltriazole, which then loses the PhC=NNPh fragment with m/z 194. The UV spectrum of (X) is similar to those of 2-substituted-3,5-diphenyl-1,2,4-triazoles [24]. This compound (X) remains unchanged on heating for 10 h in a mixture of ethanol and triethylamine (i.e., conditions used for its preparation from the uracil (III)), and gives no traces of the triazolone (VIII) (according to TLC), and is therefore in all probability not an intermediate in the foramtion of the triazolone (VIII) from the uracil (III), but rather a product of a parallel reaction.

The reactions described here enable uracil derivatives to be converted readily into compounds which fluoresce strongly, and on the other hand it is possible to cleave the heterocyclic nucleus rapidly under very mild conditions. Extension of these reactions to nucleosides and their derivatives would appear to be quite feasible, and they are therefore of considerable interest for the chemical modification of components of nucleic acids.

EXPERIMENTAL

IR spectra were obtained on UR-20 and Specord IR-75 instruments, UV spectra on a Specord UV-vis, PMR spectra on a Bruker WM-250 or a Tesla BS-467, ^{13}C NMR spectra on a Bruker WM-250 with selective proton decoupling,* mass spectra on a Varian CH-6, and the fluorescence spectrum on an Élyumin 2M, solution concentration $2.5 \cdot 10^{-6}$ mole/liter (relative to fluorescein). Electrophoresis was carried out in an 0.025 M pyridine acetate buffer at pH 4.5; 28 V/cm, 60 min. TLC was carried out on Merck F_{254} plates, layer thickness 0.2 mm, in the systems: ethyl acetate—acetone—water, 7:4:1 (A), benzene—ethyl acetate, 2:1 (B), and chloroform—methanol—water, 60:25:4 (C), the compounds being visualized under UV and with iodine vapor. Column chromatography was carried out on Silperl silica gel, 25-40 μ, the material to be chromatographed being applied together with the adsorbent. 1-Methyluracil (I) was obtained as described in [25], mp 242°C (from absolute ethanol). Phenylbenzhydrazonyl chloride (II) was obtained in 80% yield as described in [26], excess PCl_5 being destroyed with phenol followed by methanol, the reaction mixture being cooled with dry ice in acetone, mp 127-128°C (from acetone—water). 1,3-Diphenyl(4H)-1,2,4-triazol-5-one (VIII) was obtained by fusing N'-benzoyl-N-phenylhydrazine with urea at 200-210°C, followed by column chromatography, yield 23%, mp 229-230°C (from ethanol) [16], and 1,3,5-triphenylpyrazoline as described in [27], yield 98%, R_f 0.9 (benzene—heptane, 5:1).

*The authors are deeply indebted to M. I. Struchkova and A. S. Pashkov for the ^{13}C NMR spectra.

1-Methyl-3-(phenylbenzhydrazonoyl)uracil (III) and 4-(N'-Benzoyl-N-phenylhydrazino-1-methyl-1H-pyrimidin-2-one (IV). A. To a suspension of 63 mg of the uracil (I) (0.5 mmole) in 2 ml of ethanol was added 0.5 ml of 1 N NaOH. To the homogeneous solution was added immediately with stirring at room temperature a solution of 132 mg of the hydrazonoyl chloride (II) (0.6 mmole) in 6 ml of ethanol, the mixture stirred for 1.5 h at 20°C, and evaporated to dryness. The residue was dissolved in the minimum amount of ethanol, and separated preparatively on silica gel plates (layer thickness 2 mm, system A). The bands which absorbed UV were eluted with ethanol, evaporated, and dried *in vacuo* for 48 h at 20°C to give 112.7 mg (70%) of (III), R_f 0.58 (system A), dec. 100°C, pale yellow film, purified by boiling with activated charcoal in ethanol. IR spectrum (chloroform): 1600 (C=C), 1680 ($C_{(4)}$=O), 1720 ($C_{(2)}$=O), 3355 cm^{-1} (NH). UV spectrum (ethanol), λ_{max}, nm (log ε): 340 (4.39), 282 (4.13), 240 (4.29). Mass spectrum*, m/z (I, %): 320 (97), 276 (3.5), 237 (15), 194 (100), 167 (22), 126 (6), 105 (32), 104 (31), 103 (18), 91 (91), 84 (32), 77 (72). Found: C 67.0; H 5.0; N 17.8%. $C_{18}H_{16}N_4O_2$. Calculated: C 67.5; H 5.0; N 17.5%. There was obtained 14.1 mg (8.8%) of (IV), R_f 0.3 (system A), purified by boiling with activated charcoal in ethanol, followed by removal of the solvent and drying *in vacuo* to give an analytically pure sample as a film, mp 214.5-215.5°C. IR spectrum (KBr): 1740 ($C_{(2)}$=O), 1642 (C=C), 3225 cm^{-1} (NH). UV spectrum (ethanol), λ_{max}, nm (log ε): 289 (4.0); pH 10 252 (4.06), 320 (4.01); pH 2 294 (3.94). Mass spectrum, m/z (I, %): 320 (12), 277 (27), 276 (28), 227 (15), 201 (12), 200 (18), 194 (100), 172 (7), 167 (9), 157 (8), 105 (54), 104 (22), 91 (80), 77 (56). Found: C 67.3; H 5.2; N 17.4%. $C_{18}H_{16}N_4O_2$. Calculated: C 67.5; H 5.0; N 17.5%. Also obtained was 10 mg (10%) of the original 1-methyluracil.

B. The uracil (I) and the chloride (II) were first dried over P_2O_5 *in vacuo* for 48 h at 20°C. To a solution of 252 mg of (I), A2 moles in 10-12 ml of dry DMF was added with stirring 70 mg of NaH (2.5 mmoles, 80% suspension in mineral oil), the mixture stirred for 0.5 h at 20°C until evolution of hydrogen ceased, and to the resulting suspension was added all at once with vigorous stirring a solution of 520 mg of (II) (2.2 mmoles) in 10 ml of DMFA. The mixture darkened immediately, and was stirred for 1-1.5 h at 20°C, the solvent removed under reduced pressure to dryness, and the residue subjected to column chromatography. Elution was carried out with benzene, benzene–ethyl acetate (1:1), ethyl acetate, and system A to give 420 mg (65.7%) of the uracil (III), R_f 0.58, 70 mg (27.7%) of the uracil (I), R_f 0.4, and 31 mg (4.5%) of the pyrimidine (IV), R_f 0.3 (system A).

C. To a mixture of 194 mg (1.5 mmoles) of (I) and 711 mg (3 mmoles) of (II) previously dried in an oil-pump vacuum over P_2O_5 (48 h, 20°C†) were added 80 ml of benzene and 5 ml of Et_3N. The mixture was boiled under reflux for 20-30 h, the solvent removed, and the residue chromatographed on a column, eluting successively with benzene, benzene–ethyl acetate (1:1), and system A to give 377.4 mg (78.6%) of (IV), R_f 0.3, and 24.5 mg (12.5%) of (I), R_f 0.4 (system A).

6-Methyl-1,3-diphenyl-5,6-dihydro-5-oxopyrimido[4,3-c]triazolium Chloride (VII). To a solution of 280 mg (0.87 mmole) of (III) in 10 ml of ethanol was added 1.5 ml of 2 N HCl, and the solution boiled under reflux on the water bath for 1 h. The solvent was then removed, and the residue dried by evaporating with 3 × 5 ml of ethanol, finally in an oil-pump vacuum. It was then dissolved in 15 ml of ethanol, and dry ether added until no more solid separated, to give 294 mg (100%) of (VII), colorless crystals. A second reprecipitation gave 223 mg (76%) of analytically pure material, R_f 0.33 (system C), mp 163 and 204-205°C. IR spectrum (KBr): 1750 ($C_{(2)}$=O), 1620 (C=C), 1595 cm^{-1} (C=N). UV spectrum (ethanol), λ_{max}, nm (log ε): 314 (4.07), 268 (4.12); fluorescence spectrum: excitation, λ_{max} 320 nm, λf_{max} 414 nm, quantum yield 30% (relative to fluorescein. Found: C 62.0; H 5.4; Cl 9.8; N 14.9%. $C_{18}H_{15}ClN_4O \cdot C_2H_5OH$. Calculated: C 62.4; H 5.6; Cl 9.2; N 14.6%.

Acid Hydrolysis of (IV). A mixture of 80 mg (0.25 mmole) of (IV), 2 ml of 2 N HCl, 1 ml of ethanol, and 78 mg (0.37 mmole) of benzalacetophenone was heated in a sealed ampu for 24 h at 100°C, then cooled, evaporated to dryness under reduced pressure, 1 ml of glacial acetic acid added, and the mixture boiled under reflux for 1 h. The acetic acid was then distilled off, and the residue chromatographed on a column. Elution with benzene–hexane (10:1, then 5:1) followed by benzene, benzene–eth-l acetate (1:1), and system A gave 24.4 mg (30%) of starting material (IV) [R_f 0.3 (system A)], 11.7 mg (54%) of (I) [R_f 0.4 (system A), mp 242°C], 13.3 mg

*Here and subsequently, I is given as a percentage of the strongest peak.
†Glassware was dried at 170°C and cooled in a desiccator over P_2O_5. Failure to observe strictly anhydrous conditions reduces the yield of (IV) to 33-35%.

(63%) of benzoic acid [R_f 0.5 (benzene–ethyl acetate, 1:1), mp 122°C], and 8 mg (16%) of 1,3,5-triphenylpyrazoline [R_f 0.9 (benzene–heptane, 5:1)]. Mass spectrum, m/z (I, %): 1,3,5-triphenylpyrazoline: 298 (100), 296 (64), 221 (3), 194 (6), 149 (10), 105 (10), 91 (36), 77 (22); uracil (I): 126 (100), 83 (76), 55 (63); benzoic acid: 122 (61), 105 (100), 77 (78), 44 (68).

1,3-Diphenyl(4H)-1,2,4-triazol-5-one (VIII). To a solution of 80 mg (0.25 mmole) of (III) in 2.25 ml of ethanol was added 0.5 ml (0.5 mmole) of 1 N NaOH, the mixture stirred for 0.5 h at 20°C, 0.25 ml of 2 N HCl. added, and the solid filtered off, washed with water, dried, and crystallized from ethanol to give 44.1 mg (74.5%) of the triazolone (VIII), mp 240°C Mass spectrum, m/z (I, %): 237 (90), 118.5 (8), 105 (8), 103 (64), 91 (100), 77 (72). This compound (VIII) gave no depression of melting point with an authentic sample, and their IR spectra were identical.

5-[2-(N-Methyl-N-ethoxycarbonylamino)vinyl]-1,3-diphenyl-1,2,4-triazole (X). A. To 300 mg (0.9 mmole) of (III) was added 20 ml of a mixture of Et_3N and ethanol (1:1), and the mixture boiled under reflux for 60 h, until the starting material (III) was no longer present (TLC), and it was then evaporated, chromatographed on a column, and eluted with benzene–ethyl acetate (continuous gradient) to give 70 mg (32.8%) of the triazolone (VIII), R_f 0.33 (system B) and 162 mg (51.7%) of the triazole (X) (system B), colorless liquid, readily miscible with organic solvents. IR spectrum (CCl_4): 1700 (C=O), 1642 (C=C), 1600 cm^{-1} (C=N). UV spectrum ethanol), λ_{max}: 257 nm. Mass spectrum, m/z (I, %): 348 (98), 303 (3), 275 (48), 221 (25), 194 (17), 91 (100), 77 (13).

B. To a solution of 202 mg (0.6 mmole) of (VII) in 2 ml of water and 1 ml of ethanol was added 0.6 ml of 1 N NaOH at 20°C. After 10 min, the mixture was evaporated, 3 ml of water added, and extracted with benzene (3 × 5 ml). The benzene extracts were combined, washed with water (3 ml), evaporated, and dried in an oil-pump vacuum at 20°C to give 165.9 mg (79.4%) of (X), R_f 0.6 (system B), identical with the material obtained in the previous perparation in respect of its IR and mass spectra.

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REACTION OF DIAROYLETHYLENES WITH Ortho-PHENYLENEDIAMINE AND ITS DERIVATIVES

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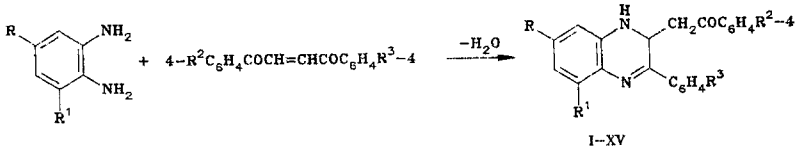
Derivatives of 1,2-dihydroquinoxaline were synthesized. The direction of the reaction of unsymmetrical diaroylethylenes with o-phenylenediamine was shown by chemical and spectral methods and the reaction mechanism was discussed.

A number of studies have been devoted to the reaction of o-phenylenediamine (PDA) with dibenzoylethylene (DBE) [1-5] but only Bass et al. [5] convincingly demonstrated that the products formed upon heating PDA and DBE at reflux in glacial acetic acid are 1-(2-aminophenyl)-2,5-diphenylpyrrole, 2-phenylquinoxaline, and 2-phenacylidene-3-phenyl-1,2-dihydroquinoxaline. Brindra and LeGoff [2] and Trattner et al. [3, 4] carried out the reaction under milder conditions (in ethanol) and obtained only 2-phenylquinoxaline, while Bass et al. [5] subsequently managed to isolate the intermediate of this synthesis, which was found to be 2-phenacyl-3-phenyl-1,2-dihydroquinoxaline.

In the present communication, we studied the controlled formation of 1,2-dihydroquinoxaline in the reactions of derivatives of PDA and DBE.

Symmetrically substituted DBE ($R^2 = R^3$) and PDA even upon heating at reflux for 10 min in methanol form the desired products I, III, VI, VIII, and XI in good yields (Table 1). Under these conditions, the other diketones form dihydroquinoxalines only in trace amounts since the secondary elimination of the acetophenone fragment leads to 2-arylquinoxalines as the major reaction products. An exception was found for VII, which was obtained in 45% yield. The same results are obtained when the reaction is carried out at room temperature. On the other hand, stirring of benzene solutions of the starting compounds at 40-50°C for 3-4 h gave dihydroquinoxalines I-XV in good yields, although the formation of small amounts of 2-arylquinoxalines occurs under these conditions. This secondary reaction is especially pronounced in the synthesis of IV and X.



I—XI R=H; XII—XV R=Cl; I—XIII R^1=H; XIV—XV R^1=Cl; I R^2=R^3=H; II R^2=H, R^3=CH_3; III R^2=R^3=CH_3; IV R^2=Cl, R^3=H; V R^2=Cl, R^3=CH_3; VI R^2=R^3=Cl; VII R^2=Br, R^3=H; VIII R^2=R^3=Br; IX R^2=Br, R^3=CH_3; X R^2=NO_2, R^3=H; XI R^2=R^3=NO_2; XII, XIV R^2=R^3=H; XIII, XV R^2=R^3=CH_3

The formation of I-XV was shown by IR, UV, PMR, and mass spectroscopy and supported by the nitrogen content determined. The purity of these compounds was also indicated by thin-layer chromatography (see Tables 1-4). We should note that the formation of two isomeric structures is possible in the reactions of unsymmetrical diaroylethylenes ($R^2 \neq R^3$) with PDA. Isomers may also be obtained in the synthesis of XII-XV. Thus, an important problem was resolution of the question of the direction of the synthesis of II, IV, V, VII, IX, X, and XII-XV.

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