Experimental

A mixture of 0.1 mole imidazole, 0.15 mole aryl bromide, 13 g powdered K_2CO_3, and 0.6 g cuprous bromide was refluxed for 30 hr, cooled, filtered, the filtrate made acid, the nitrobenzene steam-distilled off, and the solution left neutralized. The N-arylimidazole base was extracted with $CHCl_3$, and purified by distilling under reduced pressure, or by recrystallization (table).

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PYRIMIDINES

VI. Synthesis and Some Reactions of 2-Diazoacetyl-4, 6-diphenylpyrimidine*

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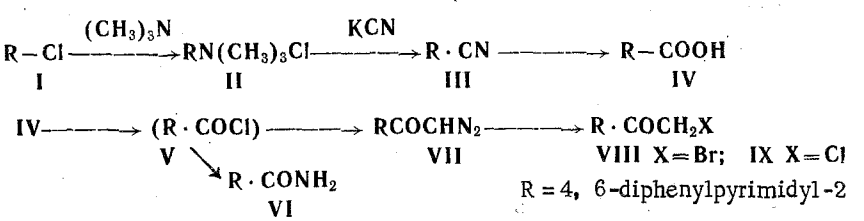
2-Diazoacetyl-4, 6-diphenylpyrimidine is prepared from 2-chloro-4, 6-diphenylpyrimidine via the nitrile and the corresponding acid, and it is readily converted to 2-bromoacetyl and 2-chloroacetyl-4, 6-diphenylpyrimidine. It was not possible to bring about the Wolff reaction.

Diazoketones are quite reactive compounds, and are often used as starting materials for synthesizing various compounds. However, only a few diazoketones of the pyrimidine series are known, and they all have the grouping $COCHN_2$ at position 4 or 5 [2, 3]. The literature does not contain any discussion of the problem of preparing 2-diazoacetylpyrimidines, or of their reactions.

It was of interest to investigate the possibility of obtaining 2-diazoacetylpyrimidines from the readily accessible 2-hydroxy derivatives, convertible in high yield to 2-chloropyrimidines [4]. Usually diazoketones are prepared by reacting acid chlorides with diazomethane. We have synthesized 4, 6-diphenylpyrimidine-2-carboxylic acid (IV) from 2-chloro-4, 6-diphenylpyrimidine (I) in the way described in [5].



The acid chloride can be prepared by treating acid IV with thionyl chloride or phosphorus pentachloride. It is unnecessary to isolate the acid chloride V for the further reactions. Its formation can be proved, and its quality assessed, by treating the impure acid chloride V with aqueous ammonia, to give 4, 6-diphenylpyrimidine-2-carboxamide (VI) in over 90% yield, so here V is pure enough for preparative purposes. Such a product was reacted with diazomethane to give 2-diazoacetylpyrimidine (VII). However, it did not prove possible to obtain VII analytically pure, but it was quite pure enough for synthetic work, judging by its reactions with hydrochloric and hydrobromic acids. In that way the hitherto unknown 2-bromoacetyl (VIII) and 2-chloroacetyl-4, 6-diphenylpyrimidine (IX) were synthesized.

One of the most interesting reactions of diazoketones, the Wolff rearrangement, gives unsatisfactory yields or does

* For Part V see [12].

not take place at all with nitrogen ring compounds [6]. Attempts to prepare acid derivatives from diazoketone VII under various conditions (action of ammonia solution of silver salt, action of ethanol in the presence of silver of copper oxide) gave no positive result.

Experimental

Melting points were determined with a Kofler block, IR spectra with a UR-10 spectrophotometer, the compounds being tabletted with KBr (concentration 0.5%).

Trimethyl (4, 6-diphenylpyrimidyl-2) ammonium chloride (II). This was synthesized from 2-chloro-4, 6-diphenylpyrimidine and trimethylamine by the method of [7], yield, 85-100%, mp 168-172° in a sealed capillary (reprecipitated from EtOH with Et_2O). Found: Cl 10.6, 10.5%. Calculated for $C_{19}H_{20}ClN_3$: Cl 10.9%.

2-Cyano-4, 6-diphenylpyrimidine (III). 9.6 g dry technical KCN was dissolved in 210 g dry acetamide, stirred and kept at 140-150°, the mixture cooled to 100-105°, and 24 g II added in small portions over 5-10 min. Then the reactants were stirred for 30 min at the same temperature, cooled, treated with 250 ml warm water (30-40°), the precipitate filtered off, washed with water, and dried in a vacuum-desiccator. Yield of III, 18.2 g (96.5%), mp 195-196° (ex benzene). Found: C 79.7, 79.3; H 4.69, 4.50; N 16.6, 16.7%. Calculated for $C_{17}H_{11}N_3$: C 79.4; H 4.31; N 16.3%.

Using pure KCN it could also be obtained in the same yield by the method of [5]. It should be mentioned that no absorption band corresponding to the CN groups could be observed in the IR spectrum of III. A similar phenomenon has also been observed for other compounds [8].

4, 6-Diphenylpyrimidine-2-carboxylic acid (IV). 17 g nitrile III was refluxed with 300 ml 10% KOH for 4 hr, then active charcoal added to the hot solution, and the whole filtered. After cooling, part of the potassium salt of IV was precipitated, the suspension was acidified with concentrated hydrochlorid acid and cooled with ice water. The acid which separated was filtered off, washed with water, and dried, first in a vacuum-desiccator, then at 90-100°. Yield of IV, 16.7 g, mp 168-170.5° (ex EtOH). Found: C 74.0, 74.2; H 4.37, 4.71; N 10.4, 10.4%. Calculated for $C_{17}H_{12}N_2O_2$: C 73.9; H 4.38; N 10.1%. IR spectrum: 1715 cm^{-1} (C=O in acids). Here and below bands are assigned according to the data of [9].

Amide (VI). 0.5 g acid III, 3.5 ml $SOCl_2$, and a few drops of dimethylformamide catalyst [10] were refluxed in 40 ml EtOH for 1 hr. The solvent was distilled off under reduced pressure, and the acid chloride (V) remaining held under vacuum (2-4 mm) for 30 min to remove volatiles. V was dissolved in 40 ml dry benzene, and 50 ml cold concentrated aqueous ammonia added with stirring, after which the mixture was left for 1 hr, then the precipitate was filtered off, washed with water, and dried in a vacuum-desiccator. Yield of VI, 0.45 g (90.5%), mp 226-228° (ex EtOH). Found: C 74.2, 74.4; H 4.92, 4.88; N 15.5, 15.4%. Calculated for $C_{17}H_{13}N_3O$: C 74.2; H 4.76; N 15.3. IR spectrum: 1658 cm^{-1} (C=O in amides).

2-Diazoacetyl-4, 6-diphenylpyrimidine (VII). A benzene solution of the acid chloride V, prepared as in the experiment above, was slowly dropped into an ether solution of CH_2N_2 (4 mole CH_2N_2 per 1 mole of acid), with stirring, at a temperature of 0-5°, after which the solution was left overnight, and after cooling with ice water, the precipitate was filtered off. The diazoketone was obtained as a finely-divided white crystalline precipitate, yield, 65-70%, mp 145-155° (decomp). IR spectrum: 1633 cm^{-1} (C=O in diazoketones) and 2112 cm^{-1} (diazo group) [11]. The product was pure enough for preparative purposes. Diazoketone VII was moderately soluble in ether, dioxane, and EtOH. It quickly decomposed when stored in the light.

2-Bromoacetyl-4, 6-diphenylpyrimidine (VIII). A few drops of hexanol were added to 40-50 ml HBr (40%) to lessen foaming, then 2.2 g diazoketone was added with stirring. After being left for 90 min the reaction products were diluted with water, and neutralized with 5% Na_2CO_3. Then the precipitate was filtered off, and dried in a vacuum-desiccator, to give 2.4 g (93%) bromoketone, mp 163-165° (ex Me_2CO). Found: C 60.7, 61.0; H 3.94, 3.84; Br 22.3, 22.4; N 8.25, 8.12%. Calculated for $C_{18}H_{13}BrN_2O$: C 61.2; H 3.71; Br 22.6; N 7.92%. IR spectrum: 1734 cm^{-1} (C=O in ketones).

2-Chloroacetyl-4, 6-diphenylpyrimidine (IX). 2.5 g VII was stirred with 40-50 ml ether, and 40 ml concentrated hydrochloric acid added dropwise with ice-water cooling. After stirring for 2.5 hr, the reaction products were worked up as in the preceeding experiment, to give an 80-85% yield of IX, mp 160-162.5° (ex Me_2CO). Found: C 70.1, 70.2; H 3.98, 3.98; Cl 11.7, 11.5; N 8.92, 9.13%. Calculated for $C_{18}H_{13}ClN_2O$: C 70.0; H 4.24; Cl 11.5; N 9.06%. IR spectrum: 1750 cm^{-1} (C=O in ketones).

*For Part V see [12].

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LETTERS TO THE EDITOR

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THE TAUTOMERISM OF 5-MERCAPTO-2-ACETYLFURAN

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By acidifying the sodium salt of 5-mercapto-2-acetylfuran (I) [1] with formic acid, we obtained for the first time 5-mercapto-2-acetylfuran (II), yellow crystals, mp 121° (ex hexane). Found: C 50.78, 51.04; H 3.83, 4.27; S 22.13%. Calculated for $C_6H_6O_2S$: C 50.68; H 4.25; S 22.55%. The IV spectrum of II was determined in octane, dioxane, and methanol. For comparison purposes, the spectrum of 5-methylmercapto-2-acetylfuran (III) was observed in the same solvents.

The spectrum of III exhibits a band with λ_{max} 302 mμ, lg ε 4.09 (in octane). With the other solvents there is a bathochromic shift of 5-10 mμ. The spectrum of II has two absorption zones, an intense band with λ_{max} 270 mμ and a less intense wide band in the 300 mμ region. Both bands vanish in alcoholic alkali, and one with λ_{max} 380 mμ appears. A similar band is found in the spectrum of the sodium salt of I (obtained by crystallization from water, after evaporating an aqueous solution under reduced pressure; yellow crystals with a violet reflex, mp 180°, decomp.)

These results make it possible to assume that, in solution, II exists as two tautomers A and B

A B

with tautomer B, which absorbs in the 270 mμ region, prevailing. We assign the band in the 300 mμ region to absorption by the thiol form A. In alkali both tautomers are converted into the sodium salt I.

We are continuing our research on the subject.

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