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NEW COMPOUNDS

Syntheses of New 1-Substituted 3,3-Diphenyl-4-(2-heteroaryl)- and 4-(1- and 2-Naphthyl)-2-azetidinones

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The reactions of 2-diazo-1,2-diphenylethanone with imines of pyrrole-2-aldehyde, thiophene-2-aldehyde, furan-2-aldehyde, and 1- and 2-naphthaldehyde give new azetidinones in excellent yields. 1,1′,4,4′-Tetraphenyl-2,2′-azinodiethanone is obtained as a minor product in these reactions.

Introduction

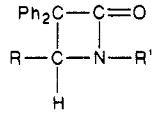
Several azetidinones having antibacterial, herbicidal, and antiinflammatory properties and activity on the central nervous system have been reported (*1*, *2*). This prompted us to investigate the reaction of 2-diazo-1,2-diphenylethanone (**1**), a precursor of diphenylketene, with *N*-2-heteroarylideneamines (**2a–g**) and *N*-1- and 2-naphthylideneanilines (**2h,i**) which resulted in the syntheses of 1-substituted 3,3-diphenyl-4-(2-heteroaryl)-2-azetidinones (**3a–g**) and 1,3,3-triphenyl-4-(1-naphthyl)- and 4-(2-naphthyl)-2-azetidinones (**3h,i**) in very good yields together with 1,1′,4,4′-tetraphenyl-2,2′-azinodiethanone (**4**) (1.5–5%). The pharmaceutical screening of these azetidinones is in progress and the results will be published elsewhere.

The reactions of diphenylketene with pyrrole and benzimidazole have been reported to occur on enamine double bond and N–H bond, respectively (**3**, **4**). Thus, the reaction of **1** with *N*-2-pyrrolideneanilines (**2a–c**) reveals the marked selective reactivity of the imino group toward diphenylketene as compared to N–H of pyrrole ring.

Results and Discussion

The azetidinone **3e** was also obtained in the photochemical reaction (irradiation of an equimolar mixture in dry benzene in a nitrogen atmosphere with UV light from a 200-W Hanovia lamp) of **1** and **2e** but the yield was lower (64%) than that obtained (82%) in the thermal reaction. The physical data of the synthesized compounds are given in Table I. The probable reaction sequence is shown in Scheme I.

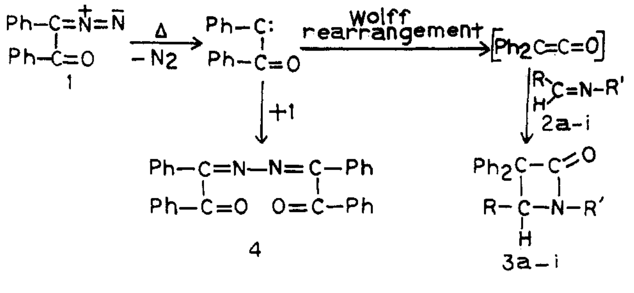
Table I. Physical Data of 1-Substituted 3,3-Diphenyl-4-(2-heteroaryl)- and 4-(1- and 2-Naphthyl)-2-azetidinones



compd no.	R	R′	mol formula[a]	mp, °C	yield, %
3a	2-pyrryl	C_6H_5	$C_{25}H_{20}N_2O$	157	72
3b	2-pyrryl	*p*-$C_6H_4{\cdot}CH_3$	$C_{26}H_{22}N_2O$	152	54
3c	2-pyrryl	*p*-$C_6H_4{\cdot}Cl$-*p*	$C_{25}H_{19}N_2OCl$	159	56
3d	2-thienyl	$CH(C_6H_5)_2$	$C_{32}H_{25}NOS$	208	90
3e	2-thienyl	*p*-$C_6H_4{\cdot}CH_3$	$C_{26}H_{21}NOS$	170	82
3f	2-thienyl	*p*-$C_6H_4{\cdot}Cl$	$C_{25}H_{18}NOSCl$	158	86
3g	2-furyl	$CH(C_6H_5)_2$	$C_{32}H_{25}NO_2$	205	91
3h	1-naphthyl	C_6H_5	$C_{31}H_{23}NO$	165	90
3i	2-naphthyl	C_6H_5	$C_{31}H_{23}NO$	190	92

[a] The microanalyses were in fair agreement with the calculated values (C, ±0.4, H and N, ±0.3).

Scheme I



Experimental Section

Melting points have been determined in capillaries on Büchi melting point apparatus and are uncorrected. NMR spectra were recorded with a Varian A-60D spectrometer, with tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer 720 spectrophotometer and UV spectra on a Cary-14 or Beckman Model DB-G grating spectrophotometer. Mass spectra were obtained on a CEC 110 double-focusing, high-resolution mass spectrometer.

***Materials*.** The aldehydes were procured from EGA Chemicals, West Germany, and the anilines from BDH, India. 2-Diazo-1,2-diphenylethanone (**1**) and imines **2a–i** were prepared by reported methods (*5–8*).

***Preparation of 2-Azetidinones 3a–i*.** A mixture of 0.01 mol of **1** and 0.01 mol of an imine **2a–i** was heated to reflux in 80 mL of dry benzene (thiophene free) for 6 h under a stream of nitrogen. The reaction mixture was kept overnight. The solvent was removed on rotatory evaporator and residual matter was crystallized from ethanol to give 2-azetidinones **3a–i**. The mother liquor after evaporation of solvent under reduced pressure and recrystallization of residual matter from *n*-hexane–ethanol (1:1) gave a yellow crystalline compound identified as 1,1′,4,4′-tetraphenyl-2,2′-azinodiethanone (**4**, 1.5–5%) by comparison (mix mp and CO-IR) with an authentic sample (**9**).

The spectral data of the azetidinones **3a–i**, prepared according to the above method, are as follows:

***1,3,3-Triphenyl-4-(2-pyrryl)-2-azetidinone (3a)*.** UV(EtOH, nm): 242(ϵ 2.7 × 10^4), 290(ϵ 0.6 × 10^4); IR(Nujol, cm^{-1}): 1735(C=O, β-lactam) and 3410(NH, pyrrole); NMR($CDCl_3$, δ ppm): 7.63(m, 2 H, aromatic); 7.06(m, 13 H, aro-

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matic); 6.31(m, 3 H, 3 CH, pyrrole ring); 5.86(bs, 1 H, NH, D_2O exchangeable); 5.73(s, 1 H, CH, β-lactam ring).

1-(4-Methylphenyl)-3,3-diphenyl-4-(2-pyrryl)-2-azetidinone (3b). UV(EtOH, nm): 244(ε 2.3 × 10^4), 295(ε 0.3 × 10^4); IR(Nujol, cm^{-1}): 1740(C=O, β-lactam) and 3410(N–H, pyrrole); NMR($CDCl_3$, δ ppm): 7.65(m, 2 H, aromatic); 7.10(m, 12 H, aromatic); 6.25(m, 3 H, three CH, pyrrole ring); 5.78(bs, 1 H, NH, D_2O exchangeable); 5.60(s, 1 H, CH, β-lactam ring); 2.25(s, 3 H, CH_3).

1-(4-Chlorophenyl)-3,3-diphenyl-4-(2-pyrryl)-2-azetidinone (3c). UV(EtOH, nm): 255(ε 2.4 × 10^4), 295(ε 0.4 × 10^4); IR(Nujol, cm^{-1}): 1745(C=O, β-lactam) and 3410(N–H, pyrrole); NMR($CDCl_3$, δ ppm): 7.55(m, 2 H, aromatic); 7.02(m, 12 H, aromatic); 6.22(m, 3 H, 3 CH, pyrrole ring); 5.72(bs, 1 H, NH, D_2O exchangeable); 5.63(s, 1 H, CH, β-lactam ring).

1-Diphenylmethyl-3,3-diphenyl-4-(2-thienyl)-2-azetidinone (3d). UV(EtOH, nm): 254(ε 0.4 × 10^4); IR(Nujol, cm^{-1}): 1740(C=O, β-lactam); NMR($CDCl_3$, δ ppm): 7.00(m, 23 H, aromatic); 5.58(s, 1 H, CH, benzhydryl); 5.46(s, 1 H, CH, β-lactam ring); Mass: *m/z* 471(M^+, 17), 304(16), 277(24), 276(43), 262(100), 261(31), 209(14), 194(98), 167(99).

1-(4-Methylphenyl)-3,3-diphenyl-4(2-thienyl)-2-azetidinone (3e). UV(EtOH, nm): 250(ε 2.6 × 10^4); IR(Nujol, cm^{-1}): 1750(C=O, β-lactam); NMR($CDCl_3$, δ ppm): 7.41(m, 17 H, aromatic); 5.91(s, 1 H, CH, β-lactam ring); 2.25(s, 3 H, CH_3).

1-(4-Chlorophenyl)-3,3-diphenyl-4-(2-thienyl)-2-azetidinone (3f). UV(EtOH, nm): 254(ε 2.8 × 10^4); IR(Nujol, cm^{-1}): 1740(C=O, β-lactam); NMR($CDCl_3$, δ ppm): 7.16(m, 17 H, aromatic); 5.93(s, 1 H, CH, β-lactam ring).

1-Diphenylmethyl-3,3-diphenyl-4-(2-furyl)-2-azetidinone (3g). UV(EtOH, nm): 258(ε 0.1 × 10^4); IR(Nujol, cm^{-1}): 1745(C=O, β-lactam); NMR($CDCl_3$, δ ppm): 7.16(m, 21 H, phenyl and furan CH_{α}); 5.98(m, 1 H, furan CH_{β}); 5.80(bs, 2 H, furan CH_{β}, and benzhydryl); 5.23(s, 1 H, CH, β-lactam ring).

1,3,3-Triphenyl-4-(1-naphthyl)-2-azetidinone (3h). UV-(EtOH, nm): 254(ε 2.8 × 10^4), 288(ε 1.4 × 10^4), 300(ε 0.9 × 10^4); IR(Nujol, cm^{-1}): 1740(C=O, β-lactam); NMR($CDCl_3$, δ ppm): 7.41(m, 22 H, aromatic); 6.50(s, 1 H, CH, β-lactam ring).

1,3,3-Triphenyl-4-(2-naphthyl)-2-acetidinone (3i). UV-(EtOH, nm): 252(ε 1.8 × 10^4), 290(ε 0.2 × 10^4), IR(Nujol, cm^{-1}): 1740(C=O, β-lactam); NMR($CDCl_3$, δ ppm): 7.25(m, 22 H, aromatic); 5.86(s, 1 H, CH, β-lactam ring).

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Registry No. **1**, 3469-17-8; **2a**, 4089-09-2; **2b**, 14479-37-9; **2c**, 51305-60-3; **2d**, 105090-43-5; **2e**, 5918-69-4; **2f**, 13533-31-8; **2g**, 54220-18-7; **2h**, 890-50-6; **2i**, 18263-29-1; **3a**, 105090-44-6; **3b**, 105090-45-7; **3c**, 105090-46-8; **3d**, 105090-47-9; **3e**, 105090-48-0; **3f**, 105090-49-1; **3g**, 105090-50-4; **3h**, 105090-51-5; **3i**, 105090-52-6; **4**, 3893-33-2.

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Phase-Transfer-Catalyzed Preparation of Triaryl Phosphorothionates

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Triaryl phosphorothionates have been prepared in good yield from thiophosphoryl chloride and three equivalents of a phenol by a phase-transfer-catalyzed process.

Triaryl phosphates are commonly prepared by treatment of phosphorus oxychloride ($POCl_3$) with three equivalents of a phenol (*1*). A number of effective catalysts have been identified to promote this reaction, such as halide salts of calcium, magnesium, and aluminum (*2*). This contrasts the behavior of thiophosphoryl chloride ($PSCl_3$) which does not react with phenol even under quite forcing conditions. In the presence of aluminum chloride, phenol and thiophosphoryl chloride remained unchanged after several hours at reflux. Triaryl phosphorothionates have been prepared from $PSCl_3$ and three equivalents of a phenol in the presence of an acid acceptor such as triethylamine (*3*) or by the oxidation of a triaryl phosphite with sulfur (*4*). This appeared to constitute a problem for us, since we were in need of large amounts of a variety of pure triaryl phosphorothionates in connection with another study.

Triaryl phosphates and diaryl benzenephosphorothionates have very recently been prepared by the phase-transfer-catalyzed reaction of phenols with $POCl_3$ (*5*, *6*) and $C_6H_5PSCl_2$ (*7*), respectively. We now wish to report a general synthesis of triaryl phosphorothionates by phase-transfer catalysis, which is both simple and effective (eq 1).

$$\underset{1}{3HOAr} + \underset{2}{PSCl_3} \xrightarrow[CH_2Cl_2,\ PTC]{NaOH/H_2O} \underset{3}{(ArO)_3P{=}S} + 3NaCl \qquad (1)$$

As can be seen from Table I, the isolated yields obtained for this process were generally in the 80 percentile range. The products were identified by their spectral data (see Table II), and melting points where known. For all new compounds satisfactory high-resolution mass spectral data as well as correct elemental analyses were obtained. The tris(*p*-chloro-

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