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REACTION OF γ-BROMODIPNONE WITH HYDRAZINES

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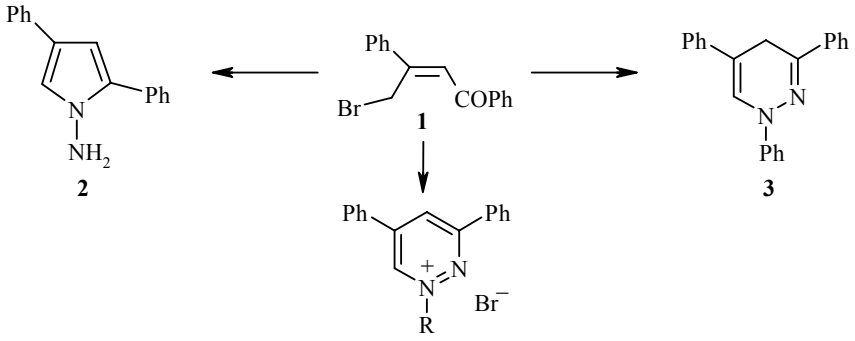
4-Bromo-1,3-diphenyl-2-buten-1-one (γ-bromodipnone) (**1**) reacts readily with amines to give N-substituted derivatives of 2,4-diphenylpyrrole [1,2]. The reaction of hydrazine with γ-halocarbonyl compounds gives, depending on their structure, derivatives of N-aminopyrrole [3] or hydrazine [4]. We have observed that on heating γ-bromodipnone **1** with hydrazine hydrate in ethanol 2,4-diphenyl-1H-pyrrol-1-amine (**2**) was formed, while with arylhydrazines under the same conditions 1-aryl-1,4-dihydropyridazine or 1-aryl-1-pyridazilium salts formed, the nature of the products depending on the nature of the substituents in the benzene ring. For example, 1,3,5-triphenyl-1,4-dihydropyridazin (**3**) was formed when a mixture of **1** and phenylhydrazine was boiled for a short time (15 min), but with 1-(2methylphenyl)- and 1-(3-methylphenyl)hydrazines the products were 1-aryl-3,5-diphenyl-1-pyridazinium bromides **4a,b**. The structures of the reaction products **2-4** were established by spectroscopic methods. Conclusive evidence of the structures of compounds 3 and 4 were obtained using homonuclear (COSY and NOESY) and heteronuclear (HMBC and HMQC) two dimensional correlation NMR spectroscopy.



2 **1** **3** **4a,b**

4 a R = 2-MeC_6H_4, **b** R = 3-MeC_6H_4

^{1}H NMR spectra of DMSO-d_6 solutions with TMS as internal standard were recorded with a Varian Mercury 400 (400 MHz) machine.

2,4-Diphenyl-1H-pyrrol-1-amine (2). A mixture of □-bromodipnone (1 g, 3.32 mmol) and hydrazine hydrate (2.6 ml 80%) in ethanol (50 ml) was heated until the □-bromodipnone had dissolved completely and the mixture was then kept for 10 h at room temperature. The precipitate was filtered off and washed with ethanol.

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Yield: 0.47 g (61%); mp 143-145°C (from 2-propanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.70 (2H, d, ^3J = 8.0, H-2',6'), 7.47 (2H, d, ^3J = 8.0, H-2",6"); 7.34 (2H, d, ^3J = 8.0, H-3',5'); 7.26 (2H, t, ^3J = 8.0, H-3",5"); 7.20 (1H, t, ^3J = 8.0, H-4'); 7.15 (1H, d, ^4J = 1.6, H-5); 7.07 (1H, t , ^3J = 8.0, H-4"); 6.46 (1H, d, ^3J = 1.6, H-3); 5.76 (2H, br. s, NH_2). Found, %: C 82.34; H 6.12; N 11.88. $C_{16}H_{14}N_2$. Calculated, %: C 82.02; H 6.02; N 11.96.

1,3,5-Triphenyl-1,4-dihydropyridazine (3). A mixture of g-bromodipnone (1 g, 3,32 mmol) and phenylhydrazine (0.33 ml, 3.32 mmol) was boiled for 15 min. The solvent was evaporated and the residue recrystallized from ethanol. Yield 0.63 g (61%); mp 131-133°C (from EtOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.00 (2H, d, ^3J = 8.0, H-2",6"); 7.72 (1H, s, H-6); 7.66 (4H, m, H-2',6',2"',6"'); 7.50-7.36 (7H, m, H-3',5',H-3"-H-5", H-3"',5"'); 7.24 (1H, t, ^3J = 8.0, H-4"') 7.04 (1H, t, ^3J = 8.0, H-4'); 3.64 (2H, s, $C_{(4)}H_2$). Found, %: C 85.41; H 5.93; N 8.99. $C_{22}H_{18}N_2$. Calculated, %: C 85.13; H 5.85; N 9.03.

1-Aryl-3,5-diphenyl-1pyridazinium bromides (4a,b). A mixture of 1-(2-methylphenyl)- or 1-(3-methylphenyl)hydrazine hydrochloride (0.53 g, 3.32 mmol) and $NaHCO_3$ (0.28 g, 3.32 mmol) was heated in ethanol (50 ml) for 10 min and the solid precipitate was filtered off. γ-Bromodipnone (1 g, 3.32 mmol) was added to the filtrate and the mixture was boiled for 30 min. The solvent was evaporated and the residue was recrystallized from AcOH.

Compound 4a. Yield 0.6 g (45%); mp 275-277°C (dec., from AcOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.59 (1H, s, H-6); 9.56 (1H, s, H-4); 8.42 (4H, m, H-2",6", H-2"',6"'); 7.97 (1H, d, ^3J = 8.0, H-6'); 7.70-7.56 (9H, m, H-3'-5', H-3"-5", H-3"'-5"'); 2.41 (3H, s, CH_3). Found, %: Br 19.85; N 6.94. $C_{23}H_{19}BrN_2$. Calculated, %: Br 19.81; N 6.95. C

Compound 4b. Yield 0.53 g (40%); mp 260-263°C (dec., from AcOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.59 (1H, s, H-6); 9.49 (1H, s, H-4); 8.43 (4H, m, H-2",6", H-2"',6"'); 8.14 (1H, s, H-2') 8.09 (1H, d, ^3J = 8.0, H-6'); 7.71-7.60 (8H, m, H-4',5', H-3"-5", H-3"'-5"'); 2.59 (3H, s, CH_3). Found, %: Br 19.79; N 6.93. $C_{23}H_{19}BrN_2$. Calculated, %: Br 19.81; N 6.95.

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