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SHORT COMMUNICATIONS

Reaction of 1-(4-Methylphenyl)-5-phenyl-2,3-dihydro-1*H*-pyrrole-2,3-dione with Tris(diethylamino)phosphine. A New Synthesis of 3,3′-Bipyrrolylidene-2,2′-dione Derivatives

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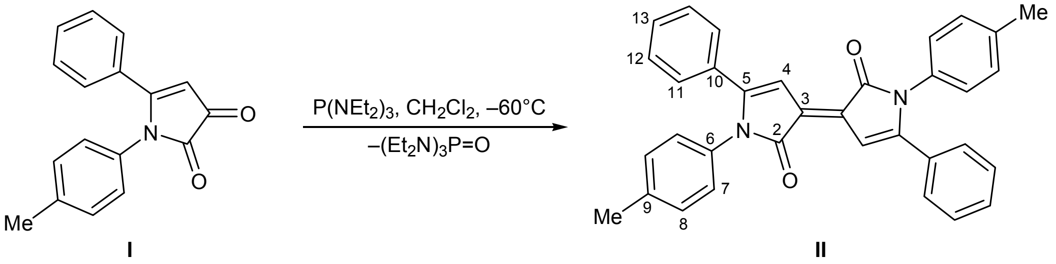
Heterocyclic α-diketones are used as starting materials for the synthesis of new heterocyclic compounds possessing useful properties, from those exhibiting specific biological activity to new functional materials [1–3]. A particular place is occupied by pyrrole-2,3-dione and 3,3′-bipyrrolylidene derivatives which have recently found increasing application in the preparation of synthetic analogs of natural chromophore systems [4], as well as in organic semiconducting and photovoltaic devices [5].

Up to now, several procedures have been reported for the synthesis of 3,3′-bipyrrolylidene-2,2′-diones from furan-2,3-dione derivatives [6, 7]. We previously showed that derivatives of another heterocyclic α-diketone, isatin, undergo mild deoxygenation by the action of tris(diethylamino)phosphine to give symmetrically substituted isoindigos in high yields [8–10].

The present communication reports on the reaction of tris(diethylamino)phosphine with 1-(4-methylphenyl)-5-phenyl-2,3-dihydro-1*H*-pyrrole-2,3-dione (**I**), which afforded 3,3′-bipyrrolylidene-2,2′-dione derivative **II** and hexaethyltriamidophosphate (CH_2Cl_2, δ_P 24 ppm). The presence of only one downfield signal at δ_C 170.14 ppm (d, $^3J_{CH}$ = 8.8 Hz) in the ^{13}C NMR spectrum of the product indicated that deoxygenation involved only the C^3=O carbonyl group.



I **II**

Our results suggest prospects in further development of this simple one-step synthesis of 3,3′-bipyrrolylidene-2,2′-dione derivatives.

1,1′-Bis(4-methylphenyl)-5,5′-diphenyl-1*H*,1′*H*-3,3′-bipyrrolylidene-2,2′-dione (II). A solution of 0.985 g of (3.8 mmol) 1-(4-methylphenyl)-5-phenyl-2,3-dihydro-1*H*-pyrrole-2,3-dione (**I**) [11] in 20 mL of anhydrous methylene chloride was cooled to –70°C, and 0.929 g (3.8 mmol) of tris(diethylamino)phosphine was added dropwise. During the addition, the originally red solution changed to dark violet. The mixture was allowed to warm up to room temperature and was kept for 8 h. The solvent was removed under reduced pressure (18 mm), and the residue (violet powder) was purified by column chromatography on silica gel using benzene as eluent. Yield 0.67 g (73%), mp >300°C. IR spectrum, ν, cm^{-1}: 1687, 1580, 1545, 1491, 1262, 1187, 1095, 1029, 802, 735, 696. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.29–7.04 m (9H, 4-H, 7-H, 8-H, 11-H, 12-H, 13-H), 2.22 s (3H, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (J, Hz) (the signal multiplicity in the proton-decoupled spectrum is given in parentheses): 170.14 d (s) (C^2, $^3J_{CH} = 8.8$), 128.76 d (s) (C^3, $^2J_{CH} = 2.6$), 103.73 d (s) (C^4, $^1J_{CH} = 182.7$), 151.87 m (s) (C^5), 135.00 m (s) (C^6), 126.69 d.d (s) (C^7, $^1J_{CH} = 162.1$, $^3J_{CH} = 7.3$), 131.11 d.m (s) (C^8, $^1J_{CH} = 158.8$), 136.66 m (s) (C^9, $^3J_{CH} = 5.5$), 130.46 m (s) (C^{10}, overlapped by a component of the C^8 signal), 127.47 d.d.d (s) (C^{11}, $^1J_{CH} = 161.0$, $^3J_{CH} = 6.6$, 5.9), 128.42 d.d (s) (C^{12}, $^1J_{CH} = 161.8$, $^3J_{CH} = 5.9$), 129.73 d.t (s) (C^{13}, $^1J_{CH} = 161.0$, $^3J_{CH} = 6.6$), 18.17 q (s) (CH_3, $^1J_{CH} = 127.3$). Found, %: C 82.30; H 5.02; N 5.37. $C_{34}H_{26}N_2O_2$. Calculated, %: C 82.57; H 5.30; N 5.66.

The ^1H, $^{31}P-\{^1H\}$, and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400 (^1H), 161.0 (^{31}P), and 150.9 MHz (^{13}C) from solutions in $CDCl_3$; the ^1H and ^{13}C chemical shifts were measured relative to the residual proton signal and carbon signal of the solvent. The IR spectrum was obtained on a Bruker Vector-22 instrument from a sample of **II** dispersed in mineral oil. The elemental composition was determined on a EuroVector 2000 CHNS-O analyzer.

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