

Notes

Michael-type Addition Reaction of Diisopropyl Azodicarboxylate to 1-Phenylpyrroles

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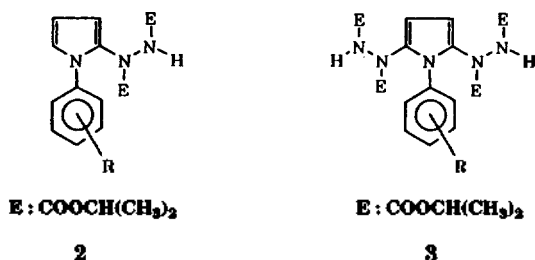
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Acyclic azodicarboxylate esters among acyclic azodicarboxylates have been used extensively as dienophiles.^{1,2} Among the diene systems examined, furan was the only heterocyclic aromatic compound which reacted with DADC (diethyl azodicarboxylate) to give a Diels-Alder adduct.³ The reactions of pyrrole and some of its derivatives with DADC have been suggested to produce no Diels-Alder adducts but 1:2 molar ratio Michael-type adducts. However, neither 1:1 adducts nor 1:2 adducts containing phenyl group have been obtained.⁴ To elucidate exact reactivity of pyrroles with azodicarboxylate ester, we have performed the reactions of 1-phenylpyrrole and some of its derivatives (1) with diisopropyl azodicarboxylate (DIPADC) in protic and aprotic solvents.

Results and Discussion

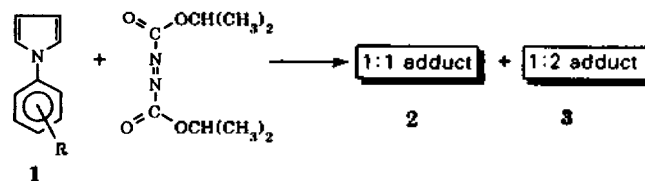
Most 1-phenylpyrroles examined in our laboratory gave 1:1 (2) and 1:2 (3) Michael-type adducts with DIPADC under the conditions specified in Table 1.

Instead of 1:2 Michael-type adducts from the reaction of pyrroles with DADC, adduct 2 and 3 were produced from the reaction with Michael-type addition of DIPADC at one or both α position of the pyrrole. This result indicates that DIPADC reacts more slowly with pyrroles than does DADC because of the bulky ester.⁵



The presence of a band at approximately 3300 cm⁻¹ in IR spectra of the adducts strongly suggests the presence of a secondary amine. Two distinctive bands at approximately 1745 and 1700 cm⁻¹ are consistent with two different carbonyl functions. Structure 3 shows that the ring and side chains are not conjugated. This is supported by the low λ_{\max} values which are in the range between 225 and 310 nm with most of the adducts. The NMR spectrum (CDCl₃, Me₄Si) of 1:1 adduct 2d shows 12 proton peaks corresponding to the diisopropyl group at δ 1.20 and double doublets indica-

Table 1. Yields and Reaction Conditions for Michael-Type Additions of Diisopropyl Azodicarboxylate to 1-Phenylpyrroles.

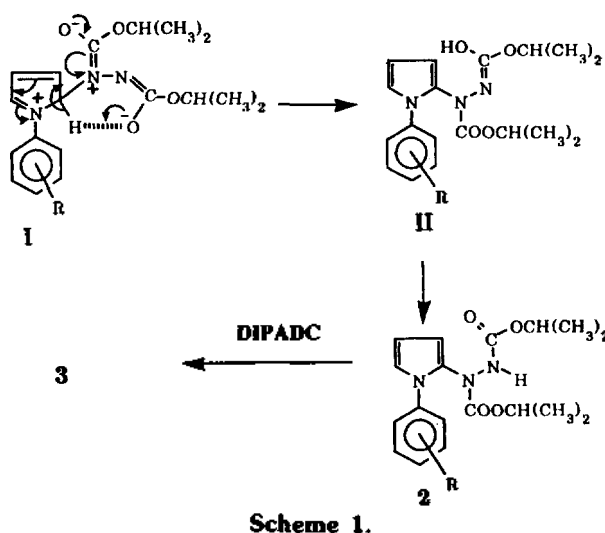


Phenyl pyrrole	R	Solvent (reflux, h)	Yield ^a (%)		mp. °C	
			2	3	2	3
1a	H	EtOH(12)	—	61	—	84-84.5
1b	<i>p</i> -OH	EtOH(14)	—	59	—	86-87
1c	<i>p</i> -F	Et ₂ O(80)	15	18	97-98	119-120
1d	<i>p</i> -Cl	EtOH(15)	20	45	90-92	121-122
		AcOH(2)	20	60		
		Et ₂ O(80)	16	20		
		Benzene(25)	5	31		
		1,4-Dioxane(25)	18	38		
		AcOH-EtOH(15)	23	38		
1e	<i>p</i> -Br	EtOH(20)	30	40	81-82	68-70
		Et ₂ O(80)	6	45		
1f	<i>p</i> -COCH ₃	EtOH(48)	26	38	122-123	96-97
1g	<i>p</i> -NO ₂	EtOH(90)	31	40	59-60	66-67
1h	<i>m</i> -F	Et ₂ O(80)	15	35	^{ab}	^{ab}
1i	<i>m</i> -Cl	Et ₂ O(80)	18	45	^{ab}	^{ab}
1j	<i>m</i> -Br	Et ₂ O(80)	20	52	^{ab}	^{ab}
1k	<i>m</i> -COCH ₃	EtOH(38)	34	45	97-98	79-81
1l	<i>m</i> -NO ₂	EtOH(40)	33	44	^{ab}	^{ab}

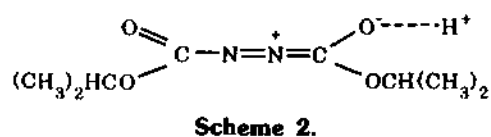
^aIsolated yield, ^boil

ting to the pyrrole C₄H at δ 6.30. The pyrrole C₃H and C₅H was observed at δ 6.45 and 6.70. Especially the NMR spectrum of 1:2 adduct 3d shows singlet of two protons (δ 6.30) corresponding to the pyrrole C₃H and C₄H, double triplets of 24 protons at δ 1.2 with $J=7.0$ Hz, double quartets of four protons indicating to the hydrogen of secondary carbon attached diisopropyl group at δ 4.9. Mass spectrum of 1:2 adduct 3d showed molecular ion peaks at m/e 581 (43%)

As shown in Table 1, the yield of the 1:2 adduct 3 varies depending upon solvents employed, reaction time, and substituents on the phenyl group. The reaction of *p*-chlorophenylpyrrole with DIPADC proceeded faster in EtOH and AcOH than in Et₂O and benzene. Also, in case of nitrophenylpyrroles (1 g, 1i) and acetylphenylpyrroles (1f, 1k), the reactions with DIPADC did not occur in Et₂O(>80h) but easily proceed to yield high yields in EtOH (30h~90h). Accordingly, the reactivity is considered to be better in the protic solvents (AcOH and ethanol) than in the aprotic solvents (ether and benzene) under the same reaction time. The yields of 2d and 3d for *p*-chlorophenylpyrrole are also better in the protic solvents (AcOH and ethanol) than in the aprotic solvents (ether and benzene).⁶ The addition of DIPADC to 1-phenylp-



Scheme 1.



Scheme 2.

pyrroles is considered initially to form a zwitterionic intermediate I (Scheme 1). An α hydrogen may then be transferred intramolecularly through a six-membered transition state in the aprotic solvent as shown in Scheme 1. The facile solvation or intermolecular protonation by the protic solvent may be an explanation for the better yield. Thus, in protic solvents, it is proposed that the protonated DIPADC (Scheme 2) formed by protonation carbonyl of oxygen of DIPADC facilitates nucleophilic attack of π electron of the pyrrole ring

Experimental Section

Melting points were determined on a Büchi 510 capillary melting point apparatus and uncorrected. Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer. Ultraviolet and visible spectra were recorded on a Shimadzu double-beam spectrophotometer. NMR spectra were recorded on a Varian EM 360-A spectrometer in CDCl_3 containing Me_4Si as an internal reference. Mass spectra were obtained by using a Finnigan model 3300 mass spectrometer.

Starting materials. DIPADC was distilled before use. 1-Phenylpyrroles were prepared by literature methods.^{7,8,9}

A typical method of preparation of the adducts in ether: 2-(*N,N'*-diisopropoxycarbonylhydrazinyl)-1-(*p*-chlorophenyl)pyrrole(2d) and 2,5-bis-(*N,N'*-diisopropoxycarbonylhydrazinyl)-1-(*p*-chlorophenyl)pyrrole(3d). A solution of 1-(*p*-chlorophenyl)pyrrole (0.53g, 3mmole) and DIPADC (1.2g 6 mmole) in anhydrous ether (10ml) was refluxed for 80 h. The solvent was removed by evaporation, and the sticky oil was chromatographed. Purification of the residue by flash chromatography with Hexane : EtOAc (20 : 1) as eluent provided 0.27g (16%) of 1:1 adduct (2d) and 0.33g (20%) of 1:2 adduct (3d): (2d) IR (KBr) 3380 (NH), 2960, 2910, 1740 (C=O), 1690, 1490, 1360, 1310, 1240, 1090 cm^{-1} ; NMR (CDCl_3) δ 1.2 (dt, 1.2H, $J=7$ Hz, C- CH_3), 4.9 (dq, 2H, OCH), 6.3 (dd, 1H, pyrrole C_4H), 6.4-6.5 (d, 1H, pyrrole C_3H), 6.7

(d, 1H, pyrrole C_5H), 7.2 (dd, phenyl 4H); UV(MeOH) 248.5 nm ($\epsilon=17840$). (3d) IR (KBr), 3300 (NH), 2990, 2970, 1740 and 1720 (C=O), 1500, 1380, 1310, 1240, 1100 cm^{-1} ; NMR (CDCl_3) δ 1.2 (dt, 24H, $J=7$ Hz, C- CH_3), 4.9 (dq, 4H, OCH), 6.3 (s, 2H, pyrrole C_3H , C_4H), 6.8 (s, 2H, NH), 7.2-7.4 (m, phenyl 4H); UV (MeOH) 248.5nm ($\epsilon=17110$); mass spectrum, m/e (%) 581 (43, m^+)

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Photoinitiated Polymerization of Acrylic acid Derivatives in Methanol

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A free radical polymerization by irradiation of UV light has advantages of both simple treatment of a reaction and saving energy using the solar radiation at horizontal surfaces. Particularly, the production process of surface coatings by polymerization of low molecular weight materials under the influence of UV light has been received a growing attention in industry. Studies on the photopolymerization using benzoin ether derivatives as a photoinitiator have extensively been made¹⁻⁹. However, to our knowledge, the quantitative investigation of the photoinitiated polymerization of acrylic