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Reaction between Azibenzil and Diarylmethanimine

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The thermal reaction of azibenzil with diarylmethanimine (**1**) leads to *N*-(diarylmethylene)diphenylacetamide (**2**) which from methanol or ethanol yields *N*-(α-alkoxydiarylmethyl)diphenylacetamide (**4**). The reduction of **2** with sodium borohydride gives *N*-(diarylmethyl)diphenylacetamide. The photochemical reaction of azibenzil and **1** results in the formation of cyano ethers besides the amido ethers **4**. A mechanism of formation of products is discussed.

Azibenzil (2-diazo-1,2-diphenylethanone) has been known to form 1,3-oxathiole[1)] in the reaction with thiobenzophenone and oxazoles[2)] with benzonitrile. It has been observed that ketocarbenes undergo cycloaddition with olefins leading to cyclopropanes.[3)] The benzoylphenylcarbene, formed from the thermal or photochemical decomposition of azibenzil, may add on carbon-nitrogen double bond of diarylmethanimine (**1**) giving rise to substituted aziridines. The interest in the attempted synthesis of aziridines[4)] prompted us to carry out the above reaction. We now report the formation of *N*-(diarylmethylene)diphenylacetamide (**2**) on treatment of a benzene solution of 2-diazo-1,2-diphenylethanone with diarylmethanimine (**1**) at refluxing temperature. The products **2** lead to amido ethers (**4**) with alcohols. On irradiation of the reaction mixture with UV light, cyano ethers (**5**) are obtained besides the amido ethers (**4**).

Results and Discussion

The product mixture, obtained by refluxing 2-diazo-1,2-diphenylethanone and diphenylmethanimine (**1a**, Ar=Ar′=C_6H_5) in benzene, was crystallized from 2-propanol; it gave *N*-(diphenylmethylene)diphenylacetamide (**2a**, 90%). The structure was assigned on the basis of analytical and spectral data (Table 1). The product **2a** resulting from an intermediate **A** presumably can be formed as an adduct of diphenylketene, generated from the decomposition of 2-diazo-1,2-diphenylethanone,[5)] and diphenylmethanimine (**1a**) (Scheme 1). A similar zwitterionic intermediate has been proposed[6)] in the formation of 2-azetidinones from the reaction of *N*-benzylideneaniline with diphenylketene. The migration of hydrogen appears to be more feasible than the cyclization of the intermediate **A** to the *β*-lactam **B** due to steric factors (presence of four bulky aryl groups on the terminal carbon atoms in **A**). The reaction of **2a** with sodium borohydride in 2-propanol at room temperature yields the reduction product **3a** (Table 1).

The crystallization of the above reaction products obtained from 2-diazo-1,2-diphenylethanone and **1a** from methanol afforded *N*-(α-methoxydiphenylmethyl)-diphenylacetamide (**4a**). Crystallization of **2a** from

Table 1. Analytical and spectral data of **2a**, **2b**, **2c**, **3a**, **3b**, and **3c**

Compound	Ar	Ar′	Yield %	Mp °C	ν_{max}^{Nujol}/cm^{-1}	NMR[a)] (δ)	Molecular formula	Found (%)	Calcd (%)
2a	C_6H_5	C_6H_5	90	110—111	1685 (C=O) 1640 (C=N)	$CDCl_3$: 7.28 (m, 20H, arom.), 4.88 (s, 1H, CH, benzhydrylic)	$C_{27}H_{21}NO$	C: 86.51 H: 5.68 N: 3.80	86.40 5.60 3.73
2b	C_6H_5	*p*-$CH_3 \cdot C_6H_4$	86	118—119	1685 (C=O) 1635 (C=N)	CCl_4: 7.25 (m, 19H, arom.), 4.80 (s, 1H, CH, benzhydrylic), 2.35 (s, 3H, Me)	$C_{28}H_{23}NO$	C: 86.28 H: 6.12 N: 3.56	86.37 5.91 3.60
2c	*p*-$CH_3 \cdot C_6H_4$	*p*-$CH_3 \cdot C_6H_4$	89	108—109	1680 (C=O) 1635 (C=N)	CCl_4: 7.21 (m, 18H, arom.), 4.80 (s, 1H, CH, benzhydrylic), 2.40 (s, 6H, 2Me)	$C_{29}H_{25}NO$	C: 86.42 H: 6.25 N: 3.51	86.35 6.20 3.47
3a	C_6H_5	C_6H_5	87	201—202	3260 (N-H) 1650 (C=O)	$CDCl_3$: 7.28 (m, 20H, arom.), 6.25—6.45 (bs, 2H, NH, CHArAr′), 5.05 (s, 1H, CH benzhydrylic)	$C_{27}H_{23}NO$	C: 86.01 H: 6.15 N: 3.90	85.94 6.10 3.71
3b	C_6H_5	*p*-$CH_3 \cdot C_6H_4$	82	185—187	3260 (N-H) 1645 (C=O)	$CDCl_3$: 7.24 (m, 19H, arom.), 6.10—6.27 (bs, 2H, NH, CHArAr′), 5.05 (s, 1H, CH benzhydrylic), 2.35 (s, 3H, Me)	$C_{28}H_{25}NO$	C: 86.17 H: 6.45 N: 3.48	85.93 6.39 3.58
3c	*p*-$CH_3 \cdot C_6H_4$	*p*-$CH_3 \cdot C_6H_4$	96	206—207	3270 (N-H) 1650 (C=O)	$CDCl_3$: 7.25 (m, 18H, arom.), 6.20—6.35 (bs, 2H, NH, CHArAr′), 5.05 (s, 1H, CH benzhydrylic) 2.35 (s, 6H, 2Me)	$C_{29}H_{27}NO$	C: 86.07 H: 6.72 N: 3.41	85.98 6.67 3.45

a) Signals are abbreviated as: s=singlet; m=multiplet; bs=broad singlet.

TABLE 2. ANALYTICAL AND SPECTRAL DATA OF AMIDO ETHERS **4a**, **4b**, **4c**, AND **4d**

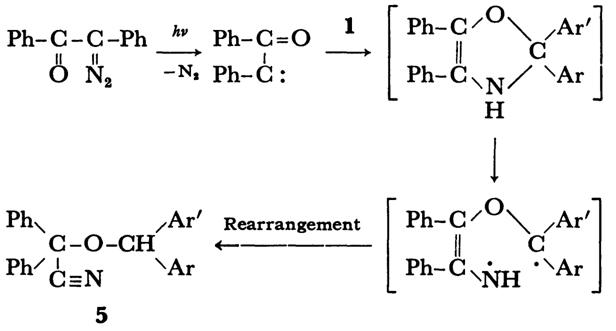
Compound	Ar	Ar′	R	Yield %	Mp °C	$\nu_{\max}^{\text{Nujol}}$/cm^{-1}	NMR[a] (δ, $CDCl_3$)	Molecular formula	Found (Calcd) (%)
4a	C_6H_5	C_6H_5	CH_3	89	199—201	3300 (N-H) 1660 (C=O) 1080 (C-O-C)	7.33 (m, 20H, arom.), 6.71 (b, 1H, NH), 5.10 (s, 1H, CH benzhydrylic), 3.18 (s, 3H, OMe)	$C_{28}H_{25}NO_2$	C: 82.85 (82.54) H: 6.03 (6.14) N: 3.40 (3.44)
4b	C_6H_5	C_6H_5	C_2H_5	82	166—167	3320 (N-H) 1675 (C=O) 1080 (C-O-C)	7.25 (m, 20H, arom.), 6.68 (b, 1H, NH), 5.08 (s, 1H, CH benzhydrylic), 3.28 (q, 2H, OCH_2, J=7 Hz), 1.20 (t, 3H, Me, J=7 Hz)	$C_{29}H_{27}NO_2$	C: 82.52 (82.66) H: 6.39 (6.41) N: 3.29 (3.33)
4c	C_6H_5	p-$CH_3\cdot C_6H_4$	CH_3	83	177—178	3300 (N-H) 1665 (C=O) 1080 (C-O-C)	7.31 (m, 19H, arom.), 6.75 (b, 1H, NH), 5.08 (s, 1H, CH benzhydrylic), 3.17 (s, 3H, OMe), 2.26 (s, 3H, Me)	$C_{29}H_{27}NO_2$	C: 82.43 (82.66) H: 6.38 (6.41) N: 3.30 (3.33)
4d	p-$CH_3\cdot C_6H_4$	p-$CH_3\cdot C_6H_4$	CH_3	82	179—180	3330 (NH) 1668 (C=O) 1080 (C-O-C)	7.32 (m, 18H, arom.), 6.75 (b, 1H, NH), 5.10 (s, 1H, CH benzhydrylic), 3.17 (s, 3H, OMe), 2.25 (s, 6H, 2Me)	$C_{30}H_{29}NO_2$	C: 82.51 (82.76) H: 6.72 (6.67) N: 3.10 (3.22)

a) Signals are abbreviated as: s=singlet; b=broad; m=multiplet; q=quartet; t=triplet.

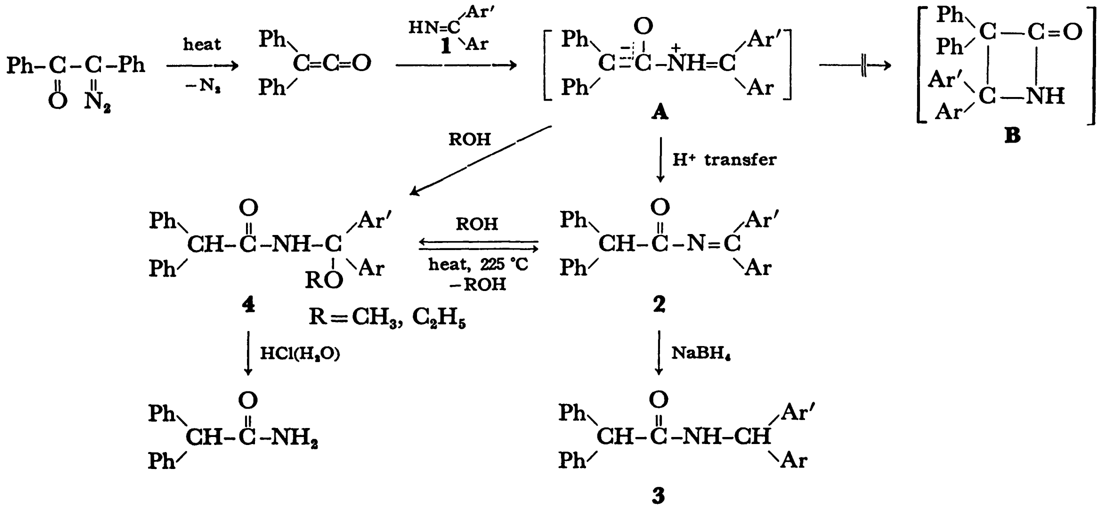
methanol also gave **4a**. The structure assignment of product **4a** has been made on the basis of analytical and spectral data (Table 2). On treatment with 0.1 mol dm^{-3} HCl the amido ethers (**4**) gave diphenylacetamide, mp 166—167 °C and the IR spectrum shows bands at 3400 (ν_{NH_2}) and 1660 cm^{-1} ($\nu_{C=O}$). The amido ether **4a** on heating at 225 °C for 15 min gave **2a** presumably with the loss of alcohol. The formation of products can be explained as shown in Scheme 1.

Similar treatment of imines **1b**—**c** gave the N-acylimines **2b**—**c** and amido ethers **4b**—**d**. The reduction of **2b**—**c** in 2-propanol gave **3b**—**c**. These products (**2a**—**c** and **4a**—**d**) were also obtained in the reaction of diphenylketene with diarylmethanimines (**1a**—**c**).

Irradiation of a solution of 2-diazo-1,2-diphenylethanone and diphenylmethanimine (**1a**) in dry benzene with UV light gave α-(diphenylmethoxy)diphenylacetonitrile (**5a**) and amido ether (**4a**). The cyano ether (**5a**)



Scheme 2.



Scheme 1.

TABLE 3. ANALYTICAL AND SPECTRAL DATA OF CYANO ETHERS **5a**, **5b**, AND **5c**

Compound	Ar	Ar′	Yield/%	Mp/°C	$\nu_{max}^{CHCl_3}$/cm^{-1}	λ_{max}^{EtOH}/nm	NMR (δ, $CDCl_3$)	Molecular formula	Found (%)	Calcd (%)
5a	C_6H_5	C_6H_5	37	178—179	2270 (C≡N) 1080 (C–O–C)	264	7.11 (m, 20H, arom.), 5.10 (s, 1H, CH benzhydrylic)	$C_{27}H_{21}NO$	C:86.51 H: 5.82 N: 3.42	86.40 5.60 3.73
5b	C_6H_5	*p*-$CH_3 \cdot C_6H_4$	34	141—142	2275 (C≡N) 1090 (C–O–C)	264	7.18 (m, 19H, arom.), 5.10 (s, 1H, CHArAr′), 2.25 (s, 3H, Me)	$C_{28}H_{23}NO$	C:86.59 H: 6.16 N: 3.67	85.38 5.91 3.60
5c	*p*-$CH_3 \cdot C_6H_4$	*p*-$CH_3 \cdot C_6H_4$	38	157—158	2270 (C≡N) 1090 (C–O–C)	268	7.15 (m, 18H, arom.), 5.16 (s, 1H, CHArAr′), 2.25 (s, 6H, 2Me)	$C_{29}H_{25}NO$	C:86.67 H: 6.10 N: 3.32	86.35 6.20 3.47

did not lead to amido ether (**4a**) on treatment with methanol. The probable reaction sequence is shown in Scheme 2.

The loss of nitrogen from 2-diazo-1,2-diphenylethanone would lead to ketocarbene, which would condense with diphenylmethanimine (**1a**) *in situ* to form 1,3-oxazole in an analogous manner as observed in the case of the reaction of 2-diazo-1,2-diphenylethanone and thiobenzophenone.[1] The oxazole may further rearrange to cyano ether (**5a**) (Scheme 2) as observed in the ring opening of 2-thiazolines.[7]

Similar irradiation of imines **1b**—**c** gave cyano ethers (**5b**—**c**) besides amido ethers (**4b**—**d**). The amido ethers (**4b**—**d**) are presumably formed from diphenylketene and **1** through zwitterionic intermediate **A** as shown in Scheme 1.

Experimental

Melting points have been determined in capillaries on Büchi apparatus and are uncorrected. The NMR spectra were recorded with a Varian A-60 D spectrometer, with tetramethylsilane as an internal standard. The IR spectra were measured on a Perkin-Elmer 720 spectrophotometer and the UV spectra on a Beckman DB-G spectrophotometer.

Preparation of N-*(Diarylmethylene) diphenylacetamide (2) and Amido Ethers (4). General Procedure From 2-Diazo-1,2-diphenylethanone*: A solution containing 3.0 g (13.5 mmol) of 2-diazo-1,2-diphenylethanone[8] (freshly prepared by the oxidation of benzil monohydrazone with yellow mercury(II) oxide) and diarylmethanimine (**1**)[9] (14.0 mmol) in 60 ml of dry benzene was heated under reflux for 6 h and kept overnight at room temperature. The solvent was removed under reduced pressure and the residue on recrystallization from 2-propanol afforded *N*-(diarylmethylene)diphenylacetamide (**2**). The analytical and spectral data are shown in Table 1.

Crystallization of the products from methanol or ethanol yielded the amido ethers (**4**). The analytical and spectral data are given in Table 2.

From Diphenylketene: A solution containing 1.94 g (10 mmol) of diphenylketene[10] in 5 ml of dry benzene and 10 mmol of diarylmethanimine (**1**) in 5 ml of dry benzene were mixed at room temperature. The vessel became hot at once and the contents were kept overnight at room temperature. Crystallization of the reaction mixture from alcohol afforded the same amido ethers (**4a**—**d**) as obtained from 2-diazo-1,2-diphenylethanone.

Preparation of Cyano Ethers 5. General Procedure: A solution containing 4.9 g (22.0 mmol) of 2-diazo-1,2-diphenylethanone and 24.0 mmol of diarylmethanimine (**1**) in 330 ml of dry benzene was irradiated by UV light from a 200 W Hanovia mercury arc lamp under a continuous slow stream of nitrogen for 6 h and kept overnight at room temperature. The solvent was removed under reduced pressure and the residual material was fractionally crystallized from benzene–methanol mixture to afford the cyano ethers (**5**, 34—38%) (Table 3) and amido ethers (**4**, 45—50%) (Table 2).

Conversion of 4a to 2a: 1.0 g of the amido ether (**4a**) was allowed to melt at 225 °C in an oil bath and was kept for 15 min at 225 °C. The flask was cooled and the residual material was recrystallized from 2-propanol to give 0.9 g (90%) of **2a**. Similarly **4b** and **4c** were converted to **2b** and **2c**, respectively.

Reduction of 2a to 3a: To a solution of 1.0 g of **2a** in 20 ml of 2-propanol was added 30 mg of sodium borohydride and was allowed to stand at room temperature (40 °C) for 30 min. The solvent was evaporated and the residual matter recrystallized from ethanol to give 0.87 g (87%) of **3a**. Similar reduction of **2b** and **2c** gave **3b** and **3c**, respectively (Table 1).

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