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STEREOCHEMISTRY AND KINETICS OF ADDITION OF AMINES TO ACETYLENIC KETONES

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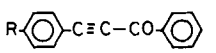
The reactions of a series of 3-(*p*-substituted phenyl)-1-phenylprop-2-yn-1-ones with piperidine and morpholine in methanol were studied and their rates measured. The products were 3-piperidino- and 3-morpholino-3-(*p*-substituted phenyl)-1-phenylprop-2-en-1-ones. ^{1}H NMR spectra were used to determine the configurations of the obtained products. A good Hammett correlation was obtained with ρ values of 1·15–1·10 and 1·15–0·53 for piperidine and morpholine, respectively, which suggest a carbanionic character of the transition state. A two-step mechanism is postulated for these nucleophilic additions.

INTRODUCTION

The nucleophilic addition of amines to activated acetylenes such as α-acetylenic esters,[1–6] sulphones,[7–9] nitriles[10] and ketones[11,12] has been studied, especially with respect to the 1:1 adducts. However, the stereochemistry of such reactions was not well elucidated, probably owing to the difficulties concerning the determination of the configuration and the possibility of isomerization of the initially formed adduct.

In this work, the reactions and kinetics of piperidine and morpholine with 3-(*p*-substituted phenyl)-1-phenylprop-2-yn-1-ones (**1a–d**) were studied, the stereochemistry of the products was assigned and a possible mechanism is suggested.



1a–d

a, R = H; b, R = CH_3; c, R = Cl; d = NO_2

RESULTS AND DISCUSSION

Many attempts to prepare **1a–d** have been reported[13,14] without much success and little of the acetylenic ketones was isolated in these cases. The synthesis of **1c** and **d** could however, be, readily achieved with fairly good yields by the reaction of triethylamine with the appropriate dibromochalcone[15] in acetone. Attempts to synthesize compounds **1a** and **b** by this method gave mainly the α-bromo-α,β-unsaturated compound and unreproducible amounts of the required acetylenic ketones. These two compounds were prepared, however, from the corresponding α-bromo-α,β-unsaturated ketones[15] by their reactions with aqueous potassium hydroxide in acetone.[16] The starting α-bromo-α,β-unsaturated ketones were prepared by the action of alcoholic fused potassium acetate on 3-(*p*-substituted phenyl)-2,3-dibromopropan-1-one. The acetylenic compounds **1a** and **b** were separated by repeated flash column chromatography [light petroleum–ethyl acetate (9:1)] and identified by continuous TLC.

The reaction of **1a–d** with piperidine and morpholine in absolute methanol gave either exclusively *Z* or a mixture of *Z* and *E* isomers of 3-(*p*-substituted phenyl)-1-phenyl-3-piperidinoprop-2-en-1-ones (**2a–d**) and 3-(*p*-substituted phenyl)-1-phenyl-3-morpholino prop-2-en-1-ones (**3a–d**), respectively. The *Z*:*E* ratio depends on the nature of the *para* substitutent in the phenyl ring at C-3. The addition occurs smoothly with the amino group β- to the activating carbonyl group, a pattern similar to acetylenic esters[17] and ketones.[18] The properties and spectral data for **2a–d** are different from those obtained from the reaction of the known[15] 2,3-dibromo-3-(*p*-substituted phenyl)propan-1-one and piperidine, which gave the known[16] 2-piperidino isomers (**4**). This is evidence for the presence of the amino group in the β-position of **2a–d** and **3a–d** rather than in the α-position.

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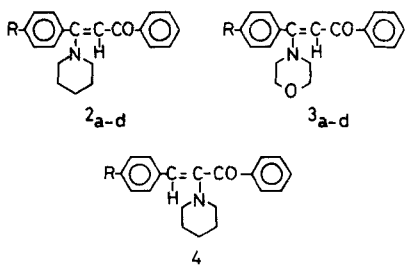
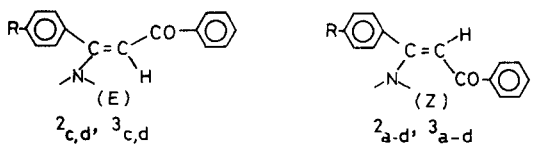
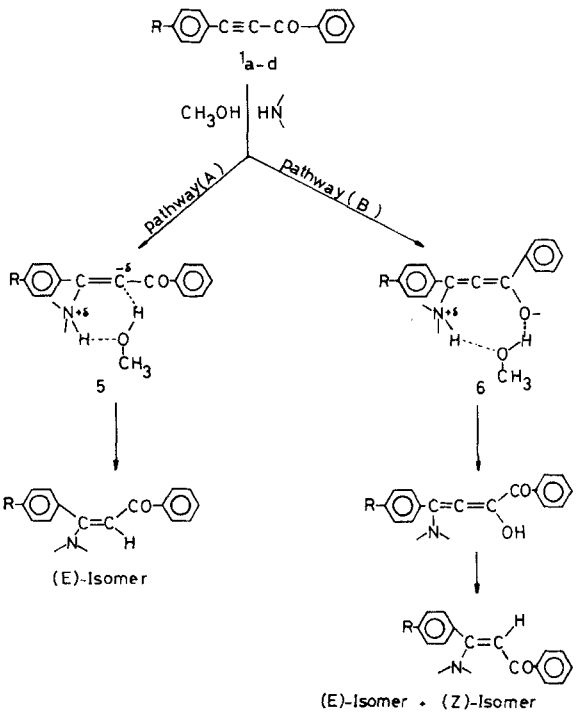


Configurational assignments of **2a–d** and **3a–d** were based on their ^{1}H NMR spectra (Tables 1 and 2). The vinylic protons of the *β-E-* isomers resonate at δ 5·60–5.64 and 5·64–5·88 ppm, whereas those of the *β-Z-* isomers resonate at δ 5·80–6·14 and 5·85–6·10 ppm for **2a–d** and **3a–d**, respectively,[17] depending on the nature of the *para* substituent in the phenyl ring. A downfield shift observed for the vinylic proton of a *β-Z-* isomer relative to that of the *β-E-* isomer is presumably due to the deshielding of this proton by the aryl group which lies on the same side of the double bond in the former isomer.





Scheme 1

Table 1. ^{1}H NMR spectra of 3-(*p*-substituted phenyl)-1-phenyl-3-piperidinoprop-2-en-1-ones (**2a–d**)

	δ(ppm)(CDCl$_3$)						
		Vinylic protons					
Compound	Aromatic protons	*Z*	*E*	α-CH$_2$N protons	β- and γ-CH$_2$N protons	*p*-CH$_3$ protons	*Z*:*E*
2a	7·95–6·90	5·80	—	2·84	1·50	—	100:0
2b	8·00–6·80	5·78	—	2·90	1·55	2·15	100:0
2c	7·85–7·24	6·04	5·60	3·20	1·64	—	81:19
2d	8·30–7·40	6·14	5·64	3·30	1·70	—	83:17

Table 2. ^{1}H NMR spectra of 3-(*p*-substituted phenyl)-1-phenyl-3-morpholinoprop-2-en-1-one (**3a–d**)

	δ(ppm)(CDCl$_3$)						
		Vinylic protons					
Compound	Aromatic protons	*Z*	*E*	O-CH$_2$ protons	N-CH$_2$ protons	*p*-CH$_3$ protons	*Z*:*E*
3a	7·75–7·35	5·95	—	3·15	3·70	—	100:0
3b	7·95–7·35	5·85	—	3·75	3·20	2·30	100:0
3c	7·80–7·25	5·85	5·64	3·20	3·75	—	83:17
3d	8·24–7·40	6·10	5·88	3·22	3·78	—	83:17

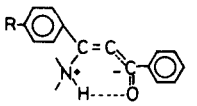
Two possible mechanisms could be proposed. The first involves a concerted mechanism in which the two possible cyclic transition states **5** and **6** include a methanol molecule as a proton carrier (Scheme 1). A similar mechanism was suggested for the reaction of *trans*-chalcone with pyrrolidine,[19] the addition of morpholine to 1,3-diphenylprop-2-yn-1-one in dioxane[20] and the addition of amines to aryl vinyl sulphones[8c] and ketones.[21] Pathway A can lead only to the *E* isomer through transition state **5**, whereas pathway B can give both *E* and *Z* isomers through transition state **6**.

The exclusive formation of the *Z* isomer in the case of **1a** and **b** and the increase in *Z*/*E* ratio in the mixture obtained from **1c** and **d** can be considered to be due to the equilibration of the *E* and *Z* intermediates during the reaction (Scheme 2). However, attempts to isomerize a mixture of (*Z*)- and (*E*)-**2c** and **d** or -**3c** and **d** under the reaction conditions resulted in the recovery of the mixture in the same ratio. A similar observation was reported where no post-isomerization was observed for β-enamino ketones.[11]

The second mechanism involves attack by the amine on the β-carbon of the acetylenic ketone with initial formation of an intramolecularly stabilized (electrostatic or hydrogen bonded) *Z* intermediate, **7** (Scheme 2). This intermediate can form the *Z* adduct only by direct protonation as in **1a** and **b** (electron-releasing substituents, kinetic control), whereas isomerization to the linear intermediate **8** leads on protonation to a mixture of *Z* and *E* isomers as in **1c** and **d** (electron-attracting substituents, thermodynamic control).

Our results are in accord with the stepwise mechanism (Scheme 2) and are inconsistent with the cyclic mechanism (Scheme 1).

The exclusive formation of the *Z* isomer in **2a** and **b** and **3a** and **b** and its extensive formation in **2c** and **d** and **3c** and **d** may be further attributed to the intramolecular π-hydrogen bonding interaction between the ammonium centre and either the aromatic ring (**10**) or the carbonyl oxygen atom[22] (**11**). Such a hydrogen bonding interaction to the π-cloud of electrons of an aromatic ring was reported earlier[9] for 1-(3,5-dimethylbenzylsulphonyl)-2-aziridinoprop-1-ene. Obviously, the substituent has a pronounced effect on the strength of this hydrogen bond[9] and on the stability of the initially formed carbanion **7** (*Z*). This hydrogen bonding presumably freezes the carbanion structure **7**, favouring the formation of the *Z* isomer.



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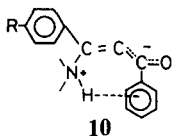

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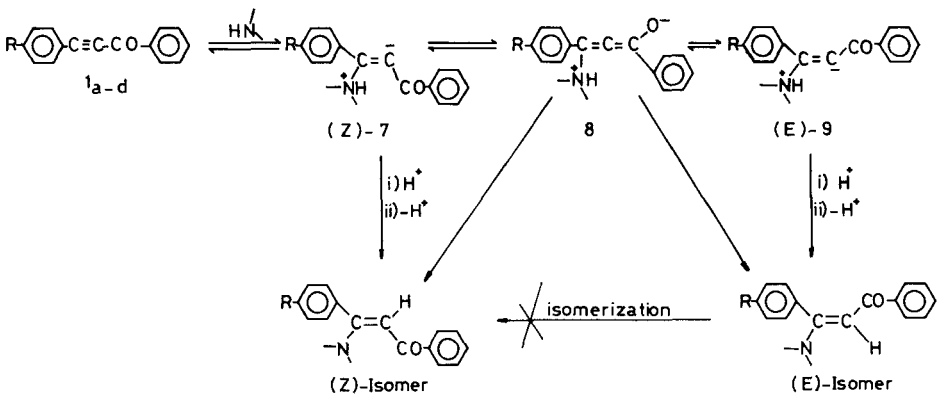
The rate constants of the reactions of **1a–d** with piperidine and morpholine in methanol were measured at five temperatures. The reaction was found to be first order with respect to the amine determined by the initial rate method. However, all reactions follow a second-order kinetic equation. The rate coefficients together with the derived Arrhenius parameters and the ρ values calculated by the least-squares method are listed in Tables 3 and 4.

The rate of addition to **1a–d** depends on the type of the amine and the nature of the substituent in the phenyl ring. Piperidine reactions are generally faster than those of morpholine ($k_{pip}/k_{morp} \approx 3$) because of the higher nucleophilic power and high basicity of the former.

Our values for the entropy of activation ($\Delta S^{\neq}$), however, are less negative than those reported for aryl vinyl sulphones in ethanol[8c] and to 1,3-diphenylprop-2-yn-1-one in dioxane.[20] These values of $\Delta S^{\neq}$ are in favour of a stepwise mechanism (Scheme 2) rather than a concerted mechanism (Scheme 1). However, the relatively low values of the entropy of activation can be considered as an indication of the participation of



Scheme 2

Table 3. Specific rate constants, activation parameters and ρ values for the reaction of **1a–d** with piperidine in methanol

Compound	Specific rate constant k_2(l min^{-1} mol^{-1}) 30 °C	35 °C	40 °C	45 °C	50 °C	E_a (kcal mol^{-1})	ΔS^* (e.u.)	ΔH^* (kcal mol^{-1})
1a	1·93	2·70	4·08	4·66	7·00	12·16 ± 0·03 (r = 0·99)	−18·9	11·53
1b	1·35	1·87	2·66	3·30	4·60	12·60 ± 0·02 (r = 0·99)	−18·3	11·98
1c	3·42	4·84	6·80	8·49	11·38	11·81 ± 0·01 (r = 0·99)	−19·0	11·18
1d	15·60	20·72	30·38	39·18	51·88	11·22 ± 0·01 (r = 0·99)	−17·0	10·59
ρ	1·15 ± 0·03	1·13 ± 0·01	1·12 ± 0·02	1·11 ± 0·03	1·10 ± 0·03			

Table 4. Specific rate constants, activation parameters and ρ values for the reaction of **1a–d** with morpholine in methanol

Compound	Specific rate constant k_2(l min^{-1} mol^{-1}) 30 °C	35 °C	40 °C	45 °C	50 °C	E_a (kcal mol^{-1})	ΔS^* (e.u.)	ΔH^* (kcal mol^{-1})
1a	0·76	0·94	1·21	1·60	2·02	9·59 ± 0·01 (r = 0·99)	−29·5	8·97
1b	0·53	0·66	0·85	1·18	1·47	9·81 ± 0·01 (r = 0·99)	−29·5	9·18
1c	1·02	1·47	1·80	2·32	3·01	9·48 ± 0·01 (r = 0·99)	−29·1	8·85
1d	3·00	3·72	4·88	6·44	7·82	9·06 ± 0·01 (r = 0·99)	−28·5	8·43
ρ	1·15 ± 0·02	0·79 ± 0·01	0·78 ± 0·02	0·77 ± 0·02	0·53 ± 0·02			

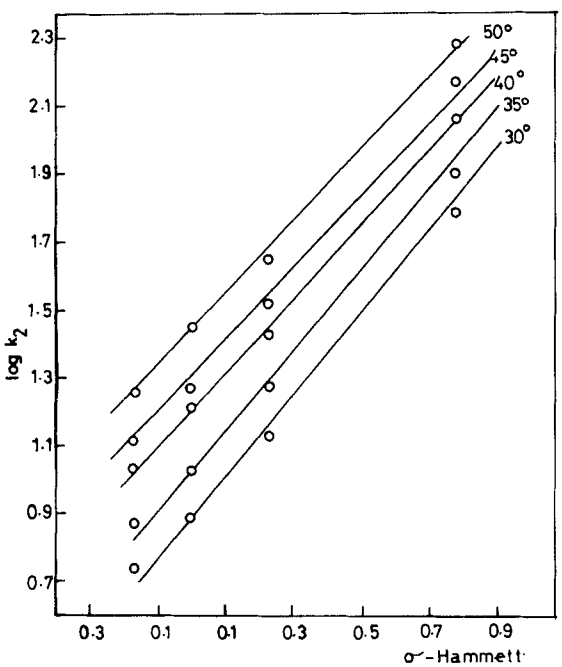


Figure 1. Plot of log k_2 for the reaction of **1a–d** with piperidine against Hammett σ-constants

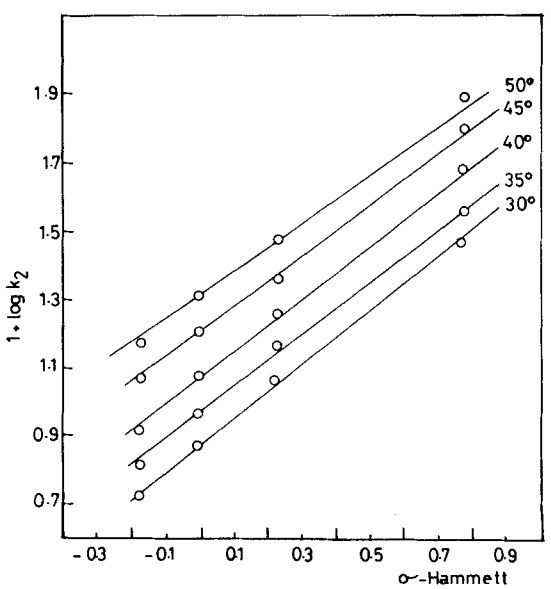


Figure 2. Plot of log k_2 for the reaction of **1a–d** with morpholine against Hammett σ-constants

π-hydrogen bonding of the benzoyl moiety with the ammonium moiety (**10** and **11**).

Plots of log k_2 vs Hammett σ-values correlate well for the piperidine and morpholine reactions (Figures 1 and 2, respectively). The ρ values range between 1·15 and 1·10 for piperidine and 1·15 and 0·53 for morpholine, indicating that a considerable anionic character is developed at the carbon atom adjacent to the carbonyl group. These ρ values are comparable to those reported for the addition of amines to aryl vinyl sluphones.[8c]

Further evidence of the stepwise mechanism came from the observation of two isosbestic points in the UV spectra (Figures 3 and 4), which is characteristic of consecutive reactions.[23]

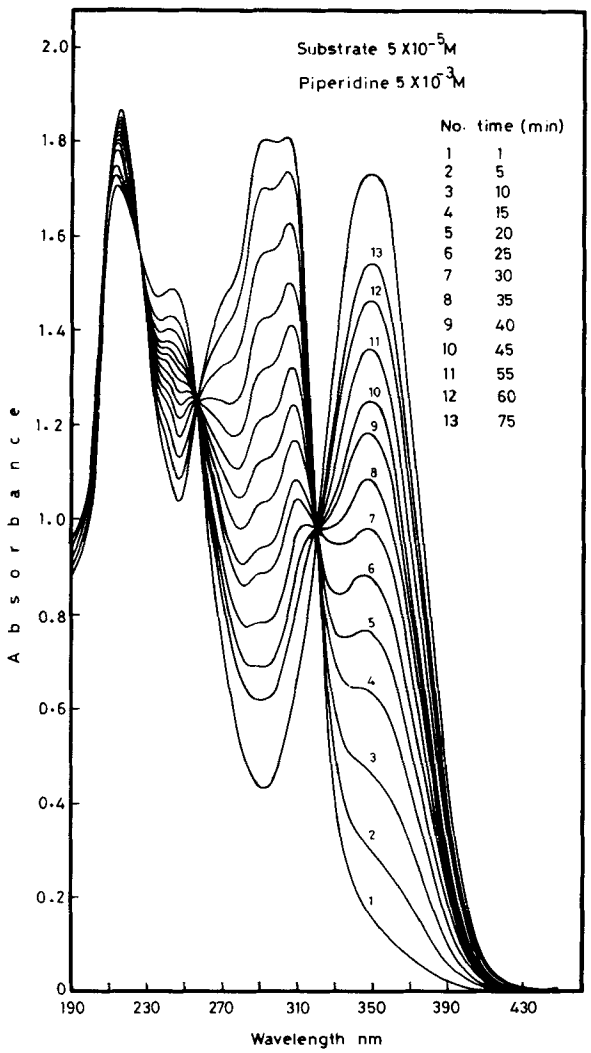


Figure 3. Variation of the electronic spectra of **1c** in the presence of piperidine as a function of time

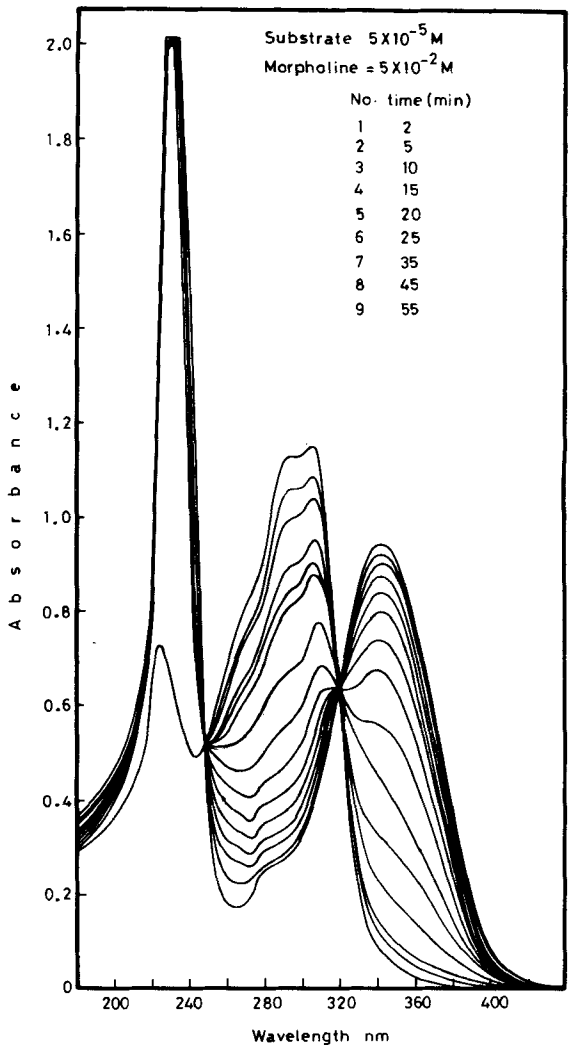


Figure 4. Variation of the electronic spectra of **1c** in the presence of morpholine as a function of time

It can be concluded that the rate-determining step for these reactions is the addition of amine followed by fast protonation of the carbanion formed, giving the final product. The possibility of delocalization of negative charge through the carbonyl group followed by ketolization cannot be excluded as a source for the formation of some *E* isomer in case of **2c** and **d** and **3c** and **d**.

EXPERIMENTAL

Infrared and ultraviolet spectra were measured on Pye Unicam SP 1025 and SP 800 spectrometers, respectively. The ^{1}H NMR spectra were measured on a Varian

EM 390 90-MHz spectrometer (Alexandria University, Egypt) and on a Bruker PW 300-MHz spectrometer (Oldenburg University, FRG) using $CDCl_3$ as the solvent. Microanalyses were done at Alexandria University, Cairo University and Mansoura University, Egypt; melting points and boiling points are uncorrected.

Solvents. Methanol and acetone were purified as reported previously,[24] whereas amines were dried over potassium hydroxide and distilled through a 25-cm fractionating column. Their physical constants are as follows: piperidine, b.p. 106 °C, n_D^{25} 1·4520; morpholine, b.p. 127 °C, n_D^{25} 1·4523.

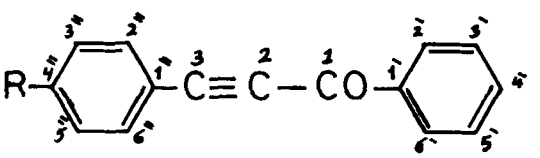
1,3-Diphenylprop-1-yn-1-one (**1a**). 2,3-Dibromo-1,3-diphenylpropan-1-one[15] was treated with fused potassium acetate as reported previously[25] to give 2-bromo-1,3-diphenylprop-2-en-1-one. The latter compound undergoes dehydrobromination[16] under the action of KOH, giving a residue which was subjected to several flash column chromatographic steps and pure **1a** was obtained as yellow crystals (14%).

3-(p-Methylphenyl)-1-phenylprop-2-yn-1-one (**1b**). 2,3-Dibromo-3-(*p*-methylphenyl)-1-phenylpropan-1-one[15] was treated with fused potassium acetate and the isolated 2-bromo-3-(*p*-methylphenyl)-1-phenylprop-2-en-1-one[25] was dehydrobrominated with KOH. The pure acetylenic compound **1b** was obtained through several flash column chromatographic steps as a pale yellow solid (27%).

3-(p-Chlorophenyl)-1-phenylprop-2-yn-1-one (**1c**). A solution of 2,3-dibromo-3-(*p*-chlorophenyl)-1-phenylpropan-1-one[15] (16 g; 0·039 mol) and triethylamine (40 ml) dissolved in acetone (160 ml) were sealed in an ampoule and heated for 40 h on a steam-bath. The reaction mixture was poured into cold water and acidified with 10% hydrochloric acid, then extracted with diethyl ether. The ethereal layer was washed with water and sodium hydrogen carbonate solution and dried over anhydrous sodium sulphate. The solvent was removed and the crude product crystallized from dilute methanol as white needles (7·29 g; 75%).

3-(p-Nitrophenyl)-1-phenylprop-2-yn-1-one (**1d**). In a sealed ampoule, a solution of 2,3-dibromo-3-(*p*-nitrophenyl)-1-phenylpropan-1-one[15] (12 g; 0·029 mol) and triethylamine (30 ml) in 120 ml of acetone was heated on a steam-bath for 40 h. The reaction mixture after work-up as in the synthesis of **1c** gave a solid that crystallized from dilute methanol as yellow crystals (4·89 g; 65%).

Table 5. IR, UV, ^{1}H NMR, mass spectra and elemental analyses of 3-(substituted phenyl)-1-phenylprop-2-yn-1-ones (**1a–d**)



1a–d

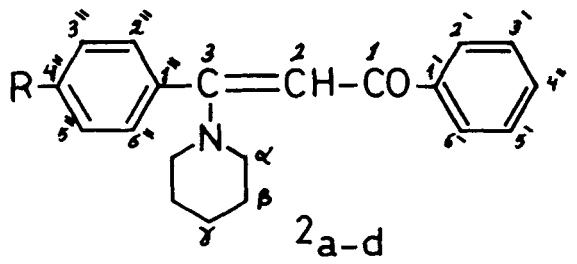
Compound	m.p.(°C)	IR (ν cm^{-1}) C≡C	C=O	C=C	UV (λ nm) (ε)	^{1}H NMR($CDCl_3$) (δ,ppm)	Formula	Calc. (Found) (%)	$(M^+)^a$ *m/z*
1a	63–64	2200	1655	1620	292 (21 900)	8·25–8·20(m,2H$_{2',6'}$) 7·68–7·62(m,3H$_{3',4',5'}$) 7·48–7·40(m,5H$_{2'',3'',4'',5'',6''}$)	$C_{15}H_{10}O$	C,87·40; H,4·89 (C,87·00; H,4·87)	206
1b	56–58	2200	1690	1620	310 (22 000)	8·23–8·04(m,2H$_{2',6'}$) 7·60–7·37(m,5H$_{3',4',5',2'',6''}$) 7·20–7·03(m,2H$_{3'',5''}$) 2·40(s,3H,*p*-CH$_3$)	$C_{16}H_{12}O$	C,87·27; H,5·45 (C,86·90; H,5·47)	220
1c	103	2210	1670	1600	296 (23 200)	8·26–8·09(m,2H$_{2',6'}$) 7·68–7·46(m,5H$_{3',4',3'',5''}$) 7·45–7·40(m,2H$_{2'',6''}$)	$C_{15}H_9OCl$	C,74·84; H,3·74; Cl,14·76 (C,74·70; H,3·60; Cl,14·30)	240
1d	146–147	2220	1640	1600	293 (26 000)	8·40–8·35(d,2H$_{3'',5''}$) 8·30–8·20(m,2H$_{2',6'}$) 7·92–7·80(m,2H$_{2'',6''}$) 7·73–7·49(m,3H$_{3',4',5'}$)	$C_{15}H_9NO_3$	C,71·71; H,3·58; N, 5·57 (C,71·10; H,3·70; N,5·66)	251

[a] Mass spectra were measured on a Nuclide 12–90 G mass spectrometer (North Eastern University, USA).

Melting points, elemental analysis and spectral data of the above starting materials **1a–d** are reported in Table 5.

Reaction products. The following procedure was adopted for all compounds **2a–d** and **3a–d**. Compound **1a**, **b**, **c** or **d** (0·59 g) was dissolved in absolute methanol and a solution of amine (three times the molarity of the compound) in absolute methanol (5 ml) was added. The mixture was thermostated at 40 °C (until the disappearance of the starting material using TLC), then cooled, poured into ice-cold water and the precipitate formed was filtered and crystallized from light petroleum–benzene. The samples used for ^{1}H NMR are those isolated from the reaction before purification.

(a) 1,3-Diphenyl-3-piperidinoprop-2-en-1-one derivatives (**2a–d**).



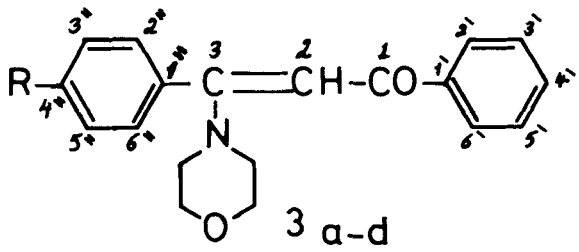
(Z)-1,3-Diphenyl-3-piperidinoprop-2-en-1-one (**2a**). Deep yellow crystals; yield 95%; m.p. 97–99 °C. Analysis: calculated for $C_{20}H_{21}NO$, C 82·47, H 7·21, N 4·81; found, C 82·32, H 7·30, N 4·61%. IR: 1680(s). 1605(s), 1380(m), 1240(m) cm^{-1}. UV, $\lambda = 348$ nm ($\varepsilon = 20\,400$). ^{1}H NMR($CDCl_3$): aromatic protons at δ 8·10–8·00 ($2H_{2',6'}$), 7·57–7·17 (m,$6H_{3',4',5',3'',4'',5''}$), 7·07–6·87 (m,$2H_{2'',6''}$); 5·80 (s, 1H, vinylic proton); 2·84 (s, 4H, α-CH_2 protons); 1·50 ppm (s, 6H, β- and γ-protons).

(Z)-3-(p-(Methylphenyl)-1-phenyl-3-piperidinoprop-2-en-1-one (**2b**). Pale yellow crystals; yield 98%; m.p. 124–125 °C. Analysis calculated for $C_{21}H_{23}NO$, C 82·62, H 7·54, N 4·59. Found, C 82·23, H 7·41, N 4·61%. IR: 1675(s), 1605(s), 1340(m), 1285(m). UV: $\lambda = 350$ nm ($\varepsilon = 17\cdot600$). ^{1}H NMR ($CDCl_3$): aromatic protons at δ 8·1–7·90 (m, $2H_{2',6'}$), 7·57–7·13 (m, $5H_{3',4',5',2'',6''}$), 6·93–6·70 (m, $2H_{3'',5''}$); 5·78 (s, 1H, vinylic proton); 2·90 (s, 4H, α-CH_2 protons); 2·15 (s, 3H, *p*-CH_3 protons); 1·55 ppm (s, 6H, β and γ-protons).

(E, Z)-3-(p-Chlorophenyl)-1-phenyl-3-piperidinoprop-2-en-1-one (**2c**). Pale yellow crystals; yield 76%; m.p. 143–145 °C. Analysis: calculated for $C_{20}H_{20}ClNO$, C 73·73, H 6·14, N 4·30, Cl 10·90; found, C 73·40, H 5·90, N 4·10, Cl, 10·70%. IR: 1648(s), 1600(s) 1375(m), 1230(m) cm^{-1}. UV: $\lambda = 350$ nm ($\varepsilon = 17\,400$). ^{1}H NMR ($CDCl_3$): aromatic protons at δ 8·04–7·74 (m, $2H_{2',6'}$), 7·55–7·25 (m, $5H_{3',4',5',3'',5''}$), 7·25–7·00 (m, $2H_{2'',6''}$); 6·04 [s, 1H, (*Z*)-vinylic proton 81%], 5·60 [s, 1H, (*E*)-vinylic proton, 19%]; 3·20 (s, 4H, α-CH_2 protons); 1·64 ppm (s, 6H, β- and γ-protons).

(E, Z)-3-(p-Nitrophenyl)-1-phenyl-3-piperidinoprop-2-en-1-one (**2d**). Yellow crystals; yield 79%; m.p. 164–166 °C. Analysis: calculated for $C_{20}H_{20}N_2O_3$, C 71·42, H 5·95, N 8·33; found, C 71·20, H 6·00, N 8·70%. IR: 1638(s), 1618(s), 1355(m), and 1220(m) cm^{-1}. UV: $\lambda = 350$ nm ($\varepsilon = 22\,800$). ^{1}H NMR ($CDCl_3$): aromatic protons at δ 8·18–8·10 (d, $2H_{3'',5''}$); 7·46–7·38 (m, $2H_{2',6'}$), 7·26–7·15 (m, $5H_{3',4',5',2'',6''}$); 6·14 [S, 1H, (*Z*)-vinylic proton, 83%]; 5·64 [s, 1H, (*E*)-vinylic proton 17%]; 3·30 (s, 4H, α-CH_2 protons); 1·70 ppm (s, 6H, β- and γ-CH_2 protons).

(b) 1,3-Diphenyl-3-morpholinoprop-2-en-1-one derivatives (**3a–d**).



(Z)-1,3-Diphenyl-3-morpholinoprop-2-en-1-one (**3a**). Pale yellow crystals; yield 97%; m.p. 72–74 °C. Analysis: calculated for $C_{19}H_{19}NO_2$, C 77·81, H 6·48, N 4·77; found, C 77·71, H 6·35, N 4·41%. IR: 1620(s), 1600(s), 1200(s), 1345(s) cm^{-1}. UV: $\lambda = 348$ nm ($\varepsilon = 16\,000$). ^{1}H NMR ($CDCl_3$): aromatic protons at δ 7·98–7·66 (m, $2H_{2',6'}$), 7·47–7·20 (m, $6H_{3',4',5',3'',4'',5''}$), 7·28–7·05 (m, $2H_{2'',6''}$); 5·95 (s, 1H, vinylic proton); 3·70 (m, 2H, CH_2-N protons); 3·15 ppm (m, 2H, O-CH_2 protons).

(Z)-3-(p-Methylphenyl)-1-phenyl-3-morpholinoprop-2-en-1-one (**3b**).
Pale yellow crystals: yield 94%; m.p. 105–106 °C. Analysis: calculated for $C_{20}H_{21}NO_2$, C 78·17, H 6·88, N 4·56; found, C 77·76, H 6·44, N 4·52%. IR: 1620 (s), 1600(m), 1345(m), 1240(m) cm^{-1}. UV: $\lambda = 348$ nm ($\varepsilon = 19\,200$), ^{1}H NMR ($CDCl_3$): aromatic protons at δ 8·13–7·87 (m, $2H_{2',6'}$), 7·60–7·20 (m, $3H_{3',4',5'}$), 7·20–7·00 (m, $4H_{2'',3'',5'',6''}$); 5·85 [s, 1H, (*Z*)-vinylic proton]; 3·75 (m, 2H, CH_2-N protons); 3·20 ppm (m, 2H, O-CH_2 protons).

(E,Z)-3-(p-Chlorophenyl)-1-phenyl-3-morpholino-prop-2-en-1-one (**3c**).
Pale yellow crystals; yield 80%; m.p. 115–117 °C. Analysis: calculated for $C_{19}H_{18}NO_2Cl$, C 69·61, H 5·49, N 4·27, Cl 10·68; found, C 69·50, H 5·80, N 3·92, Cl 10·41%. IR: 1650(s), 1610(m), 1375(s), 1220(s) cm^{-1}. UV: $\lambda = 345$ nm ($\varepsilon = 19200$). ^1H NMR ($CDCl_3$): aromatic protons at δ 8·00–7·67 (m, $2H_{2',6'}$), 7·51–7·46 (m, $2H_{2'',6''}$), 7·45–7·27 (m, $3H_{3',4',5'}$); 5·85 [s, 1H, (*Z*)-vinylic proton 83%], 5·64 [s, 1H, (*E*)-vinylic proton, 17%]; 3·75 (m, 2H, CH_2-N protons); 3·20 ppm (m, 2H, O-CH_2 protons).

(E, Z)-3-(p-Nitrophenyl)-1-phenyl-3-morpholino-prop-2-en-1-one (**3d**).
Yellow crystals; yield 85%; m.p. 154–155 °C. Analysis: calculated for $C_{19}H_{18}N_2O_4$, C 67·45, H 5·32, N 8·28; found, C 67·50, H 5·40, N 8·10%. IR: 1640(s), 1612(s), 1355(s) and 1220(s) cm^{-1}. UV: $\lambda = 350$ nm ($\varepsilon = 16800$). ^1H NMR ($CDCl_3$): aromatic protons at δ 8·33–8·20 (d, $2H_{3'',5''}$), 7·88–7·76 (m, $2H_{2',6'}$), 7·51–7·46 (m, $2H_{2'',6''}$), 7·45–7·27 (m, $3H_{3',4',5'}$); 6·10 [s, 1H, (*Z*)-vinylic protons, 83%], 5·88 [s, 1H, (*E*)-vinylic proton, 17%], 3·78 (m, 2H, CH_2-N protons); 3·22 ppm (m, 2H, O-CH_2 protons).

Kinetic measurements. The kinetics of the reactions of **1a–d** with piperidine or morpholine were studied spectrometrically using a Pye Unicam SP 800 double-beam recording spectrometer. The spectral variations of these reactions as a function of time show two isosbestic points (Table 6).

Table 6. Positions of isosbestic points for the reactions of **1a–d** with piperidine and morpholine

	Piperidine		Morpholine	
Compound	λ (nm)	λ (nm)	λ (nm)	λ (nm)
1a	316	260	317	256
1b	322	282	323	250
1c	320	256	318	252
1d	318	262	320	250

The reactions were monitored at $\lambda = 348, 350, 350$ and 350 nm for reactions of **1a**, **b**, **c** and **d**, respectively, with piperidine and at $\lambda = 348$, 348, 345 and 350 nm for the corresponding reactions with morpholine.

Methanolic solutions of the substrate and piperidine or morpholine that give a final concentration of 5×10^{-5} M and 5×10^{-3} or 5×10^{-2} M, respectively, were thermostated at the desired temperature ±0·5 °C. A 2 ml volume of the reaction mixture was transferred quickly into a well thermostated chamber containing the UV cell. The rate constant k_{obs} at any time t was obtained from the following equation:

$$\log A - A_t = \left(\frac{-k_{obs}}{2{\cdot}303}\right)t + \log(A - A_0)$$

where A_0, A_t and A are the values of the absorbance at zero, time t and infinity, respectively. The k_2 values were calculated by dividing k_{obs} by the amine concentration.

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