Mobile Keto Allyl Systems. XVII.[1] Reaction of Amines with β-Carbomethoxy Allyl Bromides

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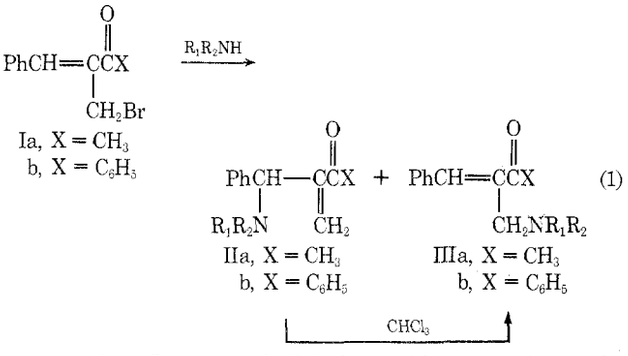
The reaction of a variety of amines with methyl α-(bromomethyl)cinnamate (**1a**) and methyl α-(bromomethyl)-4-chlorocinnamate (**1b**) in hydrocarbon solvent is described. With the exception of *tert*-butylamine, all amines reacted with **1a** or **1b** to produce substitution–rearrangement (**2**) and normal substitution (**3**) products in high yield. The product distribution was strongly dependent on the amine structure. Only **2** was formed upon reaction of *tert*-butylamine with **1a** or **1b**. All examples of **2** isomerized slowly to **3** in chloroform solvent. These reactions are discussed in terms of a variant of an SN2′ mechanism.

We have reported that the reaction of morpholine or piperidine with α-(bromomethyl)benzalacetone (Ia) in hydrocarbon solvent produced substitution–rearrangement (IIa) and normal substitution products (IIIa) in high yield (eq 1).[2] The same amines previously had been found to



react with α-(bromomethyl)chalcone (Ib) to produce substitution–rearrangement products (IIb), exclusively.[3] Compounds II required solvents of higher polarity than hexane or pentane to isomerize to the thermodynamically more stable isomers III.

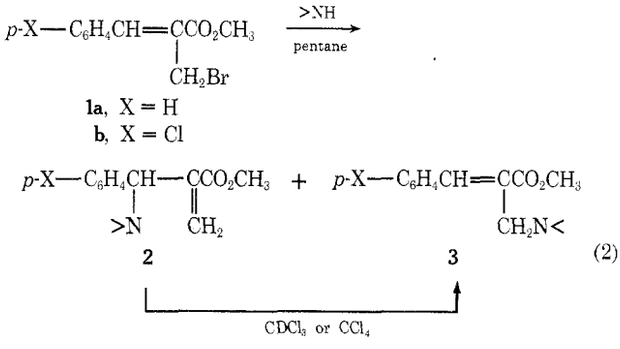
It was rationalized that the initially formed substitution–rearrangement product IIa could compete successfully with Ia for unreacted amine (morpholine or piperidine) to form IIIa. However, IIb did not compete with Ib in pentane for unreacted amine and no normal substitution product IIIb was obtained. The substituent on the β-carbo group of the allyl system in Ia and Ib appears to exert a product controlling factor upon reaction with amines.

We wished to study the reaction of amines with a β-carbomethoxy allyl bromide in hydrocarbon solvent in order to compare methoxy with methyl and phenyl groups as a product controlling factor on the β-carbo group of the allyl system and to study the effect of amine structure on product distribution.

Results

trans-Methyl α-(bromomethyl)cinnamate (**1a**) was synthesized in satisfactory yield by conventional procedures. The product was an oil and had to be distilled twice under vacuum through a Vigreux column to obtain satisfactory purity for this study. *trans*-Methyl α-(bromomethyl)-4-chlorocinnamate (**1b**) was also obtained in good yield and purified by crystallization. Both **1a** and **1b** were sufficiently soluble in pentane to undergo reactions with amines. The solubility of compounds 1 in hydrocarbon solvent is an important consideration when examining reactions with *tert*-butylamine. For example, the para nitro derivative of 1 (X = NO_2) was synthesized and found to be insoluble in pentane. Upon reaction with *tert*-butylamine in acetonitrile, substitution–rearrangement (**2**) and normal substitution (**3**) products were obtained.[4] However, in hydrocarbon solvent, the reaction of *tert*-butylamine with **1a**, **1b**, Ia, and Ib produces the substitution–rearrangement product **2**, exclusively.

The reaction of 2 mol equiv of amine with **1a** or **1b** was carried out in dilute pentane solution at room temperature; the mixture was filtered to remove amine hydrobromide, followed by evaporation of solvent to a small volume and immediate analysis by pmr. In the case of *tert*-butylamine reactions, only one product was formed, while all other amines produced two substitution products. The pentane was evaporated and the resulting oil dissolved in a few milliliters of chloroform-*d* or carbon tetrachloride and allowed to stand at room temperature for several days. Analysis by pmr showed complete isomerization of **2** to **3**.



All examples of **2** and **3** are heat-labile oils which decompose on Florisil or silica gel chromatography columns. The *tert*-butylamino derivatives of **2** and **3** and the 2,5-dimethylpyrrolidine derivative of **3** form stable hydrohalide salts. All the other amino hydrohalide derivatives of **2** and **3** are extremely hygroscopic and had to be elementally analyzed as picrates.

The substitution products are readily distinguished from each other by pmr spectroscopy (Table II). Compounds **2** exhibit three singlets (slightly broadened due to geminal and allylic coupling) assigned to the benzyl and vinylic protons. In **3**, the methoxyl and vinylmethylene singlets are characteristic.

In the case of the morpholine reaction we were able to isolate the picrate of **2c** by repeated crystallization of the picrates derived from the entire reaction mixture. By adding the morpholine slowly over 30 min to **1a**, rather than at once, a 4:1 ratio of **2c** to **3c**, respectively, was obtained as determined by pmr. Fractional crystallization afforded the picrate of **2c** which showed a mixture melting point depression with the picrate of **3c**. A mixture of the two picrates showed two spots when developed on silica gel tlc sheets.

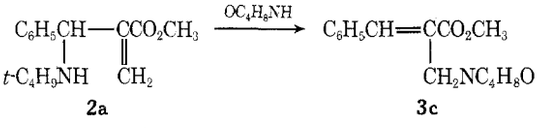
The initially formed substitution–rearrangement prod-

Table I
Amine Reactions with 1a[a]

Amount of substrate, g	Amine	Amount of amine, g	Solvent vol, ml	Reaction time, hr	% Amine HBr	Product(s)
2.57	*tert*-Butylamine	1.50	125	43.5	90.3	**2a**
1.28	Piperidine	0.85	110	1.5	96.4	**2b:3b** (79:21)
1.28	Morpholine	0.87	150	54	92.8	**2c:3c** (55:45)
1.28	*N*-Methylcyclohexylamine	1.13	150	47	89.7	**2d:3d** (67:33)
1.28	2-Methylpiperidine	0.99	200	22	93.3	**2e:3e** (25:75)
1.28	2,6-Dimethylpiperidine	1.13	115	25	14.4	Not characterized
2.56	2,5-Dimethylpyrrolidine	1.98	200	26	83.4	**2f:3f** (97:3)
1.28	*N*-Methylisopropylamine	0.73	150	42	0	
1.28	Diisopropylamine	1.01	150	50	0	
		Amine Reactions with **1b**[a]				
2.90	*tert*-Butylamine	1.50	125	41	92.3	**2g**
2.90	Piperidine	1.70	200	73	100.0	**2g:3g** (48:52)

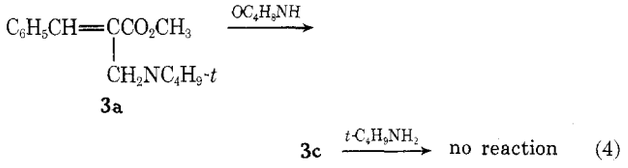
[a] In all the reactions reported here, the substrate:amine mole ratio was exactly 1:2, respectively, in pentane solvent. See Experimental Section for general procedure.

uct **2a** slowly reacted with a slight excess of morpholine in pentane solvent to produce **3c**, quantitatively.



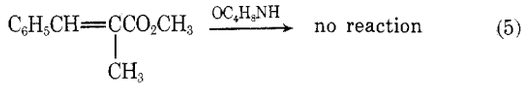
2a **3c** (3)

The same product was also obtained by treating a 7 mol excess of morpholine with **3a** over 13 days in pentane solvent. No evidence for the prior formation of **2c** or a 1,3-diamine was found. In contrast, **3c** did not react with an 8 mol excess of *tert*-butylamine in pentane for 7 days.



(4)

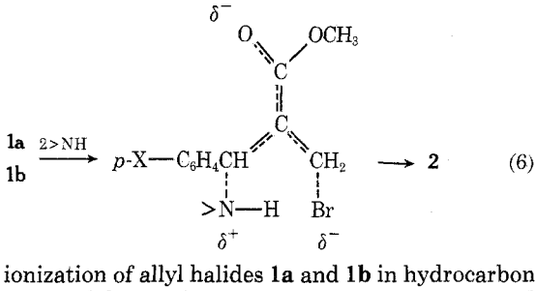
Methyl α-(methyl)cinnamate was dissolved in a 20 mol excess of morpholine without solvent at room temperature for 8 days. After removal of the morpholine, the residue was shown to be unchanged ester by its pmr spectrum.



(5)

Discussion

The formation of rearrangement–substitution products from the reaction of amines with β-carbo allyl halides has been considered to be a variant of an SN2′ mechanism in which carbon–nitrogen bond formation proceeds ahead of carbon–halogen bond breakage.[5] The oxygen atom of the β-carbo group accepts much of the developing negative charge which is ultimately carried by the leaving halide ion. This hypothesis is invoked to explain the formation of compounds **2** from the reaction of amines with **1a** or **1b.**



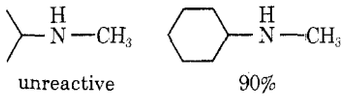
(6)

Prior ionization of allyl halides **1a** and **1b** in hydrocarbon solvent followed by nucleophilic attack on a rearranged carbocation to form **2** should not be very important. The low dielectric constant of pentane and the presence of the electron-withdrawing β-carbo substituent on the allyl system in **1a** and **1b** would depress the formation of a carbocation.[6]

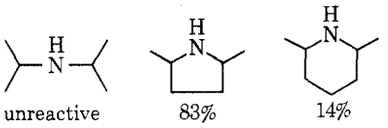
A 1,4-Michael addition of amine to **1a** or **1b** followed by elimination of hydrogen bromide to form **2** is ruled out because morpholine does not react with methyl α-(methyl)cinnamate (eq 5).

Kinetic studies on six amine reactions with Ia showed a rate retardation with increasing bulk at the α-carbon atom of the amine.[5a] Only the abnormal substitution product was obtained (eq 1).

Examination of Table I reveals a wide range of product distribution yields for the reaction of amines with **1a** as a consequence of subtle stereochemical alterations in amine structure. For example, *N*-methylisopropylamine was totally unreactive toward **1a;** however, "pinning" the methyls of the isopropyl group back slightly and forming a cyclohexyl ring results in *N*-methylcyclohexylamine which easily reacts with **1a** under the same conditions.



Diisopropylamine is also unreactive toward **1a.** When its methyl groups are "joined" to construct 2,5-dimethylpyrrolidine, we observe a reaction to 83% completion. If the pyrrolidine ring is increased by one methylene group, the yield is drastically reduced.



The reactivity of amines toward **1a** varied from (a) no reaction, (b) production of rearrangement–substitution product, exclusively, to (c) production of both rearrangement–substitution and normal substitution products. No amine was found which would produce only the normal substitution product in pentane solvent.

Stork and White demonstrated a cis geometry for the attack of piperidine to the leaving group in an SN2′ reaction for *trans*-6-alkyl-2-cyclohexen-1-yl 2,6-dichlorobenzoates.[7] The cis orientation is crowded but can be facilitated by hydrogen bonding of the amine to the carbonyl oxygen atom or the bromide atom (eq 6).[8] The differences in amine reactivity upon reaction with **1a** are best explained in terms of the steric demands of the amine structure rather than by

Table II
60-MHz Proton Magnetic Resonance Data[a]

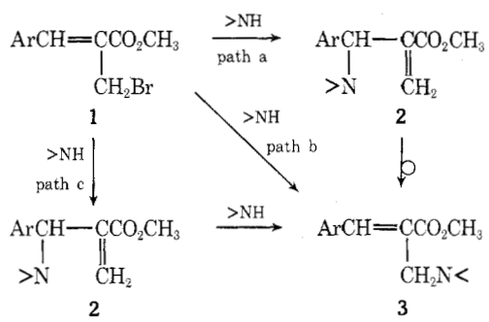
Compd	Aromatic[c]	C_6H_5CH	OCH_3	$C{=}CH_2$	CH_2N	Amino group
2a[b]	6.9–7.3	4.68	3.50	6.05, 6.15		1.05 *t*-C_4H_9
3a[b]	7.2–7.7		3.77		3.44	1.15 *t*-C_4H_9
2b[c]		4.35		6.03, 6.28		
3b[b]	6.95–7.7		3.68		3.22	2.1–2.5 CH_2NCH_2, 1.2–1.7 $(CH_2)_3$
2c[b]		4.25		6.05, 6.30		
3c[b]	7.1–7.7		3.75		3.27	3.4–3.7 CH_2OCH_2, 2.3–2.5 CH_2NCH_2
2d[b]		4.75		6.00, 6.28		
3d[b]	7.2–7.8		3.73		3.40	0.9–2.7 N-CH_3 and cyclohexyl ring
2e[d]		5.00, 5.15[f]		5.98, 6.18[e] 6.40, 6.55[e]		
3e[d]	7.4–8.1		3.97		3.30, 3.70[g]	1.0–3.0 piperidine ring and CH_3
2f[d]		5.08		5.92, 6.37		
3f[d]	7.1–7.8		3.75		3.58	2.3–3.0 CHNCH, 0.8–2.2 pyrrolidine ring, and two CH_3
2g[b]	6.9–7.1	4.68	3.50	5.85, 6.04		1.1 NH, 1.03 *t*-C_4H_9
3g[d]	7.2–7.75		3.80		3.50	2.6 N*H*, 1.03 *t*-C_4H_9
2h[d]		4.30		6.05, 6.35		
3h[d]	7.2–7.8		3.78		3.24	2.2–2.6 CH_2NCH_2, 1.3–1.7 $(CH_2)_3$

[a] Chemical shifts in δ units from internal TMS. All resonances integrated correctly for the proposed structures. [b] Carbon tetrachloride. [c] Pentane. [d] Chloroform-*d*. [e] Benzal proton ($C_6H_5CH{=}C$) resonance masked by aromatic absorption. [f] A pair of singlets due to presence of diastereomers. [g] Diastereotopic protons with J = 12 Hz. See R. E. Lyle, J. J. Thomas, and D. A. Walsh in "Conformational Analysis," G. Chiurdoglu, Ed., Academic Press, New York, N.Y., 1971, pp 157–164.

the basicity of the amine. For example, diisopropylamine is reported to be more basic than morpholine; yet, as stated, it is unreactive toward **1a** while morpholine reacts smoothly.[9]

The formation of normal substitution products **3** can be explained by at least three major pathways (Scheme I).

Scheme I



First, from path a, it is known that all examples of the rearrangement–substitution products **2** slowly isomerize in chloroform or carbon tetrachloride solvent at high concentration (30–50% by volume) to the thermodynamically more stable isomers **3** (eq 3). Qualitatively, the more polar solvent provided a faster rate of rearrangement. This solvent effect has also been observed for the self-rearrangement of Ib and considered to be an intramolecular isomerization.[3b] However, the requisite high concentrations in the more polar solvents necessary to effect this isomerization preclude the importance of this pathway for the formation of 3 under the conditions of eq 2.

A second major pathway (path b) to consider involves a direct SN2 substitution mechanism. Indeed, primary allyl halides react with amines to yield mainly normal substitution products.[10] Nevertheless, our data suggest initial attack of amine on the γ-carbon atom of the allyl system in **1**. With *tert*-butylamine, only **2a** was formed. However, when the reaction was carried out with excess amine (>2 mol), then a small amount of **3a** was found. It was also determined that the yield of **3** could be reduced appreciably while increasing the yield of **2** if the amine were slowly dripped into the pentane solution of **1a** rather than an immediate mixing of reactants. These data suggest that the most plausible explanation for the formation of **3** is by path c in Scheme I.

The β-carbo allyl bormide **1** reacts with amine to form **2** initially, which then can react with another molecule of amine to undergo a second rearrangement–substitution process to produce **3.** The possibility of this reaction is demonstrated in eq 3.[11] Compounds **1** and **2** can compete with each other for unreacted amine except when the amine is *tert*-butylamine.

The phenyl ring in **1a** appears to exert a product controlling effect from eq 4. Morpholine reacted quantitatively with **3a** to produce **3c;** however, under the same reaction conditions *tert*-butylamine would not react with **3c.** This further supports the conclusion that attack of an amine on **1** or **2** involves a rearrangement–substitution process which we consider to be a variant of an SN2′ mechanism.

It is interesting to note that in Bordwell's criticisms of the purported concertedness of the SN2′ mechanism, reactions involving bond making proceeding well ahead of bond breaking are "difficult to exclude."[12] Without kinetic data on the reactions of amines with **1** we cannot comment on the concertedness of these reactions.

Experimental Section

Melting points were determined with a Mel-Temp Laboratory Device and are uncorrected. Infrared spectra were collected on Perkin-Elmer Model 237 and 621 spectrophotometers. Nuclear magnetic resonance data were recorded on Varian Models A-60 and A-60D. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Methyl α-(Bromomethyl)cinnamate (1a). A 145-g (0.895 mol) sample of α-(methyl)cinnamic acid,[13] mp 78.5–79° (lit. 81°), in 500 ml of methanol containing *ca.* 0.5 ml of concentrated sulfuric acid was refluxed 5 days. The methanol was evaporated and the residue taken up in ether, washed with water and 10% potassium hydroxide, and again with water. The ethereal layer was dried with mag-

Table III
Elemental Analysis and Infrared Data

Compd	Calculated C	H	N	X[a]	Found C	H	N	X[a]	$\nu_{C=O}$[b]	Mp, °C
2a[c]	63.48	7.81	4.94	12.49	63.58	7.80	4.96	12.61	1710	183.5–184.5
3a[c]	63.48	7.81	4.94	12.49	63.48	7.89	4.99	12.61	1710	14–175.5
3b[d]	54.10	4.95	11.47		54.32	5.07	11.41		1711	134.5–135.5
2c[d]	51.43	4.52	11.42		51.32	4.58	11.34			180–181
3c[d]	51.43	4.52	11.42		51.62	4.71	11.22		1714	172–174
3d[d]	55.81	5.46	10.85		56.01	5.38	10.98		1714	131.5–133
3e[d]	54.98	5.22	11.15		54.85	5.16	11.18		1712	124–126.5
3f[e]	57.61	6.83	3.96	22.57	57.28	6.88	3.79	22.71	1715	170–172
2g[c]	56.60	6.65	4.40	22.28	56.70	6.73	4.21	22.01	1713	178–179
3g[c]	56.60	6.65	4.40	22.28	56.39	6.69	4.24	22.09	1701	198.5–199.5
3h[d]	50.53	4.43	10.72	6.78	50.49	4.46	10.76	6.52	1712	193–194

[a] Where X is bromide or chloride. [b] Free amine calibrated against polystyrene in CCl_4. [c] Hydrochloride. [d] Picrate. [e] Hydrobromide. [f] In $CHCl_3$.

nesium sulfate and the solvent evaporated to leave 96.1 g (61%) of methyl α-(methyl)cinnamate which solidified upon standing: mp 36–37° (lit.[14] 39°); pmr (CCl_4) δ 7.67 (m, 1, C_6H_5CH), 7.2–7.5 (m, 5, aromatic), 4.76 (s, 3, OCH_3), and 2.09 (d, J = 2 Hz, 3, vinyl CH_3); $\nu_{C=O}$ (CCl_4) 1713 cm^{-1}.

An 80-g (0.45 mol) sample of the methyl ester in 200 ml of carbon tetrachloride containing 80 g (0.45 mol) of *N*-bromosuccinimide and *ca.* 0.01 g of benzoyl peroxide was refluxed for 6 hr, cooled to room temperature, and filtered, and the solvent removed *in vacuo* with heating. The residue was distilled through a 6-in. glass Vigreux column and a light yellow oil collected at 100–140° (1–2.5 mm), 92 g (80%). A second distillation provided analytically pure product which was used for reaction with amines: pmr (CCl_4) δ 7.78 (m, 1, C_6H_5CH), 7.25–7.7 (m 5, aromatic), 4.35 (s, 2, CH_2Br), and 3.83 (s, 3, OCH_3); $\nu_{C=O}$ (CCl_4) 1712 cm^{-1}.

Anal. Calcd for $C_{11}H_{11}BrO_2$: C, 51.99; H, 4.36; Br, 31.45. Found: C, 52.03; H, 4.36; Br, 31.51.

Methyl α-(Bromomethyl)-4-chlorocinnamate (1b). α-(Methyl)-4-chlorocinnamic acid was prepared by a previously published procedure in 52% yield, mp 162–165° (lit.[15] 167°). A 37-g (0.186 mol) sample of the acid in 60 g (1.86 mol) of methanol containing 3.0 ml of concentrated sulfuric acid was refluxed 25 hr, cooled to room temperature, and taken up in ether. The ethereal solution was washed with water, saturated sodium bicarbonate, and again with water. The aqueous washings were then extracted with ether, the combined ethereal solutions dried with magnesium sulfate, and the solvent evaporated *in vacuo* with warming to leave 31.7 g (80.5%) of the methyl ester as an oil: pmr (CCl_4) δ 7.4 (m, 1, ClC_6H_4CH), 7.15–7.25 (m, 4, aromatic), 3.67 (s, 3, OCH_3), and 2.0 (d, J = 1.5 Hz, 3, CH_3); $\nu_{C=O}$ (CCl_4) 1718 cm^{-1}.

Anal. Calcd for $C_{11}H_{11}ClO_2$: C, 62.72; H, 5.26; Cl, 16.84. Found: C, 62.61; H, 5.30; Cl, 17.10.

A 31.7-g (0.149 mol) sample of the methyl ester in 175 ml of carbon tetrachloride containing 26.5 g (0.149 mol) of *N*-bromosuccinimide and a catalytic amount of benzoyl peroxide was refluxed 21 hr and filtered, and the solvent evaporated *in vacuo* with warming to leave a light yellow oil. The oil was taken up in ether–hexane (1:5, v/v) and cooled to induce crystallization of 26.4 g (6.1.2%) of white crystals: mp 35–35.5°; pmr (CCl_4) δ 7.6 (s, 1, ClC_6H_4CH), 7.4 (s, 4, aromatic), 4.26 (s, 2, CH_2Br), and 3.80 (s, 3, OCH_3); $\nu_{C=O}$ (CCl_4) 1724 cm^{-1}.

Anal. Calcd for $C_{11}H_{10}BrClO_2$: C, 45.63; H, 3.48; Br and Cl, 39.84. Found: C, 45.63; H, 3.47; Br and Cl, 39.97.

General Procedure for the Reaction of Amines with 1a and 1b. A small amount of **1a** or **1b** dissolved in pentane was treated at once with 2 mol equiv of amine in a small volume of the same solvent. The mixture was filtered to remove amine hydrobromide, followed by evaporation of solvent *in vacuo* at room temperature to a small volume for analysis by pmr. The solvent was then evaporated completely and the reaction product(s) taken up in carbon tetrachloride or chloroform-*d* and allowed to stand several days for complete isomerization to the normal substitution product which was fully characterized. See Tables I–III for results and data.

Reaction of Methyl α-(α-*tert*-Butylaminobenzyl)acrylate (2a) with Morpholine. A 0.95-g (3.85 mmol) sample of **2a** was dissolved in 10 ml of pentane containing 0.43 g (5.0 mmol) of morpholine. The contents were kept at room temperature for 5 days and analyzed by pmr to show a quantitative conversion to **3c**.

Reaction of Methyl α-(*tert*-Butylaminomethyl)cinnamate (3a) with Morpholine. To a pmr tube containing chloroform-*d* was added a small amount of **3a** and morpholine in a 1:7 mole ratio, respectively. The contents were kept at room temperature 13 days and analyzed by pmr to show complete conversion of **3a** to **3c**.

Attempted Reaction of Methyl α-(Morpholinomethyl)cinnamate (3c) with *tert*-Butylamine. A 0.58-g (2.37 mmol) sample of **3c** dissolved in chloroform-*d* containing 1.20 g (16.5 mmol) of *tert*-butylamine stood at room temperature 153 hr with no reaction observed by pmr.

Attempted Reaction of Methyl α-(Methyl)cinnamate with Morpholine. A 1.65-g (0.01 mol) sample of ester was dissolved in 17.5 ml (0.2 mol) of morpholine and was kept at room temperature for 8 days. The morpholine was evaporated *in vacuo* and the residue analyzed by pmr to show only the starting material.

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Registry No.—**1a,** 53059-43-1; **1b,** 53059-44-2; **2a,** 53059-45-3; **2a** HCl, 53059-46-4; **2b,** 53059-47-5; **2c,** 53059-48-6; **2c** picrate, 53059-49-7; **2d,** 53059-50-0; **2e** isomer a, 53059-51-1; **2e** isomer b, 53059-52-2; **2f,** 53059-53-3; **2g,** 53059-54-4; **2g** HCl, 53059-55-5; **2h,** 53059-56-6; **3a,** 53059-57-7; **3a** HCl, 53059-58-8; **3b,** 53059-59-9; **3b** picrate, 53059-60-2; **3c,** 53059-61-3; **3c** picrate, 53059-62-4; **3d,** 53059-63-5; **3d** picrate, 53059-64-6; **3e,** 53059-65-7; **3e** picrate, 53059-66-8; **3f,** 53059-67-9; **3f** HBr, 53059-68-0; **3g,** 53059-69-1; **3g** HCl, 53059-70-4; **3h,** 53059-71-5; **3h** picrate, 53059-72-6; *tert*-butylamine, 75-64-9; piperidine, 110-89-4; morpholine, 110-91-8; *N*-methylcyclohexylamine, 100-60-7; 2-methylpiperidine, 109-05-7; 2,6-dimethylpiperidine, 504-03-0; 2,5-dimethylpyrrolidine, 3378-71-0; *N*-methylisopropylamine, 4747-21-1; diisopropylamine, 108-18-9; α-(methyl)cinnamic acid, 1199-77-5; methyl α-(methyl)cinnamate, 25692-59-5; *N*-bromosuccimide, 128-08-5; α-(methyl)-4-chlorocinnamic acid, 1202-60-4; methyl α-(methyl)-4-chlorocinnamate, 53059-73-7.

References and Notes

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