the ether layer was separated, and the residue was washed thoroughly with fresh ether. Evaporation of the combined ether portions gave a yellow oil which after Cu^{2+}-catalyzed air oxidation and TLC on silica gel gave 15 mg (20%) of **23:** ir 3360 (OH), 1640 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity) 268.229 (6) (calcd for $C_{16}H_{30}NO_2$, 268.228), 228 (18), 212 (19), 196 (27), 180 (30), 164 (41), 156 (43), 123 (42), 109 (56), 95 (85), 93 (84), 81 (100), 67 (84), 55 (74), 41 (73).

2,2,4,4,6-Pentamethyltetrahydrooxazine-*N*-oxyl (26) and 3-Aza-6-hydroxy-2,2,4,4-tetramethylheptane-*N*-oxyl (29). To a solution of 76 mg (0.48 mmol) of **9** in 5 ml of dry ether with stirring at 25 °C was added 4 equiv of 2 M methyllithium in ether. After 1 h, aqueous 20% K_2CO_3 was added and the ether phase was separated and combined with several ether washings of the aqueous residue. Evaporation of the solvent gave a nearly colorless oil (79.5 mg) which was taken up in 5 ml of CH_3OH and stirred under air with 2 mg of $Cu(OAc)_2 \cdot H_2O$ for 30 min. Evaporation of the solvent and preparative tlc on silica gel gave 15 mg (18%) of nitroxide **26** (considerable loss due to volatility), mass spectrum *m/e* (rel intensity) 172.133 (5) (calcd for $C_9H_{18}NO_2$, 172.134), 157 (5), 142 (5), 114 (20), 84 (49), 69 (100), 59 (35), 43 (55), 41 (47); and 22 mg (24%) of nitroxide **29,** ir 3430 cm^{-1} (OH), mass spectrum 188.163 (12) (calcd for $C_{10}H_{22}NO_2$, 188.165), 158 (6), 132 (13), 114 (23), 88 (40), 84 (30), 83 (36), 74 (33), 56 (22), 57 (100), 45 (41), 43 (20), 41 (38).

Treatment of **26** with phenylhydrazine in $CDCl_3$[13] gave the corresponding *N*-hydroxylamine **24:** NMR δ 1.18 [3 H, d (*J* = 6 Hz)], 1.28 (6 H, s, *gem*-Me), 2.45 (3 H, s, *gem*-Me), 2.47 (3 H, s, *gem*-Me), 5.04 (1 H, m, CHO).

Treatment of **29** with phenylhydrazine in $CDCl_3$ gave the corresponding *N*-hydroxylamine **28:** NMR δ 1.28 [3 H, d (*J* = 6 Hz)], 1.30 (3 H, s, *gem*-Me), 1.34 (9 H, s, *tert*-butyl), 4.20 (1 H, m, CHO).

2-Butyl-2,4,4,6-tetramethyltetrahydrooxazine-*N*-oxyl (27). Similarly prepared by the method above was nitroxide **27** in 18% yield: mass spectrum *m/e* (rel intensity) 214.183 (12) (calcd for $C_{12}H_{24}NO_2$, 214.181), 199 (3), 157 (25), 114 (43), 101 (32), 84 (84), 69 (83), 55 (29), 43 (93), 41 (100).

Acknowledgment. This research was supported by Public Health Service Research Grant CA-17338 from the National Cancer Institute.

Registry No.—**1,** 55011-28-4; **2,** 55011-29-5; **3,** 55011-30-8; **4,** 59813-15-9; **5,** 59813-16-0; **6,** 59813-17-1; **7,** 26939-18-4; **8,** 59813-18-2; **9,** 59813-19-3; **10,** 59813-13-7; **10** dimer, 59813-14-8; **11,** 59813-20-6; **12,** 59813-21-7; **13** (R = CH_2CH_3), 55011-32-0; **13** [R = $(CH_2)_6CH_3$], 55011-33-1; **13** (R = vinyl), 55011-34-2; **14** (R = CH_2CH_3), 55011-35-3; **14** [R = $(CH_2)_6CH_3$], 55011-36-4; **14** (R = vinyl, 55011-37-5; **18,** 56348-28-8; **19,** 59813-22-8; **20,** 59813-23-9; **21,** 59813-24-0; **22,** 59813-25-1; **23,** 59813-26-2; **24,** 59813-27-3; **26,** 55179-45-8; **27,** 59813-28-4; **28,** 59813-29-5; **29,** 59813-30-8; 2-nitro-2-methylpropanol, 76-39-1; hexanoic acid, 142-62-1; oxaziridine, 6827-26-5; 1-hexyne, 693-02-7; phenylhydrazine, 100-63-0.

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Mobile Activated Allyl Systems. 19.[1] Reactions of Amines with α-(Bromomethyl)cinnamonitrile

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The reactions of a variety of amines with α-(bromomethyl)cinnamonitrile (1) in solvents of different polarities are reported. The ratio of the two products formed, namely the substitution–rearrangement (S–R) product **2** and the substitution product **3,** was found to vary with the polarity of the solvent as well as with the basicity and the steric effectiveness of the amine used. Except for the *tert*-butylamine reaction product **2a** and the diisopropylamine reaction product **2e,** all S–R products **2** isomerized to the thermodynamically more stable substitution products **3** in a polar solvent. Product **2a** was found to be susceptible to the attack of free amines to give the appropriate amine exchange product **3.** Product **2e,** however, was inert even to the highly reactive nucleophile piperidine.

Although primary allyl halides react with amines to give normal substitutions, Cromwell and Rebman[2] observed substitution–rearrangement (S–R) products upon treatment of *trans*-α-(bromomethyl)chalcone (Ia) with *tert*-butylamine and piperidine in hydrocarbon solvents. The amine reaction has been extended to other mobile allyl systems, namely, α-(bromomethyl)benzalacetone (Ib)[3] and methyl α-(bromomethyl)cinnamate (Ic).[4] In hydrocarbon solvents, morpholine and piperidine react with the above-mentioned mobile allyl systems to give both substitution and S–R products. With *tert*-butylamine, only the S–R products were isolated. It has been shown that the amine molecule attacks the mobile keto allyl system in an S_N2' manner, giving initially the S–R product (II). The substitution product (III) is a result of either

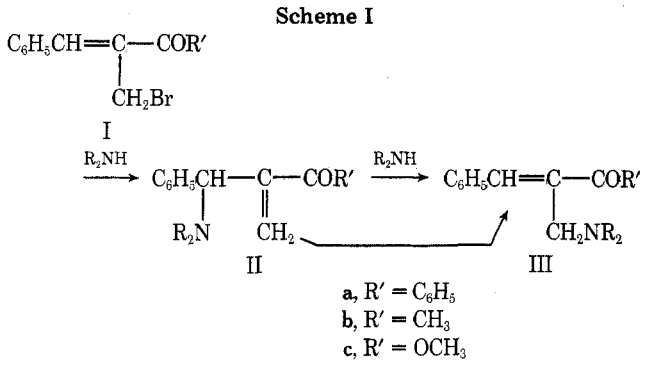
Table I. 60-HMz Proton Magnetic Resonance Data[a]

Compd	Aromatic[b]	C_6H_5CH	$C{=}CH_2$	CH_2N	Amine group
2a	7.26	4.45	5.82, 6.04		1.08 (s), *tert*-butyl
3a	7.05–7.80			3.43	1.12 (s), *tert*-butyl
2b	7.10–7.90	3.80	5.77, 5.88		2.17–2.50 (m), $-\mathbf{H_2}CNCH_2-$ 1.50 (m), $-CH_2\mathbf{CH_2}CH_2-$
3b	7.00–7.90			3.18	2.20–2.60 (m), $-CH_2NCH_2-$ 1.50 (m), $-(CH_2)_3-$
2c	7.12–7.90		5.87, 6.01		3.53–3.85 (m),[c] $-CH_2OCH_2-$ 2.26–2.62 (m) $-CH_2NCH_2-$
3c	7.00–7.90			3.21	3.56–3.78 (m) $-CH_2OCH_2$ 2.35–2.60 (m) $-CH_2NCH_2-$
2d	7.05–8.00	4.34	5.84, 5.92		2.60 (q), CH_2CH_3 0.98 (t), $-CH_2CH_3$
3d	7.00–7.90			3.30	2.57,[d] $-CH_2CH_3$, 1.00,[e] $-CH_2CH_3$
2e	7.15–7.90	4.80	5.97, 6.02		3.07 (h), $-CH(CH_3)_2$ 0.90 (d), 1.12 (d), Nonequivalent $-CH_3$
3e	7.16–7.92			3.38	3.07 (h), $-CH(CH_3)_2$ 1.02 (d), $-CH(CH_3)_2$

[a] Chemical shift in δ units from internal Me_4Si. [b] Benzal proton hidden in this region also. [c] Benzyl proton hidden in this region. [d] Overlap of 2 quartet. [e] Overlap of 2 triplet, believed to be attributable to the existence of two geometrical isomers of **3d.**

the autocatalytic rearrangement of the S–R product in a more polar solvent like chloroform, or the attack of a second mole of the appropriate amine on the S–R product in a second rearrangement–substitution. The processes are summarized in Scheme I.

Scheme I

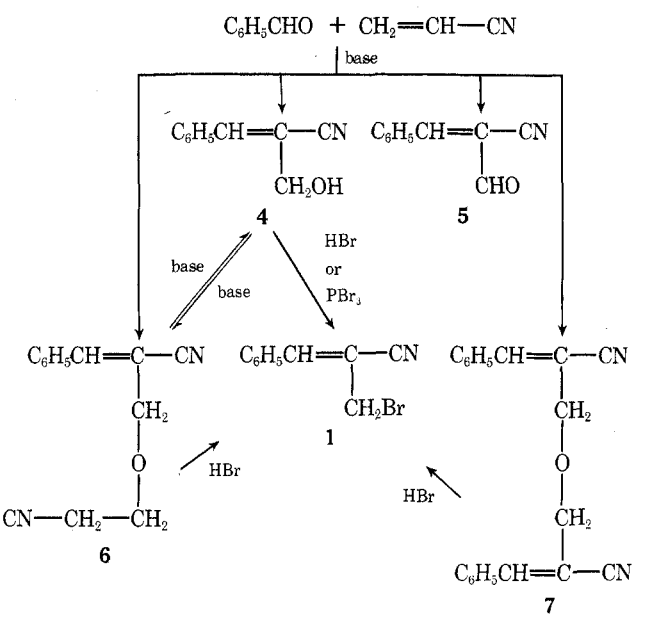


In the case of β-keto secondary allyl halides, the SN2′ mechanism is by no means the only way an amine can attack the mobile allyl system. Previously it has been reported that the direct attack of an amine at the allylic position proceeded parallel with the expected SN2′ reaction for the reaction of *tert*-butylamine with 2-(α-bromobenzyl)-4,4-dimethyl-1,4-dihydro-1-ketonaphthalene.[5] It occurred to us that studies of the reaction of amines with α-(bromomethyl)cinnamonitrile, where the β-carbonyl group has been replaced by a nitrile group, might provide further insight into the nature of the competitive reaction pathways available to these mobile allyl systems.

Results

Preparation of the starting material α-(bromomethyl)cinnamonitrile (**1**) was performed by modifying the procedure reported by Wasserman et al.[6] The base-catalyzed condensation of benzaldehyde and acrylonitrile yielded four products (Scheme II), three of which can be converted to **1.** Instead of isolating the useful compounds one by one, **4, 6,** and **7** were separated from the resulting crude oil by vacuum distillation as a mixture. The mixture was then refluxed with 48% aqueous hydrobromic acid in glacial acetic acid. Compound **1** precipitated when the reaction mixture was poured into ice water.

Scheme II



Recrystallization from hot hexane gave white, scaly crystals.

The reactions of **1** with 2 molar equiv of amines were carried out in a number of solvents. The amine hydrobromide formed during the reaction precipitated upon replacement of the solvent with ether and was removed by filtration. Evaporation of the solvent in vacuo yielded the product(s), which was analyzed immediately by ^1H NMR spectroscopy.

The two substitution products are readily distinguished from each other by ^1H NMR spectroscopy (Table I). Compound **2** exhibits three singlets (slightly broadened due to geminal and allylic coupling), assigned to the benzylic and vinylic protons. For **3,** the vinyl and methylene proton bands are characteristic (Table I).

Except in the cases when acetonitrile was used as solvent, **2** was found to be the exclusive or major product. A summary of the results is listed in Table II.

The S–R products **2b, 2c,** and **2d** were observed to rearrange to their thermodynamically more stable isomers, i.e., the substitution products **3b, 3c,** and **3d,** on standing in a polar

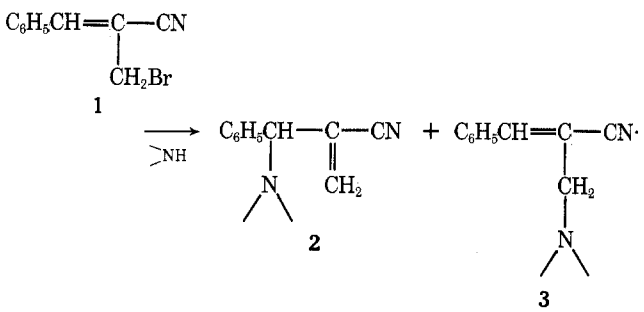
Table II. Amine Reaction with 1

Amount of substrate, mol	Amine	Amount of amine, mol	% amine hydrobromide	Solvent (ml)	Reaction time, h	Product
0.018	*tert*-Butylamine	0.071	90	*n*-Hexane (350)	48	**2a** (100)
0.0045	*tert*-Butylamine	0.009	92	Benzene (50)	48	**2a:3a** (>95:<5)
0.0045	*tert*-Butylamine	0.009	95	Chloroform (50)	48	**2a:3a** (70:30)
0.0045	*tert*-Butylamine	0.009	100	Acetonitrile (50)	8	**2a:3a** (30:70)
0.0045	Piperidine	0.009	98	*n*-Hexane (150)	0.25	**2b:3b** (>95:<5)
0.0045	Piperidine	0.009	100	Chloroform (50)	0.25	**2b:3b** (80:20)
0.0045	Morpholine	0.009	92	*n*-Hexane (150)	5.5	**2c:3c** (>95:<5)
0.0045	Morpholine	0.009	95	Chloroform (50)	3	**2c:3c** (>95:<5)
0.0045	Diethylamine	0.009	100	*n*-Hexane (150)	5.5	**2d** (100)
0.0045	Diethylamine	0.009	98	Chloroform (50)	3	**2d:3d** (70:30)
0.0045	Diisopropylamine	0.015	0	Benzene (100)	13	No reaction
0.0045	Diisopropylamine	0.015	78	Benzene (reflux) (100)	60	**2e:3e** (30:70)
0.0045	Diisopropylamine	0.015	53	*n*-Hexane (reflux) (300)	11 days	**2e** (100)
0.0045	Diisopropylamine	0.015	100	Acetonitrile (100)	3 days	**3e** (100)

Table III. Elemental Analysis and Infrared Data

	Calcd			Found				
Comp	C	H	N	C	H	N	$\nu_{C\equiv N}$	Mp, °C
2a[a]	67.06	7.50	11.17	67.00	7.73	11.40	2240	169
3a[a]	67.06	7.50	11.17	67.02	7.79	11.30	2220	244
3b[a]	68.57	7.20	10.67	68.58	7.39	10.77	2220	218
3c[b]	52.52	4.16	15.31	52.57	4.29	15.34	2220	237
3d[b]	54.18	4.70	15.80	54.13	4.83	15.78	2230	118
3e[b]	56.05	5.31	14.86	55.96	5.07	14.82	2222	197

[a] Hydrochloride. [b] Picrate.



solvent ($CDCl_3$), in the absence of additional appropriate free amine. The rate of conversion was fastest for **2b** → **3b**, while that of **2d** → **3d** was found to be the slowest among the three. However, **2a** and **2e** were found not to convert to their other isomers autocatalytically.

The reaction of **2a** with amines at room temperature in carbon tetrachloride was followed by ^1H NMR spectroscopy. The results are listed in Table IV. S–R product **2a** reacted with piperidine and morpholine to produce **3b** and **3c**, quantitatively. However, treatment of **2a** with the sterically bulky diethylamine and *tert*-butylamine did not effect such a change under these conditions. Substitution product **3a** was successfully prepared by the reaction of a large excess of *tert*-butylamine with **2a** in acetonitrile over a period of 50 days.

On standing in a polar solvent with or without the presence of excess free amine, the sterically restricted **2e** was observed not to convert to **3e** which might be expected to be the thermodynamically more stable isomer. Compound **3e** was inert even to piperidine.

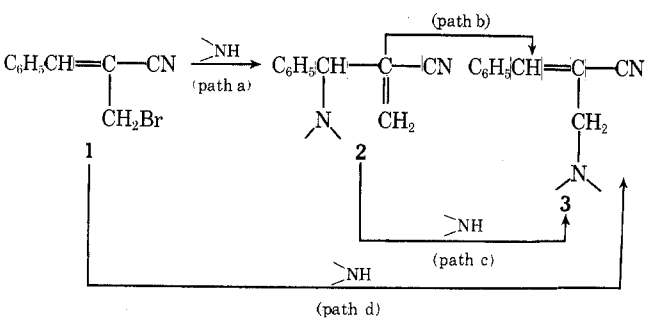
Discussion

Attack of amines on **1** can occur in two ways, namely, the amine molecule may attack the benzal carbon in a SN2′ manner, yielding **2** (Scheme III, path a), or the amine may attack the allylic position directly, yielding **3** (Scheme III, path d). The former route, which is the normal case in most of the mobile ketoallyl systems being studied, is shown by the reaction of various amines with **1** in nonpolar solvents. Compound **2** was observed to be the exclusive or major product in all cases. The latter route, although rare in other studies of similar systems, appears to occur with the mobile cyanoallyl system. Here when **1** is treated with *tert*-butylamine or di-

Table IV. Amine Exchange Reaction with 2a

Amine used	[Amine]/[precursor]	Time necessary for >90% conversion
tert-Butylamine	>3	No significant reaction
Piperidine	~3	11 h
Morpholine	~2.5	48 h
Diethylamine	~3	No significant reaction

Scheme III



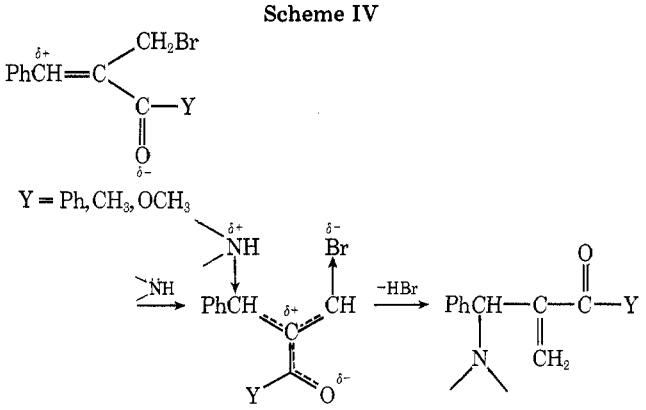
isopropylamine in a solvent more polar than a saturated hydrocarbon, both **2** and **3** were observed to form in parallel reactions. The rate for **2a** to convert to **3a** was negligible in the absence of free amine, and was slow compared to the formation of **3a** when the reaction of amine with **1** was run in a polar solvent. Also, under no circumstances could **2e** be converted to **3e.** Evidently, both pathways (path a and path d) occur in a parallel manner in the reaction of *tert*-butylamine and diisopropylamine with **1** in polar solvents.

Product **3,** arising from a second SN2′ reaction, was also observed in the mobile cyano system (Scheme III, path c). Such a mechanistic pathway for **2** → **3** conversion was established previously with β-ketoallylamines.[7,8] Results of the amine exchange reaction of different amines with **2a** are summarized in Table III. The rate of conversion was found to be a function of the basicity of the amine used. The reaction of **1** with piperidine is much faster than the reaction of **1** with other amines with lower basicity. However, basicity is not the only factor that has to be taken into account in understanding these reactions. Steric size of the free amine used plays an important role also. Diethylamine is more basic than morpholine, but diethylamine is resistant to displacing the *tert*-butylamine from **2a,** while morpholine is able to accomplish this, though slowly. Also, the fact that **2a** converts to **3a** with difficulty (in large excess of free amine and after a period of 50 days) and **2e** does not convert to **3e** (even in the presence of free amine) is believed to be attributable to the steric effectiveness of the alkyl group of the two amino groupings. This point is further illustrated by **2e** being inert even to piperidine.

Isomer **3** can also arise from autorearrangement of **2**[10] (Scheme III, path b, no excess amine present). Compounds **2b, 2c,** and **2d** were observed to isomerize in this fashion to **3b, 3c,** and **3d,** respectively, the thermodynamically more stable isomers. The fact that **2a** and **2e** do not isomerize, respectively, to **3a** and **3e** is attributed again to the steric requirements of the alkyl group of the amino function.

The formation of S–R products from the reaction of amines with β-carboallyl 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,[3,4,9] Scheme IV. The oxygen atom of the β-carbo group accepts

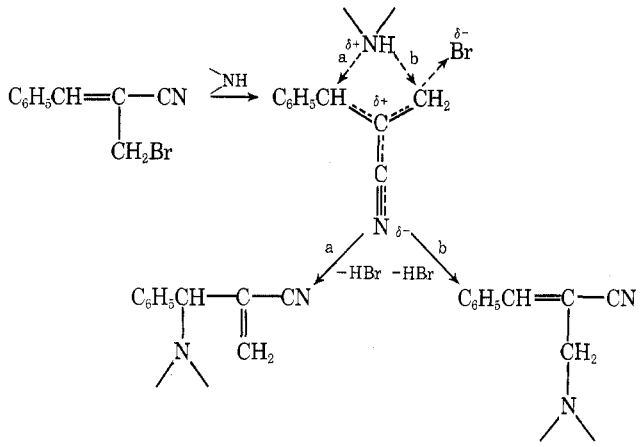
Scheme IV



much of the developing negative charge which is ultimately carried away by the leaving halide ion.

Owing to the noninterconvertibility of **2a** and **2e,** respectively, to **3a** and **3e,** autocatalytically, we suggest another mode of amine attack on the activated allyl halide in the reaction of *tert*-butylamine and diisopropylamine with the mobile cyano allyl bromide **1.** It is possible that in the more polar solvents, the carbon–bromine bond lengthens at a rate so fast that direct attack of the amine at the allylic carbon becomes a competitive pathway to the well-established SN2′ pathway as described before; see Scheme V.

Scheme V



Experimental Section

Melting points were determined from a Mel-Temp apparatus, and were uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. The proton magnetic resonance spectra were determined from a Varian Model A-60 spectrometer, utilizing tetramethylsilane as an internal standard. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill., or by Chemalytics, Inc., Tempe, Ariz. ^{1}H NMR data obtained in deuteriochloroform are listed in Table I.

Preparation of α-(Bromomethyl)cinnamonitrile (1). To a mixture of 106 g (1 mol) of benzaldehyde and 5 ml of 30% KOH/MeOH solution in 100 g of *tert*-butyl alcohol at the temperature of ice was added 106 g (2 mol) of acrylonitrile over a period of 1.5 h. The mixture was then stirred at room temperature for 8 h. The viscous solution was acidified with hydrochloric acid to pH 2–3. The solution was diluted with 500 ml of diethyl ether, and was washed repeatedly with water. The ethereal solution was washed with saturated brine and dried over anhydrous sodium sulfate. Removal of the solvent in vacuo yielded a yellow, viscous oil, which was then subjected to vacuum distillation (0.3–1 mmHg). At 120 °C, a colorless oil, which solidified on cooling, was distilled, ir $\nu_{C=O}$ 1700 cm^{-1}. Between 134 and 220 °C, 148 g of yellow oil was distilled over, ir ν_{C-O} 1115 cm^{-1}.

A sample of 25.6 g of the yellow oil obtained in the previous reaction was refluxed with 140 ml of 48% hydrobromic acid and 200 ml of glacial acetic acid for 2 h. The cooled yellow solution was poured into ice water with vigorous stirring. The precipitate thus formed was filtered off, and was washed with a large quantity of water to remove the acid. Recrystallization from light petroleum yielded 19.39 g of **1** as white crystals: mp 44–49 °C (lit. 54–55 °C); ir (KBr) ν (Nujol) 2225, 540 cm^{-1}; ^{1}H NMR (CCl_4) 4.18 (s, 2 H, $-CH_2Br$), 7.17 (s, 1 H, benzal proton), 7.25–7.90 ppm (m, 5 H, aromatic protons). A total of 106 g (48%, with respect to the benzaldehyde used) of **1** was obtained for a number of trials under similar conditions.

General Procedure for the Reaction of Amines with 1. A measured quantity of **1** dissolved in a specified quantity of solvent was treated with 2 molar equiv of the appropriate amine. After the reaction was complete the mixture was filtered to remove the amine hydrobromide, the weight of which was determined to estimate the percent yield of the reaction. In case a polar solvent, like chloroform or acetonitrile, was used, the solvent was replaced by an apolar solvent to precipitate the inorganic salt. The product oil was analyzed by ^{1}H NMR spectroscopy. Upon standing in chloroform for several days the stable product formed and was fully characterized. See Tables I–III for results and data.

Reaction of Diisopropylamine with 1 in Hexane and Then in Acetonitrile. To a solution of 1 g (4.50×10^{-3} mol) of **1** in 300 ml of *n*-hexane was added 1.5 g (1.43×10^{-2} mol) of diisopropylamine. The solution was stoppered and stirred for 12 h. No inorganic salt precipitated, implying that no reaction was taking place. The solution was then refluxed for 11 days and 440 mg (53%) of the amine hydrobromide salt was removed by filtration. Removal of the solvent in vacuo yielded a yellow oil, which was immediately identified to be a mixture of **2e** and starting material.

The acetonitrile solution of the above mixture was treated with another 1.5 g of diisopropylamine. The solution was stoppered and stirred for 4 days. The solvent was removed in vacuo. Treatment of the residue with diethyl ether yielded another 380 mg (47%) of amine hydrobromide salt. Removal of the ether in vacuo yielded a yellow oil, which was identified to be a mixture of **2e** and **3e.** It was observed that

the absorption in the ^{1}H NMR spectrum corresponding to the vinyl protons of **2e** did not change in intensity after treatment with diisopropylamine the second time.

Attempted Conversion of 2a to 3a. A 70:30 mixture of **2a:3a** was allowed to stand in deuteriochloroform for several days. No significant change was observed in the ^{1}H NMR spectrum of the product mixture. The mixture was then refluxed in chloroform (15 h) and then in acetonitrile (7 h). In neither case could significant changes be observed in the ^{1}H NMR spectrum.

General Procedure for the Amine Exchange Reaction. To a solution of 164 mg (0.000738 mol) of **2a** in 1.5 ml of carbon tetrachloride was added quickly approximately 2–3 molar equiv of the appropriate amine. The solution was filtered into a ^{1}H NMR tube. The concentration of the amine could be estimated by the intensity of the ^{1}H NMR signal relative to that of **2a**. The reaction was monitored by the relative intensity of the signals corresponding to respectively the vinylic protons of the precursor and the allylic protons of the product. Another tube holding only **2a** in carbon tetrachloride was used as a control to the experiment. See Table IV for results and data.

Attempted Reaction of 2e with Diisopropylamine. To a solution of 160 mg (0.00061 mol) of a 30:70 mixture of **2e** and **3e** in 30 ml of acetonitrile was added 287 mg (0.0028 mol) of diisopropylamine. The solution was stoppered and stirred for 13 h. Removal of the solvent and unreacted amine yielded a yellowish oil (quantitative), which was spectrally equivalent to the unreacted precursor.

Attempted Reaction of 2e with Piperidine. To a solution of 100 mg (0.00045 mol) of a 30:70 mixture of **2e** and **3e** in 10 ml of benzene was added 360 mg (0.0042 mol) of piperidine. The solution was stoppered and stirred for 13 h. Removal of the solvent and the unreacted amine yielded a yellowish oil (quantitative) which was spectrally equivalent to the unreacted precursor.

Reaction of *tert*-Butylamine with a Mixture of 2a and 3a in Acetonitrile. To a solution of 220 mg (0.001 mol) of a mixture of **2a** and **3a** (**2a:3a**, 70:30) in 30 ml of acetonitrile was added 690 mg (0.0094 mol) of *tert*-butylamine. The solution was stoppered and stirred for 53 h. Significant changes in the ratio of the two isomers were observed in the ^{1}H NMR spectrum of the worked up material. Under similar conditions, the solution was stirred for another 50 days. Removal of the solvent and excess amine yielded **3a** as a yellow oil (200 mg, 91%).

A hexane solution of the product was exposed to a stream of hydrogen chloride gas. A white solid was isolated, which on recrystallization from methanol–ether mixture yielded the crystalline amine hydrochloride salt of **3a**.

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Registry No.—**1**, 59728-94-8; **2a**, 59728-95-9; **2a** HCl, 59728-96-0; **2b**, 59728-97-1; **2c**, 59728-98-2; **2d**, 59728-99-3; **2e**, 59729-00-9; **3a**, 59729-01-0; **3a** HCl, 59729-02-0; **3b**, 4933-37-3; **3b** HCl, 59729-03-2; **3c**, 59729-04-3; **3c** picrate, 59729-05-4; **3d**, 59729-06-5; **3d** picrate, 59729-07-6; **3e**, 59729-08-7; **3e** picrate, 59729-09-8; benzaldehyde, 100-52-7; acrylonitrile, 107-13-1; *tert*-butylamine, 75-64-9; piperidine, 110-89-4; morpholine, 110-91-8; diethylamine, 109-89-7; diisopropylamine, 108-18-9.

References and Notes

(1) For the previous paper in this series, see R. J. Murray and N. H. Cromwell, *J. Org. Chem.*, in press. The general title of the series has now been broadened from "Mobile Keto Allyl Systems" to "Mobile Activated Allyl Systems" to allow coverage of activating groupings other than the keto groups.
(2) R. P. Rebman and N. H. Cromwell, *J. Org. Chem.*, **32**, 3830 (1967).
(3) M. C. Eagen and N. H. Cromwell, *J. Org. Chem.*, **39**, 911 (1974).
(4) M. C. Eagen and N. H. Cromwell, *J. Org. Chem.*, **39**, 3863 (1974).
(5) (a) N. H. Cromwell and E-M. Wu, *J. Org. Chem.*, **33**, 1895 (1968); (b) G. Glaros and N. H. Cromwell, *ibid.*, **37**, 862 (1972); (c) *ibid.*, **37**, 867 (1972).
(6) H. H. Wasserman, B. Suryanarayana, and D. D. Gassetti, *J. Am. Chem. Soc.*, **78**, 2808 (1956).
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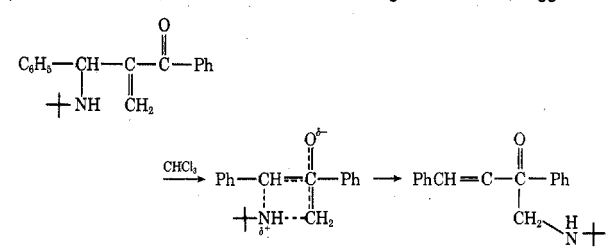
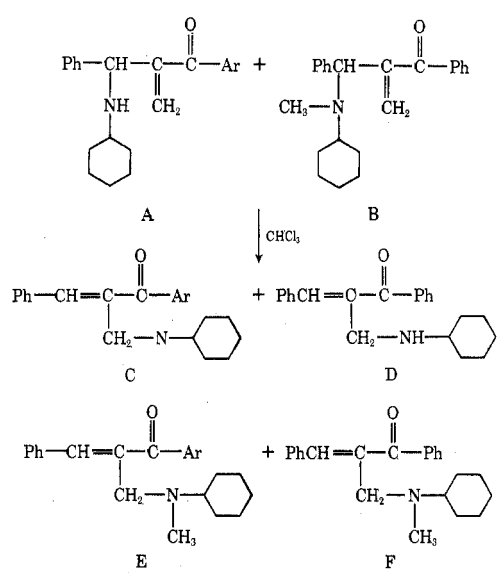
(8) G. Maury, E-M. Wu, and N. H. Cromwell, *J. Org. Chem.*, **33**, 1900 (1968).
(9) A. D. George, E. Doomes, and N. H. Cromwell, *J. Org. Chem.*, **36**, 3918 (1971).
(10) Rebman and Cromwell[1,11] postulated an intramolecular mechanism for the autocatalytic rearrangement of α-(α-*tert*-butylaminobenzyl)acrylophenone. Doomes,[12] on the basis of some rough kinetic data, suggested



that the process was not unimolecular. Eagen,[13] by a crossover experiment, showed that Doomes' suggestion was correct. An equimolar mixture of α-(α-cyclohexylaminobenzyl)-4′-phenylacrylophenone (A) and α-(α-*N*-methylcyclohexylaminobenzyl)acrylophenone (B) was dissolved in chloroform. The rates of rearrangement of A and B, respectively, to their



thermodynamically more stable direct-substitution isomers are somewhat comparable. The solution of A + B was allowed to stand to at room temperature for 72 h. The ^{1}H NMR spectrum of the reaction mixture showed four compounds, C, D, E, and F, to be present.
(11) R. P. Rebman and N. H. Cromwell, *Tetrahedron Lett.*, 4833 (1965).
(12) E. Doomes, Ph.D. Thesis, University of Nebraska, 1968.
(13) M. Eagen, Ph.D. Thesis, University of Nebraska, 1972.