# The Decomposition of Isomeric N-Nitro-N-fluorobutylamines

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N-Nitro-N-fluoro-*t*-butylamine and its primary and secondary isomers were synthesized and the kinetics of their decomposition studied in ethylcyclohexane. The major decomposition products of the tertiary isomer in refluxing carbon tetrachloride were identified as isobutylene, nitrous oxide, hydrogen fluoride, 2-methyl-2-nitropropane, and other nitro compounds having the isobutane carbon skeleton. The nitrogen isotope ratio data determined for the nitrogenous products from the decomposition of the $^{15}N$-labeled tertiary isomer suggest that the primary decomposition step may involve the *t*-butyl radical.

An earlier study[1] in which the thermal stability of N-nitro-N-fluoro-*n*-butylamine was determined suggested this investigation. Since little information is available on the decomposition of compounds containing the nitrogen–fluorine bond, this series of isomeric fluorobutylnitramines offered a practical start since they could be prepared in fair yields and good purity. The purpose of this paper is to report the observed kinetics of the isomeric fluorobutylnitramines and the major decomposition products of the tertiary isomer. Since several aliphatic nitro compounds were products of this decomposition, an $^{15}N$-labeling experiment was conducted in an attempt to determine the source of the nitrogen in the various nitrogenous decomposition products.

## Results

**Kinetics.**—Rates of decomposition and the activation parameters of N-nitro-N-fluoro-*t*-butylamine and its primary and secondary isomers in ethylcyclohexane were measured using infrared spectroscopy and are recorded in Table I. The effect of changes of solvent was investigated for the tertiary isomer and the data are listed in Table II. The rates appeared to follow first-order kinetics and were observed to be linear to over 90% reaction.

**Product Studies.**—The products from the decomposition of the N-nitro-N-fluoro-*t*-butylamine in carbon tetrachloride at 76° are summarized in Table III. The identities of these compounds were confirmed by matching the infrared and nmr spectra and the gas chromatographic retention times with authentic samples.

2-Fluoro-2-methyl-1-nitropropane was characterized from its elemental identification and its infrared and nmr spectrum. The partial structure of a carbonyl component designated as α-X-isobutyraldehyde was determined from its 2,4-dinitrophenylhydrazone derivative. The melting point and the nmr spectrum of this derivative matched exactly an authentic sample of the 2,4-dinitrophenylhydrazone of α-ethoxyisobutyraldehyde. Obviously the ethoxy group replaced the original function during the preparation of the derivative in the alcoholic 2,4-dinitrophenylhydrazone reagent. The identity of ammonium hexafluorosilicate was determined by comparison with an authentic sample using a microscopic technique.[2]

**$^{15}N$ Tracer Study.**—Since there was a variety of nitrogen-containing compounds isolated from the decomposition of N-nitro-N-fluoro-*t*-butylamine, isotopically labeled N-nitro-N-fluoro-*t*-butylamine was prepared with one of the nitrogen atoms enriched with $^{15}N$. It was hoped that the nitrogen isotope analysis might reveal the contribution of each nitrogen to the various nitrogenous decomposition products.

TABLE I

KINETICS OF N-NITRO-N-FLUORO-*t*-BUTYLAMINE DECOMPOSITION IN ETHYLCYCLOHEXANE AND CARBON TETRACHLORIDE

| Isomer | Temp, °C | $k \times 10^4$, $sec^{-1}$ | $\Delta H^*$, kcal | $\Delta S^*$, eu |
|---|---|---|---|---|
| Primary[a] | 70.1 | 2.13 ± 0.10 | 26.3 ± 0.6 | +0.9 |
| | 77.2 | 4.37 ± 0.26 | | |
| | 80.8 | 6.15 ± 0.20 | | |
| | 83.3 | 8.53 ± 0.40 | | |
| | 86.4 | 12.08 ± 0.42 | | |
| Secondary[a] | 71.4 | 1.99 ± 0.10 | 29.7 ± 1.0 | +10.9 |
| | 72.3 | 3.21 ± 0.38 | | |
| | 75.5 | 3.87 ± 0.21 | | |
| | 81.4 | 7.55 ± 0.20 | | |
| | 84.9 | 12.22 ± 0.83 | | |
| Tertiary[a] | 56.2 | 6.53 ± 0.20 | 31.6 ± 1.5 | +22.7 |
| | 58.6 | 9.72 ± 0.97 | | |
| | 61.3 | 13.63 ± 0.60 | | |
| | 66.1 | 20.00 ± 0.28 | | |
| | 77.3 | 63.33 ± 3.3 | | |
| Tertiary[b] | 55.6 | 4.26 ± 0.18 | 22.9 ± 0.4 | −4.6 |
| | 60.0 | 7.54 ± 0.21 | | |
| | 63.1 | 9.71 ± 0.38 | | |
| | 66.4 | 13.39 ± 0.77 | | |

[a] Ethylcyclohexane. [b] Carbon tetrachloride.

TABLE II

EFFECT OF VARIOUS SOLVENTS ON THE RATE OF DECOMPOSITION OF N-NITRO-N-FLUORO-*t*-BUTYLAMINE AT 61.7°

| Solvent | $k \times 10^4$, $sec^{-1}$ |
|---|---|
| Ethylcyclohexane | 14.62 |
| Carbon tetrachloride | 8.41 |
| Carbon tetrachloride–ethanol (2.5:1) | 5.64 |

TABLE III

PRODUCTS OF DECOMPOSITION OF N-NITRO-N-FLUORO-*t*-BUTYLAMINE AT 76° IN CARBON TETRACHLORIDE

| Volatiles[a] | Nonvolatiles |
|---|---|
| Isobutylene | 2-Methyl-2-nitropropane |
| Nitrous oxide | 2-Fluoro-2-methyl-1-nitropropane |
| Hydrogen fluoride | 2-Methyl-1-nitroprop-1-ene |
| Acetone | 2-Hydroxy-2-methyl-1-nitropropane |
| | α-X-isobutyraldehyde |
| | Ammonium hexafluorosilicate |

[a] Examination of the volatile products obtained from the decomposition of N-nitro-N-fluoro-*t*-butylamine under vacuum-line conditions revealed the absence of nitrogen.

(1) W. E. McQuistion, unpublished results.

(2) Microscopical analyses were performed by Mrs. E. A. Whitman, Analytical Branch, General Chemical Division, Naval Ordnance Station, Indian Head, Md.

Isotopically labeled N-nitro-N-fluoro-*t*-butylamine was synthesized starting with ethyl N-*t*-butylcarbamate containing the normal abundance of nitrogen isotopes. Following the procedures of Curry, *et al.*,[3] and Barrott, *et al.*,[4] and using $^{15}N$ enriched nitric acid, the carbamate was converted to N-nitro-*t*-butylamine in which only the nitrogen of the nitro group was reinforced with the heavier isotope. Aqueous fluorination converted this nitramine to N-nitro-N-fluoro-*t*-butylamine with a total $^{15}N$ content of 3.0%. Because the amine nitrogen contained the normal amount of $^{15}N$ (0.36%), the nitrogen of the nitro group was calculated to have 5.64% $^{15}N$.

The isotopically labeled N-nitro-N-fluoro-*t*-butylamine was decomposed in refluxing carbon tetrachloride, the nitrogenous decomposition products were isolated, and their nitrogen isotope ratios were measured by mass spectroscopy. The results of these determinations are listed in Table IV.

TABLE IV

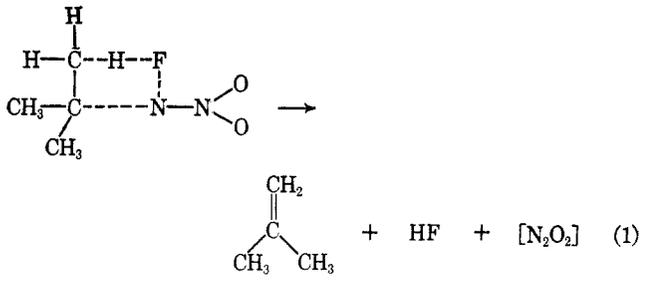
NITROGEN ISOTOPE DETERMINATION OF THE NITROGENOUS DECOMPOSITION PRODUCTS OF $^{15}N$-LABELED N-NITRO-N-FLUORO-*t*-BUTYLAMINE[a]

| Product | $^{15}N$, % |
|---|---|
| Nitrous oxide | 3.2 |
| Ammonium hexafluorosilicate | 4.02 |
| 2-Methyl-2-nitropropane | 3.63 |
| 2-Fluoro-2-methyl-1-nitropropane | 4.07 |
| 2-Hydroxy-2-methyl-1-nitropropane | 4.01 |

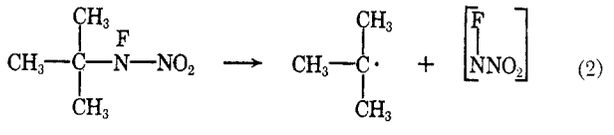
[a] The total $^{15}N$ per cent of the N-nitro-N-fluoro-*t*-butylamine was found to be 3.0; since the amine nitrogen contained only the normal isotope abundance (0.36%), the nitro nitrogen was calculated to have 5.64%.

## Discussion

Examination of Tables I and III reveals that the thermal decomposition of N-nitro-N-fluoro-*t*-butylamine is a complex multiproduct reaction involving complex kinetics featuring considerable rate changes with various solvents and drastically different activation parameters in carbon tetrachloride and ethylcyclohexane. A mixed mechanism is suggested to account for the various types of decomposition products obtained in carbon tetrachloride. One pathway may involve a five-membered cyclic activated complex that could lead to the isobutylene derived compounds (eq 1). The other pathway may involve the homolytic cleavage of the amine C–N bond to yield the *t*-butyl radical[5] (eq 2). The results of the nitrogen isotope measurement may be interpreted to support this mechanism. The *t*-butyl group in the isotopically prepared N-nitro-N-fluoro-*t*-butylamine was bonded to the nitrogen having only the natural isotope abundance; however, the newly formed decomposition product, 2-methyl-2-nitropropane, contained an isotopically enriched nitrogen. This suggests that the original C–N bond was broken and the *t*-butyl fragment recombined with the nitrating species either as a radical or as a carbonium ion. This evidence favors the radical because the alternative carbonium ion would require an unlikely negatively charged nitrating species.



+ HF + $[N_2O_2]$ (1)



(2)

Several attempts were made to show the free-radical nature of this decomposition: (1) acrylonitrile was easily polymerized in the presence of the isomeric fluorobutylnitramines at 70°; (2) an attempt to trap out the *t*-butyl radical with the long-lived free radical ("Galvinoxyl") was unsuccessful; (3) the decomposition of the isomeric fluorobutylnitramines in toluene yielded no detectable bibenzyl; (4) no match was obtained in the vapor phase chromatographic analyses of the decomposition products of the tertiary isomer with an authentic sample of 2,2,3,3-tetramethylbutane, a product that is often found in the production of the *t*-butyl radical. Failure to trap out the *t*-butyl radical may be caused by its short life and the presence of other reactive free radicals produced by the decompositions (such as $NO_2$) with which *t*-butyl radical would react preferentially.

## Experimental Section

The N-nitrobutylamines were prepared according to the methods of Curry, *et al.*,[3] and Barrett, *et al.*[4] The carbon tetrachloride and ethylcyclohexane were spectroquality reagents.

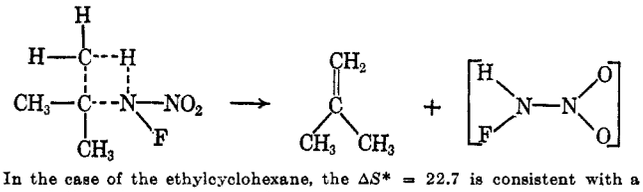
Infrared spectra were recorded on a Beckman IR-8 spectrophotometer, ultraviolet spectra with a Bausch and Lomb 505 spectrophotometer, and nuclear magnetic resonance spectra by a Varian Associates Model DP 60 spectrometer using tetramethylsilane as the internal standard ($\delta = 0$) and deuteriochloroform as the solvent. Vapor phase chromatographic analyses were performed with a Perkin-Elmer 820 chromatograph using a 2-m column containing 20% didecylphthalate supported on Chromosorb W.

**General Preparation of N-Nitro-N-fluorobutylamines.**—Following the procedure of Grakauskas,[6] a mixture of nitrogen and fluorine (4:1) was passed into an agitated solution of 23.6 g (0.2 mole) of the N-nitrobutylamine, 16.0 g (0.4 mole) of sodium hydroxide, and 400 ml of water at a rate that maintained the temperature between 5 and 10° with the aid of an ice–water cooling bath. Fluorination was continued until the reaction mixture became acidic. After purging with nitrogen, the oily product was separated, washed with water, and dried over anhydrous

(3) H. M. Curry and J. P. Mason, *J. Am. Chem. Soc.*, **73**, 5043 (1951).

(4) J. Barrott, U. N. Denton, and A. H. Lamberton, *J. Chem. Soc.*, 1998 (1953).

(5) One referee has suggested that the wide difference in the entropy of activation for the tertiary isomer in carbon tetrachloride and ethylcyclohexane is caused by a change in mechanism. The $\Delta S^* = -4.6$ in carbon tetrachloride suggests an elimination mechanism similar to the gas-phase four-center elimination of $HNO_2$ from 2-nitropropane to give propene.



In the case of the ethylcyclohexane, the $\Delta S^* = 22.7$ is consistent with a homolytic radical cleavage mechanism.

(6) V. Grakauskas, patent applied for.

sodium sulfate. Distillation at reduced pressure yielded the desired N-nitro-N-fluorobutylamines. The boiling points and analytical data for these compounds are given in Table V.

TABLE V

PHYSICAL CONSTANTS OF N-NITRO-N-FLUOROBUTYLAMINES

| Isomer | Yield, % | Bp, °C (mm) | $n^{25}D$ | Empirical formula | Nitrogen, % Calcd | Nitrogen, % Found |
|---|---|---|---|---|---|---|
| Primary[a] | 35.0 | 35 (17) | 1.4020 | $C_4H_9FN_2O_2$ | | |
| Secondary | 40.0 | 24 (14) | 1.4007 | $C_4H_9FN_2O_2$ | 20.59 | 19.97 |
| Tertiary | 50.0 | 27 (8) | 1.4009 | $C_4H_9FN_2O_2$ | 20.59 | 20.33 |

[a] V. Graukakas reported bp 40–41° (25–28 mm), $n^{25}D$ 1.4040.

**Kinetic Measurements.**—The solvent (40.0 ml) was heated to temperature in a constant-temperatue bath and purged with prepurified nitrogen for 15 min. Next, the N-nitro-N-fluorobutylamine sample (about 0.3 g) was added and the nitrogen stirred solution was sampled at intervals. The cooled samples were examined in the infrared spectrum from 5 to 7 $\mu$ *vs.* pure solvent in sodium chloride cells (0.078 mm). The amount of the unchanged N-nitro-N-fluorobutylamine was obtained from the intensity of the $NO_2$ stretching vibration of the fluorobutylamine at 1610 $cm^{-1}$. There was no interference of this band with that of the decomposition products. A calibration curve of the concentration of the N-nitro-N-fluorobutylamine *vs.* the absorbance of the 1610-$cm^{-1}$ band was determined for each isomer.

**Volatile Decomposition Products of N-Nitro-N-fluoro-*t*-butylamine.**—In an atmosphere of nitrogen, 0.5 g of N-nitro-N-fluoro-*t*-butylamine was decomposed at reflux temperature in 25 ml of carbon tetrachloride and the effluent decomposition products were collected in a trap containing carbon tetrachloride cooled to −20°. The infrared spectrum of the trap solution revealed the presence of isobutylene, nitrous oxide, and a carbonyl component. Vpc analysis *vs.* authentic samples of isobutylene and nitrous oxide confirmed the identity of these components.

The effluent products of another decomposition were led into a trap containing a 2,4-dinitrophenylhydrazine reagent solution prepared as described by Shriner and Fuson.[7] The resulting yellow precipitate was recrystallized from 95% ethanol. A mixture melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of acetone did not depress the melting point. Tlc and infrared analysis confirmed the identification. The effluent vapors gave a strong acid test and a positive fluoride ion test by the zirconium–alizarin procedure;[7] this revealed hydrofluoric acid as a product of the decomposition.

**Nonvolatile Products from the Decomposition of N-Nitro-N-fluoro-*t*-butylamine.**—The decomposition of the N-nitro-N-fluoro-*t*-butylamine was studied in both Teflon and glass reactors. Product composition remained the same except for the small amount of white crystalline precipitate reported in the glass reactor. The reaction mixture from the decomposition of 7.0 g of the title compound in refluxing carbon tetrachloride was filtered to collect a white insoluble crystalline precipitate (about 0.1 g). Next, the solvent was removed under reduced pressure, leaving 2.8 g of a greenish oily residue of decomposition products. The white crystalline product was identified as a mixture of $(NH_4)_2SiF_6$ and $Na_2SiF_6$ by microscopy.[2]

Analytical gas chromatography revealed four major components and several minor ones. These components were also separated by a Perkin-Elmer Model 154 preparative gas chromatographic fractometer using a thermal conductivity detector. The 3 m × 25 mm column was packed with 20% didecylphthalate on Chromosorb W: temperature, 125°; helium pressure, 10 psi. Table VI lists the components in the order of their retention times and their approximate relative area per cent. The major components were separated and identified through comparison with known samples, principally *via* infrared and nmr spectroscopy and vpc retention times. The low-boiling components 1, 2, and 3 were identified as nitrous oxide, isobutylene, and acetone by comparison of their infrared spectra and vpc retention times with authentic samples.

Component 5 was obtained substantially pure and was identified as 2-methyl-2-nitropropane by comparison of its infrared and nmr spectrum and vpc retention time with an authentic sample. Component 6 was isolated in approximately 95% purity. The infrared spectrum and elemental identification

(7) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p 171.

TABLE VI

GAS CHROMATOGRAPHIC DATA OF THE DECOMPOSITION PRODUCTS OF N-NITRO-N-FLUORO-*t*-BUTYLAMINE

| Component | Identity | Retention time, min | Relative area, % |
|---|---|---|---|
| 1 | Nitrous oxide | 0.4 | 5.5 |
| 2 | Isobutylene | 0.6 | 1.6 |
| 3 | Acetone | 0.8 | 5.7 |
| 4 | Carbon tetrachloride | 2.0 | |
| 5 | 2-Methyl-2-nitropropane | 4.0 | 17.5 |
| 6 | 2-Fluoro-2-methyl-1-nitropropane | 7.1 | 19.5 |
| 7 | 2-Methyl-1-nitroprop-1-ene | 12.6 | 5.6 |
| 8 | Unknown | 16.0 | 7.4 |
| 9 | Unknown | 18.6 | 13.0 |
| 10 | 2-Hydroxy-2-methyl-1-nitropropane | 23.6 | 24.2 |

suggested both a fluorine and nitro group. The nmr spectrum in carbon tetrachloride using tetramethylsilane as an internal standard showed a doublet centered at $\delta$ 1.55 ($(CH_3)_2CF$–) with $J_{HF}$ value of 34 cps and another doublet centered at $\delta$ 4.42 (–$CFCH_2NO_2$–) with $J_{HF}$ value of 23 cps. 2-Fluoro-2-methyl-1-nitropropane is the only structure which completely satisfied the nmr data. Component 7 was identified as 2-methyl-1-nitroprop-1-ene by comparison of its infrared and nmr spectra and vpc retention time with an authentic sample. Component 10 was identified as 2-hydroxy-2-methyl-1-nitropropane by comparison of its infrared and nmr spectrum and vpc retention time with an authentic sample.

Another carbonyl component was isolated as a 2,4-dinitrophenylhydrazone derivative by treating the nonvolatile residual oil with a 2,4-dinitrophenylhydrazine reagent, prepared according to Shriner and Fuson.[6] The resulting yellow precipitate was recrystallized from 95% ethanol. A mixture melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of $\alpha$-ethoxyisobutraldehyde prepared according to Stevens and Gilles[8] was not depressed. The nmr spectrum of the derivative matched the nmr spectrum of the authentic sample exactly.

**$^{15}N$-Labeled N-Nitro-N-fluoro-*t*-butylamine Preparation.**—Isotopically labeled 99% nitric acid (2.0 g, atom % $^{15}N$, 99) obtained from Isomet Corp. was mixed with 98% nitric acid (17.9 g) containing the natural abundance of nitrogen isotopes. The resulting mixture was added dropwise with stirring to acetic anhydride (40.0 g, 0.392 mole) while maintaining the temperature below 10°. The mixture was used to convert ethyl N-*t*-butylcarbamate (27.0 g, 0.193 mole) to 12 g of N-nitro-*t*-butylamine according to the procedures of Curry, *et al.*,[3] and Barrott, *et al.*[4]

The 12.0-g sample of the $^{15}N$-labeled N-nitro-*t*-butylamine was diluted with an equal amount of N-nitro-*t*-butylamine having the natural nitrogen isotope abundance. This mixture was dissolved in a solution of sodium hydroxide (16.0 g, 0.4 mole) and water (400 ml) and fluorinated in the manner described above. The yield of the title compound was 16.0 g and contained 3.0% $^{15}N$ by mass spectroscopic analysis.

**The Isolation of the $^{15}N$-Labeled N-Nitro-N-fluoro-*t*-butylamine Decomposition Products.**—A 15.0-g sample of the $^{15}N$-labeled N-nitro-N-fluoro-*t*-butylamine (3.0% $^{15}N$) was decomposed in 150 ml of refluxing carbon tetrachloride under an atmosphere of nitrogen. The effluent products were led into a trap containing 50 ml of carbon tetrachloride cooled by an ice–salt bath in order to obtain a sample of nitrous oxide. After the decomposition was complete, the reaction mixture was filtered to collect the mixed crystalline precipitate of ammonium hexafluorosilicate and sodium hexafluorosilicate. Next, the filtrate was distilled under reduced pressure to remove the solvent. There remained 4.0 g of a green oily liquid. From this residue were isolated three nitro products by preparative gas chromatography which were identified as 2-methyl-1-nitropropane, 2-fluoro-2-methyl-1-nitropropane, and 2-hydroxy-2-methyl-1-nitropropane. Each component analyzed pure by analytical gas chromatography.

**Measurement of the Nitrogen Isotope Ratio.**—Nitrogen samples from the three nitro products from the above decomposition along with the ammonium hexafluorosilicate were prepared by the usual procedure[9] and were measured on a Bendix Model 12-101 time-of-flight mass spectrometer. The nitrous oxide

(8) C. L. Stevens and B. T. Gilles, *J. Am. Chem. Soc.*, **79**, 3450 (1957).

(9) D. Rittenberg, "Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Publishers, Ann Arbor, Mich., 1948, p 31.

sample was transferred from the carbon tetrachloride trap to a sampling tube in a vacuum line and its $^{15}N$ content determined from the various $N_2O$ isotopic mass peaks.

**Registry No.**—Primary isomer, 14233-86-4; secondary isomer, 14233-87-5; tertiary isomer, 14233-88-6; $^{15}N$-labeled tertiary isomer, 14233-89-7.

**Acknowledgment.**—Microanalyses were performed by Mrs. Phyllis P. Wheeler, nmr spectra were determined by Mr. Rupert D. Barefoot, and mass spectra were determined by Mr. G. Morgan King and Dr. M. J. Kraeutle. This work was supported by the Foundational Research Program of the Director of Naval Laboratories; additional funding was obtained from Task Assignment ORD-033 101/067 1/F009-06-01.

# Mobile Keto Allyl Systems. IV.[1] Reaction of Amines with α-(Bromomethyl)chalcone and Allylic Rearrangements with β-Ketoallylamines

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*trans*-α-(Bromomethyl)chalcone, a β-ketoallyl bromide, has been found to react with both primary and secondary amines to produce as primary products 2-(α-substituted aminobenzyl)acrylophenones in which the allyl system has been inverted. The rearrangement of the primary products to the thermodynamically more stable α-(substituted aminomethyl)chalcones proceeds about ten times as fast in the more polar solvent chloroform as in benzene. The amine exchange–rearrangement reactions of the 2-(α-substituted aminobenzyl)acrylophenones to give α-(substituted aminomethyl)chalcones involve a second inversion of the allyl system. Possible mechanisms for these reactions are discussed.

In a preliminary report[2] of some of this work it was pointed out that rearrangements of allylamines had not been reported previously.[3] The allyl system present in β-ketoallylamines has been found to be quite mobile and we now report a more detailed study of the reactions of the β-ketoallyl halide, *trans*-α-bromomethylchalcone **3**, with both primary and secondary amines, which lead to highly mobile β-ketoallylamines.

## Results

*trans*-α-Methylchalcone (**1**)[4] was prepared in excellent yield by the hydrogen bromide catalyzed condensation of benzaldehyde with propiophenone.[5] The bromine addition derivative **2** is reported for the first time as a crystalline product.[5] Hydrogen bromide added readily to α-(bromomethyl)chalcone (**3**)[2] to produce a good yield of 2-(bromomethyl)-3-bromo-3-phenylpropiophenone (**4**). The structure of **4** was clearly indicated by its conversion in good yield to the known[6] *trans*-1-phenyl-2-benzoylcyclopropane (**5**). When **4** was refluxed with *t*-butylamine, the known[2] α-(*t*-butylaminomethyl)chalcone (**11**) was obtained in excellent yield.

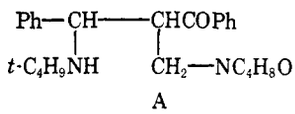
Reaction of the bromo ketone **3** with the amines morpholine or N-methylcyclohexylamine in ether solution at room temperature gave good yields of the corresponding α-(substituted aminomethyl)chalcones **6** and **8**, respectively. Three new 2-(α-substituted aminobenzyl)acrylophenones were isolated on careful treatment of **3** with 2 molar equiv of amine in pentane solution at lowered temperatures. In this way 2-(α-cyclohexylaminobenzyl)acrylophenone (**9**) was obtained as the free base while the piperidino, **12**, and morpholino, **13**, analogs were isolated as their hydrochlorides.

2-(α-Morpholinobenzyl)acrylophenone (**13**) was shown by nmr studies to rearrange quantitatively to the chalcone **6** on standing for 24 hr at room temperature in deuterated chloroform.

The β-ketoallyl bromide **3** reacted with other nucleophiles such as iodide and chloride ions to produce the direct exchange products, **14** and **15**, respectively.

Previously[2] it was reported that the acrylophenone **10** rearranged to the chalcone **11** in deuteriochloroform apparently by a monomolecular mechanism showing first-order kinetics. It has now been found that this rearrangement takes place in the solvents benzene, carbon tetrachloride, and deuteriochloroform, the relative rates of which are roughly of the order of 1:2:10, and parallel to the relative polarities of these solvents.

The amine exchange–rearrangement of **10** with morpholine to give **6** took place readily in pentane at room temperature, and nmr analyses during the course of reaction gave no indication of a stable intermediate product such as a diamino ketone, A.



A

The chalcone **11** was much more resistent to amine exchange than the isomeric acrylophenone **10**. Thus in pentane solution **11** was recovered unchanged after standing with an excess of morpholine. However, when pentane was replaced by methanol, **11** was converted quantitatively to **6**. On the other hand **6** gave no change when allowed to stand under the same conditions with an excess of *t*-butylamine in methanol solution (Scheme I).

The structures of the α-(aminomethyl)chalcones and

(1) For paper III in this series, see N. H. Cromwell and Earl Doomes, *Tetrahedron Letters*, No. 34, 4037 (1966).

(2) R. P. Rebman and N. H. Cromwell, *ibid.*, No. 52, 4833 (1965).

(3) R. H. DeWolfe and W. G. Young in "The Chemistry of Alkenes," S. Patai, Ed., Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1964, p 691.

(4) W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **77**, 5134 (1955).

(5) R. D. Abell, *J. Chem. Soc.*, **79**, 928 (1901).

(6) R. J. Mohrbacher and N. H. Cromwell, *J. Am. Chem. Soc.*, **79**, 401 (1957).