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.

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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.

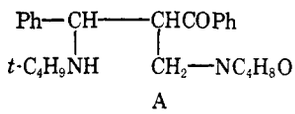
Reaction of the bromo ketone **3** with the amines morpholine or N-methylcyclohexylamine in ether solution at room temperature gave good yields of the corresponding α-(substituted aminomethyl)chalcones **6** and **8**, respectively. Three new 2-(α-substituted aminobenzyl)acrylophenones were isolated 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).

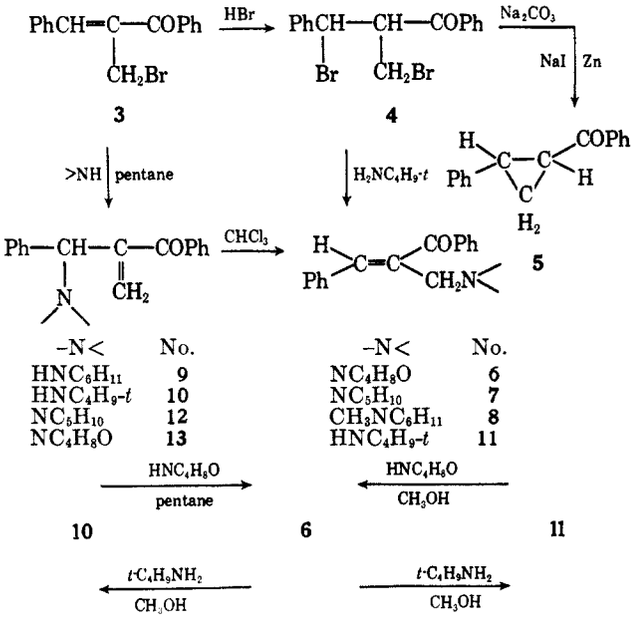
(3) R. H. DeWolfe and W. G. Young in "The Chemistry of Alkenes," S. Patai, Ed., Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1964, p 691.

(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).

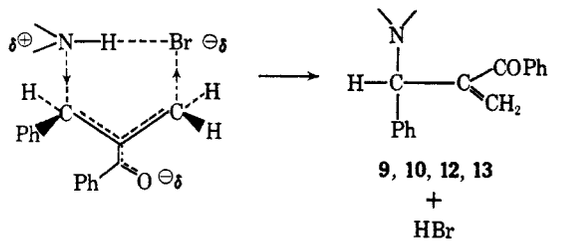
SCHEME I



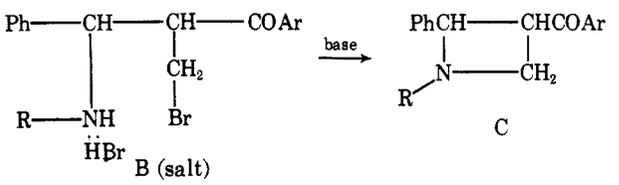
of the 2-(α-aminobenzyl)acrylophenones were readily established by elemental analysis and spectral studies (nmr, ultraviolet, and infrared); see the Experimental Section.

Discussion

The reaction of the dibromo ketone **4** with *t*-butylamine to produce the known[2] α-(*t*-butylaminomethyl)-chalcone (**11**) probably involved the primary loss of hydrogen bromide to give **3** which then reacted with more *t*-butylamine to form the acrylophenone **10**,[2] which in turn was readily rearranged by the excess *t*-butylamine to give the final product **11**. In a similar fashion the α-(substituted aminomethyl)chalcones **6** and **8** undoubtedly resulted from an aminotropic rearrangement of the first formed 2-(α-substituted aminobenzyl) acrylophenones. Since kinetic evidence is lacking at this time, any conclusions regarding the mechanisms of these reactions are somewhat speculative. For the reaction of the β-ketoallyl bromide **3** with primary and secondary amines to give as primary products the 2-α-(substituted aminobenzyl)acrylophenones **9, 10, 12,** and **13,** the available facts are accommodated by a variant of an SN2′ type of mechanism. On the other hand the



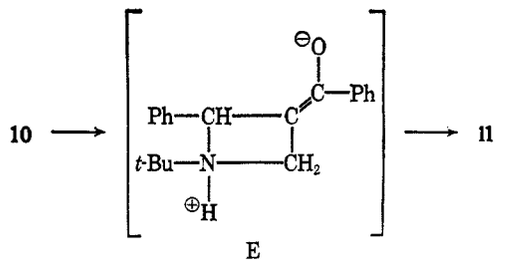
reaction of **3** with the negative nucleophiles Cl^- and I^-, which gave only nonrearranged products, may result from SN2 reactions. As has been pointed out previously by Young and his co-workers,[7a] coulombic attractions between the adjacent partially positive entering group (amine) and the partially negative leaving group (bromine) supplies energy of stabilization for the SN2′ transition state. On the other hand when the entering group is a negatively charged nucleophile (Cl^- or I^-) the SN2′ transition state is destabilized by electrostatic repulsions between the partially negative entering and leaving groups and the SN2 mechanism might be expected to be favored. That intermediate bromoamino ketones B are not formed in appreciable amounts during the reaction of **3** with amines is clearly indicated by the finding[8] that compounds of structure B, on being released from their hydrobromide salts, rapidly close a four-membered ring to give the new class of azetidines, the 2-aryl-3-aroylazetidines C.



Dittmer and Marcantonio[9] using deuterated and nondeuterated amines in displacements with α-methylallyl chloride found no kinetic isotope effect and therefore concluded that there is no hydrogen participation in the transition state[3] as implied in D.

The amine exchange reaction of the β-ketoallylamines also appears to be best described as a variant of an SN2′ displacement and not as a Michael addition of the attacking amine followed by a reverse Michael elimination of the amine originally present in the β-ketoallylamine.[10] In any case, there was no evidence obtained for the formation of a stable intermediate diamino ketone A in measurable amounts in any of these reaction mixtures with various solvent media. The SN2′ exchange would be expected to be sensitive to steric factors and this is found to be the case.

The intramolecular SN1 type rearrangement of the 2-(α-substituted aminobenzyl)acrylophenones to α-substituted aminomethylchalcones, *i.e.*, **10** → **11**,



is very sensitive to the polarity of the solvent, showing at least a tenfold increase in rate in changing from benzene to chloroform. This fact along with the very low energy of activation, E_a ~5.5 kcal/mole, and quite negative entropy of activation, ΔS^* ~−66 cal/deg mole, in the range of 35–42°, previously re-

(7) (a) W. G. Young, J. D. Webb, and H. L. Goering, *ibid.*, **73**, 1076 (1951); (b) W. G. Young, R. A. Clement, and C.-H. Shih, *ibid.*, **77**, 3061 (1955); (c) W. G. Young and I. J. Wilk, *ibid.*, **79**, 4793 (1957).

(8) (a) N. H. Cromwell and E. Doomes, *Tetrahedron Letters*, No. 34, 4037 (1966); (b) J.-L. Imbach, E. Doomes, R. P. Rebman, and N. H. Cromwell, *J. Org. Chem.*, **32**, 78 (1967).

(9) D. C. Dittmer and A. F. Marcantonio, *Chem. Ind.* (London), 1237 (1960).

(10) This suggestion was made by S. G. Levine in footnote 18 of D. F. Morrow, M. E. Butler, W. A. Neuklis, and R. M. Hofer, *J. Org. Chem.*, **32**, 86 (1967).

ported,[2] suggests a highly polar transition state[11] or dipolar cyclic intermediate E, wherein bond making is far ahead of bond breaking, thereby significantly reducing the energy "debt."[12]

Kinetic studies of this type of rearrangement are being continued to observe the effects of solvent variation and alterations in the structure of the β-ketoallylamines upon rates and thermodynamic parameters.

Experimental Section[13]

trans-α-**Methylchalcone**[4] (1).—Dry hydrogen bromide gas was passed into a mixture of 67.1 g (0.500 mole) of propiophenone and 53.0 g (0.500 mole) of benzaldehyde and was cooled to 0°. The reaction mixture solidified. After warming to room temperature for 24 hr the water and excess hydrogen bromide were removed *in vacuo*. To the reaction mixture was added 500 ml of ethanol, 49.0 g (0.500 mole) of potassium acetate, and 69.1 g (0.500 mole) of potassium carbonate. This was refluxed for 8 hr and the ethanol was removed *in vacuo* with warming. The residual material was taken up in ether and washed free of halide ion with water. The halogen-free product was obtained in 90% yield: bp 158–160° (1 mm); λ_{max} 256, 290 mμ (ε 12,400, 16,300) in 95% ethanol; $\nu_{C=O}$ 1654 cm^{-1}; nmr in CCl_4, multiplet, 2.1–3.0 (one benzal and ten aromatic protons), singlet 7.77 (three α-methyl protons).

2,3-Dibromo-2-methyl-3-phenylpropiophenone (2).[5]—A solution of 33.6 g (0.210 mole) of bromine in 60 ml of glacial acetic acid was added as rapidly as decolorization took place to a stirred solution of 44.4 g (0.200 mole) of **1** in 60 ml of the same solvent. After standing at room temperature for 5 hr, the mixture was poured into 1 l. of water and the product was extracted with chloroform. The chloroform extract was washed with water, dried, and evaporated to give an oil which solidified and was then recrystallized from petroleum ether (bp 60–70°) to give 60 g (78% yield) of white crystals: mp 53–55°; $\nu_{C=O}$, 1694 cm^{-1}. The nmr spectrum in CCl_4 showed ten aromatic protons at 1.8–2.8, a sharp peak for the benzyl proton at 4.08, and a singlet, three protons strong, for the α-methyl group at 7.88.

Anal. Calcd for $C_{16}H_{14}Br_2O$: C, 50.29; H, 3.69; Br, 41.83. Found: C, 50.41; H, 3.79; Br, 41.65.

2-(Bromomethyl)-3-bromo-3-phenylpropiophenone (4).—A 15.1-g (0.050 mole) sample of α-(bromomethyl)chalcone (**3**)[2] in 300 ml of ethyl ether was cooled to 0° and saturated with hydrogen bromide for 1 hr. Evaporation of the ether and recrystallization of the crude product from petroleum ether gave 13.4 g (70% yield) of white crystals, mp 123.5–124°; $\nu_{C=O}$, 1683 cm^{-1}; the nmr spectrum showed ten aromatic protons at 2.0–3.0, the benzyl proton at 4.73 (J = 11 cps) the proton α to C=O at 5.13–5.53, and two protons (bromo-methylene) at 5.75–6.05.

Anal. Calcd for $C_{16}H_{14}Br_2O$: C, 50.29; H, 3.69; Br, 41.83. Found: C, 50.14; H, 3.88; Br, 41.48.

trans-**1-Phenyl-2-benzoylcyclopropane** (5).—A 3.82-g (0.010 mole) sample of **4** was dissolved in 400 ml of 80% ethanol and stirred with 1.06 g (0.010 mole) of sodium carbonate, 1.35 g (0.020 mole) of zinc dust, and 0.30 g (0.002 mole) of sodium iodide.[14] This mixture was refluxed for 48 hr, filtered, cooled, and again filtered. After evaporation of the solvents, the residue was extracted with ether, the ether extract washed with water, dried, and evaporated to give 1.44 g (65% yield) of a pale yellow oil: λ_{max} 247 mμ (ε 14,200) in 95% ethanol; $\nu_{C=O}$, 1675 cm^{-1}, and the entire spectrum was identical with that of an authentic sample of **5**.[6]

α-(**Substituted aminomethyl**)**chalcones.**—A 6.02-g (0.020 mole) sample of **3** dissolved in 200 ml of ethyl ether was mixed with a 2 M amount of the amine dissolved in 100 ml of the same solvent and stirred for 24 hr, then filtered to remove a near quantitative amount of the amine hydrobromide, and the filtrate was washed with water and dried. Removal of the ether produced a product which was recrystallized from petroleum ether to give colorless crystals.

α-(**Morpholinomethyl**)**chalcone** (6) was prepared in 96% yield with mp 62–63°; λ_{max} 256, 285 mμ (ε 14,300, 16,100) in 95% ethanol; $\nu_{C=O}$ 1654 cm^{-1}; nmr signals at 2.0–2.6 (ten aromatic protons), 2.68 (one benzal proton), 6.2–6.5 (two α-N-methylene protons and four α-O-morpholino protons), 7.4–7.6 (four α-N-morpholino protons).

Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.14; H, 6.89; N, 4.56. Found: C, 78.15; H, 6.90; N, 4.74.

Hydrochloride of 6 was found to have mp 140–141°; λ_{max} 284 mμ (ε 13,500) in methanol; $\nu_{C=O}$ 1654 cm^{-1} (KBr).

Anal. Calcd for $C_{20}H_{22}ClNO_2$: Cl, 10.31. Found: Cl, 10.19.

α-(**Piperidinomethyl**)**chalcone** (7)[2] **hydrochloride** had mp 132–133; λ_{max} 282 mμ (ε 14,600) in methanol; $\nu_{C=O}$ 1647 cm^{-1} (KBr).

Anal. Calcd for $C_{21}H_{24}ClNO$: Cl, 10.37. Found: Cl, 10.24.

α-(**N-Methylcyclohexylaminomethyl**)**chalcone** (8) was prepared in 56% yield with mp 53–54°; λ_{max} 253, 279 mμ (ε 13,800, 13,700) in 95% ethanol; $\nu_{C=O}$ 1654 cm^{-1} (CCl_4); nmr signals at 2.0–2.8 (ten aromatic protons), 2.83 (one benzyl proton), 6.33 (two α-N-methylene protons), 7.81 (three N-methyl protons), 8.1–9.2 (eleven cyclohexyl protons).

Anal. Calcd for $C_{23}H_{27}NO$: C, 82.84; H, 8.16; N, 4.20. Found: C, 82.75; H, 8.04; N, 4.23.

Reaction of 4 with *t*-Butylamine.—A 3.82-g (0.010 mole) sample of **4** was heated under reflux with 25 ml of *t*-butylamine to give a 94% yield of α-(*t*-**butylaminomethyl**)**chalcone** (**11**);[2] the **hydrochloride of 11** had mp 227–228°; λ_{max} 285 mμ (ε 15,700); $\nu_{C=O}$ 1647 cm^{-1} (KBr).

Anal. Calcd for $C_{20}H_{24}ClNO$: Cl, 10.75. Found: Cl, 10.60.

2-(α-Cyclohexylaminobenzyl)acrylophenone (9).—A 6.02-g (0.020 mole) sample of **3** dissolved in 500 ml of pentane was added to a solution of 4.1 g (0.040 mole) of cyclohexylamine in 25 ml of the same solvent and allowed to stand for 15 hr. The cyclohexylamine hydrobromide, 3.51 g (98% yield), was removed and the filtrate washed and dried. Evaporation of the pentane *in vacuo* and several recrystallizations from petroleum ether gave 4.43 g (69% yield) of white crystals: mp 96.5–97.5°; λ_{max} 250, 282 mμ (ε 13,200, 7000) in 95% ethanol; $\nu_{C=O}$ 1662 cm^{-1}; nmr signals at 2.2–3.0 (ten aromatic protons), 3.92 and 4.30 (=CH_2), 4.86 (benzyl proton), 7.4–9.2 (NH and cyclohexyl protons).

Anal. Calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; H, 4.38. Found: C, 82.91; H, 8.15; N, 4.45.

2-[α-(N-*t*-Butylamino)benzyl]acrylophenone (10)[2] **hydrochloride** was found to have mp 183–184°; λ_{max} 255 mμ (ε 10,000); $\nu_{C=O}$ 1658 cm^{-1} (KBr).

Anal. Calcd for $C_{20}H_{24}ClNO$: Cl, 10.75. Found: Cl, 10.84.

2-(α-Piperidinobenzyl)acrylophenone (12) **Hydrochloride.**—A 3.01-g (0.010 mole) sample of **3** dissolved in 500 ml of pentane was added to 1.70 g (0.020 mole) of piperidine in 100 ml of the same solvent with stirring. After 1 hr, the mixture was cooled to 0° and stirring was continued for 5 hr. The mixture was filtered to remove piperidine hydrobromide and exposed to a stream of dry hydrogen chloride for 5 min with cooling. The precipitated salt was filtered and washed with ethyl ether. Several recrystallizations from methanol–ethyl ether gave 2.14 g (63% yield) of white crystals: mp 120–121°; λ_{max} 257 mμ (ε 8600); $\nu_{C=O}$ 1660 cm^{-1} (KBr).

Anal. Calcd for $C_{21}H_{24}ClNO$: C, 73.78; H, 7.07; Cl, 10.37; N, 4.10. Found: C, 73.49; H, 7.16; Cl, 10.49; N, 4.17.

2-(α-Morpholinobenzyl)acrylophenone (13) **Hydrochloride.**—This compound was prepared in the same manner as the hydrochloride of **12** in 50% yield: mp 139–140°; λ_{max} 258 mμ (ε 9800); $\nu_{C=O}$ 1659 cm^{-1} (KBr).

Anal. Calcd for $C_{20}H_{22}ClNO_2$: C, 69.86; H, 6.45; Cl, 10.31; N, 4.07. Found: C, 69.75; H, 6.69; Cl, 10.17; N, 4.08.

In a second experiment, after filtration of the morpholine hydrobromide by-product, the pentane was evaporated *in vacuo*, using no heat, to yield a pale yellow oil, **13**; there were nmr signals at 2.1–3.0 (ten aromatic protons), 3.83 and 4.33 (=CH_2), 5.50 (one benzyl proton), 6.3–6.6 (four protons α to morpholino oxygen), 7.4–7.8 (four protons α to morpholino nitrogen). When the nmr sample cell had stood at room temperature for 24 hr the nmr spectrum was nearly identical with that of **6** indicating that the first formed 2-(α-morpholinobenzyl)acrylophenone (**13**) had rearranged to the chalcone **6**.

(11) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 137.

(12) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1960, pp 178–181.

(13) Ultraviolet spectra of methanol solutions (unless otherwise indicated) were determined with a Cary Model 11-MS recording spectrophotometer. Infrared spectra of CCl_4 solutions (unless otherwise indicated) were obtained using a Perkin-Elmer Model 21 instrument. Proton magnetic resonance spectra of $CDCl_3$ solutions (unless otherwise indicated) were measured with a Varian A-60 instrument using a trace of tetramethylsilane (τ 10.00) as an internal reference; the results are reported as τ values.

(14) H. B. Hass, *et al.*, *Ind. Eng. Chem.*, 1179 (1936).

α-(Iodomethyl)chalcone (14).—To a solution of 3.01 g (0.010 mole) of **3** in 50 ml of dry acetone was added a solution of 2.25 g (0.015 mole) of NaI in 100 ml of dry acetone. After standing for 24 hr the acetone was evaporated and the residue was extracted with ethyl ether. The ether extract was washed with water, dried, and evaporated to give a product which after recrystallization from petroleum ether produced yellow crystals: mp 75–76°; λ_{max} 255, 290 mμ (ε 15,000, 17,100) in isooctane; $\nu_{C=O}$ 1660 cm^{-1}; there were nmr signals at 2.1–2.8 (ten aromatic protons), 3.03 (one benzal proton), 5.59 (two α-iodomethyl protons).

Anal. Calcd for $C_{16}H_{13}IO$: C, 55.19; H, 3.76; I, 36.45. Found: C, 55.14; H, 3.84; I, 36.52.

α-(Chloromethyl)chalcone (15).—A 1.50-g (0.0050 mole) sample of **3** and 4.98 g (0.030 mole) of tetraethylammonium chloride were added to 25 ml of acetonitrile and heated under reflux for 16 hr. The acetonitrile was evaporated and the product was extracted with ether. Evaporation of the ether and recrystallization from petroleum ether gave white crystals (0.75 g, 58% yield): mp 62–63°; λ_{max} 261, 281 mμ (ε 14,200, 17,000) in isooctane; $\nu_{C=O}$ 1660 cm^{-1}; nmr 2.0–2.7 (ten aromatic protons), 2.75 (one benzal proton), 5.37 (two α-chloromethyl protons).

Anal. Calcd for $C_{16}H_{13}ClO$: C, 74.85; H, 5.11; Cl, 13.81. Found: C, 74.84; H, 5.21; Cl, 13.93.

Relative Rates of Rearrangement of 10 to 11 in Various Solvents.—Three nmr sample cells labeled A, B, and C, each containing 100 mg of **10** and 0.5 ml of solvent, benzene, carbon tetrachloride, or deuteriochloroform, respectively, were allowed to stand for 6 days. Periodic analysis by nmr showed that the relative rates of rearrangement of the contents of cells A, B, and C were roughly 1:2:10.

Reaction of 10 with Morpholine.—A 2.93-g (0.010 mole) sample of **10** was dissolved in 50 ml of pentane and 8.71 g (0.010 mole) of morpholine was added. After standing for 48 hr the pentane was evaporated *in vacuo* and the residue was taken up in ether, which after water washing, drying, and evaporation gave 2.8 g (91% yield) of **6**. Periodic nmr analysis during the course of the reaction showed the presence of only **10** and **6**.

Reaction of 11 with Morpholine.—When the above described experiment was repeated using **11** in place of **10**, 90% of the starting material was returned; but when the pentane was replaced by 25 ml of methanol and the reaction mixture was allowed to stand at room temperatur for 3 days **11** was quantitatively converted to the morpholino analog **6**.

It was found that **6** was unchanged after standing 4 days in a methanol solution containing 10 molar equiv of *t*-butylamine.

Registry No.—**1,** 14182-01-5; **2,** 14181-91-0; **3,** 14181-92-1; **4,** 14181-93-2; **6,** 14182-00-4; **6** hydrochloride, 14271-42-2; **7** hydrochloride, 14182-02-6; **8,** 14181-94-3; **9,** 14181-95-4; **10** hydrochloride, 14271-48-8; **11** hydrochloride, 14182-03-7; **12** hydrochloride, 14181-96-5; **13,** 14181-97-6; **13** hydrochloride, 14181-98-7; **14,** 14271-43-3; **15,** 14181-99-8.

Acknowledgment.—This work was supported in part by Grant CA-02931 from the National Cancer Institute, U. S. Public Health Service.

The Versatility and the Mechanism of the *n*-Butylamine-Catalyzed Reaction of Thiols with Sulfur

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The *n*-butylamine-catalyzed reaction of alkyl thiols with sulfur has been investigated in detail. By proper selection of reaction variables, alkyl di-, tri-, or in some cases tetrasulfides can be formed in good yields. These variables are (1) moles of thiol/g-atoms of sulfur ratio, (2) polarity of solvent, (3) reaction time, and (4) temperature. The appropriate combination is selected after consideration of the steric requirements of the thiol. The reaction probably proceeds by a mechanism similar to that proposed for the interaction of both inorganic and organic thiophilic nucleophiles with sulfur. Intermediates were isolated. The intermediates were identified by nmr spectroscopy even in complex mixtures of the reactants.

The base-catalyzed reaction of thiols with sulfur is well known; however, it has found little utility, because a mixture of alkyl polysulfides is the usual consequence.[1,2]

A major obstacle preventing a detailed investigation of the mechanism and scope of this reaction has been lack of a reliable analytical tool. A method which would permit analysis of the polysulfide mixtures at ambient temperatures was needed, since the higher polysulfides are known to undergo disproportionation at elevated temperatures.

Recently, Grant and Van Wazer[3] utilized nuclear magnetic resonance to analyze mixtures of alkyl polysulfides. They showed that as the number of sulfur atoms increased the chemical shifts of the α-protons are shifted downfield. Their technique seemed to be an appropriate analytical procedure to use in a study of the thiol–sulfur reaction. Indeed, this method has proven an effective tool, particularly for the *t*-butyl system, since only one type of proton and hence one peak for each polysulfide is observed. For this reason and because it reacts at a convenient rate, *t*-butyl thiol was selected for most of the mechanistic studies. Once an insight into the reaction was obtained using nmr, a gas chromatography (gc) method was developed. This was especially useful for alkyl polysulfides, such as the isopropyl or *sec*-butyl compounds where splitting of the α-protons made nmr analysis more difficult.

Our recent report showed that alkyl trisulfides could be obtained by the controlled reaction of most thiols with sulfur.[4] The versatility of this general base-catalyzed reaction has been expanded to include the formation of alkyl di-, tri-, or in some cases tetrasulfides in good yields. Several variables must be considered when a particular alkyl polysulfide is desired. These variables are (1) the moles of thiol/g-atoms of sulfur ratio, (2) the polarity of the solvent, (3) the reaction time, and (4) temperature. The

(1) For a review of polysulfide chemistry, see E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, p 387.

(2) W. A. Pryor, "Mechanism of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 9.

(3) D. Grant and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 3012 (1964).

(4) B. D. Vineyard, *J. Org. Chem.*, **31**, 601 (1966).