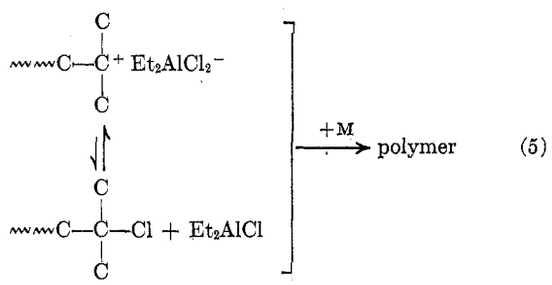
methylaluminum chloride anion. (We thank one of the referees for pointing this out.)

In the reaction of cyclohexene with $Me_3Al$ and HCl, the order of addition of the reagents influences the extent of conversion (lines 2 and 3, Table I). We propose that, when $Me_3Al$ is added to an olefin such as cyclohexene, a Lewis acid–olefin complex is formed, which lowers the reactivity of the Lewis acid and the olefin toward HCl. However, when the Lewis acid is added last, the possibility of complex formation is minimized, resulting in a higher yield of chlorocyclohexane. Complex formation between olefins and alkylaluminum compounds may be a general phenomenon.[3] We have also found that the rate of cationic polymerization of isobutylene initiated by the trimethylaluminum-*tert*-butyl bromide initiator system can be considerably accelerated by adding the alkylaluminum last.[4] Complex formation between olefins and Lewis acids such as $SnCl_4$, $BF_3$, $AlBr_3$, etc., has been demonstrated.[5]

Experiments described in this paper (*i.e.*, lines 2 and 3 in Table I) suggest the formation of chlorinated intermediates in similar other reactions as well. A consequence of these results is the possibility that cationic polymerizations may also involve covalent halides. The direct insertion of monomer into the covalent C–Cl bond, however, is considered to be much less likely.[6] The relative concentration of the conventional ion pairs and the covalent chlorides in the equilibrium (eq 5) is determined by the structure of the




(5)

monomer (or the stability of the propagating cation) and the particular Lewis acid used. For example, the polymerization of isobutylene by *t*-Bu$^+$$Et_2AlCl_2^-$ (derived from *t*-BuCl and $Et_2AlCl$) might involve predominantly conventional ion pairs (eq 5). Termination would occur when the counterion is in a favorable orientation to alkylate the positive center.

### Experimental Section

All the experiments and manipulations were performed in a stainless steel enclosure under $N_2$ atmosphere (<30 ppm moisture level).[7] Trimethylaluminum (Texas Alkyl, Inc.) was used as received. Cyclohexene (Aldrich Chemical Co.) and 1-methylcyclohexene (Columbia Organic Chemicals Co.) were dried over molecular sieves and distilled before use. Authentic samples of chlorocyclohexane, methylcyclohexane, and 1,1-dimethylcyclohexane for glpc comparison were obtained commercially. Gas chromatography was done on an HP 5750 instrument equipped with FID on a 6 ft × 0.125 in. silicone gum rubber UC-W-98 column using He (35 ml/min) as the carrier gas. All unknown peaks were identified by peak superposition using authentic materials for comparison. All reactions were generally run for 30 min; however, the reactions were virtually complete in *ca.* 10 min. A representative experiment is described. A three-neck flask equipped with a mechanical stirrer, glass-jacketed addition funnel, and a thermometer was cooled to −50°. Cyclohexene, 5.1 ml (50 mmol), dissolved in 25 ml of EtCl (~1.5 *M*) was placed in the flask followed by 1.5 ml (50 mmol) of liquid hydrogen chloride dissolved in 25 ml of EtCl. Trimethylaluminum, 4.8 ml (50 mmol), was dissolved in 25 ml of EtCl and was added dropwise through the precooled addition funnel. Upon addition of the first few drops of trimethylaluminum the temperature of the pot rose by ~10°. After addition was complete, the reaction was quenched by the dropwise addition of 5 ml of prechilled methanol. The aluminum alkoxide was coagulated by the addition of a saturated aqueous solution of sodium potassium tartrate. The organic product was extracted into pentane, washed, dried, and analyzed by glpc. *N*-Nonane was used as an internal standard. The products arising from the reaction of cyclohexyl cation with cyclohexene (1-cyclohexylcyclohexene) and from the skeletal rearrangement of the cyclohexyl cation (1-methylcyclopentene, 1,1-dimethylcyclopentane) were shown to be absent.

**Registry No.**—Cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; trimethylaluminum, 75-24-1; hydrogen chloride, 7647-01-0.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research,

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(4) P. D. Trivedi, unpublished observations, Akron, Ohio, 1972.

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## Base-Catalyzed Reaction of β-Amino Alcohols with Ethyl Trihaloacetates

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*January 12, 1973*

The reaction of β-hydroxyalkylamines with ethyl trihaloacetates has been investigated in some detail only by Lesher and Surrey,[1] who obtained 2-oxazolidinones[2] by treatment of *N*-benzylethanolamines with ethyl trichloroacetate (ETC). According to the same authors, N-unsubstituted β-amino alcohols failed to afford any 2-oxazolidinones.

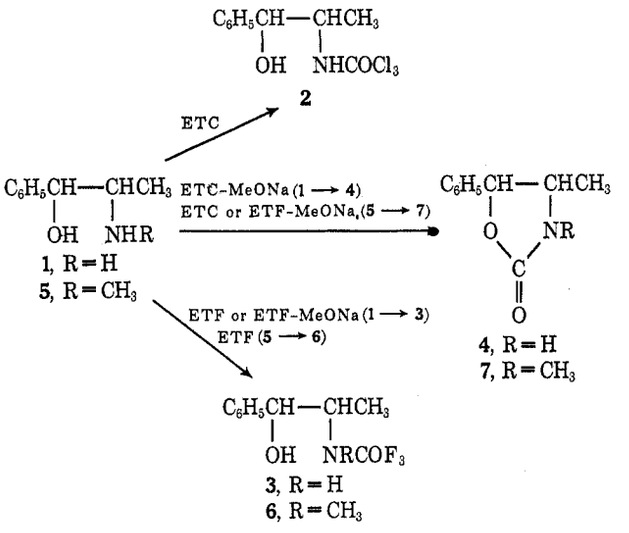
We have investigated the reaction of DL-phenylpropanolamine (**1**) and L-ephedrine (**5**) with ETC and ethyl trifluoroacetate (ETF) and the influence of a basic catalyst on the course of this reaction.

Treatment of **1** with ETC and ETF afforded the corresponding aminolysis products **2** and **3**, respectively. Addition of catalytic amounts of methanolic sodium methoxide increased the conversion rate of **1** into **3**, while added base resulted in the formation of the N-unsubstituted 2-oxazolidinone **4**, as the only product of the reaction with the trichloro ester.

Reaction of **5** with ETF afforded the trifluoroacetamide **6** in the absence of catalyst, while an almost complete conversion into 2-oxazolidinone **7** was obtained

(1) G. Y. Lesher and A. R. Surrey, *J. Amer. Chem. Soc.*, **77**, 636 (1955).

(2) For a comprehensive review on 2-oxazolidinones, see M. E. Dyen and D. Swern, *Chem. Rev.*, **67**, 197 (1967).




in the presence of sodium methoxide.[3] The same oxazolidinone **7** was obtained by treatment of **5** with ETC also in absence of sodium methoxide.

The isolation of **6** and the tlc identification of **2** during the base-catalyzed reaction of **5** with ETF and **1** with ETC, respectively, indicates that the formation of the 2-oxazolidinones proceeds through the corresponding trihaloacetamides.[4]

The conversion of *N*-benzylethanolamines to oxazolidinones has been suggested to occur either through an initial O-acylation, followed by splitting of chloroform, or through an initial haloform-type cleavage to a *N*-carboethoxy derivative, followed by an intramolecular alcoholysis.[1] Our results do not support these hypotheses, but suggest a reaction pattern involving an initial aminolysis of the halo ester, followed by a nucleophilic intramolecular attack by the alkoxide ion on the carbonyl group and loss of haloform.

Deprotonation at nitrogen may compete with cyclization in the case of the secondary trihaloacetamides[5] and this may account for their reduced ability to afford 2-oxazolidinones. A stronger inductive effect favors the N deprotonation of trifluoro- more than trichloroacetamides. This may contribute to the failure of **3** to cyclize, although the greater reactivity of trichloro- *vs.* trifluoroacetamides can be more generally determined by the superior leaving group ability of the trichloromethyl moiety.[6]

### Experimental Section

Melting points were taken in a capillary apparatus and are uncorrected. Optical rotations were determined in dioxane at 24° unless otherwise stated. Ir spectra were measured in Nujol mull on a Perkin-Elmer 457 instrument. Tlc was run with 9:1 benzene–acetone on 250-$\mu$-thick layers of silica gel (C. Erba, Milan, Italy), containing 1% fluorescence indicator (S5 grün/1, Leuchstoffwerk GmbH and Co., Heidelberg, West Germany) and spots were visualized under short-wave uv light (254 m$\mu$). Microanalyses were performed by Ilse Beetz Microanalytisches Laboratorium, Kronach, West Germany.

DL-**Trifluoro-*N*-(2-hydroxy-1-methyl-2-phenylethyl)acetamide** (**3**).—A solution of **1** (1 g) in ETF (5 ml) and EtOH (2 ml) was kept at room temperature for 60 min. Evaporation of the solvent under reduced pressure afforded **3** (1.5 g, 91.7%): mp 131–132° (benzene); $\nu_{max}$ 3460, 3230, 3100, 1700 cm$^{-1}$.

*Anal.* Calcd for $C_{11}H_{12}F_3NO_2$: C, 53.44; H, 4.78; N, 5.66. Found: C, 53.37; H, 4.81; N, 5.64.

Following the same procedure but using ETC, trichloroacetamide **2** was obtained (60%): mp 72–76° (hexane); $\nu_{max}$ 3420, 3300, 1680 cm$^{-1}$. This compound was fully characterized as the *O*-benzoate: mp 148–150° (MeOH); $\nu_{max}$ 3460, 1710, 1690 cm$^{-1}$.

*Anal.* Calcd for $C_{18}H_{16}Cl_3NO_3$: C, 53.96; H, 4.02; Cl, 26.55; N, 3.49. Found: C, 53.79; H, 4.06; Cl, 26.73; N, 3.35.

L-**Trifluoro-*N*-(2-hydroxy-1-methyl-2-phenylethyl)-*N*-methylacetamide** (**6**).—A solution of **5** (7 g) in ETF (10 ml) was kept at room temperature for 150 min and then processed as above to give **6** (10 g, 90.3%): mp 63–65° (hexane); $\nu_{max}$ 3440, 1680 cm$^{-1}$; $[\alpha]_D$ −8° (*c* 4).

*Anal.* Calcd for $C_{12}H_{14}F_3NO_2$: C, 55.17; H, 5.40; N, 5.36. Found: C, 54.92; H, 5.64; N, 5.26.

The *O*-benzoate had mp 111–113° (MeOH); $\nu_{max}$ 1728, 1685 cm$^{-1}$; $[\alpha]_D$ +36° (*c* 1).

*Anal.* Calcd for $C_{19}H_{18}F_3NO_3$: C, 62.47; H, 4.96; N, 3.38. Found: C, 62.42; H, 4.90; N, 3.80

DL-**4-Methyl-5-phenyloxazolidin-2-one** (**4**).—A solution of **1** (3.02 g) in ETC (2.1 ml) was treated with 1 *M* MeONa (2 ml) and kept at room temperature for 150 min. Concentration under reduced pressure and dilution with water afforded **4** (2.9 g, 82%): mp 147–149° (benzene) (lit.[7] mp 145–147°); $\nu_{max}$ 3380, 1745, 1720 cm$^{-1}$. Tlc at 30-min intervals revealed the presence of amide **2**, which disappeared at the end of the reaction.

L-**3,4-Dimethyl-5-phenyloxazolidin-2-one** (**7**).—A solution of **5** (4 g) in ETF (6 ml) was treated with 1 *M* MeONa (3 ml), kept under stirring at room temperature for 150 min, and worked up as above to give **7** (4.3 g, 93%): mp 91–92° (EtOH); $[\alpha]_D$ −125° (*c* 1, $CHCl_3$); $\nu_{max}$ 1735 cm$^{-1}$ [lit.[8] mp 91–92°; $[\alpha]^{20}D$ −110.6° ($CHCl_3$)].

When the reaction was allowed to proceed for only 5 min, the trifluoroacetamide **6** was isolated.

**B.**—A solution of **5** (3 g) in ETC (2.1 ml) was kept at room temperature for 180 min and worked up as above to yield **7** (2.6 g, 75%), mp 90–92°.

**Registry No.**—**1**, 14838-15-4; **2**, 39663-72-4; **2** *O*-benzoate, 39663-73-5; **3**, 39663-74-6; **4**, 39663-75-7; **5**, 299-42-3; **6**, 39663-77-9; **6** *O*-benzoate, 39663-78-0; **7**, 16251-46-0; ETF, 383-63-1; ETC, 575-84-4.

(3) *N*-Benzylethanolamine has been reported to afford the corresponding salt by reaction with ETF.[1]

(4) Evidence for the formation of an intermediate showing tlc behavior reasonable for the trichloroacetamido derivative was obtained also in the reaction of **5** with ETC.

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(6) *Cf.* C. A. Panetta and T. G. Casanova, *J. Org. Chem.*, **35**, 4275 (1970).

(7) A. H. Homeyer, U. S. Patent 2,399,118 (1946); *Chem. Abstr.*, **40**, 4084 (1946).

(8) J. B. Hyne, *J. Amer. Chem. Soc.*, **81**, 6058 (1959).

## Cyclohexadienyl Cations. V. Concerning the Acidity Dependence of the Dienone–Phenol Rearrangement

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*Received February 22, 1973*

In the previous papers[1,2] in this series we have suggested that the kinetic acidity dependence in concentrated acid solutions of the acid-catalyzed dienone–phenol rearrangement can be understood in terms of two factors: (a) the equilibrium protonation acidity

(1) V. P. Vitullo and E. A. Logue, *J. Org. Chem.*, **37**, 3339 (1972).

(2) V. P. Vitullo and N. Grossman, *J. Amer. Chem. Soc.*, **94**, 3844 (1972).