

The Friedel-Crafts Reactions of 2-Substituted Oxetanes*

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The aluminium chloride-catalyzed Friedel-Crafts reactions of 2-phenyloxetane and 2-methyloxetane with solvent benzene, toluene, and mesitylene have been studied and found to give 3-aryl-3-phenylpropan-1-ols and 3-aryl-3-methylpropan-1-ols, respectively, as the main condensation products.

3-Phenylpropan-1-ol and diarylmethanes were formed as side products in the reactions of 2-phenyloxetane, while 3-chlorobutan-1-ol and 4-chlorobutan-2-ol were minor components from the reactions of 2-methyloxetane.

The relative rate constants for the main hydroxyalkylation reactions have been determined by the competitive method. The reactions are subject to a relatively low intermolecular selectivity.

It has been suggested for these reactions that the rate is determined by a slow formation of a π -complex, but in the transition state of 2-phenyloxetane the new carbon-carbon bond has been partially formed.

In contrast to oxirans, oxetanes are relatively stable toward nucleophiles in neutral solution but, like oxirans, smoothly undergo a wide variety of nucleophilic substitution reactions in acidic conditions.^{1,2} It is also well established that oxirans can be used in the Friedel-Crafts hydroxyalkylation of aromatic hydrocarbons.³

Searles⁴ has found that oxetane reacts with benzene and mesitylene in the presence of aluminium chloride to yield 50–70 % of the corresponding 3-hydroxypropyl derivative. Later, Japanese workers⁵ studied the reactions of oxetane and 2-methyloxetane with benzene. However, detailed knowledge of the effect of Lewis acid-type catalysts on the reactions of oxetanes is still limited. We report here the results of our studies concerning the aluminium chloride-catalyzed reactions of 2-phenyloxetane and 2-methyloxetane with benzene, toluene, mesitylene, and other compounds.

* Presented in part at the Symposium on Synthetic Chemistry at Kemian Päivät, Helsinki, Finland, November 1973.

RESULTS AND DISCUSSION

Experiments for examining the products of the reactions were performed by adding oxetane dissolved in hydrocarbon to a suspension of aluminium chloride in hydrocarbon, under conditions similar to those usually employed for the Friedel-Crafts reactions of oxirans.

3-Phenylbutan-1-ol and 3-chlorobutan-1-ol were isolated from the products of the reaction between 2-methyloxetane and benzene. Determined by gas-chromatography from the reaction mixture, they amounted to 75 % and 4 %, respectively. About 1 % of 4-chlorobutan-2-ol was also detected.

The reaction of 2-phenyloxetane with benzene gave 3,3-diphenylpropan-1-ol (rel. amount 83 %), diphenylmethane (10 %), and 3-phenylpropan-1-ol (7 %). The yield of the main product was 28 % calculated on equimolar starting quantities of 2-phenyloxetane and aluminium chloride. This implies that polymerization and other side reactions play a considerable role in these reactions.

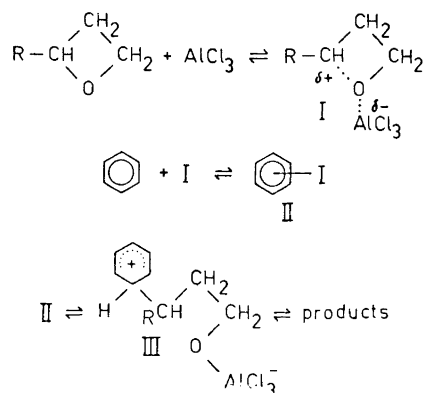
The aluminium chloride-catalyzed reactions of propylene oxide with benzene has been reported to give a 64 % yield of 2-phenylpropan-1-ol and no 1-phenylpropan-2-ol.⁶ When benzene was alkylated by 1,2-dimethyl,⁷ 1,1-dimethyl,⁷ or 1-methyl-2-phenyloxirane,⁸ only minor quantities of the expected alcohols were isolated from the reaction mixtures.

It is now generally accepted that the acid-catalyzed reactions of oxirane and oxetane occur by a borderline S_N2 -mechanism, and the same seems to be reliable for the 2-methyl- and 2-phenyl-substituted compounds as well. Thus Berti *et al.*⁹ have found that the extent of inversion in the reaction of styrene oxide with hydrogen chloride greatly depends on the solvent, varying from 24 % in dioxane to 83 % in chloroform. Chapman and co-workers¹⁰ have recently reported that 89 % inversion of configuration occurs in the acid-catalyzed methanolysis of styrene oxide. They interpreted this observation in terms of a borderline S_N2 -mechanism. The same conclusion has been drawn from the values of the entropy of activation and the Hammett ρ -values for the acid-catalyzed alcoholysis of substituted styrene oxides.¹¹

Although the hydrogen ion-catalyzed reactions of oxetanes take place by a bimolecular nucleophilic substitution reaction, this is no proof that the aluminium chloride-catalyzed reactions must also do so. The bond-polarizing effect of the latter catalyst seems to be stronger, as we will show later in this discussion.

A collection of the available information¹² suggests the following course for the formation of the main product. A donor-acceptor complex or an intimate ion-pair (I) is first formed from oxetane and aluminium chloride. Thereafter an intermediate benzenium ion (III), *i.e.* a σ -complex, is formed in a two-step process which involves a π -complex (II) as the first intermediate. The benzenium ion is then converted into the products by hydrogen transfers.

Ring fission in the reactions of 2-phenyloxetane studied in this work took place solely between the oxygen atom and substituted carbon atom. The same is evident in the reaction of 2-phenyloxetane with hydrogen chloride in benzene,¹³ aqueous solvents,¹³ and dioxane,¹⁴ and in the reaction of 2-phenyloxetane with acetyl chloride,¹³ but not in the reductive cleavage of 2-phenyl-



oxetane with lithium aluminium hydride or lithium borohydride,¹⁵ nor in the reaction of 2-phenyloxetane with methyl magnesium bromide.¹ Clearly the former reaction group includes reactions where powerful catalysts function.

In the acid-catalyzed reaction between 2-methyloxetane and hydrogen chloride in ten solvents or solvent mixtures, and in the concurrent acid-catalyzed methanolysis in four solvents, the main product has been found to result from the ring fission between oxygen and the unsubstituted carbon atom.¹⁶ In these reactions the product ratios vary with changes in the nucleophilicity of the attacking reagent and in the polarity of the reaction medium.

A higher positive charge exists on the carbon atom of the reaction centre in the transition state when the catalyst is aluminium chloride than when it is hydrogen ion, and this can explain the product ratios observed in this work. This charge is located more favourable on the secondary carbon atom than on the primary, and is higher in the case of 2-phenyloxetane than that of 2-methyloxetane.

Consequently, in the reaction of 2-methyloxetane with chloride ion, more secondary chloride is formed when aluminium chloride functions as catalyst than in the hydrogen ion-catalyzed reaction. In the aluminium chloride-catalyzed reaction of 2-methyloxetane with the less nucleophilic aromatic hydrocarbons, and in the catalyzed reactions of 2-phenyloxetane, the bond stretching is so important that it dominates all other forces controlling the course of the reaction.

Diphenylmethane was one of the products from the reaction of 2-phenyloxetane with benzene. This compound has probably been formed from formaldehyde and benzene through the influence of aluminium chloride, for the corresponding product in the reaction of toluene was a mixture of 4,4'-, 2,4'-, and 2,2'-dimethyldiphenylmethanes. This composition was confirmed by gas-chromatographic comparison with authentic samples of all three isomers prepared individually by Grignard reactions.

A mixture of 4,4'- and 2,4'-dimethyldiphenylmethanes was obtained when hydrogen chloride gas was passed into a mixture of toluene, paraformaldehyde, and hydrochloric acid at 60–70°C.

2-Phenyloxetane has been found to fragment by electron impact partly to formaldehyde.¹⁷ Raising the temperature has been reported to lead to an increasing removal of formaldehyde from 2-phenyloxetane. Thus, at least partly, this is a thermal reaction.

3-Phenylpropan-1-ol was formed in the reactions of 2-phenyloxetane with benzene, toluene, and mesitylene. The product is evidently a result of hydride-ion transfer. The source of hydride-ions may well be diarylmethane, by analogy with the cycloalkylations reported by Ipatieff *et al.*¹⁸

The main Friedel-Crafts hydroxyalkylation products were isolated from the reactions of 2-methyloxetane and 2-phenyloxetane with benzene, toluene, and mesitylene.

Chlorobenzene reacted more slowly and gave more side products. The main product in the reaction of 2-phenyloxetane amounted to about 40 % of the volatile components, but at least fifteen others were observed. The corresponding reaction of 2-methyloxetane gave about 70 % of two products with closely similar retention times. We have abandoned further study of these reactions because of their complexity.

The kinetic Friedel-Crafts hydroxyalkylation experiments were performed by the competitive method. To minimize the contribution of disturbing side reactions, the oxetane solution was added gradually to the stirred aluminium chloride suspension in hydrocarbon mixtures or in ethylene dichloride solution at 0°C. After the aluminium chloride had dissolved, samples were withdrawn from the reaction mixture, quenched and analyzed by gas-chromatography.

The kinetic results are collected in Tables 1–3. Owing to the decomposition and polymerization reactions, and to the partly heterogeneous conditions, the accuracy of the rate constants is not high. Nevertheless, we consider them sufficiently reliable to draw the following brief conclusions which we believe are useful as a guide.

As may be seen from the tables, the reactions investigated imply a decreasing intermolecular selectivity in the sequence: 2-phenyloxetane in hydrocarbons, 2-methyloxetane in hydrocarbons, 2-methyloxetane in ethylene dichloride. The selectivities are lower than those observed in acylation reactions, but resemble those reported for the various alkylation reactions.¹⁹

For comparison, the relative rate constants obtained are collected in Table 4 together with those for aluminium chloride-catalyzed acylation with benzoyl chloride in ethylene dichloride²⁰ and for aluminium chloride-catalyzed alkylation with benzyl chloride in nitromethane.²¹ The relative stabilities of the π -complexes of the aromatic compounds with iodine and iodine monochloride in carbon tetrachloride²² are also included in the table.

The relative rate constants of 2-methyloxetane closely resemble the relative stabilities of the π -complexes formed by iodine and iodine monochloride. The selectivity of the reactions of 2-phenyloxetane is lower than that of benzoyl chloride but higher than that of benzyl chloride.

The values 2.4 and 1.64 have been obtained for the kinetic isotope effect (k_H/k_D) in the aluminium chloride-catalyzed benzoylation of, respectively, *p*-deuteriotoluene and hexadeuteriobenzene in benzoyl chloride.²⁴ Isotope effects of considerable magnitude have also been reported for other acylation reactions.²⁵ These values reveal that proton elimination is part of the rate-

Table 1. The relative rates of the aluminium chloride-catalyzed reactions of 2-methyl-oxetane in ethylene dichloride.

Hydrocarbons	Molarity mol/l	Ratio of rate constants	Relative rate	Yield %
Toluene	0.512	$\frac{k_T}{k_B} = 1.7$	1.7	16
Benzene	0.537		1.0	
<i>m</i> -Xylene	0.456	$\frac{k_{m-X}}{k_T} = 1.3$	2.2	21
Toluene	0.435			
<i>o</i> -Xylene	0.434	$\frac{k_{o-X}}{k_T} = 1.4$	2.4	24
Toluene	0.565			
<i>p</i> -Xylene	0.473	$\frac{k_{p-X}}{k_T} = 1.6$	2.7	22
Toluene	0.462			
Mesitylene	0.535	$\frac{k_M}{k_{m-X}} = 1.9$	4.2	35
<i>m</i> -Xylene	0.522			

Table 2. The relative rates of the aluminium chloride-catalyzed reactions of 2-methyl-oxetane in mixtures of hydrocarbons.

Hydrocarbons	mmol	Ratio of rate constants	Relative rate	Yield %
Toluene	6.1	$\frac{k_T}{k_B} = 2.7$	2.7	34
Benzene	19.3		1.0	
Mesitylene	6.0	$\frac{k_M}{k_B} = 8.2$	8.2	56
Benzene	19.3			
Mesitylene	6.6	$\frac{k_M}{k_T} = 4.5$	(12)	62
Toluene	15.3			

Table 3. The relative rates of the aluminium chloride-catalyzed reactions of 2-phenyl-oxetane in mixtures of hydrocarbons.

Hydrocarbons	mmol	Ratio of rate constants	Relative rate	Yield %
Toluene	31.1	$\frac{k_T}{k_B} = 35$	35	44
Benzene	37.5		1.0	
Mesitylene	22.4	$\frac{k_M}{k_T} = 1.9$	67	84
Toluene	29.2			
Mesitylene	3.4	$\frac{k_M}{k_B} = 36$		93
Toluene	3.7			
Benzene	52.1	$\frac{k_T}{k_B} = 27$		

Table 4. The relative rates of the aluminium chloride-catalyzed reactions of methyl-substituted benzenes with 2-phenyloxetane, 2-methyloxetane, benzoyl chloride, and benzyl chloride, and the relative stabilities of iodine and iodine monochloride complexes.

Aromatic compound	Relative rate constants					Relative stabilities	
	2-Phenyl-oxetane ^a	2-Methyl-oxetane ^a	2-Methyl-oxetane ^b	Benzoyl chloride ^c	Benzyl chloride ^d	Iodine ^e	Iodine mono-chloride ^e
Benzene	1.0	1.0	1.0	1.00	1.00	1.0	1.0
Toluene	35	2.7	1.7	117	3.20	1.1	1.6
<i>m</i> -Xylene			2.2	698	4.64	2.1	2.6
<i>o</i> -Xylene			2.4	1076	4.25	1.8	2.3
<i>p</i> -Xylene			2.7	106	4.35	2.1	2.8
Mesitylene	67	8.2	4.2	125 000 ^f	5.20	5.5	8.5

^a This work, in aromatic hydrocarbons. ^b This work, in ethylene dichloride. ^c Ref. 20, in ethylene dichloride. ^d Ref. 21, in nitromethane. ^e Ref. 22, in carbon tetrachloride. ^f Ref. 23, in nitromethane.

determining step. Accordingly, a σ -complex transition state must be accepted for these reactions.

From the observed relative rate constants and other results for aluminium chloride-catalyzed alkylation with benzyl chloride, Olah and co-workers²¹ have suggested that the transition state in the displacement step could best be represented as an oriented π -complex containing a partially formed carbon-carbon bond and a partially broken carbon-chloride bond.

To account for the data, we consider that the rate for the aluminium chloride-catalyzed Friedel-Crafts reactions of 2-methyloxetane and 2-phenyloxetane is most probably determined by the slow formation of a π -complex. This step is followed by a faster isomerization of the complex to the benzenium ion. In the transition state of 2-phenyloxetane the new carbon-carbon bond from oxetane to the aromatic compound has been partially formed. This is reflected in the increased intermolecular selectivity.

EXPERIMENTAL

Chemicals. 2-Methyloxetane and 2-phenyloxetane were synthesized by the methods described previously.^{14,16}

Benzene and the alkylbenzenes were purified and used at purities comparable to those used in an earlier investigation.¹² Chlorobenzene was distilled from phosphorus pentoxide. Ethylene dichloride, a *purum* product from Fluka AG, was shaken with sodium hydroxide pellets, allowed to stand over phosphorus pentoxide and fractionally distilled from fresh P₂O₅. A middle fraction, b.p. 83.5°, was used in the kinetic experiments.

Aluminium chloride, a *zur Synthese* product from Merck AG, was sublimed several times *in vacuo*.

Reaction of 2-methyloxetane with benzene. 2-Methyloxetane, 5.22 g (0.0725 mol) in 20 ml of benzene was added over 90 min to a magnetically stirred mixture of 9.70 g (0.0727 mol) of aluminium chloride in 31.5 ml of benzene under nitrogen. The temperature was held at 5–10° with the aid of the ice-water bath. After the aluminium chloride had dissolved, the reaction mixture was allowed to attain room temperature and was left over night. The mixture was then poured gradually into a mixture of 170 g of ice and

50 ml of concentrated hydrochloric acid and mixed until the precipitated aluminium hydroxide had dissolved. The benzene layer was separated and the aqueous layer extracted twice with benzene. The combined benzene solutions were washed with water, 5 % sodium bicarbonate and again water. After drying with magnesium sulphate, the solution was analyzed by gas-chromatography. It contained 75 % of a main product and 5 % of side products calculated on the equimolar quantities of 2-methyloxetane and aluminium chloride. The products were isolated by distillation.

The side products, b.p. 65°/11 torr, n_D^{25} 1.4399, were shown to be composed of 3-chlorobutan-1-ol and 4-chlorobutan-2-ol in the ratio of 4:1 by comparison with known compounds using gas-chromatography.

4-Chlorobutan-2-ol was prepared from 2-methyloxetane and hydrogen chloride in dioxane.¹⁶ 3-Chlorobutan-1-ol was synthesized by allowing the neutral sulphate of 1,3-butanediol to react with hydrochloric acid, as described by Lichtenberger and Lichtenberger.²⁶

The identity of the main product, b.p. 120–121°/11 torr, n_D^{25} 1.5178 (lit.:²⁷ b.p. 132.5–135°/18–19 torr, n_D^{25} 1.5184), was confirmed by its PMR and mass spectra as 3-phenylbutan-1-ol. PMR spectrum: δ 1.22 (3 H) (doublet, methyl protons), 1.72 (2 H) (multiplet, C-2 methylene protons), 2.83 (1 H) (multiplet, benzylic proton), 3.40 (2 H) (triplet, C-1 methylene protons), 7.16 (5 H) (singlet, aromatic protons). Mass spectrum: m/e M^+ 150 (36 %), 132 (41 %), 117 (100 %), 106 (64 %), 105 (75 %), 91 (72 %), 79 (39 %), 77 (45 %).

Reaction of 2-methyloxetane with toluene. This was run as in the preceding experiment, except that the mixing time at room temperature was 4 h. 2-Methyloxetane, 5.07 g (0.0704 mol), 9.66 g (0.0724 mol) of aluminium chloride, and 45 ml of toluene gave, by GLC, 73 % of 3-(4'-methylphenyl)-butan-1-ol, b.p. 150–152°/24 torr, n_D^{25} 1.5186. PMR spectrum: δ 1.18 (3 H) (doublet, methyl protons), 1.69 (2 H) (multiplet, C-2 methylene protons), 2.28 (3 H) (singlet, methyl protons), 2.82 (1 H) (multiplet, benzylic proton), 3.32 (2 H) (multiplet, C-1 methylene protons), 6.97 (4 H) (multiplet, aromatic protons).

Reaction of 2-methyloxetane with mesitylene. Using a procedure similar to that of the preceding experiment, 2-methyloxetane, 4.19 g (0.0582 mol), 8.00 g (0.0600 mol) of aluminium chloride, and 40 ml of mesitylene gave, by GLC, 88 % of 3-(2',4',6'-trimethylphenyl)-butan-1-ol, b.p. 156–158°/15 torr, n_D^{25} 1.5265. PMR spectrum: δ 1.23 (3 H) (doublet, methyl protons), 1.88 (2 H) (multiplet, C-2 methylene protons), 2.27 (9 H) (singlet, methyl protons), 2.90–3.55 (3 H) (multiplet, C-1 methylene and benzylic protons), 6.67 (2 H) (singlet, aromatic protons).

Reaction of 2-phenyloxetane with benzene. With the same procedure as for 2-methyloxetane, 2-phenyloxetane, 10.02 g (0.0746 mol), 10.00 g (0.0750 mol) of aluminium chloride, and 80 ml of benzene gave a mixture of 82 % (rel. amount by GLC) of 3,3-diphenylpropan-1-ol, 10 % of diphenylmethane, and 9 % of 3-phenylpropan-1-ol. On distillation, 4.48 g (28 % of theory) of 3,3-diphenylpropan-1-ol were collected, b.p. 133–137°/0.1 torr, n_D^{22} 1.5827 (lit.²⁸: b.p. 164–166°/2.5 torr, n_D^{25} 1.5814). PMR spectrum: δ 2.15 (2 H) (multiplet, C-2 methylene protons), 4.05 (1 H) (triplet, benzylic proton), 7.10 (10 H) (singlet, aromatic protons). Mass spectrum: m/e M^+ 212, 168 (45 %), 167 (100 %), 165 (35 %), 118 (33 %), 105 (30 %), 92 (30 %), 91 (57 %), 77 (37 %).

Reaction of 2-phenyloxetane with toluene. 2-Phenyloxetane, 10.15 g (0.0757 mol), 10.23 g (0.0767 mol) of aluminium chloride, and 84 ml of toluene gave a mixture of 91 % (rel. amount by GLC) of 3-(4'-methylphenyl)-3-phenylpropan-1-ol, 7 % of a mixture of 2,2',-2,4',- and 4,4'-dimethyldiphenylmethanes, and 2 % of 3-phenylpropan-1-ol. 8.52 g (50 % of theory) of the main product were isolated by distillation, b.p. 131–132°/0.1 torr, n_D^{22} 1.5771. PMR spectrum: δ 2.15 (2 H) (multiplet, C-2 methylene protons), 2.24 (3 H) (singlet, methyl protons), 3.41 (2 H) (triplet, C-1 methylene protons), 4.00 (1 H) (triplet, benzylic proton), 6.96 (4 H) (singlet, aromatic protons), 7.10 (5 H) (singlet, aromatic protons).

Preparation of 2,2',-2,4',- and 4,4'-dimethyldiphenylmethanes. These compounds were prepared by known Grignard syntheses from methylphenyl bromides and methylbenzyl chlorides or bromides. The GLC retention times were 14.8, 14.4, and 14.2 min for the 4,4',-2,4',- and 2,2'-substituted compounds, respectively. A 2 m column of 10 % Silicone Gum Rubber SE-30 on Chromosorb W, NAW, was used at 160°.

Reaction of toluene with formaldehyde. Hydrogen chloride gas was passed into a mixture of 100.0 g (1.09 mol) of toluene, 20.0 g (0.667 mol) of paraformaldehyde, and 220 ml of

concentrated hydrochloric acid at 60–70°. The reaction time was 2.5 h. The organic layer was separated, washed with ice-water, 5 % sodium bicarbonate and water, and dried with magnesium sulphate. 1.86 g of a fraction boiling at 157–166°/14 torr were collected and shown by GLC, PMR, and MS to be composed of 49 % 4,4'- and 51 % 2,4'-dimethyldiphenylmethanes.

Reaction of 2-phenyloxetane with mesitylene. 2-Phenyloxetane, 10.0 g (0.0747 mol), 10.0 g (0.0752 mol) of aluminium chloride, and 85 ml of mesitylene reacted to give a mixture of 90 % (rel. amount by GLC) of the main product, about 0.5 % of 3-phenylpropan-1-ol, and traces of other products. When distilled, 4.05 g of a solid fraction boiling at 130–132°/0.08 torr were collected. After recrystallization from light petroleum (b.p. 40–65°), 3.75 g (20 % of theory) of 3-(2',4',6'-trimethylphenyl)-3-phenylpropan-1-ol, m.p. 85.5–88° were obtained. PMR spectrum: δ 2.14 (6 H) (singlet, methyl protons), 2.22 (3 H) (singlet, methyl protons), 2.42 (2 H) (multiplet, C-2 methylene protons), 3.55 (2 H) (triplet, C-1 methylene protons), 4.64 (1 H) (triplet, benzylic proton), 6.74 (2 H) (singlet, aromatic protons), 7.12 (5 H) (singlet, aromatic protons).

Competitive experiments. Oxetane solution was added to a suspension of aluminium chloride in either a mixture of two or three hydrocarbons or their solution in ethylene dichloride at 0°C. The reaction mixture was then allowed to attain room temperature. After the aluminium chloride had dissolved (about 10 min in the case of 2-methyloxetane, about 20 min for 2-phenyloxetane), 0.5 ml samples were withdrawn and arrested by adding 1 ml of 1 M sodium hydroxide solution. The organic layer was then analyzed by GLC and the relative rate constants calculated from the product ratios corrected by the mean concentrations of the aromatic hydrocarbons during the reactions

$$\frac{k_1}{k_2} = \frac{X_1}{C_1^\circ - X_1/2} \bigg/ \frac{X_2}{C_2^\circ - X_2/2}$$

where C_1° and C_2° are the initial concentrations of the hydrocarbons and X_1 and X_2 the concentrations of the corresponding hydroxyalkylation products.

Apparatus. The gas-chromatograms were run on a Perkin-Elmer Model 452 gas-chromatograph with a hot-wire detector or on a Perkin-Elmer Model F11 gas-chromatograph with a flame ionization detector. The PMR spectra were run on a Varian T-60 NMR spectrograph employing carbon tetrachloride as solvent and tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E double focusing mass spectrometer.

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Received June 29, 1973.