

the formolysis of *trans*- and *cis*-2-bromocyclohexyl brosylate. In the case of the *trans* isomer where β -bromine assistance is possible, the rate of formolysis relative to that of the parent cyclohexyl brosylate was decreased by a factor of 2.8. In the case of the *cis* isomer where β -bromine assistance is impossible, the inductive effect of the bromine decreased the reaction rate by a factor of 8500.⁸ On the other hand, the effect of an α -bromine in the case of the solvolysis of some benzhydryl dibromides was to speed up solvolysis.⁹ Based on an estimate that the half-life for the reaction (eq 1) was less than 6 min, the solvolysis of the α,β -dibromo tosylate **6** is faster than that of 2-butyl tosylate by at least a factor of 35.¹⁰ The cited literature suggests that both α - and β -bromine assistance occur in the formolysis of **6**.

Finally, it may be noted that the reaction of α,β -dibromo tosylates with formic acid may be of synthetic value, as it provides an alternative to a standard preparation of α -bromo ketones and aldehydes through the bromination of enol acetates.¹¹

(8) (a) J. E. Duddey, Ph. D. Thesis, St. Louis University (1967). (b) These results may be compared with the acetolysis data from the literature: E. Grunwald, *J. Amer. Chem. Soc.*, **73**, 5458 (1951), and S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(9) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw Hill Book Co., New York, N. Y., 1962, p 102.

(10) P. E. Peterson, R. E. Kelley Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965).

(11) (a) E. R. H. Jones and D. J. Wluka, *J. Chem. Soc.*, 907 (1959); (b) P. Z. Bedoukian, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 127.

Experimental Section

Infrared spectra were determined on a Beckman Model IR-5A double-beam spectrophotometer. Gas chromatographic analysis was carried out on a Hewlett-Packard Model 5750 gas chromatograph. Nmr spectra were determined on a Varian Model HA-100D spectrometer.

Addition of Bromine to 2-Buten-2-yl Tosylates.—*trans*-2-Buten-2-yl tosylate (0.0358 g, 1.585×10^{-4} mol) was dissolved in 0.5 ml of CCl_4 and cooled in an ice bath. Bromine (0.025 g, 0.1585 mmol) was added and the mixture kept cold until the nmr spectrum was taken (2–5 min; cf. Figure 1): nmr (CCl_4) δ 1.83 and 1.85 (2d, $J = 6$ Hz, CH_3CHBr –), 2.34 and 2.46 (2s, CH_3COTsBr –), 2.45 (s, $\text{CH}_3\text{C}_6\text{H}_4$ –), 4.59 and 4.34 (2q, $J = 7$ Hz, CH_3CHBr –), 7.72 (m, aromatic). To show that two peaks were present at δ 4.45 and 4.46, 20% benzene was added to the solution. The $\text{CH}_3\text{C}_6\text{H}_4$ – peak was shifted upfield to δ 2.32 and the CH_3COTsBr – peak shifted upfield only to δ 2.43. The spectrum remained constant in the proportions of isomers after 36 hr at room temperature, indicating no interconversion of isomers. The addition to the *cis* isomer was carried out in a similar manner. The nmr spectrum showed that the minor component from the previously described addition reaction was now the predominant isomer present.

Isolation Experiment.—The *trans* isomer (0.0026 mol) was brominated. The solution was washed with distilled water and saturated NaCl solution and dried (MgSO_4). Removal of the solvent on a rotary evaporator yielded 91% of a mixture of diastereomers. Several crystallizations from hexane gave *erythro*-2,3-dibromo-2-butyl tosylate: mp 77.9–79.8; nmr (CCl_4) δ 1.83 (d, 3, $J = 6$ Hz, CH_3CHBr –), 2.34 (s, 3, CH_3COTsBr –), 2.45 (s, 3, $\text{CH}_3\text{C}_6\text{H}_4$ –), 4.59 (q, 1, $J = 7$ Hz, CH_3CHBr –), 7.52 (m, 4, aromatic).

Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{Br}_2\text{O}_3\text{S}$: C, 34.22; H, 3.65. Found: C, 34.22; H, 3.65.

Formolysis of *erythro*-2,3-Dibromo-2-butyl Tosylate.—To a weighed quantity of dibromobutyl tosylate formic acid (0.125 M in sodium formate) was added to form a solution 0.1 M in tosylate. The tosylate was slow to dissolve, but did so after 10 min. At that time, nmr indicated that no starting material was present. The solution was neutralized with NaHCO_3 and extracted with CCl_4 . The sole product of the reaction was identified by ir and nmr to be 3-bromo-2-butanone.

In a similar experiment, glpc of the reaction mixture, employing a base forecolumn,¹² indicated quantitative conversion into the bromo ketone.

Registry No.—Bromine, 7726-95-6; **5**, 22461-42-3; **6**, 22461-43-4.

(12) P. E. Peterson and E. Tao, *J. Org. Chem.*, **29**, 2322 (1964).

Quaternary Carbons by the Alkylation of Tertiary Halides with Aluminum Alkyls. A Model for Initiation and Termination in Cationic Polymerization

J. P. KENNEDY

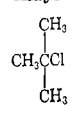
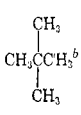
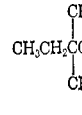
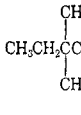
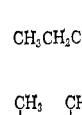
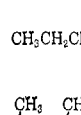
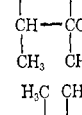
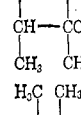
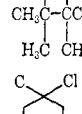
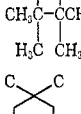
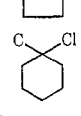
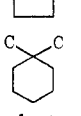
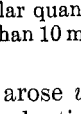
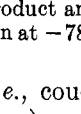
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The reactions of halo hydrocarbons with aluminum alkyls have been studied previously.¹ The best report in this field is by Miller,¹ who investigated the interaction between aluminum triethyl and a variety of halogen-containing hydrocarbons in ethyl ether at room or higher temperatures. Product analysis showed medium to high conversions into a variety of products

(1) D. B. Miller, *J. Org. Chem.*, **31**, 908 (1966), and references cited therein.

TABLE I
SYNTHESIS OF QUATERNARY CARBON ATOM CONTAINING COMPOUNDS BY
REACTION OF TERTIARY ALKYL CHLORIDES WITH $\text{Al}(\text{CH}_3)_3^a$

Alkyl halide	Registry no.	Product	Solvent	
			Methyl chloride	Cyclopentane
	507-20-0		c	No appreciable reaction for 15 min at -25° ; complete reaction in less than 10 min at -21°
	594-36-5		d	e
	4325-48-8		d	No appreciable reaction for 4 days at -78° ; complete clean reaction after 12 hr at room temperature
	4398-65-6		d	No appreciable reaction for 4 days at -78° ; complete, clean reaction after 12 hr at room temperature
	918-07-0		d	Partial reaction after 24 hr at -70°
	6196-85-6		d	Partial reaction after 24 hr at -70° ; ca. 1% olefin present
	931-78-2		d	Partial reaction after 24 hr at -70° ; ca. 1% olefin present

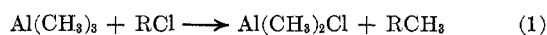
^a Molar quantities of $\text{Al}(\text{CH}_3)_3$ and RCl reacted. Product analysis by nmr. ^b Also confirmed by gc. ^c Quantative, clean reaction in less than 10 min at -78° . ^d Quantative, clean reaction at -78° . ^e Not examined.

which arose *via* a variety of reaction paths, *i.e.*, coupling, reduction, elimination (dehydrohalogenation), polymerization, etc.

In the course of our studies on the mechanism of cationic polymerizations, we carried out experiments to elucidate the polymerization-catalytic action of $\text{AlR}_3\text{-RCl}$ initiator systems.^{2,3} Aluminum trialkyls (*e.g.*, AlMe_3 , AlEt_3 , $\text{Al}i\text{Bu}_3$) in the presence of certain alkyl halides are efficient initiators for the polymerization of cationically initiatable monomers, *e.g.*, isobutylene, styrene, etc.^{2,3} It was observed that the introduction sequence of the reactants is of decisive importance for successful polymerization. Thus efficient polymerization commences when the introduction sequence is monomer- $\text{AlMe}_3\text{-RCl}$; however, no or very little polymer is formed when the sequence is $\text{AlMe}_3\text{-RCl}$ -monomer. This initial observation was followed up experimentally to elucidate the reaction(s) between AlR_3 and various alkyl halides. This work provided important insight into the initiation and termination mechanisms of olefin polymerizations with $\text{AlR}_3\text{-RCl}$ initiator systems and, in addition, resulted in the definition of an alkylation (coupling) reaction for the synthesis of branched hydrocarbons in general and quaternary carbon compounds in particular.

Results

Table I summarizes the results obtained with a series of tertiary chlorides and AlMe_3 . All reactions proceeded by eq 1. Alkylation was very rapid in



methyl chloride solvent and complete conversion into final products was obtained by the time of nmr analysis (usually less than 10 min). In cyclopentane the reactions were slower but proceeded without disturbing side reactions (*e.g.*, elimination) as well.

Table II shows the results obtained with AlMe_3 and various primary, secondary, allyl, and benzyl chlorides. The conversion of 1-chloroethylbenzene into cumene was complete in less than the time of nmr analysis (*ca.* 10 min). Allyl, isopropyl, and isobutyl chloride did not react at -78° during the times shown in Table II; however, the expected methylated hydrocarbons formed at a higher temperature. It should be noted that the sole product from isobutyl chloride was neopentane (*cf.* below). There was no evidence for disturbing side reactions (elimination, etc.) in any of these experiments. Benzyl chloride, which gives polybenzyl ($-\text{C}_6\text{H}_4\text{CH}_2-$) in the presence of Lewis acids,⁴ gave *ca.* 20% ethylbenzene and *ca.* 80% polymer. Ethyl chloride did not react with AlMe_3 .

Table III shows the results of a series of experiments with various aluminum trialkyls and *t*-butyl chloride. Again, the reactions proceeded rapidly and without the formation of by-products.

Experiments were also carried out to study the stoichiometry of the *t*-BuCl + $\text{Al}(\text{CH}_3)_3$ reaction by the addition of increasing amounts of *t*-BuCl to the $\text{Al}(\text{CH}_3)_3$. No complications occurred upon the addition of up to 3 mol of *t*-butyl chloride to 1 mol of $\text{Al}(\text{CH}_3)_3$ in methyl chloride solvent at -78° . Product analysis by nmr indicated the formation of stoichiometric amounts of neopentane. Further addition

(2) J. P. Kennedy in "Polymer Chemistry of Synthetic Elastomers," J. P. Kennedy and E. Tornqvist Ed., Interscience Publishers, Inc., New York, N. Y., 1968, part 1, Chapter 5A, p 291.

(3) J. P. Kennedy, Belgian Patent 663,319 (1965).

(4) J. P. Kennedy and R. B. Isaacson, *J. Macromol. Chem.*, **1**, 541 (1966).

TABLE II
SYNTHESIS OF VARIOUS HYDROCARBONS BY REACTION OF ALKYL AND ARALKYL CHLORIDES
WITH $\text{Al}(\text{CH}_3)_3$ IN METHYL CHLORIDE SOLUTION^a

Halide	Product	Remarks
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3^b$	Ca. 20% ethylbenzene formed in the temperature range of -78 to 20° ; by-product polybenzyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_5\text{CHCl} \\ \text{CH}_2=\text{CHCH}_2\text{Cl} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_5\text{CHCH}_3^b \\ \text{CH}_2=\text{CHCH}_2\text{CH}_3 \end{array}$	Complete, clean reaction at -78° No reaction for 24 hr at -78° . Slow reaction at room temperature: ca. 30% conversion after 4 days, 100% conversion into 1-butene after 9 days
$(\text{CH}_3)_2\text{CHCl}$	$(\text{CH}_3)_2\text{CHCH}_3$	No reaction at -78° . Slow reaction when heated to room temperature: ca. 50% conversion into isobutane after 9 days
$(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CCH}_3 \\ \\ \text{CH}_3 \end{array}$	No reaction for 2 hr at -78° ; complete conversion into neopentane after 4 days at room temperature
$\text{CH}_3\text{CH}_2\text{Cl}$...	No reaction for 2 weeks at room temperature

^a Molar quantities reacted; product analysis by nmr. ^b Confirmed by gc.

TABLE III
SYNTHESIS OF HYDROCARBONS BY REACTION OF VARIOUS ALUMINUM TRIALKYLS
WITH *t*-BUTYL CHLORIDE IN METHYL CHLORIDE SOLUTION^a

Aluminum trialkyl	Product	Remarks
$\text{Al}(\text{CH}_3)_3$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2\text{CCH}_3 \end{array}$	Immediate complete reaction at -78° . The $[\text{Al}(\text{CH}_3)_3]_2/t$ -butyl chloride ratio was 0.5:1
$\text{Al}(\text{C}_2\text{H}_5)_3$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \\ \\ \text{CH}_3\text{CCH}_2\text{CH}_3 \end{array}$	Immediate reaction at -78° . The $[\text{Al}(\text{C}_2\text{H}_5)_3]_2/t$ -butyl chloride ratio was 0.5:1
$\text{Al}(i\text{-C}_4\text{H}_9)_3$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CCH}_2\text{CHCH}_3 \\ \\ \text{CH}_3 \end{array}$	Partial reaction at -78° . The $\text{Al}(i\text{-C}_4\text{H}_9)_3/t$ -butyl chloride ratio was 1:1

^a Product analysis by nmr.

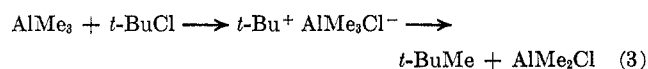
of *t*-butyl chloride resulted in the formation of a white precipitate, and the nmr spectra became difficult to interpret.

Discussion

The reaction represented by eq 2, where R and R' are



alkyl or aralkyl groups, most likely proceeds by a carbonium ion mechanism.¹ For example, the reaction between aluminum trimethyl and *t*-butyl chloride to neopentane can be visualized as follows (eq 3). The



reaction is very rapid in methyl chloride solvent at -78° and it is complete before the nmr spectroscopic analysis can be performed (<10 min). The reaction in methyl chloride, the more polar solvent (ϵ ca. 18 at

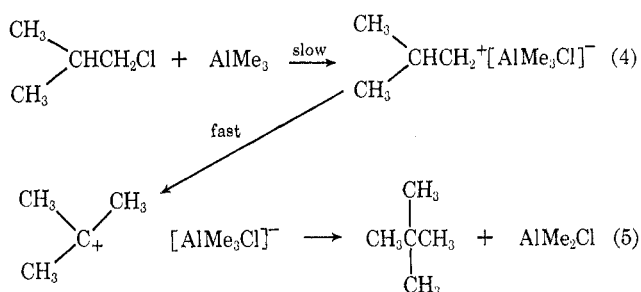
-78°), is faster than in cyclopentane. In cyclopentane the reaction is slow at -25° , but occurs rapidly at -21° . Similar observations were also made with the other tertiary chlorides, as shown in Table I.

All the reactions proceeded selectively to the quaternary carbon compound indicated. The synthesis of organic molecules with quaternary carbon atoms is quite difficult with present-day techniques. The Grignard reaction commonly used for this purpose is slow and is beset by disturbing complications, *e.g.*, elimination, reduction, etc., and therefore usually gives low yields. The reaction with aluminum alkyls and tertiary alkyl halides, particularly in inert polar solvents at low temperatures, proceeds very rapidly and selectively.

Under our conditions tertiary halides react very rapidly with aluminum trimethyl, secondary halides react much more slowly, and normal primary halides do not react at all. *E.g.*, isopropyl chloride gives

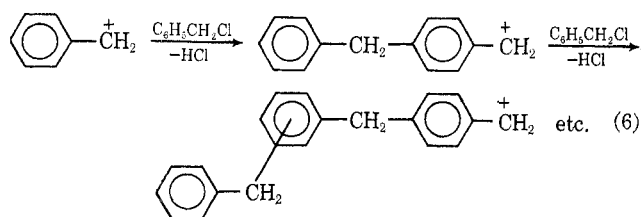
isobutane with a half-life of *ca.* 9 days at room temperature, whereas ethyl chloride remains unchanged even after 14 days at room temperature.

The isobutyl chloride experiment (*cf.* Table II) is important, as it provides insight into the reaction mechanism. Isobutyl chloride gives exclusively neopentane in a relatively slow reaction (no reaction after 2 hr at -78° , complete conversion in 4 days at room temperature). These results are interpreted by assuming a slow reaction in which the chlorine is removed by the aluminum trialkyl, followed by a fast isomerization *via* hydride shift to the more stable tertiary butyl cation, which captures a methyl group (methine anion) from the Gegen ion and gives neopentane (eq 4 and 5). Neopentane formation from iso-

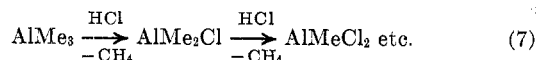


butyl chloride strongly supports a carbonium ion mechanism.

Among the benzyl halides, 1-chloroethylbenzene gave cumene selectively and rapidly in 100% yield at -78° . Benzyl chloride produced *ca.* 20% ethylbenzene and *ca.* 80% white powdery product, polybenzyl ($-\text{C}_6\text{H}_4\text{CH}_2-$). Evidently, with benzyl chloride a competitive side reaction occurs in which benzyl cations (and/or growing benzyl cations) are consumed by ring benzylation (eq 6). The dehydrochlorination



which accompanies each benzylation step most likely gives rise to AlMe_2Cl_2 (eq 7), a strong chlorine acceptor;



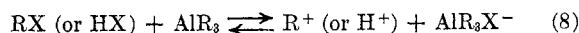
so that this reaction is probably autocatalytic for polybenzyl formation. The polyalkylation reaction of benzyl chloride to polybenzyl is a well-investigated, extremely facile reaction and proceeds with high rate even at -130° .^{4,5}

With 1-chloroethylbenzene no polymer formation was observed. Apparently, in this case the repetitive alkylation of the aromatic rings with the methyl phenyl carbonium ion ($\text{C}_6\text{H}_5\text{CH}^+\text{CH}_3$) is retarded owing to steric hindrance.

Allyl chloride gave exclusively 1-butene in a relatively slow reaction. In this experiment no reaction occurred

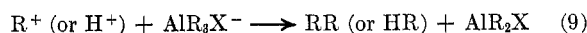
at -78° , *ca.* 30% conversion was found after 4 days at room temperature, and 100% after 9 days.

The reaction between aluminum alkyls and alkyl halides can be viewed as a model for the initiation and termination reactions in carbonium-ion polymerizations. Thus initiation of cationic polymerizations occurs by the generation of a suitable carbonium ion. The polymerization initiator is usually a Lewis acid the function of which is to help generate the first carbonium ion (or proton) by, *e.g.*, eq 8. This step is



identical with the first step of the alkylation reaction discussed above. The R^+ (or H^+), in the presence of a cationically active monomer, initiates polymerization which, depending on a series of important parameters (*e.g.*, structure of the monomer, temperature, solvent, etc.), might proceed to high polymer.

In the absence of a cationically initiatable monomer, the electrophile (R^+ or H^+) is stabilized by alkylation or by a variety of other processes, *e.g.*, elimination, etc. (eq 9). This reaction has been referred to in our earlier publication.⁶



This process can be regarded as a model for the termination in carbonium-ion polymerizations initiated with $\text{AlR}_3\text{-RX}$ systems. In these polymerizations the growing cation is converted into a high molecular weight hydrocarbon (eq 10).



Experimental Section

All the experiments and manipulations were performed in a stainless-steel enclosure under N_2 atmosphere (*ca.* 30 ppm moisture).⁶ The aluminum alkyls (Texas Alkyls Co.) and other chemicals used were commercially available materials (K & K Laboratories or Matheson Coleman and Bell) and were freshly distilled *in vacuo* before use. 2-Chloro-2,3-dimethylbutane and 2-chloro-2,3,3-trimethylbutane were produced by hydrochlorination of the corresponding olefins by known methods. Both gas chromatography and nmr spectroscopy were used to ascertain the purity of the starting materials. Most experiments were carried out in nmr tubes. A representative experiment was performed as follows. Separate molar solutions of *t*-butyl chloride and aluminum trimethyl in methyl chloride (or cyclopentane) solvent were prepared at -78° . Into nmr tubes 2-ml aliquots of these solutions were filled and mixed at -78° . The tubes were capped, frozen in liquid N_2 , and sealed. Subsequently, the temperature of the samples was brought back to -78° for nmr spectroscopy. Nmr analysis was performed as soon as feasible after sample preparation by the use of a Varian 60 nmr spectrometer. If no reaction occurred at -78° , the tubes were stored at this temperature and/or warmed to higher temperatures to effect conversion.

Selected samples were also analyzed by gas chromatography. A Perkin-Elmer 226 instrument (0.01 in. \times 300 ft capillary, DC 550 silicon oil at 40° , He carries gas) and a flame ionization detector were used. In these instances the samples were prepared in test tubes, and the reactions were quenched by the introduction of an excess of cold methanol. Upon methanol treatment a voluminous white precipitate formed. Gc analysis was performed by removing aliquots of the supernatant liquid.

Registry No.— $\text{Al}(\text{CH}_3)_3$, 75-24-1; $\text{Al}(\text{C}_2\text{H}_5)_3$, 97-93-8; $\text{Al}(i\text{-C}_4\text{H}_9)_3$, 100-99-2.

(6) J. P. Kennedy and G. Milliman, *Advances in Chemistry Series*, No. 91, American Chemical Society, Washington, D. C., 1969, Chapter 18, p 287.

(5) P. Finocciaro and R. Passerini, *Ann. Chim. (Rome)*, **58**, 418 (1968).

Acknowledgment.—The help of Dr. M. A. Melchior and F. Cassidy in the interpretation of nmr and gc spectra, respectively, is gratefully acknowledged. The advice of Dr. G. E. Milliman during the initial phase of this work was of great value. Most of the experimental operations were carried out with greatest competence by Mr. R. R. Phillips.

Direction of Cyclization of 1,2-Bis-(cyanomethyl)benzenes^{1a}

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2-Amino-3-cyano-1H-indenes bearing a single chlorine substituent on the benzene ring were required as synthetic intermediates.^{1b} A convenient route to amino nitriles of this type is the base-catalyzed Thorpe cyclization of 1,2-bis(cyanomethyl)benzenes, which has been reported for the unsubstituted parent compound, **1a**.² Unsymmetrically substituted dinitriles, such as 4-chloro-1,2-bis(cyanomethyl)benzene (**1b**) and 3-chloro-1,2-bis(cyanomethyl)benzene (**1c**), can each give rise to two isomeric products, depending on which cyanomethyl group undergoes anion formation most easily in the presence of base. This note describes a useful chemical method to establish the direction of cyclization of these dinitriles with complete certainty. This method, outlined in Scheme I, may be of general interest and applicability for similar systems.

Cyclization of the unsymmetrical dinitriles **1b** and **1c** afforded the corresponding cyano ketones; alkylation gave the cyano enol ethers, which were oxidized to homophthalic acids with chromic acid under mild conditions. The direction of cyclization of the dinitriles, which proved to be in accordance with predictions based on classical electronic effects, was confirmed by identification of the homophthalic acids.

Dinitriles **1b** and **1c** were prepared by bromination of 4-chloro-*o*-xylene³ and 3-chloro-*o*-xylene, and reaction of the resulting 1,2-bis(bromomethyl) compounds with sodium cyanide in aqueous ethanol.⁴ Cyclization of the dinitriles was accomplished in absolute ethanol in the presence of a catalytic amount of sodium ethoxide according to the method previously described for the cyclization of **1a**.² The amino group in amino nitriles **2b** and **2c** was hydrolyzed by refluxing in 6 *N* sulfuric acid for 3 hr. Treatment of the strongly enolic cyano ketones **3b** and **3c** with ethereal diazo-

methane yielded the corresponding enol ethers, **4b** and **4c**. All the chloro-substituted indenenes prepared in this work were sharp melting and appeared to be single compounds by thin layer chromatography. Gas-liquid chromatography of the enol ethers also failed to reveal the presence of more than one component. Thus, it seemed likely that dinitriles **1b** and **1c** were both undergoing cyclization unidirectionally. Since the structures of the cyclization products could not be determined by physical methods, it was necessary to resort to chemical degradation.

Attempted ozonolysis of **3a** gave only unchanged starting material. However, gentle oxidation of ethyl enol ether **4a**⁵ with 1 equiv of chromic acid gave a mixture of unreacted starting material and a product which proved to be ethyl *o*-carboxyphenylacetate (**5a**).⁶ When the oxidation was carried out with 2 equiv of chromium trioxide, the product appeared to be a mixture of **5a** and another compound, which is probably the intermediate acyl cyanide shown in Scheme I. This assignment was supported by the infrared spectrum of the mixture, which contained a nitrile band at 2230 cm⁻¹ and a carbonyl peak at 1780 cm⁻¹. The latter peak lies in the high wave number region characteristically ascribed to C=O functions attached directly to strong electron-attracting groups.⁷ The presence of a small amount of the presumed acyl cyanide was also indicated by the nmr spectrum, which contained, in addition to the signals arising from **5a**, a minor second set of peaks displaced by only about 2 cps.

Similar oxidation of **4b** with 1 equiv of chromium trioxide, gave, in addition to some unchanged **4b**, a product whose analysis and spectra were consistent with structure **5b**. On the other hand, oxidation with 2 equiv of chromium trioxide and direct saponification of the crude product afforded a 63% yield of 4-chlorohomophthalic acid (**6b**). Since no unchanged **4b** was recovered, it was clear that the employment of 2 equiv of oxidant had resulted in a more complete reaction. The identification of **6b** was made by comparison of its infrared spectrum with that of an authentic specimen,⁸ and also by mixture melting point determination. The formation of **6b** during the oxidation of **4b** established unequivocally that the Cl substituent in indenenes **2b**–**4b** was attached to the 5 rather than the 6 position. Hence, the base-catalyzed cyclization of dinitrile **1b** had to proceed *via* preferential ionization of the cyanomethyl group *meta* to the Cl atom.

Oxidation of **4c** with 2 equiv of chromium trioxide gave a 48% yield of a single product identified as 6-chlorohomophthalic acid (**6c**) by comparison with an authentic sample prepared as shown in Scheme II.

(5) Compound **4a** was prepared directly from **2a** by refluxing with ethanol in sulfuric acid as described by Moore and Thorpe.^{2a}

(6) This compound has been claimed previously as the product of the reaction of *o*-carboxyphenylacetone nitrile with ethanol and sulfuric acid: H. W. Johnston, C. E. Kaslow, A. Langsjoen, and R. L. Shriner, *J. Org. Chem.*, **13**, 477 (1948). The material isolated by these workers was a liquid, bp 164–169° (19 mm), whereas our product was a solid, mp 98–100° (see Experimental Section). It is probable that the material described by Johnston and coworkers was actually a mixture of at least two compounds.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, p 125.

(8) We are very grateful to Dr. P. A. S. Smith, of the Department of Chemistry, University of Michigan, for furnishing us with a sample of 4-chlorohomophthalic acid.

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