and an intermediate "enolate" radical as shown in eq 3 and 4. Such an intermediate was discounted by both

$$R_2CHCHO + Cu(II) \rightarrow R_2CCHO + H^+ + Cu(I) \quad (3)$$

$$R_2CCHO + Cu(II)Cl_x \rightarrow R_2CClCHO + Cu(I)Cl_{x-1} \quad (4)$$

Kochi[3] and Kosower[6] because Kochi reported no effect of benzoquinone on the acetone reaction. However, the very high rate of ligand transfer reactions between $CuCl_2$ and carbon radicals which has now been demonstrated[14] makes this criticism dubious, and dimers of such species have actually been found in some Cu(II) oxidations of carbonyl compounds (although under rather different conditions—base catalysis in the presence of amines and triphenylphosphine).[15]

In summary, while our data serve to rule out ordinary acid-catalyzed enolization as a step in the $CuCl_2$–aldehyde reaction and imply a direct, acid-catalyzed bimolecular process, there are still a number of alternatives for a detailed formulation of this interesting and rapid reaction.

Experimental Section

Reagents were commercial materials, purified by conventional means and purity checked by physical constants. Reference samples of α-chlorobutyraldehyde (bp 108-110°) and α-chloroisobutyraldehyde (bp 87–88°) were prepared by SO_2Cl_2 chlorination of the aldehydes as described by Stevens.[16]

$CuCl_2$–Butyraldehyde Reactions.—One hundred and ten cubic centimeters of a reaction mixture that was 1.02 *M* in freshly distilled *n*-butyraldehyde and 1.02 *M* in $CuCl_2$ isopropyl alcohol–water 3:1 by volume was refluxed (81°) for 1 hr under nitrogen. After 15 min CuCl began to precipitate and, at the end of the reaction 4.5 g had separated from the green solution. Titration of aliquots showed 0.0945 mole of copper to be reduced and 0.0475 mole of HCl produced. The yield of α-chloroaldehyde by glpc was 98% on the basis of copper consumed, and it was identified by collection and comparison with authentic material. Only a few minor by-products were detected and most of the excess aldehyde remained unreacted. Experiments in acetone–water and *t*-butyl alcohol–water gave similar results, while one in 4:1 methanol–water apparently yielded chiefly the dimethyl acetal of α-chlorobutyraldehyde. Refluxing 50 cc of aldehyde with 4 g of $CuCl_2$ in the absence of solvent gave complete reduction of the copper, but 2-ethyl-2-hexenal as the chief product, identified by comparison with authentic material.

$CuCl_2$–Isobutyraldehyde.—Eighty-five cubic centimeters of a solution that was 1.3 *M* in isobutyraldehyde and $CuCl_2$ in 2:1 acetone–water was refluxed under nitrogen (60–65°) for 1.5 hr. At the end of this time the solution was almost colorless, and copper reduction was 94.5% and 5.5 g of CuCl had precipitated. Analysis showed a 96% yield of α-chloroisobutyraldehyde, identified by isolation and comparison with authentic material. Again only minor by-products and no α-chloroacetone were detected. Under similar conditions in 4:1 isopropyl alcohol–water at 76° reaction was almost complete in 5 min, yield 95%. A number of other experiments were carried out similarly.

Kinetic experiments were conducted in a thermostat with stirring under nitrogen and followed by removal of aliquots, addition of KI, and titration with thiosulfate. Rate plots were close to linear to 30–50% reaction and initial rates are summarized in Table I. Added methyl methacrylate or benzoquinone had little effect on rate, although the latter increased total yield of chlorination products by reoxidation of cuprous ion.

Registry No.—Cupric chloride, 7447-39-4; butyraldehyde, 123-72-8; isobutyraldehyde, 78-84-2.

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[14] *Cf. e.g.*, J. K. Kochi and R. V. Subramanian, *J. Am. Chem. Soc.*, **87**, 4855 (1965).

[15] W. Brackman and H. C. Volger, *Rec. Trav. Chim.*, **85**, 446 (1966).

[16] C. L. Stevens and B. T. Gillis, *J. Am. Chem. Soc.*, **79**, 3449 (1957).

The Silver Tetrafluoroborate Induced Rearrangement of N-Chloroketimines[1a,b]

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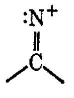
Silver tetrafluoroborate reacts with N-chloroketimines in aqueous dioxane to produce amides of rearranged structure. The group *trans* to the nitrogen–chlorine bond migrates to the nitrogen atom as the silver ion assists the removal of the chlorine. The resulting nitrilium ion has been trapped in aprotic solvents. No evidence was found for the intermediacy of a methylenimine cation.

The methylenimine cation 1 is a particularly intriguing species for it is theoretically capable of existing in either a singlet or triplet state. Lansbury,[2] observing an insertion of cationic nitrogen into the carbon–hydrogen bond, has recently presented strong evidence for the intermediacy of methyleniminium ions in the Schmidt and Beckmann rearrangements of substituted indanones and their derivatives. It is widely believed that methyleniminium ions are normally not intermediates in the Beckmann or Schmidt rearrangements[3] but it has been postulated that the particular geometry of the indanone system does not permit facile participation of the aryl group in the loss of the positively charged group from nitrogen.[2,4]



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The interesting theoretical and synthetic possibilities posed by the methyleniminium ion have resulted in an exploration in these laboratories of synthetic routes which might provide a greater structural variety of such cations. An essential feature of any such synthesis must be the removal of the leaving group from the nitrogen without anchimeric assistance and concomitant rearrangement of either of the groups attached to the adjacent carbon atom. Such a situation might arise if the intramolecular assistance to ionization were replaced by a suitable external driving force. The reaction of N-chloroketimines with silver ion appeared to be a good candidate to test this hypothesis.

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[1] (a) A portion of this work was supported by Petroleum Research Fund Grant 654 G-1. (b) Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., 1967. (c) NSF undergraduate research participant, 1965.

[2] P. T. Lansbury, J. G. Colson, and N. R. Mancuso, *J. Am. Chem. Soc.*, **86**, 5225 (1964); P. T. Lansbury and N. R. Mancuso, *ibid.*, **88**, 1205 (1966).

[3] P. A. S. Smith in "Molecular Rearrangements," Vol. 1, P. deMayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 483.

[4] R. Huisgen, J. Witte, and I. Ugi, *Chem. Ber.*, **90**, 1844 (1957).

It was expected that the silver ion might provide such electrophillic assistance to the ionization of the nitrogen–chlorine bond as to obviate anchimeric assistance provided by one of the groups bound to the trigonal carbon atom.

The literature[5,6] contains several reports of attempts to bring about the Beckmann-like rearrangement of N-haloimines with a diversity of catalysts such as aluminum chloride,[5a,b] sulfuric acid,[5c] boron trifluoride,[5a] stannic chloride,[5a] phosphorus pentachloride,[5b,d] and alkali.[5d] The only Beckmann-like rearrangement of N-haloimines which has been reported involved an attempt by Theilacker and Mohl[5b] to determine the configuration of the two isomeric N-chloroimines of 4-chlorobenzophenone. When N-chlorobenzophenonimine and antimony pentachloride were mixed together in carbon tetrachloride, a 1:1 insoluble complex was formed in which the benzophenone structure was still intact. This complex proved to be remarkably stable to hydrolytic conditions but rearranged at 40–45° in carbon tetrachloride to give rise to benzanilide after hydrolysis. Similar experiments with the pure *cis*- or *trans*-N-chloroimine of 4-chlorobenzophenone led to the isolation of 50% yields of the same mixture of the two possible amides. It was concluded without supporting evidence that isomerization was occurring prior to rearrangement but the precise nature of the complex was left to speculation. No extensive study of the catalytic requirements of this rearrangement has been performed. Antimony pentachloride failed to produce the rearrangement of the N-chloroimines of cyclohexanone and acetone but these are extremely unstable compounds.[5a] Theilacker noted that other Lewis acids such as phosphorus pentachloride and aluminum chloride would not induce the rearrangement of N-chlorobenzophenonimine. N-Bromo- and N-iodoimines are not very suitable for rearrangement studies since the nitrogen–halogen bond in these compounds is so prone to homolysis.[7] None of the previously reported work sheds much light on the availability of methyleniminium ions from N-haloimines.

The purpose of this work was, therefore, to test the ability of the silver ion to bring about the rearrangement of N-chloroimines and to examine the mechanism of the rearrangement for the possible intervention of a methylenimine cation intermediate.

The Rearrangement of N-Chlorobenzophenonimine.—The N-chloroimine of benzophenone was prepared from the corresponding imine according to the method of Petersen.[6] This compound is easily purified and was found to be stable in all the aprotic solvents employed in this work at temperatures up to 120° in the absence of intense light.[7] The reaction of N-chlorobenzophenonimine (**2**) with a twofold excess of silver tetrafluoroborate in 75% dioxane–water for 4 hr at 80–100° gave rise to 65–70% yields of benzanilide (**3**). Other than silver chloride the only by-product of this reaction was benzophenone which resulted from the hydrolysis of **2**. Employment of equal molar quantities of **2** and silver tetrafluoroborate reduced the yield of benzanilide to 33% and increased the extent of the competing hydrolysis reaction. The rearrangement was examined in several aprotic solvents in order to gain some qualitative insight into the effect of solvents of varying polarity.

The reaction of **2** with silver tetrafluoroborate in dry N,N-dimethylformamide (DMF), like the reaction in aqueous dioxane, did not precipitate silver chloride at room temperature for up to 48 hr. When the reaction was carried out with equal concentrations of reactants at 80–100°, silver chloride precipitated quite rapidly but addition of water followed by work-up gave **3** in only 20–30% yields. Gas–liquid partition chromatographic (glpc) analysis of samples which were withdrawn from the reaction mixture at regular intervals and immediately quenched with a small amount of water showed that the relative yield of benzanilide increased up to a reaction time of 45–50 min. The relative amount of benzanilide then decreased steadily while the concentration of several lower molecular weight products increased. It appeared that an intermediate was being produced which in the absence of water was reacting further to give the lower molecular weight products. Careful analysis of the product mixture after a classical acid–base separation by column chromatography substantiated this belief. The acid and basic fractions each contained a single component, benzoic acid (**6**) and N,N-dimethyl-N′-phenylformamidine (**7**), respectively. The neutral fraction consisted of benzophenone, benzanilide, and a small amount of the formamidine. Benzoic acid and the formamidine were found not to arise from the reaction of either benzanilide with DMF under the conditions of the reaction or of **2** with DMF in the absence of the silver salt. The reaction of N-phenylbenzimidoyl chloride (**5**) with silver tetrafluoroborate in DMF under the same conditions, however, did produce a product mixture which was identical with the one just described except for the absence of benzophenone. Benzanilde, benzoic acid, and N,N-dimethyl-N′-phenylformamidine must, therefore, all arise from the nitrilium ion **4** (Scheme I). These results indicate that the rearrangement produces **4** which in the absence of water slowly reacts with the solvent to produce a more stable cation, probably **10**. The cation **10** would be expected to be more stable than its immediate predecessor **9** due to relief of strain and would reasonably give rise to the observed products on hydrolysis. Analysis of the reaction mixture by glpc prior to hydrolysis indicated that **6** and **7** were not produced before the addition of water.

The intermediacy of **4** in the rearrangement was further substantiated by its trapping with sodium ethoxide in 1,2-dimethoxyethane to give ethyl N-phenylbenzimidate (**11**) as well as a small amount of **3**. Such an intermediate is not unexpected for nitrilium ions have been postulated to explain the diversity of products from the Schmidt and Beckmann rearrangements.[3] No products (benzonitrile and substituted benzenes) which could be construed to have arisen through a fragmentation process of the type recently investigated by Hill and co-workers were found.[8]

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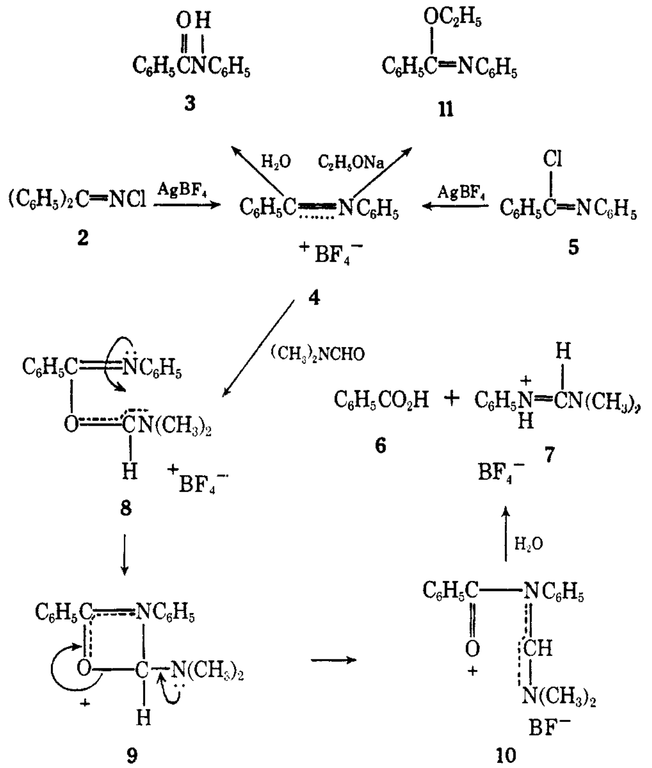
[5] (a) S. L. Reid and D. B. Sharp, *J. Org. Chem.*, **26**, 2567 (1961); (b) W. Theilacker and H. Mohl, *Ann.*, **563**, 99 (1949); (c) E. J. Moore and E. H. Huntress, *J. Am. Chem. Soc.*, **49**, 2618 (1927); (d) J. Stieglitz and P. H. Watkins, unpublished work referred to in ref 6.

[6] P. P. Petersen, *Am. Chem. J.*, **46**, 325 (1911).

[7] D. Y. Curtin and C. G. McCarty, *J. Org. Chem.*, **32**, 223 (1967).

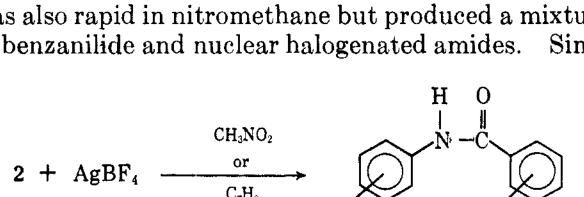
[8] R. K. Hill, R. T. Conley, and O. T. Chortyk, *J. Am. Chem. Soc.*, **87**, 5646 (1965). For a review of the Beckmann cleavage, see C. A. Grob and P. W. Shiess, *Angew. Chem. Intern. Ed. Engl.*, **6**, 9 (1967).

SCHEME I



Benzanilide yields in the range of 65–70% could routinely be obtained if a twofold excess of silver tetrafluoroborate was employed in DMF and the reaction was stopped after 45 min to cut down on the competing side reactions of **4**.

The effect of other solvents on the rearrangement was the subject of a cursory investigation. The precipitation of silver chloride from a dimethyl sulfoxide solution of the reactants was rapid even at room temperature but the products were large in number and involved extensive reaction with the solvent. Small amounts of benzanilide were obtained but the reaction mixture was not investigated further. The reaction was also rapid in nitromethane but produced a mixture of benzanilide and nuclear halogenated amides. Similar product mixtures were obtained from the reactions of **1** with silver tetrafluoroborate in acetonitrile and toluene although the reaction was much slower in these solvents. The formation of halogenated derivatives of benzanilide could be the result of (1) silver ion catalyzed halogenation either before or after rearrangement,[9] (2) solvent-promoted dissociation of silver tetrafluoroborate into boron trifluoride and silver fluoride which subsequently catalyze halogenation, or (3) traces of moisture which promote the formation of N-chlorobenzanilide which then undergoes rearrangement to the halogenated amides.[10] The data at hand do not permit a decision on the mode of halogenation although it may be noted that no chlorinated amides were obtained from reaction in aqueous dioxane, a fact which would argue against the last pathway.



Still another result was obtained when the reaction was carried out in absolute ethanol. The addition of silver tetrafluoroborate led to the simultaneous precipitation of silver chloride and the formation of an intense deep red-violet color. Upon work-up the reaction mixture gave an ill-characterized highly colored solid and a small amount of ethyl benzoate as the only identifiable product. It appears probable that the ethyl N-phenylbenzimidate was oxidized possibly to the corresponding free-radical cation[11] soon after its formation. This possibility is being examined further.

Qualitative observation of the enhanced rate of silver chloride precipitation as a function of the solvent employed for the reaction permits the establishment of the following order: acetonitrile $<$ toluene $<$ dimethoxyethane $<$ 75% dioxane–water $<$ DME $\ll$ nitromethane $\approx$ dimethyl sulfoxide. With the exception of acetonitrile the reaction rate increases as the ability of the solvent to support ionization increases.[12] The anomalous behavior of acetonitrile may be attributed to its complexation of the silver ion[13] and in so doing reducing its effective electrophilicity. Similar solvent effects have been observed for the Beckmann rearrangement of O-tosyl oximes.[14] This reaction, however, differs from the one being considered here in that an ion (the silver ion) is producing another ion which is presumed *vide infra* to have a higher degree of charge dispersal than the silver ion. The rate of such a reaction should show an increase as one goes to less polar solvents,[12] while the converse is true for the ionization of an O-tosyl oxime. In seeking an answer to this apparent discrepancy between theory and experiment, one must consider such factors as the effect of solvent change on $\Delta S^{\ddagger}$ as well as $\Delta H^{\ddagger}$, competitive complexation of the silver ion by the substrate and the solvent, and the degree of dissociation of silver tetrafluoroborate in the solvents under study. Although speculation might lead one to a suitable explanation, the resolution of the problem must await more definitive data.

The Rearrangement of *cis*- and *trans*-N-Chloro-4-chlorobenzophenonimines.—Although no evidence set forth so far indicates the presence of the methyleniminium ion along the reaction coordinate for the rearrangement of N-chloroimines, it is possible that its lifetime may be so short that it rearranges to the more stable iminocarbonium ion before it can react with anything in the solution. If the methyleniminium ion were an intermediate it is highly probable that it would give rise to indiscriminate migration of either group attached to the trigonal carbon atom. Such an unselective migration would be produced by either a symmetrical cation where the original two electrons of the nitrogen unshared pair now occupy separate orbitals or rapid inversion of the electron pair in the cation prior to rearrangement. Thus indiscriminate migration of either group in an unsymmetri-

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[9] L. Birckenbach and J. Goubeau, *Chem. Ber.*, **65**, 395 (1932).

[10] K. J. P. Orton, *et al.*, *J. Chem. Soc.*, 782, 998 (1928).

[11] S. Siegfried, *Chem. Eng. News*, **44**, No. 41, 103, (1966).

[12] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 345; C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965).

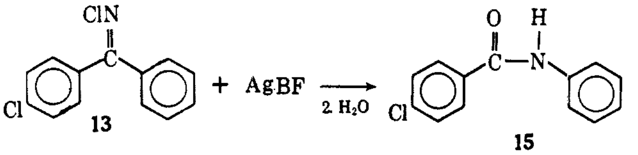
[13] S. E. Manahan and R. T. Iwamoto, *J. Electro anal. Chem.*, **14**, 213 (1967).

[14] W. Z. Heldt, *J. Org. Chem.*, **26**, 1695 (1961).

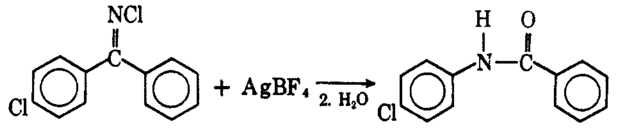
cal N-chloroketimine would imply the intermediacy of a methyleniminium ion.

In order to test this hypothesis, the *cis*- and *trans*-N-chloroimines of 4-chlorobenzophenone were subjected to the rearrangement conditions. The stereochemical assignments and the geometrical isomerism of these N-chloroimines has been the subject of a recent investigation by Curtin and McCarty[15] who found these isomers to possess remarkable configurational stability (the half-life for the isomerization is 500 hr at 140°), indicating that there should be almost no isomerization under the reaction conditions. This was found to be the case. The isomeric N-chloroketimines were prepared and separated by the method of Curtin and McCarty and their individual physical and spectroscopic properties were found to be identical with those reported in the literature.

The silver tetrafluoroborate induced rearrangement of *cis*-N-chloro-4-chlorophenylphenylmethylenimine (**13**) in both dimethylformamide and 75% dioxane–water gave N-phenyl-4-chlorobenzamide (**13**) as the only amide. The other possible amide, 4-chlorobenzanilide (**16**), could be separated from **15** by glpc and no indication of its presence in the reaction mixture was found. The rearrangement in 75% dioxane–water was not allowed to proceed to the complete consumption of all of the starting material and the unisomerized remaining N-chloroimine was recovered. The only other product of this reaction was 4-chlorobenzophenone (**17**). *trans*-N-Chloro-4-chlorophenylphenylmethylenimine (**14**) led to rearrangement in both solvent systems to give **16** and none of the isomeric amide **15**.

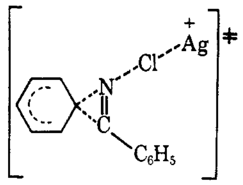


13 **15**



14 **16**

Just as the configuration of the hydroxyl group attached to the nitrogen of an oxime directs the course of the Beckmann rearrangement, it is apparent that the configuration of the nitrogen–chlorine bond is commanding the direction of the similar rearrangement of N-chloroimines reported here. Certain conclusions can, therefore, be drawn concerning the nature of the transition state for the rearrangement. The aryl group *trans* to the chlorine assists in the removal of this atom as the nitrogen–chlorine bond is polarized by the silver ion. Although the presence of the silver ion in the activated complex has not been kinetically demonstrated this formulation is highly probable since the rearrangement failed to occur in its absence in a variety of solvents. It could be argued that the presence of silver tetrafluoroborate merely increases the polarity of the media to the point where heterolysis of the nitrogen–chlorine bond is energentically favorable. Although this possibility has not been eliminated in every solvent system studied, it bears pointing out that the rearrangement proceeded extremely slowly in acetonitrile where silver tetrafluoroborate (which is isosteric with silver perchlorate) is completely dissociated[16] and the silver ion is complexed to the nitrile function.[13] Such reasoning obviously leaves no room on the reaction coordinate for the intervention of a free methyleniminium ion. The transition state depicted for this rearrangement is, of course, extremely similar to that currently accepted for the Beckmann rearrangement.[3] Inasmuch as the Beckmann rearrangement can be used to determine the stereochemistry of oximes, the rearrangement described here supports the stereochemical assignments of Curtin and McCarty.



The Rearrangement of N-Chloro-2-methylbutyrophenonimine.—The lesser ability of aliphatic groups compared with aryl groups to assist anchimerically ionization of the type being examined here led to a consideration of the rearrangement of acylic aliphatic N-chloroketimines. Unfortunately, the ease with which the parent ketimines undergo self-catalyzed condensation reactions[17] renders their synthesis and the subsequent preparation of the N-chloroimines difficult. The relatively hindered imine of 2-methylbutyrophenone was prepared[18] and successfully converted to its N-chloro derivative. This compound was too unstable for successful elemental analysis and had to be freshly distilled under high vacuum prior to each experiment. The details of its characterization are given in the Experimental Section. The nuclear magnetic resonance (nmr) spectrum of this substance exhibited two different methinyl proton resonance signals which were separated by 0.78 ppm at 60 Mc. The integrated ratio of the low- to the high-field multiplet was 2:3. In analogy with the recent work of Karabatsos and Hsi[19] on the nmr spectral characteristics of oxime O-methyl ethers and the published spectra of several oximes,[20] the low-field proton has been tentatively assigned to the N-chloroimine with the chlorine *cis* to the 2-butyl group **18** and the high-field proton to the *trans* compound **19**.

When subjected to the rearrangement conditions the isomer with the chlorine *trans* to the phenyl group would certainly be expected to give rise to the migration of this group. On the other hand, since the alkyl group can not participate as well in the ionization of the nitrogen-chlorine bond, the isomer with the chlorine *trans* to the 2-butyl group might lead to a methylenimine cation which could undergo indiscriminate rearrangement or insertion into the C_4–H bond to give a pyrroline. The reaction of the isomeric mixture of

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[15] D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Am. Chem. Soc.* **88**, 2775 (1966).

[16] Y. Pocker and D. N. Kevill, *ibid.*, **87**, 4760, 4771, 4778 (1965), and reference contained therein.

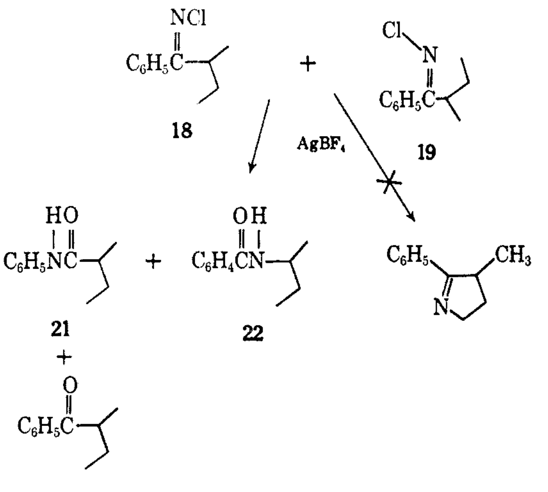
[17] P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, **26**, 4886 (1961).

[18] J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5085 (1965).

[19] G. J. Karabatsos and N. Hsi, *Tetrahedron*, **23**, 1079 (1967).

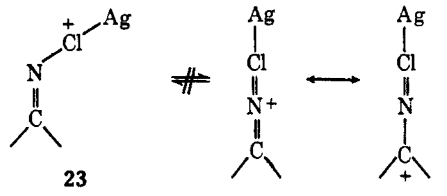
[20] NMR Spectra Catalog, Vol. 2, N. S. Bhacca, D. P. Hollis, L. J. Johnson, and E. A. Pier, Ed., Varian Associates, 1963, Spectra No. 373 and 420.

N-chloroimines with silver tetrafluoroborate gave a product mixture the composition of which was 2-methylbutyrophenone (**20**) (58%), N-phenyl-2-methylbutanamide (**21**) (31%), and N-*sec*-butylbenzamide (**22**) (11%). The fact that no basic products were formed coupled with the observation that the amide ratio corresponds roughly to the ratio of isomeric N-chloroimines makes it highly unlikely that a methylenimine cation is involved in this rearrangement of N-chloroimines. The lack of a precise correspondence between the N-chloroimine isomer ratio and the ratio of amides produced can be explained if one considers that the rearrangement of the N-chloroimine with the nitrogen–chlorine bond *trans* to the phenyl probably occurs more rapidly than the other isomer which is consumed by competitive hydrolysis.



The facile rearrangement of certain O-acyloximes[21,22] has led to the suggestion that N-chloroimines might undergo uncatalyzed rearrangement in highly polar solvents.[23] The stability of N-chlorobenzophenonimine in such solvents as dimethyl sulfoxide, DMF, and nitromethane illustrates that the assistance to ionization provided by the polar solvent is not sufficient to bring about rearrangement. The data presented here, in fact, show that the ionization of the nitrogen–chlorine bond is facilitated by and even dependent upon the synchronous action of three different factors: electrophilic assistance resulting in a substantial increase in the polar character of the N–Cl bond, internal stabilization of the developing positive charge by the migrating group, and a similar external stabilization by the solvent.

Definitive knowledge on the role of the silver ion in the rearrangement of N-chloroimines must await kinetic experiments. It is reasonable to assume that the silver ion is reversibly complexed to the chlorine atom and that the complex undergoes rearrangement fairly rapidly. Precedence for such a complex comes from the numerous studies on the silver-assisted solvolysis of alkyl halides.[13,24] The exceedingly slow rearrangement of **2** in acetonitrile supports the idea that the solvent is effectively competing for the complexation of the silver ion. Furthermore, if the nitrogen–chlorine bond cleavage were concerted with chlorine–silver bond formation, one would expect the intervention of a methylenimine cation. The complex **23** could seek stabilization through resonance forms such as **24a** and **b** by expansion of the valence shell of chlorine but this process requires a linear arrangement of the nitrogen and chlorine atoms and cannot be important here. This type of stabilization in the antimony pentachloride complex would explain the results of Thielacker.



23 **24a** **24b**

In conclusion, it can be stated that silver tetrafluoroborate appears to be quite general in its ability to bring about the rearrangement of N-chloroimines. The inability of other workers to induce rearrangement with similar Lewis acid catalysts is probably the result of several factors including use of solvents unable to provide the necessary assistance to ionization of the complex if formed, irreversible complex formation at some site other than the chlorine atom in the molecule, and instability of the N-chloroimines. Although not proven here, the wealth of data on the silver ion assisted solvolyses of alkyl halides supports the assumption that the silver ion is weakly complexed to the chlorine prior to rearrangement. Thus, silver–chlorine bond formation must be far advanced prior to the formation of the activated complex, setting the stage for participation of the migrating group in the loss of silver chloride and precluding the formation of a free methyleniminium ion. Such a view is in complete harmony with the mass of information on Beckmann-type rearrangements. The intermediacy of methyleniminium ions in solvents such as dimethyl sulfoxide and nitromethane is of course possible but not too probable since their ability to support ionization is comparable to that of DMF.

Experimental Section

General.—Glpc was performed on a Micro-Tek GC2000R dual-column instrument fitted with both thermal conductivity and flame-ionization detectors. All glpc work was done on either matched 4-ft 25% S.E. 30/Chromosorb W or 25% Carbowax/Chromosorb W columns and retention times were checked against authentic samples. Infrared spectra were taken on a Perkin-Elmer Infracord 237 and nmr spectra were recorded on a Varian Associates A-60. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are corrected. Boiling points are uncorrected. All solvents were dried and purified by recommended procedures prior to use. Anhydrous silver tetrafluoroborate was obtained from Alpha Inorganics.

The Preparation of Ketimines.—Benzophenonimine was obtained from the reaction of benzonitrile with phenylmagnesium bromide according to the method of Pickard and Tolbert,[17] bp 100° (0.025 mm). 2-Methylbutyrophenonimine was prepared

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[21] The sensitivity of Beckmann-type rearrangements to the nature of the leaving group is emphasized by the fact that among all the imine derivatives of appropriate structure only the picryl- and aryl sulfonyloximes undergo uncatalyzed rearrangement.[8,22]

[22] A. H. Blatt, *Chem. Rev.*, **12**, 215 (1933); M. Kuhara and T. Kainoko, *Mem. Coll. Eng. Kyoto Imp. Univ.*, **1**, 254 (1906); C. R. Hauser and D. S. Hoffenberg, *J. Org. Chem.*, **20**, 1482 (1955).

[23] P. A. S. Smith in "Molecular Rearrangements," P. DeMayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 507.

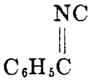
[24] D. J. Pasto and K. Graves, *J. Org. Chem.*, **32**, 778 (1967).

from the reaction of 2-butylmagnesium bromide with benzonitrile by Roberts' method,[18] bp 75° (0.75 mm). The nmr spectral assignments for this and related compounds are reported in Table I. 4-Chlorobenzophenonimine hydrochloride was prepared by the method of Petersen,[7] mp 290° dec.

The Preparation of N-Chloroketimines.—All N-chloroimines were prepared by the method of Petersen[7] which involved adding the imine or its hydrochloride to a cold aqueous solution of sodium hypochlorite followed by extraction into chloroform. Nearly quantitative yields were obtained in every case. N-Chlorobenzophenonimine (2) was recrystallized from low-boiling petroleum ether (bp 30–60°) or ethanol, mp 38° (lit.[7] mp 37°). The *cis*- and *trans*-N-chloroimines of 4-chlorobenzophenone were fractionally recrystallized from low-boiling petroleum ether as previously described.[16] The infrared spectra of the two isomers agreed with the spectra published in McCarty's Ph.D. thesis;[25] *cis*-N-chloro-4-chlorophenylphenylketimine,[13] mp 105° (lit.[15] mp 103–104°), and *trans*-N-chloro-4-chlorophenylphenylketimine,[14] mp 55° (lit.[15] mp 55°). N-Chloro-2-methylbutyrophenonimine (**18** and **19**) was distilled twice, bp 70° (0.025 mm), but decomposed slowly and an acceptable analysis was not obtained. It could be repurified by careful distillation and was characterized in the following way. Treatment with aqueous hydroiodic acid liberated 98% of the theoretical amount of iodine by titration with a standard thiosulfate solution. It could be hydrolyzed to the known ketone. The infrared spectrum showed no carbonyl or NH absorption. The nmr spectral assignments for this substance are given in Table I along with other related compounds which could contaminate the product. It can be seen that the methinyl proton resonances for these compounds are all different and an impurity would easily show up in the spectrum of the N-chloroimine. No contamination was observed and the two methinyl resonance signals in the spectrum were assigned to the *cis*- and *trans*-N-chloroimines as described in the Discussion section.

Table I

Chemical Shift Values[a] for $\underset{b}{CH_3}\underset{d}{CH}(-Y)\underset{c}{CH_2}\underset{a}{CH_3}$

Y	a	b	c	d
C_6H_5CO	0.89	1.14	1.6	3.33
C_6H_5CONH	0.90	1.18	1.49	4.08
C_6H_5NHCO	0.90	1.18	1.58	2.30
C_6H_5CNH	0.93	1.10	1.51	2.85
 $\overset{NCl}{\overset{\|}{C_6H_5C}}$	0.93	1.21	1.52	3.58
 $\overset{ClN}{\overset{\|}{C_6H_5C}}$	0.93	1.11	1.52	2.80

[a] Spectra were taken of 30% $CDCl_3$ solutions. Values reported are (δ) in parts per million.

General Procedure for the Reaction of N-Chloroimines with Silver Tetrafluoroborate in DMF and 75% Dioxane–Water.—The following description typifies the best conditions for the rearrangement of N-chloroimines. In obtaining these conditions the length of reaction time and the temperature were varied but the mode of work-up was always the same. The amides were compared with authentic samples prepared by the well-known Schotten–Baumann method. In one experiment, 3.9 g (0.02 mole) of silver tetrafluoroborate was dissolved in 50 ml of dry DMF. The solution was heated with stirring to 95° under nitrogen and 2.51 g (0.01 mole) of N-chlorobenzophenonimine **2** in 10 ml of DMF was added dropwise to the solution over a 15-min period. The precipitation of silver chloride began immediately. The reaction mixture was allowed to stir for 45 min at 100°. The silver chloride was removed by rapid filtration and weighed 1.18 g (0.0085 mole). A 1-ml sample of the filtrate was added to 0.1 ml of water and set aside for glpc analysis. The filtrate was then poured into 200 ml of water containing 5 g of sodium chloride. The resulting mixture was filtered again and the filtrate was set aside. The solid residue, a mixture of silver chloride and organic material, was digested with 50 ml of 30–60° petroleum ether and filtered. The remaining solid was digested with 100 ml of acetone and filtered. The first aqueous filtrates were extracted with four 50-ml portions of chloroform, dried over sodium sulfate, and stripped of solvent at reduced pressure to yield 150 mg of benzanilide (**3**) after recrystallization from ethanol. The acetone filtrate was concentrated to give a solid which yielded 1.2 g of benzanilide (**3**), mp 162–163° (lit.[26] 161°), after recrystallization from ethanol. The over-all yield of benzanilide was 1.35 g (75%). The petroleum ether solution on concentration and cooling gave 51 mg of starting material, mp 37°. The reaction of 0.01 mole of the N-chloroketimine with 0.01 mole of silver tetrafluoroborate in 50 ml of 75% dioxane-water gave a 68:32 ratio of benzophenone and benzanilide after a reaction time of 4 hr. The material balance was 89%. The benzophenone was obtained from the petroleum ether extract. Doubling the quantity of silver salt resulted in a 91% yield of a mixture which contained 68% benzanilide and 32% benzophenone. Yields were based on the over-all isolation of crude material and upon the glpc analysis.

The Reaction of N-Chlorobenzophenonimine with Silver Tetrafluoroborate in Dimethyl Sulfoxide.—The reaction of 2.51 g (0.01 mole) of **2** with 1.95 g (0.01 mole) of silver tetrafluoroborate in 50 ml of dimethyl sulfoxide was carried out in the manner just described. The precipitation of silver chloride occurred at room temperature and was quantitative. Glpc analysis of the reaction mixture indicated the presence of at least ten components. The only identifiable compound was benzanilide (approximately 8% of the mixture). The odor of dimethyl sulfide was very apparent and the reaction mixture was not investigated further.

The Reaction of N-Chlorobenzophenonimine with Silver Tetrafluoroborate in Toluene.—The reaction of 0.01 mole of the N-chloroimine (**2**) and 0.01 mole of the silver salt was carried out at 95° for 2 hr in 50 ml of toluene. The reaction mixture yielded 360 mg (0.0025 mole) of silver chloride on filtration. The filtrate was washed with water, dried over sodium sulfate, and stripped of solvent at reduced pressure to produce an oil. The oil was digested with petroleum ether which yielded 1.5 g of starting material on cooling. The solid residue from the digestion gave 390 mg of material, mp 141–155°, which on glpc analysis was found to consist of 93% benzanilide, retention time 10 min/200°, and 7% N-4-chlorophenylbenzamide,[16] retention time 12.5 min/200°. Repeated recrystallization of this material gave benzanilide, mp 161–162°.

The Reaction of N-Chlorobenzophenonimine with Silver Tetrafluoroborate in Nitromethane.—The reaction was carried out in the manner just described except that the toluene was replaced with 50 ml of nitromethane. The precipitation of silver chloride occurred at room temperature. Filtration of the reaction mixture after 1.5 hr gave 1.15 g of silver chloride (80%). Petroleum ether extraction of the solid product after removal of the nitromethane did not give any starting material. Analysis of the solid product by glpc showed that it was a mixture of 10% N-4-chlorophenylbenzamide and 90% benzanilide. The solid product (wt 1.32 g) was fractionally recrystallized from ethanol to give small but pure samples of benzanilide, mp 160–161°, and N-4-chlorophenylbenzamide, mp 191–192° (lit.[27] mp 193°).

The Reaction of N-Chlorobenzophenonimine with Silver Tetrafluoroborate in Acetonitrile.—The reaction of 0.01 mole of the N-chloroimine with 0.01 mole of the silver salt in 50 ml of acetonitrile at the reflux temperature of the solvent gave only a 12% yield of silver chloride after 2 hr. When double quantities of all materials were employed and the reaction was allowed to continue at reflux for 15 hr the yield of silver chloride was 39.5%. Analysis of the product mixture by thin layer chromatography (tlc) showed a mixture of five compounds. Separation of this mixture was not attempted but glpc indicated the presence of 4-chlorobenzanilde, N-4-chlorophenylbenzamide, N-2-chlorophenylbenzamide, benzanilide, and benzophenone ketazine by comparison of the retention times with those of authentic samples.

The Reaction of N-Chlorobenzophenonimine with Silver Tetrafluoroborate in Ethanol.—Silver tetrafluoroborate (9.75 g, 0.05 mole) was dissolved in 150 ml of ethanol and stirred at the reflux temperature while 10.7 g of N-chlorobenzophenonimine in 50 ml of ethanol was added dropwise to the stirring mixture. The precipitation of silver chloride was quite rapid and a deep

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(25) C. G. McCarty, Ph.D. Thesis, University of Illinois, 1963, p 107.

(26) L. Claisen, *Chem. Ber.*, **27**, 3182 (1899).

(27) E. E. Slossen, *Am. Chem. J.*, **29**, 305 (1903).

red-violet color developed simultaneously. The mixture was stirred at reflux for several hours, then filtered, and stripped of solvent at reduced pressure. A dark black-purple semisolid resulted. The material was sparingly soluble in chloroform and no meaningful spectral data could be obtained. The product mixture was extremely soluble in ethanol, acetone, and water but could not be crystallized from any of these solvents; chloroform was also unsuitable. The color was unaffected by acid or base and the compound burned with a residue. The mixture was washed with ether and the ether solution was stripped of solvent and distilled to give 1 g of ethyl benzoate, bp 100° (25–30 mm). The remaining material could not be characterized and was not investigated further.

The Rearrangement of N-Chlorobenzophenonimine in DMF. A Product vs. Time Study.—Solutions containing 1.15 g of N-chlorobenzophenonimine and 2 g of silver tetrafluoroborate in 10 and 25 ml of DMF, respectively, were mixed and stirred at 100°. Samples (1 ml) were taken every 10 min for the first 2 hr and every hour thereafter and were quenched with 0.1 ml of water. Samples were taken up to 12-hr total reaction time. The samples were analyzed by glpc (column temperature programmed from 150 to 210° at 10°/min). The relative yield of benzanilide increased steadily from 0 to 45 min. After that time it decreased while the relative concentration of what was later found to be N,N-dimethyl-N′-phenylformamidine increased steadily. Benzanilide could barely be detected after 12-hr reaction time. Analysis of these samples at lower temperatures did not show the presence of benzonitrile.

The Rearrangement of N-Chlorobenzophenonimine in DMF. A Product Study.—N-Chlorobenzophenonimine (10.775 g, 0.05 mole) was dissolved in 50 ml of dry DMF and stirred while a solution of 10 g of silver tetrafluoroborate in 100 ml of DMF was added. The reaction mixture was stirred at 110° for 15 hr under nitrogen. A sample was taken for glpc analysis and the solution was filtered from the precipitated silver chloride (6.9 g, 0.048 mole). The filtrate was poured into 500 ml of water containing 10 g of sodium chloride, and the mixture was filtered again. The precipitate (100 mg of silver chloride) was washed with acetone, and the filtrates were combined and extracted with four 200-ml portions of chloroform. The aqueous layer was made basic with 5% sodium hydroxide and reextracted with three 150-ml portions of ether to give extract B. The chloroform extract was extracted with three 75-ml portions of 5% of sodium hydroxide solution to leave the chloroform extract N. The aqueous basic extract was acidified with hydrochloric acid and back-extracted into chloroform to give extract A. All extracts were analyzed by glpc and extract B contained a single component. Extract A possessed nothing and extract N contained three components two of which were identified as benzophenone and benzanilide by comparison of their retention times with authentic samples. The third component of this mixture, barely detectable, had a retention time identical with the compound in B. Evaporation of the chloroform from A gave 963 mg of benzoic acid **6**, mp 122° (lit.[28] mp 122°). Extract B gave after evaporation of the solvent a clear oil which was distilled to give 2.87 g of a substance, bp 74–75° (0.25 mm). The nmr spectrum of this substance showed absorption at δ 2.80 (s) and 6.6–7.4 (m), the integrated ratio of which was 1:1. The infrared spectrum showed strong absorption at 1645 cm^{-1} and no NH absorption and was in perfect accord with the published spectrum of N,N-dimethyl-N′-phenylformamidine[29] (**10**). This compound formed a hydrochloride, mp 236–237° (lit.[30] mp 239–241°), whose nmr spectrum (30% in dimethyl sulfoxide-d_6) gave the following absorptions: CH_3, δ 3.31 and 3.42; phenyl; H, δ 7.5; and NH, δ 8.80. Extract N was taken to dryness (wt, 5.5 g) and chromatographed on 800 g of alumina. Elution with 50% benzene–petroleum ether afforded 841 mg of benzophenone (**12**), mp 48° (lit.[31] mp 49°), γ_{C-O} 1665 cm^{-1}. Continued elution with 20% ethyl acetate–benzene gave 3.012 g of benzanilide (**3**), mp 162° (lit.[21] mp 161°), γ_{C-O} 1660 cm^{-1}, γ_{NH} 3400 cm^{-1}. Elution of the column with 20% methanol–ethyl acetate gave an additional 415 mg of N,N-dimethyl-N′-phenylformamidine (**10**).

The Reaction of N-Phenylbenzimidoyl Chloride with Silver Tetrafluoroborate in DMF.—A solution of 2.5 g of silver tetrafluoroborate in 25 ml of DMF was added to a solution of 2.15 g (0.01 mole) of N-phenylbenzimidoyl chloride[32] **5** in 10 ml of DMF. The reaction mixture was stirred under nitrogen at 95° for 15 hr. The silver chloride was filtered and the mixture was worked up in a manner identical with the experiment just described. Glpc analysis of the various extracts showed the presence of benzanilide and N,N-dimethyl-N′-phenylformamidine by comparison of the retention times with authentic samples. The acid extract on evaporation of the solvent gave 196 mg of benzoic acid, mp 122°.

The Reaction of N-Chlorobenzophenonimine with Silver Tetrafluoroborate in 1,2-Dimethoxyethane Followed by Sodium Ethoxide.—A solution of 2.15 g (0.01 mole) of N-chlorobenzophenonimine in 10 ml of 1,2-dimethoxyethane (which had previously been distilled from lithium aluminum hydride) was added to a stirred solution of 2 g of silver tetrafluoroborate (dried under vacuum prior to use) in 20 ml of 1,2-dimethoxyethane. The reaction mixture was stirred at the reflux temperature of the solvent under nitrogen for 90 min. The mixture was cooled to room temperature and a 4-ml solution of 0.01 mole of sodium ethoxide in ethanol was added rapidly. The solution began to turn dark red-violet but the color development was quenched by the addition of 1 g of lithium chloride. The mixture was filtered rapidly and poured into 100 ml of water. This mixture was rapidly extracted with three 75-ml portions of ether. The ether solution was dried over sodium sulfate and analyzed by glpc. The glpc analysis showed the presence of 23% ethyl benzoate, 39% ethyl N-phenylbenzimidate (**11**), 28% benzophenone, and 10% benzanilide by comparison of retention times with authentic samples on two different columns and at several different column temperatures. The weight of crude material was 1.73 g.

The Reaction of *cis*-N-Chloro-4-chlorophenylphenylmethylenimine with Silver Tetrafluoroborate.—The reaction of 2.4 g (0.0095 mole) of *cis*-N-chloro-4-chlorophenylphenylmethylenimine (**13**) (mp 105°) with 4 g (0.0205 mole) of silver tetrafluoroborate in 50 ml of DMF was carried out in the manner described in the general procedure to give 844 mg of N-phenyl-4-chlorobenzamide (**15**), mp 195–196° (lit.[33] 194°), undepressed by an authentic sample but depressed by a sample of 4-chlorobenzanilide, mp 193°. Glpc analysis of the reaction mixture under conditions which would separate the isomeric amides showed the presence of only N-phenyl-4-chlorobenzamide. The same reaction of 2.52 g (0.01 mole) of the N-chloroimine (**13**) and 4 g of silver tetrafluoroborate in 50 ml of 75% dioxane–water gave 2.1 g of a mixture which contained 30% N-phenyl-4-chlorobenzamide, 39% 4-chlorobenzophenone, and 31% starting material by glpc. Small samples of each of the three components for the purposes of characterization were obtained in the following way. The starting N-chloroimine, mp 105°, was separated from the mixture by extraction into and recrystallization from low-boiling petroleum ether, while the ketone, mp 77° (lit.[34] mp 77–78°), and the amide, mp 195°, which were sparingly soluble in petroleum ether, were separated by crystallization of the amide from ethanol followed by crystallization of the ketone.

The Reaction of *trans*-N-Chloro-4-chlorophenylphenylmethylenimine with Silver Tetrafluoroborate.—The reaction of the *trans*-N-chloroimine (**14**) with silver tetrafluoroborate was carried out in both solvent systems as described for the *cis* isomer. The reaction of 1.11 g (4.4 moles) of *trans*-N-chloro-4-chlorophenylphenylmethylenimine (**14**) with 1.95 g (10 moles) of silver tetrafluoroborate in 25 ml of DMF gave rise to 553 mg of 4-chlorobenzanilide (**16**), mp 192–195° (lit.[27] mp 193°), undepressed by an authentic sample but depressed when mixed with a sample of N-phenyl-4-chlorobenzamide. Glpc analysis showed the reaction mixture to be free of N-phenyl-4-chlorobenzamide. The reaction of 1.26 g of the N-chloroimine with 1.95 g of silver tetrafluoroborate in 25 ml of 75% dioxane water gave 876 mg of a mixture which contained 34% 4-chlorobenzanilide, 42% 4-chlorobenzophenone (**17**), and 26% starting N-chloroimine. The recovered starting material was recrystallized from low-boiling petroleum ether, mp 54–55°.

The Reaction of N-Chloro-2-methylbutyrophenonimine with Silver Tetrafluoroborate.—The reaction of 5.13 g (0.026 mole)

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[28] H. Kopp, *Ann.*, **94**, 303 (1855).

[29] "Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa. 25009, 1965.

[30] H. Bredereck, R. Gompper, K. Klemm, and H. Rempfer, *Chem. Ber.*, **92**, 837 (1959).

[31] E. Linnemann, *Ann.*, **133**, 4 (1865).

[32] W. M. Lauer and C. S. Benton, *J. Org. Chem.*, **24**, 804 (1959).

[33] O. Emmerling, *Chem. Ber.*, **8**, 882 (1875).

[34] M. Kollaritis and V. Merz, *ibid.*, **6**, 547 (1873).

of freshly distilled N-chloro-2-methylbutyrophenonimines (**18** and **19**) with 6 g (0.03 mole) of silver tetrafluoroborate in 75 ml of 75% dioxane–water at 80° was carried out in the manner described in the general procedure to give 3.4 g of a product mixture. The mixture was analyzed by glpc which showed the presence of three components, one of which was 2-methylbutyrophenone (**20**). The two amides, N-phenyl-2-methylbutanamide and N-(2-butyl)benzamide, expected from this reaction could not be completely resolved on several columns under a variety of conditions. The glpc trace of the product mixture indicated the presence of both amides but their relative amounts could not be ascertained. The ketone to amide ratio was 58:42. The relative amounts of 2-methylbutyrophenone and N-(2-butyl)benzamide (**22**) could be determined by integration of the methinyl proton resonance signals in the nmr (Table I); this permitted the calculation of the constitution of the amide mixture to be 73% N-phenyl-2-methylbutanamide (**21**) and 27% N-(2-butyl)benzamide (**22**). Extraction of the reaction mixture with aqueous acid followed by basification and back-extraction into ether gave nothing. Similarly, extraction of the basified aqueous extract in the initial work-up with ether gave nothing. Chromatography of the reaction mixture on alumina resulted in the separation of the ketone from the amides but did not separate the amides. The ketone was characterized by comparison of its infrared and nmr spectra with that of the authentic compound. Recrystallization of the amide mixture from ethanol resulted in a pure sample of N-phenyl-2-methylbutanamide (**21**), mp 109–111° (lit.[35] mp 110–111°), whose infrared and nmr spectra were identical with the authentic compound. The nmr spectrum of the amide mixture was similar (identical except for relative intensities) to the nmr spectrum of a synthetic mixture of the two amides. Furthermore, the presence of N-(2-butyl)benzamide in the reaction mixture was demonstrated by tlc in two different solvent systems.

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[35] P. E. Verkade, *Rec. Trav. Chim.*, **36**, 204 (1917).

Lead Tetraacetate. V. Effects of a Phenyl Group on the Formation of Ethers from Phenyl-Substituted Alkyl Alcohols[1,2]

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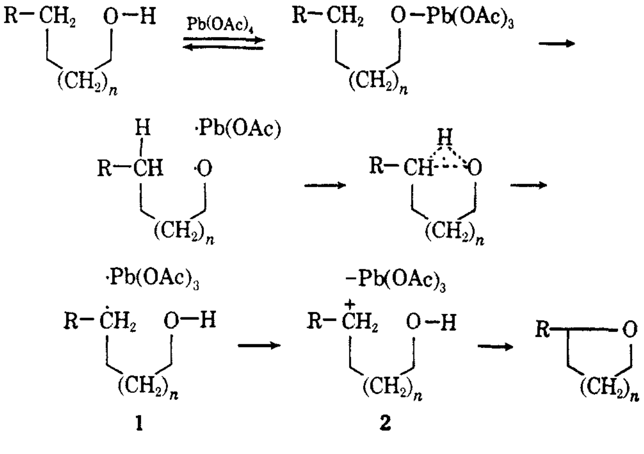
The reactions of lead tetraacetate with phenyl-substituted alcohols were studied in order to determine the effects of a phenyl group on the course of the reaction. 3-Phenylpropanol yielded chroman, and 4-phenylbutanol and 5-phenylpentanol gave tetrahydrofuran derivatives but no tetrahydropyran derivatives. 1-Phenyl-1-butanol and 1-phenyl-2-pentanol yielded cleavage products and no cyclization products. Reaction mechanisms and possible intermediates are discussed in light of these results.

The reaction of lead tetraacetate with saturated, acyclic alcohols has been extensively studied by a number of workers.[3] One of the principal products is a tetrahydrofuran derivative, although a small amount of the corresponding tetrahydropyran derivatives have also been isolated.

Mihailovic[3b] has proposed the following mechanism for the formation of cyclic ethers (see Scheme I).

On the other hand, it was found that an ether oxygen, substituted at the proper carbon, caused the formation of six-membered ethers.[3b] Presumably, the oxygen atom stabilizes such an intermediate as **1** or **2**, causing the formation of the six-membered ethers. With these results in mind, the reactions of lead tetraacetate with 3-phenylpropanol, 4-phenylbutanol, and 5-phenylpentanol were investigated in order to study the effect of a phenyl group on the course of the reaction.

Scheme I



Results

The results of these reactions are shown in Scheme II. The percentages listed are obtained from gas chromatographic analysis of the reaction mixtures. The products were isolated by gas chromatography and identified by comparison of their infrared and nmr spectra with those of authentic samples.

In an attempt to obtain authentic samples of **9** and **12**, 1-phenyl-1-butanol (**14**) and 1-phenyl-2-pentanol (**15**), respectively, were treated with lead tetraacetate. Neither of the cyclization products were obtained, but considerable amounts of carbon–carbon bond cleavage products were obtained (Scheme III).

Authentic samples of **9** and **12** were obtained as shown in Scheme IV. The over-all yields were low. Therefore, lead tetraacetate oxidation of **8** and **11** is a

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[1] Part IV: S. Moon and W. J. Campbell, *Chem. Commun.*, 470 (1966).

[2] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[3] For leading references, see (a) R. Criegee, "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, pp 278–366; (b) M. Lj. Mihailovic and M. Miloradovic, *Tetrahedron*, **22**, 723 (1966); (c) K. Heusler and J. Kalvoda, *Angew. Chem. Intern. Ed. Engl.*, **3**, 525 (1964).