less than that of N–H–O and O–H–O bonds, hence the addition of chloroform and monofluorodichloromethane does not cause dissociation in compounds associated by means of hydrogen bonding between two oxygen atoms, or a nitrogen atom and an oxygen atom. In this connection it should be recalled that it has been known for a long time that the haloforms behave essentially as non-polar solvents similar to benzene and hexane in cryoscopic measurements on alcohols, acids, and amides.

The considerations outlined above also should be applicable to the solution of solid organic compounds in monofluorodichloromethane, or other halogenated hydrocarbons of the type CHX_3, C_2HX_5, etc. (and to a lesser extent to the type CH_2X_2), and should allow the qualitative prediction of solubility in such cases.

Summary

The concept of C–H ← O bonds between a hydrogen of a halogenated hydrocarbon and donor atoms in solvents has been shown readily to correlate solubility data on solutions of halogenated hydrocarbons in a large number of solvents of different types.

The most important factors governing the solubility of the types of compounds investigated are: (1) the donor properties of atoms in the solvent for forming C–H ← O or C–H ← N bonds; (2) the presence or absence of intermolecular association through hydrogen bonding in the solvent.

It has been shown that it is possible to predict the type of association occurring in a liquid by means of a solubility measurement. The presence of large linear polymers in the solvent inhibits the solution of monofluorodichloromethane but if the polymerization stops at the dimer stage nearly normal solubility is observed.

URBANA AND BLOOMINGTON, ILLINOIS

RECEIVED AUGUST 29, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

The Reaction of Esters with Aluminum Isopropoxide

BY ROBERT H. BAKER

Aluminum alkoxides react with alcohols[1,2] and catalyze the alcoholysis of esters,[3] but their reaction with esters alone has been studied very little.[1,4]

For the simple esters the reaction is one of exchange of groups and possibly may be of use in the preparation of alkoxides whose alcohols themselves are either unstable or which fail to react with amalgamated aluminum. The reaction also may be used in the preparation of esters.

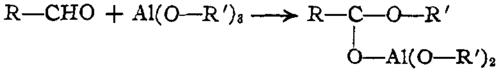
In this work the equilibrium

$$3R\text{—}COOR' + Al(O\text{—}i\text{-}Pr)_3 \longleftrightarrow 3R\text{—}COO\text{—}i\text{-}Pr + Al(O\text{—}R')_3$$

has been shifted as far to the right as possible by carrying out the reaction under a fractionating column which permits the removal of only the isopropyl ester. *t*-Butyl acetate failed to react completely, the reaction stopping when two of the isopropyl (or isopropoxide) groups had been replaced. This is in accord with the observations of Tischtschenko,[1] who found that the tertiary alkoxides reacted best with the alcohols.

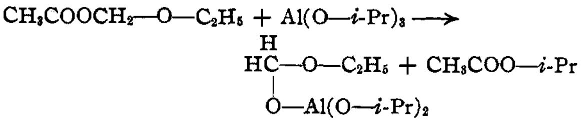
The isopropoxide, which is easily made and purified and which gives rise to low boiling esters, has been used exclusively in this work.

Only one ester, ethoxymethyl acetate, gave rise to reduction products similar to those which the simple esters give with sodium alkoxides.[5] This ester was used in an attempt to prepare an alkoxide of the type which Verley[6] postulated as an intermediate in both the Tischtschenko reaction[4] and in the reduction of aldehydes. This aluminate of a hemiacetal, which Verley claims is formed thus



$$R\text{—}CHO + Al(O\text{—}R')_3 \longrightarrow R\text{—}\underset{\substack{|\\ O\text{—}Al(O\text{—}R')_2}}{\overset{H}{C}}\text{—}O\text{—}R'$$

was expected to be formed as follows



$$CH_3COOCH_2\text{—}O\text{—}C_2H_5 + Al(O\text{—}i\text{-}Pr)_3 \longrightarrow \underset{\substack{|\\ O\text{—}Al(O\text{—}i\text{-}Pr)_2}}{\overset{H}{HC}}\text{—}O\text{—}C_2H_5 + CH_3COO\text{—}i\text{-}Pr$$

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[1] Tischtschenko, *J. Russ. Phys.-Chem. Soc.*, **31**, 694, 784 (1899); *Chem. Zentr.*, **71**, I, 10, 585 (1900).

[2] Adkins and Cox, THIS JOURNAL, **60**, 1151 (1938).

[3] Fehlandt and Adkins, *ibid.*, **57**, 193 (1935); Hatch and Adkins, *ibid.*, **59**, 1694 (1937).

[4] Tischtschenko, *J. Russ. Phys.-Chem. Soc.*, **38**, 355, 482 (1906); *Chem. Zentr.*, **77**, II, 1309, 1552 (1906).

[5] Magnani and McElvain, THIS JOURNAL, **60**, 813 (1938).

[6] Verley, *Bull. soc. chim.*, **37**, 537, 871 (1925).

TABLE I

			Aluminum alkoxide					
							Al, %	
Ester used	n^{20}D	Isopropyl ester, %[a]	%	M. p., °C.	B. p., °C.	Mm.	Calcd.	Found
n-Butyl acetate	1.3950	85	88[e]		280–284	12		
t-Butyl acetate	1.3838	66	98[b]	165–167	Subl. 160	14	11.64	11.64
s-Butyl formate	1.3865	81	57		165–166	3		
Allyl acetate	1.4050	95	100[c,e]	145–150	dec.			
n-Hexadecyl acetate	1.4438	100	98[e]	44			3.60	3.70
Ethyleneglycol diacetate	1.4184	80	120[d]	dec.			24.05	21.20

[a] Calcd. from fractions of isopropyl acetate n^{20}D 1.3770–1.3786 and of isopropyl formate n^{20}D 1.3720–1.3735. A dry refractionated synthetic sample of the latter had distillation range (Widmer) 66.9–67.0°; n^{20}D 1.3716; d^{20}_4 0.8726; *M*D calcd., 22.33, found 22.92. [b] Assumed to be aluminum di-*t*-butoxide monoisopropoxide, pure *t*-butyl acetate could be distilled from this even after heating together at 150° for two hours. [c] Attempts to purify this for analysis were unsuccessful. It begins to distill at 220° (5 mm.) and then decomposes violently. The crude product melts over a narrower range than that reported.[1] [d] A very light powder retaining ester even at 150° (2 mm.) for two hours. Completely insoluble in xylene, but retains xylene which is removed only at 150° (2 mm.). [e] These alkoxides gave a negative iodoform test after hydrolysis.

Such a compound was not isolated and no evidence for or against its formation[7] can be gained from the experiment, but it is of interest that the products of the reaction were those which one would expect from Tischtschenko reactions, reductions, and group exchanges between alkoxides and esters.

Experimental

Reagents.—Aluminum isopropoxide, b. p. 134° (5 mm.), m. p. 118°, was prepared in 91% yield by the method of Adkins.[8] Before each experiment the powdered material was tested for complete solubility, without opalescence, in dry benzene. The esters were prepared by the standard methods and distilled through a Widmer column, refractive index and boiling range rather than the boiling point being used as a criterion of purity. The esters were tested for moisture immediately before use by adding a few drops of a benzene solution of aluminum isopropoxide to a few cc. of the ester. If opalescence did not appear within a few minutes, the esters were considered to be dry. Ethoxymethyl acetate n^{20}D 1.3950, distillation range 129.5–130.0°, was prepared by the method of Farren[9] except that the final distillation was through the Widmer column.

The general procedure was to mix 0.4 mole of the ester with 0.1 mole of aluminum isopropoxide in a flask protected from moisture and fitted to a Widmer column equipped with a partial condensation head. Slow distillation was carried out collecting 1- or 2-g. fractions and following the fractionation by means of the refractive index. When all the isopropyl ester had distilled and the index corresponded to that of the starting ester, the remainder was distilled by diminished pressure to leave the alkoxide in weighable form. The results from several esters are found in Table I.

***n*-Butyl benzoate,** n^{20}D 1.5001, 53.4 g. (0.3 mole) and aluminum isopropoxide 20.4 g. (0.1 mole) were heated at 130° for two hours, cooled, poured into cold water containing 25 cc. of 6 *N* sulfuric acid, and extracted with ether. The ether solution was washed successively with water, saturated solution of calcium chloride, saturated solution of potassium carbonate, and then was dried over anhydrous magnesium sulfate. The ether solution gave upon fractionation through the Widmer column isopropyl benzoate n^{20}D 1.4975–1.4978, 27.0 g. (0.165 mole), and *n*-butyl benzoate n^{20}D 1.4998–1.5001, 18.9 g. (0.105 mole). This is a 90% recovery of the esters and, since the acidic hydrolysate gave negative tests for aldehydes and ketones, no reverse Tischtschenko reactions[5] take place.

Ethoxymethyl acetate, 35.4 g. (0.3 mole) and aluminum isopropoxide 20.4 g. (0.1 mole) were heated in an oil-bath from 50 to 150° over a period of eight hours. The reaction started quickly, as the odor of formaldehyde or acetaldehyde could be noticed. The exhaust gases were passed first through a drying tube and then through water. The water gave a positive Schiff test for aldehydes, but a negligible quantity of their 2,4-dinitrophenylhydrazones. Seven fractions, 36.2 g., distilling between 50 and 85° were collected and refractionated into fifteen fractions, b. p. 40–87°; n^{20}D 1.3570–1.3770. Four "flats" appeared in the refractive index-weight distilled diagram at n^{20}D 1.3640, 1.3680, 1.3730, and 1.3770. These constants, their respective distillation ranges, 56–58, 62–67, 71–75, and 80–87° and the fact that they were all saponifiable, were interpreted as indicating the presence of methyl acetate, isopropyl formate (possibly), ethyl acetate, and isopropyl acetate. The weights of the fractions in these "flats" were 4.4, 4.6, 6.6, and 7.7 g., respectively. Although acetone was found throughout the first six fractions, it was concentrated mainly, along with formate esters, in the first two, 3.7 g., from which it was identified (dibenzylideneacetone, m. p. 111–111.5°). The residue in the distilling flask, 16.5 g., was a mixture of alkoxides; when hydrolyzed it gave negative tests for aldehydes, esters, and acids.

Acknowledgment.—The author is indebted to Professor Charles Barkenbus for his coöperation and helpful suggestions.

Summary

The alkoxyl groups of esters and aluminum alkoxides are easily interchangeable and the resulting equilibrium has been shifted so as to prepare new alkoxides in good yield.

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(7) For more definite information concerning the probability of definite compound formation between aldehyde and catalyst see Child and Adkins, THIS JOURNAL, **47**, 798 (1925).

(8) Adkins, *ibid.*, **44**, 2175 (1922).

(9) Farren, Fife, Clark and Garland, *ibid.*, **47**, 2419 (1925).

The reaction of ethoxymethyl acetate with aluminum isopropoxide gave no isolable aluminate of the hemiacetal, but gave acetone, esters which were typical products of Tischtschenko reactions, and a mixture of methyl, ethyl, and isopropyl aluminates.

LEXINGTON, KY. RECEIVED SEPTEMBER 8, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

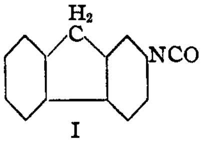
Fluorene Compounds. Nitrogen Derivatives

BY FRANCIS EARL RAY AND GEORGE RIEVESCHL, JR.

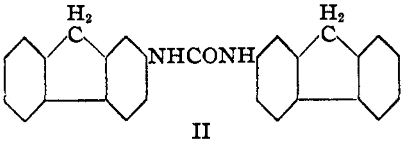
In the present work we undertook the preparation of new derivatives of 2-aminofluorene and of 9-N substituted 2-benzoylfluorene.

The preparation of 2-aminofluorene was first accomplished by Strasburger[1] from 4-aminodiphenic acid. A more convenient synthesis by the reduction of the normal mono-nitration product of fluorene is described in "Organic Syntheses."[2]

When we attempted to prepare 2-fluoryl-isocyanate, I, from the amine and phosgene, the *sym*-di-urea resulted, II.



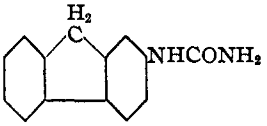
I



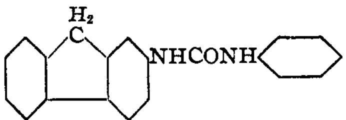
II

The isocyanate, I, was obtained by the modification of Hardy.[3] When dry it was quite stable but moisture caused its conversion into the di-urea, II. This di-urea was formed quantitatively when equimolar solutions of 2-aminofluorene and 2-fluoryl isocyanate were mixed.

When treated with ammonia, the mono-urea, III, was obtained. *sym*-Phenyl-2-fluorylurea, IV, was prepared in two ways: by treating 2-fluoryl isocyanate with aniline and by treating 2-aminofluorene with phenyl isocyanate.



III



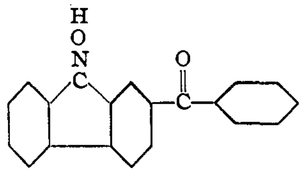
IV

Due to the sensitivity of 2-fluoryl isocyanate to water and the insolubility of the resulting di-urea in ether, acetone, etc., it may be a useful reagent to detect small amounts of water. The factor is 0.0464.

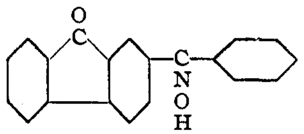
The methyl, ethyl and *n*-propyl urethans were prepared from 2-fluoryl isocyanate and the corresponding absolute alcohol.

Derivatives of 2-Benzoylfluorene

In 1902 Fortner[4] prepared a monoxime from 2-benzoylfluorenone which he described as bright yellow leaves from alcohol which sintered at 185° and melted at 199°. Fortner did not determine which of the configurations, V or VI, this compound possessed.



V



VI

As it seemed probable that the 9-position of the fluorene would be the more active, we set out to prepare V by methods that would leave no doubt as to its constitution.

Using Nenitzescu and Isăcescu's[5] method we condensed benzyl chloride with potassium 2-benzoyl-9-*aci*-nitrofluorene[6] and obtained an oxime melting at 207–208°.

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[1] Strasburger, *Ber.*, **16**, 2346 (1883).

[2] *Org. Syntheses*, **13**, 74 (1933).

[3] Hardy, *J. Chem. Soc.*, 2011 (1934).

[4] Fortner, *Monatsh.*, **23**, 921 (1902).

[5] Nenitzescu and Isăcescu, *Ber.*, **63**, 2484 (1930).

[6] Ray and Palinchak, in press.