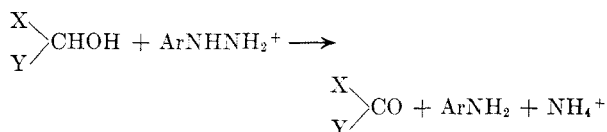Experiments were made with different amounts of acid as the catalyst, so as to ascertain the influence of the acid concentration on the yields of the product. It was found that mixtures of 5 g. of trityl alcohol and 5 g. of DNP in 200 ml. of ethanol refluxed for 2 hr. gave about the same yields irrespective of the amount of the added aqueous concentrated hydrochloric acid, which was varied between 10 and 100 ml. On the other hand, an attempt to carry out the reaction in concentrated sulfuric acid as the solvent, proved unsuccessful. Here, probably, the DNP is converted into an unreactive salt, which is uncapable of attack even though the trityl carbonium ion is present in a high concentration in concentrated sulfuric acid.[9]

The reaction gave no results with *p*-nitrotriphenylcarbinol and with tri(*p*-nitrophenyl)carbinol. It seems that only carbinols in which the heterolysis of the C—OH bond is strongly promoted can react in the manner described, whereas in nitro-substituted aralkyl alcohols, the electron attracting substituents hinder the heterolysis. Neither does any reaction take place with less reactive alcohols, e.g., benzyl alcohol.[4]

A further limitation of this reaction is the fact described by Braude[4] that easily oxidizable alcohols yield derivatives of the corresponding aldehyde or ketone. According to Braude the alcohol is oxidized as follows:

$$\begin{array}{c} X \\ Y \end{array}\!\!\!\!\diagdown\!CHOH + ArNHNH_2{}^+ \longrightarrow$$

$$\begin{array}{c} X \\ Y \end{array}\!\!\!\!\diagdown\!CO + ArNH_2 + NH_4{}^+$$

Braude did not prove the presence of either the ammonium ions or of the 2,4-dinitroaniline in the reaction mixture. Several alternative mechanisms could be proposed for Braude's reaction, such as self-oxidation of diphenylcarbinol with formation of benzophenone and diphenylmethane, or primary formation of a hydrazine derivative with subsequent oxidation to the hydrazone, or again an oxidation of diphenylcarbinol by the nitro groups of the DNP. We repeated therefore part of Braude's work with diphenylcarbinol and searched for byproducts, especially for 2,4-dinitroaniline and for diphenylmethane. None of these attempts was successful. Owing to the low yields and the reactivity of these by-products the negative results can be relied upon probably only in the case of diphenylmethane, for which a sensitive and specific color test[10] exists and was used. The absence of diphenylmethane from the mixture seems to support although does not yet prove, Braude's reaction scheme.

Some 1,1-diarylethylenes, especially 1,1-di(*p*-anisyl)- and 1,1-di(*p*-chlorophenyl)ethylene are

known to give stable carbonium ions in the presence of acids.[11] We thought, therefore, that products similar to those obtained from carbinols and DNP might also be obtained from the corresponding ethylenes and DNP, as e.g., both 1,1-diphenylethanol and 1,1-diphenylethylene can give rise to the same carbonium ion in acid solutions. Several attempts were therefore made to react DNP with 1,1-diphenylethylene and also with 1,1-di(*p*-anisyl)- and 1,1-di(*p*-chlorophenyl)ethylene but all these attempts failed. Probably the acidity of ethanolic hydrochloric acid is not sufficiently great, and concentrated sulfuric acid cannot be used, as the DNP is deactivated in this solvent, owing to salt formation (see above).

EXPERIMENTAL

Reaction of carbinols with DNP. An excess (50–100%) of DNP was refluxed with the carbinol in a mixture of ethanol and concentrated HCl, until no more precipitate formed. The mixture was filtered while hot and the precipitate crystallized from chloroform or from carbon tetrachloride. (See Table I.)

Attempted reaction of trityl alcohol with DNP in conc. sulfuric acid. Five grams of trityl alcohol and 5 g. of DNP were dissolved in 200 ml. of concentrated sulfuric acid. The mixture was stirred at room temperature for 1 hr., poured on ice, and worked up as usual. Only the starting materials could be recovered.

Attempted reaction of DNP with diarylethylenes. Two grams of either 1,1-diphenyl-, 1,1-di(*p*-chlorophenyl)- or 1,1-di(*p*-anisyl)ethylene in 100 ml. of ethanol and 15 ml. of concentrated HCl was refluxed with 2.5 g. of DNP for 2 hr. Only resinous products (probably polymers of the ethylenes) and DNP could be recovered.

Reaction of DNP with trityl chloride in ether. Fourteen grams of tritylchloride and 20 g. of DNP were refluxed in 200 ml. of dry ether for 1 hr. Worked up as usual, the product was obtained in 88% yield and was proved to be identical to the product from the reaction of trityl alcohol with DNP.

Spectra. The infrared spectra of the substances were determined in KBr, on a Baird-Atomic Inc., I.R. Spectrophotometer. Ultraviolet spectra were determined on a Beckman Model DU spectrophotometer.

(11) V. Gold, B. W. V. Hawes, and F. L. Tye, *J. Chem. Soc.*, 2167, 2172, 2181, 2184 (1952).

## Preparation of Fluoroalkyl Iodides from Fluorinated Acid Chlorides

C. G. KRESPAN

Fluoroalkyl iodides can generally be prepared in excellent yield by the reaction of the anhydrous

(9) For references see: R. J. Gillespie and J. A. Leisten, *Quart. Reviews (London)*, VIII, 49 (1954).

(10) S. Hilpert and L. Wolf, *Ber.*, **46**, 2217 (1913).

silver salts of fluorinated carboxylic acids with iodine.[1] Another route has been reported that involves preparation of the fluorinated acid iodide and pyrolysis of this intermediate in a stream of iodine, but the yields are low.[2]

It has now been found that fluoroalkyl iodides can be prepared easily by reaction of the fluorinated acid chlorides with potassium iodide at 200°. The acid iodide that might be formed by halogen exchange is unstable at the temperature of the reaction, so the decomposition products are obtained instead. In contrast to the 10% over-all yields of fluoroalkyl iodides obtained previously by isolation and pyrolysis of the acid iodides, the new one-step route has given yields of 60–70% in the two cases examined.

$$H(CF_2)_xCOCl + KI \longrightarrow H(CF_2)_xI + KCl + CO$$
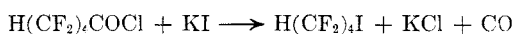
EXPERIMENTAL

ω-H-Octafluoro-n-butyl iodide. A mixture of 66.4 g. (0.40 mole) of potassium iodide and 53.2 g. (0.20 mole) of ω-H-octafluoro-*n*-valeryl chloride, b.p. 86–88°, was heated at 200° for 6 hr. under autogenous pressure in a 500-ml. shaker tube lined with "Hastelloy B." The product was stirred with 200 ml. of ice water, and the lower layer was separated, dried over anhydrous calcium chloride, filtered, and distilled. There was obtained in this way 39.7 g. (61% conversion based on acid chloride) of ω-H-octafluoro-*n*-butyl iodide, b.p. 90–91°; n_D^{25} 1.3500.

Anal. Calcd. for C_4HF_8I: F, 46.35; I, 38.70. Found: F, 46.35; I, 38.08.

The structure was confirmed by determination of the F^{19} and H^1 spectra by nuclear magnetic resonance. A CF_2 peak split into a doublet by H, another CF_2 peak shifted to an extent similar to that observed for tetrafluoroethylene diiodide, and two additional CF_2 peaks were observed, as well as a triplet for the proton resonance.

Trifluoromethyl iodide. Reaction of 33.2 g. (0.20 mole) of reagent grade potassium iodide and 27 g. (0.20 mole) of trifluoroacetyl chloride was carried out at 200° for 6 hr. under autogenous pressure in a 500-ml. static tube lined with "Hastelloy B." The volatile products were cooled in liquid nitrogen, and carbon monoxide was pumped off. The residue from this evacuation weighed 26.8 g. and was identified by its infrared spectrum as a nearly equimolar mixture of trifluoroacetyl chloride and trifluoromethyl iodide. Assuming an equimolar mixture, the yield of trifluoromethyl iodide was 69% and the conversion was 41%. No hexafluoroethane, a possible coupling product, was detected in the product.

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(1) J. H. Simons and T. J. Brice, *Fluorocarbon Chemistry,* in J. H. Simons, *Fluorine Chemistry,* Vol. II, p. 367, Academic Press, 1954.
(2) R. N. Haszeldine, *J. Chem. Soc.,* 584 (1951).

Reaction of Oxamic Acid Hydrazide with Phosgene[1]

RUDI RÄTZ AND HANSJUERGEN SCHROEDER

The asymmetric isomer of cyanuric acid, 3,5,6-trihydroxy-1,2,4-triazine (I), is still unknown. In an attempt to synthesize I by a ring-closure reaction between oxamic acid hydrazide (II) and phosgene, an unexpected result was obtained. Under a wide variety of conditions the only isolated condensation product corresponded to the empiric formula $(CHNO)_n$, but instead of being the desired I it proved to be a triazole derivative, 4-oxamido-1-oxamoyl-1,2,4-triazolidine-3,5-dione (III). This triazolidine was formed by condensation of two moles of II with two moles of phosgene.

Compound III possessed slightly acidic properties, forming dibasic salts with alkali metals and silver ions. Diazomethane converted III into a dimethyl derivative IV. Alkaline hydrolysis led to the conversion of the carbonamido groups into carboxylic groups. Upon acidification the corresponding acid V was obtained which reacted di- and tetra-basic with alkali and amines.

Diazomethane and V yielded the tetramethyl-derivative VI. Since V has the structure of an α-keto acid, two moles of carbon dioxide were evolved on heating. The resulting 1-formyl-4-formylamino-1,2,4-triazolidine-3,5-dione (VII) was found to be identical with a product obtained previously by O. Diels by a different route.[2] The German author, however, ascribed formula IX to this compound, a structure which is highly improbable in view of the strain involved in such a three-membered ring. The correctness of our formula $(CHNO)_4$ as compared to Diels' formula $(CHNO)_2$ was proven by molecular weight determination.

The partial hydrolysis of VII to the known parent compound VIII, 4-amino-1,2,4-triazolidine-3,5-dione (urazine) could not be accomplished. Even under mild conditions only hydrazine, formic acid, and carbon dioxide were produced as the result of the complete degradation of the ring structure. Likewise, attempts to formylate VIII to VII were not successful.

Regarding the constitution of VII, it appears to be noteworthy to mention Diels' synthesis of VII from guaiacyl formylhydrazine carboxylate (X), while guaiacyl hydrazine carboxylate (XI) yielded urazine (VIII). Both reactions were performed by thermal degradation and, assuming an analogous course of reaction with elimination of ROH and

(2) O. Diels, *Ber.,* **47,** 2183 (1914).