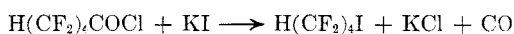


silver salts of fluorinated carboxylic acids with iodine.¹ Another route has been reported that involves preparation of the fluorinated acid iodide and pyrolysis of this intermediate in a stream of iodine, but the yields are low.²

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.



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 $\text{C}_4\text{HF}_8\text{I}$: 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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CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON, DEL.

Reaction of Oxamic Acid Hydrazide with Phosgene¹

RUDI RÄTZ AND HANSJUERGEN SCHROEDER

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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 $(\text{CHNO})_n$, 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 $(\text{CHNO})_4$ as compared to Diels' formula $(\text{CHNO})_2$ 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

(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).

(1) This article is based on work performed under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corporation, New York, N. Y.

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

shown to be identical with IX, the structure proposed by Diels.

Anal. Calcd. for $C_8H_9N_4O_4$: C, 27.93; H, 2.32; N, 32.55; mol. W., 172. Found: C, 27.92, 27.96; H, 2.25, 2.26; N, 32.20, 32.30; Mol. W. (Rast), 195, 196.

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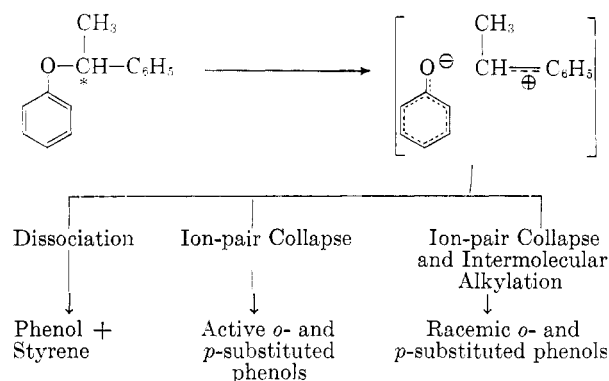
THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION
COLUMBUS 10, OHIO

Stereochemical Control by Solvent in the Thermal Rearrangement of Aryl α -Phenethyl Ethers

HAROLD HART AND JOHN R. KOSAK^{1,2}

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In the thermal rearrangement of alkyl aryl ethers to alkylphenols, it was shown³ that an α -phenethyl group migrated (ortho or para) with retention of configuration. But when the reaction was necessarily intermolecular (as in the cross-alkylation of phenol with optically active α -phenethyl mesityl ether) optically inactive product was obtained. These stereochemical results were taken as evidence for an intramolecular thermal rearrangement, very likely proceeding *via* ionic intermediates.³ This mechanism was made more explicit by Cram⁴ who suggested the intermediacy of ion-pairs (Scheme 1).



Scheme 1. A Mechanism for Thermal Rearrangement of α -Phenethyl Aryl Ethers

Several alternatives may ensue following ionization. Dissociation could yield phenol and styrene,

(1) Taken from a portion of the Ph.D. thesis of J. R. K. submitted to Michigan State University, 1957.

(2) Research Corporation Fellow 1956-57.

(3) H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, **76**, 519 (1954).

(4) D. J. Cram in M. S. Newman's *Steric Effects in Organic Chemistry*, John Wiley and Sons, New York, 1956, p. 298.

products always found in these reactions. Ion-pair collapse might give active or racemic alkylphenols, depending upon the degree to which the cationic part of the ion-pair maintains configuration. Alkylation by an intermolecular process would also give racemic alkylphenols.⁵

If an ion-pair mechanism of this type were operative, one would anticipate that retention of optical purity (and configuration) should be high in solvents of low ionizing power, but that in good ionizing solvents separation of the ion-pair partners into separately solvated ions should increase the chance for racemization of the cationic fragment, thus decreasing the overall stereospecificity of the rearrangement. Previous work³ was done without a solvent; we wish here to report on the rearrangement of several α -phenethyl aryl ethers in 1M solutions in β -methylnaphthalene, phenyl ether, and diethylene glycol. The ethers had *p*-aryl substituents (CH_3 , Cl, OCH_3) so that a single isomer (*o*-alkyl) would be formed on rearrangement.

Table I gives the yields and rotations of the several ethers and ortho- α -phenethylphenols prepared by the alkylation (O— and C—) of certain *p*-substituted phenols with optically active α -phenethyl chloride.⁶ The ethers were rearranged thermally in several solvents, as shown in Table II. The per cent retention of optical purity was calculated as the ratio ($\times 100$) of rotations of *o*- α -phenethyl-*p*-X-phenol obtained by ether rearrangement to that obtained by direct synthesis (Table I). Suitable control experiments showed essentially no racemization of the products under rearrangement conditions.

The data in Tables I and II give additional³ examples of thermal migration of an α -phenethyl

TABLE I
STEREOCHEMISTRY OF α -PHENETHYL ARYL ETHERS AND *o*- α -PHENETHYLPHENOLS PREPARED FROM CERTAIN *p*-X-PHENOLS

X	Rotation of RCl^a	α -Phenethyl Aryl Ether		<i>o</i> - α -Phenethyl- <i>p</i> -X-phenol	
		Yield %	Rotation	Yield %	Rotation
CH_3	+27.2	89.0	+2.52 ^b	2.5	+6.25 ^c
Cl	+42.5	57.3	+1.48 ^b	4.6	+4.90 ^b
OCH_3	+65.2	60.2 ^d	+9.77 ^a	6.8	+14.10 ^b

^a R = α -phenethyl, observed rotations at 25°, l = 1 dm., neat. ^b $[\alpha]_D^{25}$, c = 40, benzene. ^c $[\alpha]_D^{25}$, c = 20, benzene. ^d This ether is new; m.p. 21-21.5°, b.p. 138-141°/1 mm. Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.9; H, 7.11. Found: C, 78.68; H, 7.0.

(5) Another alternative, collapse of the ion-pair to active or racemic ether, has not been tested experimentally.

(6) The procedure, using potassium carbonate suspended in acetone, was that of H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, **76**, 516 (1954). It is assumed in the present work (but was proved previously) that the ether and ortho-alkylphenols have identical configurations, opposite to that of the α -phenethyl chloride used. It is further assumed that they also have equal optical purity.