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 onestep route has given yields of 60-70% in the two cases examined.

 $H(CF_2)_{\ell}COCl + KI \longrightarrow H(CF_2)_{\ell}I + KCl + CO$

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 "Hastellov 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 C₄HF₈I: 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.

Contribution No. 491 Central Research Department Experimental Station E. I. du Pont de Nemours and Company Wilmington, Del. 2017

Reaction of Oxamic Acid Hydrazide with Phosgene¹

RUDI RÄTZ AND HANSJUERGEN SCHROEDER

Received June 30, 1958

The asymmetric isomer of cyanuric acid, 3,5,6trihydroxy-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-1oxamoyl-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 tetramethylderivative 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

⁽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).

ring formation between two molecules, the product from X has the structure of a 1-formyl-4-formylamino-1,2,4-triazolidine-3,5-dione (VII).



 $R = C_6 H_2 OC H_3(o)$

EXPERIMENTAL³

4-Oxamido-1-oxamoyl-1,2,4-triazolidine-3,5-dione (III). Oxamic acid hydrazide (15.5 g., 0.15 mole) was dissolved in a cold solution of 12 g. of sodium hydroxide in 180 ml. of water and placed in a 750 ml. three-neck flask fitted with stirrer and dropping funnel. A solution of 20 g. of phosgene in 85 ml. of toluene was added dropwise with stirring and external ice-cooling over a period of 2 hr. In order to maintain the pH at 8.5, the dropwise addition of 6 g. NaOH in 90 ml. of H₂O was necessary, simultaneously with the last parts of phosgene. After filtering off some solid impurities, the solution was acidified with HCl. The separated white crystals (14.5 g., 73%) were collected on a Buchner funnel and recrystallized from water; m.p. 247-248°.

Anal. Caled. for $C_6H_6N_6O_6$: C, 27.93; H, 2.32; N, 32.55. Found: C, 27.93; H, 2.43; N, 32.55.

The disodium salt of III was prepared by dissolving 25.8 g, of III in a solution of 21.2 g. of sodium carbonate in 180 ml. of water at 60° . On evaporation the salt separated and the compact crystals were recrystallized from water and dried in a vacuum desiccator at room temperature.

Anal. Calcd. for C₆H₄N₆O₆Na₂·H₂O: Č, 22.65; H, 1.88; N, 26.41; Na, 14.45. Found: C, 22.75, 22.59; H, 1.17, 1.12; N, 26.63, 26.47; Na, 13.54, 13.42.

Dipotassium salt of III. An amount of 2.58 g. of III was dissolved in 25 ml. of ice-cooled 5% KOH. On scratching with a glass rod crystallization occurred. The salt was recrystallized once from a small amount of water.

Anal. Calcd. for $C_6H_4N_6O_6K_2$: C, 21.58; H, 1.20; K, 23.38. Found: C, 21.31; H, 1.21; K, 23.51.

Disilver salt of III. This salt was prepared by adding a warm solution of III to an excess of aqueous silver nitrate. The colorless precipitate was washed several times with water.

Anal. Caled. for $C_6H_4N_6O_6Ag_2$: N, 17.80; Ag, 45.80. Found: N, 17.76; Ag, 46.04.

An aqueous solution of the disodium salt hydrate of III was treated with aqueous $AgNO_3$ to give the disilver salt of

(3) Melting points are uncorrected (Fisher-Johns); analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Spang Microanalytical Laboratory, Ann Arbor, Mich. III which was identical with that obtained from III and $AgNO_3$.

4-N-Methyl-oxamido-2-methyl-1-oxamoyl-1,2,4-triazolidine-3,5-dione (IV). The amount of 1 g. of III was added to an ethereal solution of 3 g. of diazomethane. Nitrogen evolution started immediately. After four days 1.15 g. of crystalline material was collected on a Buchner funnel. Small needles, m.p. 191.5-193° after crystallization from methanol.

Anal. Calcd. for $C_8H_{10}N_6O_6$: C, 33.60; H, 3.49; N, 29.53. Found: C, 34.30; H, 3.43; N, 28.89.

4-Oxalamido-1-oxaloyl-1,2,4-triazolidine-3,5-dione (V). The amount of 50 g. of III was dissolved in a solution of 36 g. of sodium hydroxide in 200 ml. of water. NH₃ evolution was observed. After two hours standing, 87.12 g. of the disodium salt of V was obtained by addition of 200 ml. of ethanol. The sodium salt was dissolved on a steam bath at 60° in 500 ml. dilute HCl (1:4) within 30 min. After filtering, the filtrate was cooled to 0° and saturated with HCl gas. NaCl was precipitated almost quantitatively and removed by filtration. The filtrate was evaporated to dryness in a vacuum of 10 mm. at 40–50°. A total of 48 g. of crystalline residue remained from which 37.5 g. (99%) of pure V were extracted with hot acetone. After distilling off the acetone, the crystals were recrystallized from ethanol, m.p. 176–178°. Anal. Calcd. for C₆H₄N₄O₈: C, 27.70; H, 1.54; N, 21.58. Found: C, 27.76; H, 1.02; N, 21.75.

Tetrasodium salt of V. An amount of 2.52 g. of V was dissolved in 10 ml. of water and a solution of 1.55 g. of NaOH in 30 ml. of water added. After cooling, the solution was filtered and the equal volume of ethanol was added. The precipitated tetrasodium salt (3.75 g.) was recrystallized from a small amount of water.

Anal. Caled. for C₆N₄O₈Na₄·6H₂O: C, 15.78; H, 2.63; N, 12.28; Na, 20.18. Found: C, 15.73; H, 3.05; N, 12.77; Na, 20.28.

Diammonium salt of V. The solution of 1 g. of V in aqueous ammonia was evaporated on a steam bath to dryness. The remaining product was recrystallized from a small portion of water, glittering leaflets, m.p. 204° (Fisher-Johns), 182° (Thiele) with loss of NH₃.

Anal. Caled. for $C_6H_{10}N_6O_8$: C, 24.45; H, 3.41; N, 28.51. Found: C, 24.37; H, 3.44; N, 28.69.

Tetrammonium salt of V. An amount of 1 g. of V was added to an excess of 30% aqueous ammonia. After cooling the hot solution, the crystalline ammonium salt separated, m.p. $202-203^{\circ}$ with loss of NH₃ after one recrystallization from water.

Anal. Caled. for $C_{6}H_{16}N_{8}O_{8};$ C, 22.45; H, 4.99; N, 34.95. Found: C, 22.20; H, 4.98; N, 34.99.

Analogously were prepared the tetraanilium salt of V (fine needles from water or ethanol, m.p. 205–206°; calcd. for $C_{30}H_{30}N_8O_8$: C, 57.00; H, 5.07; N, 17.73. Found: C, 56.51; H, 4.93; N, 18.51), the tetrahydrazonium salt of V (crystals from aqueous ethanol, m.p. 159–160°; calcd. for $C_{6}H_{20}N_{12}O_8$: C, 18.55; H, 5.16; N, 43.31. Found: C, 18.62; H, 5.15; N, 43.38), and the bis-1,6-diaminohexane salt of V (crystals from water, m.p. 173–175° (decomp.); calcd. for $C_{18}H_{36}N_8O_8$: C, 43.95; H, 7.32; N, 22.78. Found: C, 43.39; H, 7.52; N, 22.84).

4-N-Methyl-methoxamido-2-methyl-1-methoxamoyl-1,2,4triazolidine-3,5-dione (VI). An amount of 1.23 g. of finely ground V was added to an ethereal solution of 3 g. diazomethane. Within one hour almost complete solution was effected. After standing overnight, the ether was removed by distillation. The remaining crystals (1.42 g.) were twice recrystallized from methanol, m.p. 77-78°.

Anal. Calcd. for $\rm C_{10}H_{12}N_4O_8;$ C, 38.00; H, 3.80; N, 17.72. Found: C, 38.45; H, 3.74; N, 17.50.

1-Formyl-4-formylamino-1,2,4-triazolidine-3,5-dione (VII). An amount of 3 g. of V was placed into a vacuum sublimation apparatus. On heating at $170^{\circ}/3$ mm. carbon dioxide was split off with formation of VII (1.6 g., 81%), m.p. 120° from methanol or water. By mixed melting point VII was shown to be identical with IX, the structure proposed by Diels.

Anal. Calcd. for C₄H₄N₄O₄: 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.

Acknowledgment. The authors are very much indebted to the Olin Mathieson Chemical Corporation for their generous support of this work. They also wish to thank Dr. C. J. Grundmann for his interest in the work and for stimulating discussions.

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}

Received July 3, 1958

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 (CH₃, Cl, OCH₃) 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 $o-\alpha$ -Phenethylphenols Prepared from Certain p-X-Phenols

I HENOLS					
	Rota-	α -Phenethyl Aryl Ether		$o-\alpha$ -Phenethyl- p-X-phenol	
х	tion of RCl ^a	%Yield	Rota- tion	% Yield	Rota- tion
${c H_3 \atop Cl \\ OCH_3}$	+27.2 + 42.5 + 65.2		$+2.52^{b}$ +1.48 ^b +9.77 ^a	$2.5 \\ 4.6 \\ 6.8$	$+6.25^{c}$ +4.90 ^b +14.10 ^b

^a R = α-phenethyl, observed rotations at 25°, l = 1 dm., neat. ^b $[\alpha]_{\rm D}^{25}$, c = 40, benzene. ^c $[\alpha]_{\rm D}^{25}$, c = 20, benzene. ^d This ether is new; m.p. 21–21.5°, b.p. 138–141°/1 mm. *Anal.* Calcd. for C₁₅H₁₆O₂: 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 orthoalkylphenols have identical configurations, opposite to that of the α -phenethyl chloride used. It is further assumed that they also have equal optical purity.