Table IV. Infrared Absorption Maxima (Cm.$^{-1}$) of Monoamides

Compound	Aryl Group	N—H	Carboxyl CO	Amide I CO	CH Out-of-Plane Deformation
2c	m-$CH_3C_6H_4$	3300 (s)	1720 (vs)	1640 (vs)	768 (vs)
2d	o-$CH_3OC_6H_4$	3400 (vs)	1690 (vs)	1625 (vs)	752 (vs)
2e	p-$CH_3OC_6H_4$	3240 (vs)	1666 (vs)	1630 (vs)	820 (vs)
2h	p-ClC_6H_4	3300 (vs)	1700 (vs)	1625 (vs)	756 (vs) 813 (vs)
2i	m-ClC_6H_4	3300 (s)	1710 (vs)	1600 (vs)	768 (vs)

Monoamides of o-Phthalic Acid (2). Acidification of the filtrates from preparation of the diamides sometimes resulted in formation of 2 (see above). Monoamides were recrystallized from acetonitrile. The monoamide (2c) was obtained in a quantity too small for complete characterization. However, identification was established on the basis of its infrared spectrum, which was identical with that of an authentic sample (*11*).

Analyses. Calculated for 2d, and 2e, $C_{15}H_{15}NO_4$: C, 66.42; H, 4.79; N, 5.16. Found: 2d: C, 66.31; H, 4.76; N, 5.19. 2e: C, 66.34; H, 4.74; N, 5.25. Calcd. for 2h and 2i, $C_{14}H_{10}ClNO_3$: C, 61.00; H, 3.63; N, 5.08; Cl, 12.9. Found: 2h: C, 61.10; H, 3.65; N, 4.99; Cl, 12.86. 2i: C, 61.01; H, 3.83; N, 5.38; Cl, 12.85.

Formation of Monoamides (2) from N-Arylphthalimides (3). The *N*-arylphthalimides [3d (*1*) and 3i (*9*)] in ethanolic sodium ethoxide were subjected to treatment described for production of monoamides of *o*-phthalic acid. The monoamides (2d and 2i) were isolated in yields of 70%.

Analysis of Crude Reaction Mixtures. Crude reaction mixtures from preparation of 1d and 1i were evaporated to dryness under nitrogen at room temperature. Repeated washing with small amounts of dry ether and dry alcohol yielded white powders which were subjected to infrared analysis. Absorption peaks typical of 1d, 3d, 1i, and 3i were apparent.

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Synthesis of Perfluoroallyl-Substituted 1,3,5-Triazines

HENRY C. BROWN and MING T. CHENG
Department of Chemical Engineering and Department of Chemistry, University of Florida, Gainesville, Florida 32601

2,4,6-tris(Perfluoroallyl)-1,3,5-triazine and 2,4-bis(perfluoroallyl)-6-perfluoropropyl-1,3,5-triazine were synthesized and their physical properties were determined.

AS AN EXTENSION of a study of the perfluoroalkyl-substituted 1,3,5-triazines (*3*), the authors desired to investigate the properties of a symmetrical triazine with carbon-carbon unsaturation in the substituent fluorinated alkyl groups. Although considerable information was available concerning the chemical characteristics of both the perfluoroalkyl-substituted triazines and fluorinated olefins, no specific conclusions could be drawn concerning the effect of the aromatic, nitrogen-containing ring in an allylic position on the reactivity of the carbon-carbon double bond or, conversely, the influence of the chain unsaturation on the behavior of the perfluoroalkyl-substituted ring system.

A synthesis was designed, therefore, to produce 1,3,5-triazines with perfluoroallyl groups in two or three of the 2, 4, and 6 positions, with perfluoroalkyl groups in the remaining positions as shown in Table I.

The starting material required for this synthesis was 3,4-dichloropentafluorobutyric acid, prepared from the chlorinated dimer, $CF_2ClCFClCF_2CFCl_2$, of chlorotrifluoroethylene by the method of Barnhart and Wade (*1*). This acid was converted to the methyl ester, the ester converted to the amide by treatment with ammonia, and the amide in turn converted to 2,3-dichloropentafluorobutyronitrile by dehydration with phosphorous pentoxide.

3,4-Dichloropentafluorobutyronitrile was converted to the corresponding amidine by treatment with liquid ammonia (*4*); heating this amidine at atmospheric pressure until ammonia evolution ceased produced the corresponding 2,4,6-tris (2,3-dichloropentafluoropropyl)-1,3,5-triazine. The dechlorination of the substituent groups by treatment with zinc in dioxane produced 2,4,6-(perfluoroallyl)-1,3,5-triazine.

For preparation of triazine with both perfluoroallyl and perfluoroalkyl substituent groups, 3,4-dichloropentafluorobutyronitrile was mixed with heptafluorobutyronitrile, the mixture subject to deammonation to produce a mixture of substituted triazines. These compounds were separated by fractional distillation and subsequently dehalogenated to form both 2,4-bis(perfluoroallyl)-6-perfluoropropyl-1,3,5-triazine and 2-perfluoroallyl-4,6-(perfluoropropyl)-1,3,5-triazine. The latter compound was not purified.

Although perfluoroallyl cyanide was prepared from 3,4-dichlorobutyronitrile, the use of this compound to prepare

Table I. Properties of Perfluoroallyl-Substituted 1,3,5-Triazines and Intermediates

Compound	B.p., °C. (mm. Hg)	n_D^{25}	d^{25}	Analyses Calcd., % F	Analyses Calcd., % Cl	Analyses Found, % F	Analyses Found, % Cl
$CF_2ClCFClCF_2COOH$	54(3)	1.3748	1.7324	38.5	28.5	38.1	28.5
$CF_2ClCFClCF_2COOCH_3$	145(atm.)	1.6166	...	36.5	26.2	36.0	27.0
$CF_2ClCFClCF_2CONH_2$	57(m.p.)	...	...	38.7	28.4	38.2	28.7
$CF_2ClCFClCF_2CN$	72(atm.)	1.3360	...	41.6	31.2	41.0	30.8
$CF_2{=}CFCF_2CN$[a, b]	26(atm.)[c]			60.5	...	60.0	...
$(CF_2ClCFClCF_2CN)_3$[d]	113(2)	1.4047	1.8350	41.8	31.0	40.9	31.4
$(C_3F_7CN)\ (CF_2ClCFClCF_2CN)_2$	115(5)	1.3706	1.8016	49.7	21.8	48.9	20.1
$(C_3F_7CN)_2(CF_2ClCFClCF_2CN)$	86(6)	1.3410	1.7660	58.4	11.5	57.9	11.0
$(CF_2{=}CFCF_2CN)_3$[e]	65(4.5)	1.3600		60.5	...	60.2	...
$(C_3F_7CN)\ (CF_2{=}CFCF_2CN)_2$	173(atm.)	1.3434		63.5	...	63.2	...

[a] Infrared spectra showed absorption at 5.6 microns (C=C) and at 4.4 microns (C≡N). [b] Molecular weight (Dumas)160; calcd. 157. [c] Lit. 43–48. [d] Infrared spectra showed strong absorption at 6.45 microns (characteristic ring absorption for polyfluoroalkyl-substituted 1,3,5-triazines. [e] Infrared spectra showed strong absorption at 5.60 (C=C) and 6.43 microns (ring stretching). Calcd: C, 30.5; N, 8.91. Found: C, 30.5; N, 8.71.

perfluoroallyl-substituted triazines by conversion of the nitrile to amidine or by catalytic trimerization with a small amount of ammonia could not be carried out since reaction between the carbon-carbon double bond and ammonia was very rapid, as might be expected for a fluorinated olefin.

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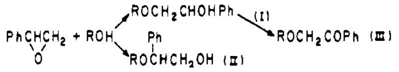
The Alkali-Catalyzed Reaction of Styrene Oxide with Saturated Fatty Alcohols

J. K. WEIL, ELIZABETH A. DIAMOND, and A. J. STIRTON
Eastern Regional Research Laboratory, Philadelphia, Pennsylvania 19118

The alkali-catalyzed reaction of styrene oxide with 12-, 14-, 16-, and 18-C long-chain alcohols gave $ROCH_2CHOHC_6H_5$ as the main product. Structure was confirmed by CrO_3 oxidation to the phenacyl ether, $ROCH_2COC_6H_5$.

THE REACTION of styrene oxide with short chain primary alcohols such as methyl (*2*) or allyl (*1*) alcohol under alkaline catalysis apparently takes place to yield a mixture of two isomers (I, II), in which the secondary alcohol predominates.



The present paper is a continuation of an investigation of the alkali-catalyzed reaction of long chain alcohols (dodecanol, tetradecanol, hexadecanol, octadecanol) with epoxides (ethylene oxide, propylene oxide, 1,2-butylene oxide) (*4, 5, 6*). In the present investigation, oxidation to the phenacyl ether (III) agrees with other evidence (*4*) to show that for each of the three unsymmetrical oxides the ring opens in the same way, under alkaline catalysis, to give a secondary alcohol as the main product.

Gas liquid chromatography of the distilled ether alcohol fraction showed two peaks, a minor forerun and a major component representing about 85% of the fraction. The minor component was formed in too small an amount to be isolated in a pure state. Low temperature crystallization from acetone removed the minor component in the filtrate and gave the pure ether alcohol (I) listed in Table I.

The two components are apparently the isomers I and II since a fraction obtained from the acetone filtrate, or as a forerun on redistillation, rich in the lesser component (II), has the same molecular weight, refractive index, and per cent hydroxyl as the isolated ether alcohol (I). The infrared spectra are the same except for subtle differences in the 1600-, 1350-, and 1100-cm.$^{-1}$ regions.

Chromic acid oxidation of I gave the phenacyl ether (III) listed in Table I, identified by elemental analysis and infrared spectra, proving I to be a secondary alcohol.

EXPERIMENTAL

Materials. Normal primary alcohols purified from good commercial grades by redistillation and low temperature crystallization from acetone had the following constants: dodecanol, n_D^{25} 1.4409; tetradecanol, n_D^{40} 1.4383, m.p. 37.4–38.4°; hexadecanol, n_D^{60} 1.4361, m.p. 49.3–49.6°; octadecanol, n_D^{60} 1.4380, m.p. 57.9–58.4°. Purity by GLC, 97–99%.

Styrene oxide was redistilled, from a good laboratory grade, through a 13-inch column packed with Berl saddles, collecting the fraction $b_{7.5}$ 67–67.5°.

Analysis for terminal epoxide (*3*): theory, 13.32%; found: 13.20%.