only *N*-perfluoropropionyl-*N'*-phenylurea, m.p. 143–145° (see below for proof of structure).

*Hydrolysis of N-n-perfluoropropyl-N'-phenylurea to the acyl ureide.* Refluxing an acetone solution of a small sample of *N*-*n*-perfluoropropyl-*N'*-phenylurea for a few minutes and addition of water produced a white precipitate. Recrystallization from acetone-water gave *N*-perfluoropropionyl-*N'*-phenylurea, m.p. 145.5–146°.

*Anal.* Calcd. for $C_{10}H_7F_5N_2O_2$: C, 42.56; H, 2.50; N, 9.93. Found: C, 42.67; H, 2.39; N, 9.81.

*N-Perfluoropropionyl-N'-phenylurea.* The structure of this compound was proved by an independent synthesis.[7] A solution of 2.01 g. (0.0123 mol.) of perfluoropropionamide and 1.45 g. (0.0122 mol.) of phenyl isocyanate in 10 ml. of dry toluene was refluxed for 48 hr. After storing at 0° for 3 days, the precipitate which formed was isolated and recrystallized from acetone-water to give 1.50 g. (43% yield) of *N*-perfluoropropionyl-*N'*-phenylurea, m.p. 144.5–146.5. A mixed m.p. with the hydrolysis product of *N*-*n*-perfluoropropyl-*N'*-phenylurea showed no depression.

*Reaction of N-perfluoropropionyl-N'-phenylurea with excess aniline.* A mixture of 1.00 g. (.00354 mol.) of the *N*-perfluoropropionyl-*N'*-phenylurea and 3.25 ml. (0.0357 mol.) of aniline was heated to 90° for 20 hr., cooled, and then acidified with 30 ml. of 10% hydrochloric acid. The aqueous acid solution was extracted with four 50-ml. portions of ether. The combined ether extracts, dried over magnesium sulfate, were evaporated to dryness and the solids treated with 30 ml. of boiling ligroin. Filtration of the hot solution gave an insoluble residue from which by fractional crystallization from ethanol-water was isolated 0.30 g. of *sym*-diphenylurea (m.p. 234–235°) and 0.08 g. of phenylurea (m.p. 137–141°). The identities were established through further purification and mixed m.p. with authentic samples.

Evaporation of the ligroin solution to 15 ml., chilling to −60°, and filtering gave 0.56 g. of white crystals, m.p. 95–97°. Recrystallization from ethanol-water gave pure perfluoropropionanilide, m.p. 97.5–98.5°.

*Anal.* Calcd. for $C_9H_6F_5NO$: C, 45.20; H, 2.53; N, 5.86; mol. wt. 239.16. Found: C, 45.25; H, 2.53; N, 6.10; mol. wt. 247.

The identity was confirmed by a mixed m.p. with an authentic sample of perfluoropropionanilide prepared by passing perfluoropropionyl chloride into a solution of aniline in ether.

*Reactions of benzylamine with perfluoropropyl isocyanate.* To prove the generality of the above sequence of reactions, the entire series through the ultimate solvolysis to benzyl urea was successfully repeated using benzyl amine.

*N,N-Methylphenyl-N',N'-methylphenylcarbamylperfluoropropionamidine.* Over a period of 40 min., 3.44 ml. (0.0318 mol.) of methylaniline in 30 ml. of dry ether was slowly added at −60° to 6.7 g. (0.0317 mol.) of perfluoropropyl isocyanate in 30 ml. of dry ether. After an additional 1.5 hr. at −60° and 6 hr. at room temperature, the mixture was stored at −30° for 2 weeks. Vacuum evaporation of the ether left an oily residue which was dissolved in 10 ml. of ligroin and 10 ml. of benzene. Vacuum evaporation of the mixture gave three successive crops of crystals, 4.27 g. (70%), m.p. 68.5–70°. Recrystallization from acetone-water and decolorizing with Norit gave white, crystalline *N,N*-methylphenyl-*N',N'*-methylphenylcarbamylperfluoropropionamidine, m.p. 71–72°.

*Anal.* Calcd. for $C_{15}H_{16}F_5N_3O$: C, 56.10; H, 4.19; N, 10.90; mol. wt., 385. Found: C, 56.27; H, 4.29; N, 11.09; mol. wt., 378; (m.p. depression of benzene).

CLEVELAND, OHIO

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[7] P. F. Wiley, *J. Am. Chem. Soc.*, **71**, 1310 (1949).

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

# Fluorinated Paraffins

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Paraffins with fluorinated clusters at one end, both ends, or in the middle of the chain have been synthesized from perfluorinated acids and their derivatives.

Many propanes and butanes are known[2] which have clustered fluorine atoms as in $CF_3C_3H_7$, $CF_3CH_2CH_2CF_3$, or $CF_3CF_2CF_2CH_3$. One pentane, $CF_3C_4H_9$, has been reported,[3] but no longer paraffin. The present paper shows the synthesis of hexanes and heptanes with their fluorinated groups diversely spaced, namely $C_3F_7C_3H_7$, $C_2H_5C_2F_4C_2H_5$, $C_3F_7CH_2CH(CH_3)_2$, and $CF_3(CH_2)_4CF_3$. They were prepared for an examination of their physical properties and the character of their carbon-hydrogen bond to be reported separately.[4]

The syntheses of these hexanes and heptanes involved basically a reduction starting with readily available perfluorinated acids. Particularly advantageous would be a reduction to a carbonyl function from an acid or derivative by use of Grignard or similar reagent. The carbonyl could be further reduced to the desired paraffin.

Esters of perfluorinated acids were unsuitable as they were known to give alcohols exclusively on treatment with $LiAlH_4$ or Grignards.[5] Anhydrides of unfluorinated acids yielded some carbonyl compounds at low temperatures[6] which was explained

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[1] Present address: Department of Chemistry, University of Hartford, Hartford, Conn.

[2] A. L. Henne, J. W. Shepard, and E. J. Young, *J. Am. Chem. Soc.*, **72**, 3577 (1950).

[3] R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949).

[4] This phase of the work will be published by A. L. Henne. It has been orally presented by A. L. H. at the International Symposium on Fluorine Chemistry, at Birmingham, England in July 1959.

[5] E. Gryskiewicz-Trochimowski, *Rec. trav. chim.*, **66**, 427 (1947).

[6] M. S. Newman and Fr. O'Leary, *J. Am. Chem. Soc.*, 68, 258 (1946).

in terms of the possible stability of the intermediate organometallic complexes,[7] and hence it seemed worth-while to extend this reaction to perfluorinated acid anhydrides in the hope of achieving carbonyl products.

The anhydride of trifluoroacetic acid, $(CF_3CO)_2O$, on reduction with $LiAlH_4$ gave a mixture of alcohol, acid, ester, and aldehyde in which the latter amounted to 21.5%. With $CH_3MgBr$, there was only a trace of $CF_3COCH_3$ in the products, while with $(CH_3)_2CHMgBr$, the main products were the acid, $CF_3COOH$, and a secondary alcohol, $CF_3CHOHCH(CH_3)_2$, made by reduction of the intermediate. From the anhydride of perfluorobutyric acid, $(C_3F_7CO)_2O$, and $CH_3MgBr$, no ketone was isolated. The main products were the acid and the ester of the acid, $C_3F_7CO_2C(CH_3)_2C_3F_7$.

Recent work[8] has indicated that some perfluorinated monobasic acids could be converted to ketones with Grignard reagents. In this investigation, this work was extended to include perfluorinated dibasic acids. The reaction of perfluorosuccinic acid, $(CF_2)_2(COOH)_2$, with $CH_3MgBr$ gave 45% of the diketone, $CH_3COCF_2CF_2COCH_3$. The next perfluorinated homolog, perfluorinated glutaric acid, $(CF_2)_3(COOH)_2$, with $CH_3MgBr$ gave, however, a mixture, in which two products boiling respectively at 147° and 177° predominated; the lower boiling one was probably a mixture of $CH_3CO(CF_2)_3COCH_3$ and $CH_3CO(CF_2)_3C(CH_3){=}CH_2$, while the higher boiling one was the cyclic hemiketal, $CH_3\underbrace{C(OH)(CF_2)_3C}_{O}(CH_3)_2$. Infrared spectra of the lower boiling fragment indicated a carbonyl and olefin function and tests with $Br_2$, $MnO_4^-$ and 2,4-DNPH were all positive. On this basis, it could be (a) $CH_3CO(CF_2)_3C(CH_3){=}CH_2$ or (b) $CH_3CO(CF_2)_3CH{=}CH_2$. The first (a) could involve addition of $CH_3MgBr$ to the diketone $CH_3CO(CF_2)_3COCH_3$ followed by loss of water; the second, (b) would require reduction of the carbonyl without addition of an alkyl group which has not been observed with $CH_3MgBr$. A 2,4-DNPH formed from the 147° material gave an analysis [% N found 13.86, calculated for mono derivative of (a) 13.52, calculated for mono derivative of (b) 14.47] which favored (a) but analysis of the 147° mixture [%C, % H found 38.79, 2.47; calculated for (a) 41.03, 3.42; calculated for (b) 38.18, 2.73) favored structure (b)]. This contradiction can be resolved by assuming a mixture of $CH_3CO(CF_2)_3COCH_3$ (% C, % H calculated 35.59, 2.54) and (a). The 2,4-DNPH formed would be the derivative of (a); any formed from the diketone was presumably lost in purification by recrystallization.

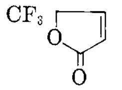
Guided by these considerations and the fact that fluorinated ketones could not be reduced directly to paraffins in a Clemmensen or Wolff-Kishner procedure, the following synthesis were settled as follows:

*$C_3F_7C_3H_7$.* $C_3F_7CH{=}CHCH_3$, prepared by addition of $C_2H_5MgBr$ to $C_3F_7CO_2CH_3$ followed by dehydration with $P_2O_5$ in accord with reported procedures[9,10] was hydrogenated in presence of Raney nickel to give a 41% yield of $C_3F_7C_3H_7$.

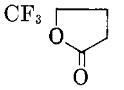
*$C_3F_7CH_2CH(CH_3)_2$.* $C_3F_7CH{=}C(CH_3)_2$, prepared by reduction of $C_3F_7CO_2CH(CH_3)_2$ with $LiAlH_4$ followed by dehydration with $P_2O_5$ in accord with reported procedures[9,10] was hydrogenated in presence of $PtO_2$ to give a 89% yield of $C_3F_7CH_2CH(CH_3)_2$.

*$C_2H_5C_2F_4C_2H_5$.* $CH_3COCF_2CF_2COCH_3$, prepared by the reaction of $CH_3MgBr$ on the perfluorinated succinic acid, was reduced in 64% yield to give $CH_3CHOHCF_2CF_2CHOHCH_3$. This diol, on treatment with $P_2O_5$, gave only a cyclic ether, $CH_3\underbrace{CHCF_2CF_2CH}_{O}CH_3$ in 72% yield. Therefore reduction to the paraffin was achieved by acetylation of the diol with $(CH_3CO)_2O$ in 92% yield to the diacetate, $CH_3CH(OCOCH_3)CF_2CF_2CH(OCOCH_3)CH_3$, pyrolysis of this diacetate to the diene $CH_2{=}CHCF_2CF_2CH{=}CH_2$ in 67% yield and finally hydrogenation of the diene in 85% yield to the paraffin $C_2H_5C_2F_4C_2H_5$.

*$CF_3(CH_2)_4CF_3$.* $CF_3CO_2C_2H_5$ was reacted with diethyl succinate and $NaOC_2H_5$ in the usual Claisen condensation followed by decarboxylation to give a 65% yield of the unsaturated lactone,



which was then hydrogenated in 80% yield to give



This saturated lactone was reacted with $CF_3CO_2C_2H_5$ and $NaOC_2H_5$ in a second Claisen condensation which gave on decarboxylation a 67% yield of the hemiketal, $\underbrace{CF_3C(OH)CH_2CH_2CH}_{O}CF_3$. Reduction of the hemiketal with $LiAlH_4$ gave a 75% yield of diol, $CF_3CHOHCH_2CH_2CHOHCF_3$. Dehydration of the diol with $P_2O_5$ gave only tar and acrid fumes. Therefore, dehydration was achieved by acetylation of the diol in essentially quantitative yield to the diacetate, $CF_3CH(OCOCH_3)CH_2CH_2CH(OCOCH_3)CF_3$, followed by pyrolysis in 83% yield to

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[7] M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Non-metallic Substances*, Prentice-Hall, Inc., New York, 1954, p. 549.

[8] K. T. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78**, 2269 (1956).

[9] E. T. McBee, O. R. Pierce, and M. C. Chen, *J. Am. Chem. Soc.*, **75**, 2325 (1953).

[10] F. Swarts, *Bull. sci. roy. acad. Belg.*, **8**, 343 (1922).

the diene, $CF_3CH{=}CHCH{=}CHCF_3$. Finally the diene was hydrogenated in 94% yield to the paraffin $CF_3(CH_2)_4CF_3$.

In this last synthesis, the first Claisen presumably gave a gamma keto acid which in acid media formed the unsaturated lactone. This is in accord with expectations based on unfluorinated analogs. The second Claisen presumably gave a keto alcohol which as expected formed the stable hemiketal by reaction of the two functional groups.

The identity of the new compounds was established from analysis, method of preparation, subsequent reactions and optical refractivity computations as detailed below. Infrared red spectra was used to confirm the structure.

## EXPERIMENTAL

*Reaction of* $(CF_3CO)_2O$ *with* $LiAlH_4$. $(CF_3CO)_2O$ was prepared from the corresponding acid by the method of Swarts[11] and modified by Paridon.[12] A slurry of $LiAlH_4$ (10 g., 0.263 mole in 300 ml. of dry ether) was refluxed for 3 days under an atmosphere of nitrogen with continuous stirring under the refluxing of a water condenser leading to a dry ice trap and $CaCl_2$ drying tube. This $LiAlH_4$ solution, determined by titration to contain 0.12 mole, was added dropwise in 2 hr. to $(CF_3CO)_2O$ (48.5 g., 0.23 mole) in 100 ml. of dry ether at −55° to −45°. The mixture was protected from moisture as before and stirred overnight at −45°. Decomposition was achieved by addition of 10 ml. of water followed by 25 ml. of concentrated $H_2SO_4$ in 55 ml. of water and allowing the mixture to reach room temperature. The ether layer and ether extracts of the aqueous layer were dried over $Na_2SO_4$ and then fractionated to give:

i. 16.2 g. boiling between 45–70°, mostly 60–65°.
ii. 4.2 g. boiling between 70–85°.
iii. 20.0 g. pot residue, which on fractionation gave:
iv. 1.4 g. boiling between 78–103°.
v. 22.4 g. boiling between 103–106°.

v with $P_2O_5$ gave a material, boiling at −19°, which formed a 2,4-DNPH, melting at 148°; mixed m.p. with 2,4-DNPH of $CF_3CHO$ was 148°.

Refractionation of i, ii, and iii combined gave:

vi. 3.4 g. boiling between 47–52°.
vii. 1.4 g. boiling between 52–60°.
viii. 12.0 g. boiling between 68–74°.

vi on the basis of infrared spectra (max. at 5.56 μ) and boiling point (compared to known 52–55°[11]) and preparation of amide, $CF_3CONH_2$ (m.p. 75°, mixed m.p. 75°) was identified as the ester $CF_3CO_2CH_2CF_3$. viii, by infrared spectra (max. at 3.00 μ) and boiling point comparison (known b.p. 74°[11]) was identified as $CF_3CH_2OH$. v was strongly acidic and gave a positive 2,4-DNPH test. Titration of an aliquot with base indicated 10.1 g. of $CF_3COOH$ (0.089 mole, 19.3%). Reaction of another aliquot with 2,4-DNPH indicated 9.7 g. of $CF_3CHO$ (0.099 mole, 21.5%).

*Reaction of* $(CF_3CO)_2O$ *with excess* $CH_3MgBr$. $CH_3MgBr$ (about 0.7 mole) in 300 ml. of dry ether was added dropwise in 1.25 hours to $(CF_3CO)_2O$ (50 g., 0.238 mole) in 100 ml. of dry ether at 0°. The solution was continuously stirred and protected from moisture as previously described. After addition, the temperature was allowed to rise to room temperature and the solution stand overnight. The complex was then decomposed at 0° by dropwise addition of 120 ml. of saturated $NH_4Cl$ solution with continuous stirring. A small aliquot was treated with 2,4-DNPH and gave only traces of the 2,4-DNPH derivative of $CF_3COCH_3$ (m.p. 138°, mixed m.p. 138°). The main portion of the mixture was treated with dilute HCl and the ether layer and ether extracts of the aqueous layer treated as before after a washing with dilute $Na_2CO_3$ solution. Fractionation gave $CF_3C(CH_3)_2OH$ (25.3 g., 0.198 mole, 42%), boiling between 76–80° (known b.p. 81°[13,14]) and having an index of refraction of 1.3350 at 20° (known 1.3350[13,14]). Continuous ether extraction of the acidified aqueous layer resulted in isolation of $CF_3COOH$ (15.7 g., 0.138 mole, 29%).

The reaction of $(CF_3CO)_2O$ with equimolar amounts of $CH_3MgBr$ gave comparable results.

*Reaction of* $(CF_3CO)_2O$ *with* $(CH_3)_2CHMgBr$. $(CH_3)_2CH$-MgBr (prepared from 0.7 mole of $(CH_3)_2CHBr$) in 500 ml. of dry ether was added dropwise in 2 hr. to $(CF_2CO)_2O$ (59 g., 0.28 mole) in 100 ml. of dry ether at 0°. After reaction with protection from moisture, the mixture stood overnight at room temperature and was then decomposed by addition of 100 ml. of saturated $NH_4Cl$ solution at 0°. Fractionation after washing the ether layer and extracts with dilute $Na_2CO_3$ solution and drying over $Na_2SO_4$ gave:

| | | | |
|---|---|---|---|
| i. | 8.2 g. | b.p. 35–62° | $n_D^{20}$ 1.3520 |
| ii. | 13.0 g. | 62–87° | 1.3440 |
| iii. | 11.8 g. | 87– | 1.3515 |
| iv. | 4.0 g. | residue | |

Infrared spectra indicated i to be essentially ether, ii alcohol, $CF_3CHOHCH(CH_3)_2$ (max. at 2.92 μ), and iii an alcohol and ester mixture (max. at 2.92 μ and 5.56 μ). Continuous ether extraction of the acidified aqueous layer gave $CF_3$-COOH (20 g., 0.175 mole, 31%). The alcohol could not be purified for analysis and was prepared by reaction of $CF_3CO_2C_2H_5$ and $(CH_3)_2CHMgBr$ at 0° with a yield of 55%.[15] Comparison of the infrared spectra of the alcohol present in ii and that of the synthesized sample indicated them to be the same.

*Reaction of* $(C_3F_7CO)_2O$ *with* $CH_3MgBr$. $(C_3F_7CO)_2O$ was prepared from $C_3F_7COOH$ and $P_2O_5$ by the method of Minnesota Mining and Mfg. Co.[16] modified by the use of some concentrated $H_2SO_4$ (10 ml. per 129 g., 0.603 mole of $C_3F_7$-COOH and 85 g., 0.589 mole of $P_2O_5$) in 85% yield. $CH_3$-MgBr (containing about 0.24 mole) in 200 ml. of dry ether was added dropwise in 1.5 to 2 hr. to $(C_3F_7CO)_2O$ (46 g., 0.112 mole) in 150 ml. of dry ether at 0°. After reaction and subsequent standing overnight at room temperature, the mixture at 0° was decomposed by dropwise addition of 40 ml. of saturated $NH_4Cl$ solution. Treatment of the ether layer and extracts was as before and fractionation gave:

| | | | |
|---|---|---|---|
| i. | 2.2 g. | b.p. 37–97° | $n_D^{24}$ 1.3225 |
| ii. | 2.8 g. | 97–110° | 1.3226 |
| iii. | 5.2 g. | 110–125° | 1.3270 |
| iv. | 3.5 g. | residue | |

Infrared spectra indicated i, ii, and iii to be mainly ester in character (max. at 5.56 μ). A small aliquot gave a (−) test for ketone with 2,4-DNPH. Continuous ether extraction of the acidified aqueous layer gave $C_3F_7COOH$ (24.8 g., 0.116 mole, 50.2%). Inasmuch as attempts to purify the ester were unsatisfactory, a synthesis of the ester was effected by repeating the reaction with excess $CH_3MgBr$ to form the tertiary alcohol, $C_3F_7C(OH)(CH_3)_2$ converting it to the sodium alcoholate and reacting this alcoholate with $C_3H_7$-COCl. Using $CH_3MgBr$ (prepared from 0.3 mole of $CH_3Br$) in 175 ml. of dry ether and $(C_3F_7CO)_2O$ (32 g., 0.078 mole) in 150 ml. of dry ether, the tertiary alcohol (11.3 g., 0.0496 mole, 31.8%), boiling between 105–107°, $n_D^{20}$ 1.3279 was

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(11) F. Swarts, *Compt. rend.*, **197**, 1261–4 (1933).

(12) L. Paridon, private communication, March 1955.

(13) F. Swartz, *Bull. soc. chim. Belg.*, **36**, 191 (1927).

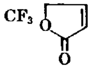
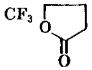
(14) F. Swarts, *Bull. soc. chim. Belg.*, **38**, 99 (1929).

(15) E. T. McBee, O. R. Pierce, and W. F Marzluff, *J. Am. Chem. Soc.*, **75**, 1609 (1953).

(16) Minnesota Mining & Mfg. Co., Literature, Sept. 1, 1949.

TABLE I

NEW COMPOUND

| Compound | M.P.[a] | B.P.[a] | $n_D^{20}$ | $d_4^{20}$ | M.R. | ARF | % C[b] Calcd. | % C[b] Found | % H[b] Calcd. | % H[b] Found | % N[b] Calcd. | % N[b] Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3F_7CO_2C(CH_3)_2C_3F_7$ | | 146° | 1.3082 | 1.572 | 51.7 | 1.22 | 28.30 | 28.15 | 1.41 | 1.68 | | |
| $CH_3CO(CF_2)_2COCH_3$ | | 129° | 1.3520 (25°) | 1.311 (25°) | 30.70 | 1.29 | 38.71 | 39.03 | 3.23 | 3.40 | | |
| di-2,4-DNPH | 283–284° dec. | | | | | | | | | | 20.51 | 20.17 |
| $C_3H_7C_3F_7$ | | 64–65° | 1.30000 | 1.260 (25°) | | | 33.97 | 33.58 | 3.30 | 3.58 | | |
|  | | 83/12–13 mm. | 1.3853 | 1.444 | 24.68 | 1.02 | 39.49 | 39.42 | 1.97 | 2.72 | | |
|  | | 78–79/25 mm. | 1.3748 | 1.413 | 24.97 | 1.18 | 38.96 | 38.90 | 3.24 | 3.30 | | |
| $CF_3\underbrace{C(OH)CH_2CH_2CH}_{O}CF_3$ | | 140 | 1.3468 (25°) | 1.525 (25°) | 31.11 | 1.14 | 32.14 | 32.13 | 2.68 | 2.84 | | |
| $(CF_3CHOCOCH_3CH_{2-})_2$ | 65° | 133/75 mm. | 1.3630 (26°) | 1.310 (26°) | 52.25 | 1.20 | 31.86 | 31.63 | 3.54 | 3.68 | | |
| $CF_3CH{=}CHCH{=}CHCF_3$ | | 85.5–86.5 | 1.3403 (25°) | 1.286 (25°) | 30.995 | 1.22 | 37.89 | 38.09 | 2.11 | 2.38 | | |
| $CH_3CHOHCF_2CF_2CHOHCH_3$ | | 201 | 1.3865 (25°) | 1.359 (25°) | 32.875 | 1.08 | 37.90 | 38.08 | 5.26 | 5.45 | | |
| $(CH_3CHOCOCH_3CF_{2-})_2$ | | 205 | 1.3870 (25°) | 1.246 (25°) | 51.78 | 1.12 | 43.80 | 43.97 | 5.11 | 5.19 | | |
| $CH_3\underbrace{CHCF_2CF_2CH}_{O}CH_3$ | | 91 | 1.3425 (24°) | 1.229 (24°) | 29.53 | 1.14 | 41.86 | 40.05 | 4.66 | 4.66 | | |
| $CH_2{=}CHCF_2CF_2CH{=}CH_2$ | | 75.5–76.5 | 1.3415 | 1.135 | 28.55 | 1.00 | 46.75 | 46.45 | 3.90 | 4.14 | | |
| $C_2H_5C_2F_4C_2H_5$ | | 78.5–79.5 | 1.3292 (25°) | 1.089 (25°) | 29.54 | 1.01 | 45.57 | 45.70 | 6.33 | 6.49 | | |
| $C_3F_7CH_2CH(CH_3)_2$ | | 81.5 | 1.3130 | 1.220 | 36.02 | 1.33 | 37.17 | 37.40 | 3.98 | 4.25 | | |
| $CH_3\underbrace{C(OH)CF_2CF_2CF_2C}_{O}(CH_3)_2$ | | 177 | 1.3781 | 1.433 | 40.375 | 1.14 | 38.09 | 37.75 | 3.97 | 4.35 | | |
| $CH_2{=}\underbrace{C(CF_2)_3C}_{O}(CH_3)_2$ | | 136 | 1.3650 | 1.350 | 38.74 | 1.20 | 41.04 | 41.04 | 3.19 | 3.42 | | |
| $CH_3\underbrace{CH(CF_2)_3C}_{O}(CH_3)_2$ | | 139 | 1.3571 | 1.332 | 38.791 | 1.13 | 40.67 | 40.81 | 4.23 | 4.43 | | |
| $CH_3CHOH(CF_2)_3CH(CH_3)_2$ or $CH_3CH_2(CF_2)_3C(OH)(CH_3)_2$ | | 165 | 1.3670 | 1.339 | 39.91 | 0.98 | 40.43 | 40.41 | 5.04 | 5.19 | | |
| $C_3F_7COCH_3$ as semicarbazone | 107° | | | | | | 26.76 | 26.44 | 2.24 | 2.64 | 15.61 | 15.67 |
| $CF_3CHOHCH_2CH_2CHOHCF_3$ | 75–120° | | | | | | 31.86 | 31.63 | 3.54 | 3.68 | | |
| $CF_3CHOHCH_2CH_2CONH_2$ | 46° | | | | | | | | | | 8.19 | 8.22 |

[a] All temperatures uncorrected. [b] Analysis by Galbraith Laboratories.

formed. Its identity was established by comparison with known constants (b.p. 105–107°, $n_D^{20}$ 1.3279[15]) and confirmed by infrared spectra (max. at 2.92 $\mu$). This alcohol (45.6 g., 0.2 mole) was added dropwise to Na sand (4.6 g., 0.2 mole) prepared in hot toluene and suspended in 250 ml. of dry ether, as rapidly as refluxing under a water condenser permitted. The mixture was protected from moisture. $C_3F_7COCl$ (48.5 g., 0.208 mole) prepared from $C_3F_7COOH$ and $PCl_5$ in accord with the procedure of Minnesota Mining and Mfg. Co.,[16] was added dropwise to the suspension of the sodium alcoholate as rapidly as refluxing of the water condenser permitted with continuous stirring. Fractionation gave the ester (63.5 g., 0.15 mole, 75%) boiling 140–146°. Infrared spectra indicated it to be alcohol free and identical to the ester formed by reaction of $CH_3MgBr$ with $(C_3F_7CO)_2O$.

*Reaction of* $(CF_2)_2(COOH)_2$ *with* $CH_3MgBr$. Two identical runs were made in which $(CF_2)_2(COOH)_2$ (220 g., 1.157 moles) in 300 ml. of dry ether was reacted in 4.5 hr. with $CH_3MgBr$ (prepared from 545 g., 5.85 moles $CH_3Br$ and 146 g., 6 g.a.a. Mg) in 2000 ml. of dry ether using the procedure outlined earlier. The residue from the ether layers and extracts of both runs were combined and treated as before, and then fractionated to give the diketone, $CH_3COCF_2CF_2COCH_3$, (198 g., 1.06 moles, 45%) boiling 128–130°. In addition, a forecut (85 g.) boiling 65–125° and a tarry residue (45 g.) were isolated. The aqueous phase contained $F^-$ and continuous ether extraction of it gave only traces of $(CF_2)_2(COOH)_2$. The diketone was identified on the basis of its mode of preparation, subsequent reactions, atomic refractivity computations, and analysis. A solid 2,4-DNPH melted at 283–284° with decomposition. Infrared spectra (max. at 5.62 $\mu$) confirmed this structure.

*Reaction of* $(CF_2)_3(COOH)_2$ *with excess* $CH_3MgBr$. Two identical runs were made simultaneously by reacting $(CF_2)_3(COOH)_2$ (1.5 equivalents on the basis of titration of a small aliquot with base) in 500 ml. of dry ether in 2.5 hr. with $CH_3MgBr$ (prepared from 6 moles $CH_3Br$ and 6.05 g.a.a. Mg) in 750 ml. of dry ether at 0°. (The Grignard reagent was used in large excess because the very hydroscopic acid was thought to contain some water.) Fractionation of the residue from the combined ether layers and extracts, treated as before, gave a mixture containing an olefin and ketone function (174 g., 0.814 mole, 54.3% including estimates in the fore and tail cuts) boiling mostly at 147°, and a hemiketal (82.4 g., 0.327 mole, 21.8% including estimates in fore and tail cuts) boiling mostly at 177°. The 147° material gave a 2,4-DNPH melting at 120°, positive tests for olefin with $MnO_4^-$ and $Br_2$, and an infrared spectra (max. at 5.62 $\mu$ and 6.02 $\mu$) which confirmed presence of double bond and carbonyl. Infrared spectra of the hemiketal, $CH_3\underbrace{C(OH)(CF_2)_3C}_{O}(CH_3)_2$, showed characteristic alcohol band (max. 2.85 $\mu$) and absence of olefin and carbonyl bands.

*Hydrogenation of* $C_3H_7CH{=}CHCH_3$. $C_3F_7CH{=}CHCH_3$ (70 g., 0.333 mole) in 250 ml. of dry ether was placed in a glass lined high pressure steel autoclave (capacity 1 l.) with 4 g. Raney nickel and enough hydrogen to produce a pressure of 106.7 atmospheres. The autoclave was mechanically rocked and heated to 100°. Fractionation of the product gave the hydrocarbon, $C_3F_7C_3H_7$ (29 g., 0.137 mole, 41%) as the main product boiling 64–65°. Infrared spectra confirmed that the product was olefin free.

*Hydrogenation of* $C_3F_7CH{=}C(CH_3)_2$. $C_3F_7CH{=}C(CH_3)_2$ (30.8 g., 0.138 mole) in 50 ml. of dry ether was placed in a 220 ml. glass bottle in a Parr hydrogenation apparatus with 50 mg. of $PtO_2$ and enough hydrogen to produce a pressure of 3.3 atmospheres at room temperature. In 36 hr., a total of 2.54 atmospheres was absorbed. Fractionation of the product gave $C_3F_7CH_2CH(CH_3)_2$ (19 g., 0.083 mole, 60% practical yield, 89% including estimates on fore and tail cuts) boiling mostly 80–82°. Infrared spectra confirmed the absence of the olefin band. (The constant for the apparatus is 1.87 to 2 atmospheres per 0.1 mole of hydrogen absorbed.)

*Reduction of* $CH_3COCF_2CF_2COCH_3$ *with* $LiAlH_4$. $LiAlH_4$ (25 g., 0.658 mole) in 500 ml. of dry ether was refluxed for 3 hr. with suitable precautions to exclude moisture. $CH_3COCF_2CF_2COCH_3$ (173.5 g., 0.933 mole) was added with continuous stirring to this solution in 2.5 hr. at 0°. After standing overnight at room temperature, the mixture was decomposed at 0° by dropwise addition with continuous stirring of 50 ml. of ice water followed by 50 ml. of concentrated $H_2SO_4$ in 150 ml. of ice water. The dried ether layer and extract gave on fractionation the diol, $CH_3CHOHCF_2CF_2CHOHCH_3$ (112.5 g., 0.592 mole, 64% including estimates on fore and tail cuts) boiling at 201°. A forecut (17 g., 0.093 mole, 10%) of starting material was also recovered. Continuous ether extraction of the aqueous layer gave 22 g. of material, consisting of diol and diketone. The identity of the diol was confirmed by infrared spectra (max. 3.06 $\mu$).

Direct reduction of the ketones to paraffins was tried without success by Clemmensen and Wolff-Kishner procedures. Using $CF_3COCH_3$ and also $CF_3COC_4H_9$ and the usual Clemmensen procedure, no reaction occurred. The Wolff-Kishner reaction was tried using $C_3F_7COCH_3$ (prepared by a Claisen condensation between $C_3F_7CO_2C_2H_5$ and $CH_3CO_2C_2H_5$ in the presence of $NaOC_2H_5$ with a yield of 46% in addition to 37% recovered ethyl acetate and 19% diethyl carbonate) and $CF_3COCH_3$ as semicarbazones. In both cases decomposition occurred giving $CF_3H$, CO, $CO_2$ and $NH_3$ in the case of $CF_3COCH_3$ and $C_3F_7H$, CO, $CO_2$ and $NH_3$ in the case of $C_3F_7COCH_3$.

*Acetylation of* $CH_3CHOHCF_2CF_2CHOHCH_3$. The diacetate was prepared in the usual manner by adding $(CH_3CO)_2O$ (118 g., 1.15 moles) dropwise with continuous stirring in 1.5 hr. to $CH_3CHOHCF_2CF_2CHOHCH_3$ (100 g., 0.526 mole) containing 2 drops of concentrated $H_2SO_4$. The mixture was maintained at 100° for 3 hr. and then fractionated to give the diacetate, $CH_3CH(OCOCH_3)CF_2CF_2CH(OCOCH_3)CH_3$ (126.6 g., 0.462 mole, 87% yield, 92% including estimates in fore and tail cuts). Infrared spectra (max. at 5.72 $\mu$) confirmed the presence of acetate esters and absence of alcohol.

Dehydration of the diol with $P_2O_5$ gave a 72% yield of $CH_3\underbrace{CHCF_2CF_2CH}_{O}CH_3$, boiling between 90–92° and having an olefin, alcohol, and carbonyl-free infrared spectra.

*Pyrolysis of* $CH_3CH(OCOCH_3)CF_2CF_2CH(OCOCH_3)CH_3$. This pyrolysis was carried out using the method of Hinkamp.[17] In all 5 passes were made and the product (47 g., 0.306 mole, 67% practical yield) obtained on fractionation, boiling 75.5–76.5° was confirmed by infrared spectra (max. at 5.75 $\mu$ and 6.05 $\mu$) as the diene, $CH_2{=}CHCF_2CF_2CH{=}CH_2$. The usual positive tests with $MnO_4^-$ and $Br_2$ were noted. The rate of addition of diacetate was 1 drop/6 to 8 seconds; nitrogen inlet rate 2 bubbles/second, and temperature 460–480°.

*Hydrogenation of* $CH_2{=}CHCF_2CF_2CH{=}CH_2$. Hydrogenation of the diene was effected in the same manner as that used with $C_3F_7CH{=}C(CH_3)_2$. The hydrocarbon, $C_2H_5C_2F_4C_2H_5$ (16.3 g., 0.103 mole, 72% practical yield, 85% including estimates in fore and tail cuts) isolated showed negative tests with $Br_2$ and $MnO_4^-$ and absence of olefin bands in its infrared spectra.

*Dehydration of* $CH_3\underbrace{C(OH)(CF_2)_3C}_{O}(CH_3)_2$. The hemiketal (14.4 g., 0.057 mole) and $P_2O_5$ (15 g., 0.104 mole) were heated together and the product distilled out. The main product (9.8 g., 0.042 mole, 73.7%) boiled at 136°. This olefin, $CH_2{=}\underbrace{C(CF_2)_3C}_{O}(CH_3)_2$, showed the usual tests with $Br_2$ and $MnO_4^-$ and had an infrared spectra (max. at 5.92 $\mu$) which confirmed the olefin and showed absence of alcohol and carbonyl bands.

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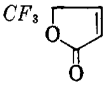
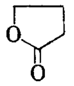
[17] A. L. Henne and P. Hinkamp, *J. Am. Chem. Soc.*, **76**, 5147 (1954).

*Hydrogenation of* $CH_2{=}\underbrace{C(CF_2)_3C}_{O}(CH_3)_2$. The olefin (32.6 g., 0.139 mole) in 50 ml. of dry ether with 50 mg. of $PtO_2$ absorbed 3.41 atmospheres of hydrogen in 37 hr. in the Parr Hydrogenation apparatus. Fractionation gave: $CH_3\underbrace{CH(CF_2)_3C}_{O}(CH_3)_2$ (22.1 g., 0.094 mole, 67.3% including estimates in fore and tail cuts) boiling mostly at 138–140°. Infrared spectra of the oxide showed no olefin or carbonyl group. An alcohol (8.8 g., 0.037 mole, 26.6% including estimates in fore and tail cuts) boiling mostly at 165° was also isolated. The infrared spectra of this material showed an alcohol band (max. at 2.92 μ).

*Condensation of* $(CH_2)_2(CO_2C_2H_5)_2$ *with* $CF_3CO_2C_2H_5$ *in presence of* $NaOC_2H_5$. $NaOC_2H_5$ (4 moles) was prepared from Na sand (92 g., 4 g.a.a.) and $C_2H_5OH$ (184 g., 4 moles) and suspended in 1 liter of dry ether. $CF_3CO_2C_2H_5$ (586 g., 4 moles) was added with some external cooling to the $NaOC_2H_5$ slurry. Half of the $(CH_2)_2(CO_2C_2H_5)_2$ (174 g. of 348 g., 2 moles) was added dropwise at room temperature in 1.25 hr. to the continuously stirred solution. The mixture was refluxed under a water condenser which led to a dry ice trap for 12 hr. The remainder of the $(CH_2)_2(CO_2C_2H_5)_2$ was added in 2.75 hr. and the mixture refluxed for 24 hr. The solvent was then removed and on fractionation of it, small amounts of recovered ester, $CF_3CO_2C_2H_5$, and $CF_3COCH_3$, characterized as $CF_3CONH_2$ (m.p. 75°, mixed m.p. 75°) and 2,4-DNPH of $CF_3COCH_3$ (m.p. 138°, mixed m.p. 138°) respectively; ethyl alcohol (170 g., 3.7 moles), and a small amount of unfluorinated carbonyl containing compound in the tails. The remaining solid mass was neutralized with 1200 ml. of 25% $H_2SO_4$ solution and the resulting organic layer (885 g.) was added to 200 ml. of 25% $H_2SO_4$ solution. The two layer system, continuously stirred, was refluxed under a reflux head whose outlet led to a dry ice receiver and trap for 2.5 days, at which time no further evidence of $CO_2$ evolution was noted. In the dry ice trap, 45 g. of material was isolated and identified as before as mostly $CF_3CO_2C_2H_5$ and lesser amounts of $CF_3COCH_3$. The ether extract of the main organic layer was dried and fractionated to give small amounts of $CF_3CO_2C_2H_5$, an intermediate cut consisting largely of ethyl alcohol, and a main fraction of a high boiling material and tar. Fractionation of this main cut gave a yellowish product (236 g.) boiling between 170–172° and tar (50 g.). Refractionation of the yellowish product gave a slightly yellow liquid (200 g.) boiling at 76°/16 mm. Infrared spectra (max. at 5.62 μ and 6.24 μ) confirmed other evidence that it was an unsaturated lactone. The structure of this entity was ascertained by a study of comparative reactions of it and alpha and beta angelicalactones as follows:

| Reaction with: | α angelicalactone gave: | β angelicalactone gave: | This lactone gave: |
|---|---|---|---|
| $H_2$[18] | Acid | Saturated lactone | Saturated lactone |
| Aniline[19] | Anilide | No reaction | No reaction |
| Alcoholic HCl | Ester of keto acid | No reaction | No reaction |
| $Br_2$ | Decolorized | No reaction | No reaction |
| $MnO_4^-$ | $MnO_2$ | $MnO_2$ | $MnO_2$ |

*Hydrogenation of* $CF_3$  . The unsaturated lactone (7.5 g., 0.05 mole) in 40 ml. of dry ether with 100 mg. of $PtO_2$ was hydrogenated in the Parr hydrogenation apparatus to give a product (6.0 g., 0.039 mole, 80%) boiling 78–79°/25 mm. Infrared spectra showed loss of double bond and presence of lactone group (max. at 5.60 μ). Larger runs gave nearly quantitative results. The product on treatment with liquid $NH_3$ gave a crystalline product melting at 46° and confirmed by infrared spectra (max. at 3.10 μ, 6.05 μ and 6.22 μ) to be the amide.

*Condensation of* $CF_3$  *with* $CF_3CO_2C_2H_5$ *in presence of* $NaOC_2H_5$. $CF_3CO_2C_2H_5$ (284 g., 2 moles) was added with some external cooling to a slurry of $NaOC_2H_5$ in 700 ml. of dry ether. Using a similar procedure as that in previous condensation, the saturated lactone (308 g., 2 moles) was added in 3 hr. and refluxed for 40 hr. Fractionation of the removed solvent gave 3 moles of ethyl alcohol and small amounts of $CF_3CO_2C_2H_5$. The residue was treated with 500 ml. of 25% $H_2SO_4$ solution for neutralization and then 70 ml. of concentrated $H_2SO_4$ was added. Decarboxylation was effected in 84 hr. Fractionation of the dried ether extract of the organic layer gave a hemiketal, $CF_3\underbrace{C(OH)CH_2CH_2CH}_{O}CF_3$ (294 g., 1.31 moles, 67% including estimates on fore and tail cuts) boiling between 139–141°. The hemiketal gave a (−) test with 2,4-DNPH and its infrared spectra (max. at 3.00 μ) showed an alcohol but no carbonyl band.

*Reduction of* $CF_3\underbrace{C(OH)CH_2CH_2CH}_{O}CF_3$ *with* $LiAlH_4$. The hemiketal (264.7 g., 1.18 moles) was added dropwise in 2.6 hr. to $LiAlH_4$ (30 g., 0.80 mole) in 750 ml. of dry ether at 0°. The excess $LiAlH_4$ was decomposed by dropwise addition of $CH_3CO_2C_2H_5$ (35 g., 0.4 mole) at 0° and the complex decomposed by addition of 60 ml. of ice water followed by 60 ml. of concentrated $H_2SO_4$ in 180 ml. of ice water. The ether layer and extracts were washed with dilute $Na_2CO_3$ and dried over $Na_2SO_4$. On fractionation after removal of a forecut of starting material (47 g.), the remainder of the material solidified on cooling. This solid (198.5 g., 0.78 mole, 75%) was confirmed by infrared spectra (max. at 3.08 μ) as the diol. Sublimation of the solid gave a crystalline material melting between 75–120°, presumably a mixture of D, L, and *meso* forms.

*Acetylation of* $CF_3CHOHCH_2CH_2CHOHCF_3$. The diol (190 g., 0.84 mole) in 200 ml. of glacial acetic acid was acetylated by addition of $(CH_3CO)_2O$ (225 g., 2.20 moles, 30% in excess) in the usual manner to give a quantitative yield of crude diacetate boiling at 133°/75 mm., which solidified on standing and melted at 65° on recrystallization from ethyl alcohol. Infrared spectra (max. at 5.67 μ) confirmed presence of acetate esters.

*Pyrolysis of* $CF_3CH(OCOCH_3)CH_2CH_2CH(OCOCH_3)CF_3$. This pyrolysis was carried out in the manner already described. The diacetate (99 g., 0.319 mole) on two passes gave the diene (40 g., 0.21 mole, 66% yield, 83% including estimates in fore and tail cuts) boiling 85.5–86.5°. The rate of diacetate addition, nitrogen flow, and temperature were the same as in the previous case. Infrared spectra (max. at 5.82 μ and 6.06 μ) confirmed the diene structure. Attempts to prepare the adduct with maleic anhydride were unsuccessful indicating the material to be probably *cis*. Carr[20] in this laboratory simultaneously prepared a diene having nearly the same constants (differences probably due to isomers in Carr's material) which gave on hydrogenation the same paraffin.

*Hydrogenation of* $CF_3CH{=}CHCH{=}CHCF_3$. The diene

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(18) F. A. Kuehl, R. P. Winstead, and B. A. Orkin, *J. Chem. Soc.*, 2213 (1950).

(19) W. A. Jacobs and A. B. Scott, *J. Biol. Chem.*, **87**, 601 (1930).

(20) R. L. K. Carr, Ph.D. dissertation to Ohio State University, 1955.

(26.5 g., 0.14 mole) in 40 ml. of dry ether with 50 mg. of $PtO_2$ was hydrogenated to give the paraffin (25.5 g., 0.132 mole, 94% including estimates in fore and tail cuts) boiling 97.5-99.5°. The olefin free spectra was superimposable with that obtained by Carr on a sample prepared by another method and having the constants: b.p. 99°, $n_D^{20}$ 1.3103, and $d_4^{20}$ 1.231. (My data for a purified sample: b.p. 99°, $n_D^{20}$ 1.3105, and $d_4^{20}$ 1.232.)

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COLUMBUS, OHIO

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[CONTRIBUTION FROM THE ROHM & HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION]

# Preparation of Esters of Pentaerythritol Arsenite and of Other Pentaerythritol Esters

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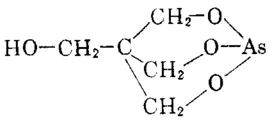
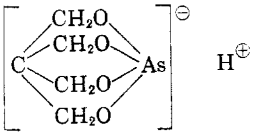
Several esters of pentaerythritol arsenite (I) have been prepared. The arsenite ester portion of these compounds was found to be selectively hydrolyzed, acetolyzed, or nitrolyzed to produce the corresponding pentaerythritol monoester, the pentaerythritol ester triacetate, or the ester of pentaerythritol trinitrate.

Esters of pentaerythritol can be prepared in several ways,[1] but selective partial esterification is not easily carried out. One obvious method of preparation of pentaerythritol monoesters would be that of blocking three of the hydroxyl groups with some functional group that could be removed readily. Such a monofunctional pentaerythritol, the product obtained by merely heating a mixture of arsenic trioxide and pentaerythritol and removing the water formed, is pentaerythritol arsenite, I.[2] This compound, m.p. 106–107°, also has been formulated as II and designated pentaerythritol arsenious acid.[3] However, the infrared spectrum of pentaerythritol arsenite which possessed the characteristic hydroxyl absorption at 3420 cm.$^{-1}$ (Nujol mull), and the facile esterification of the arsenite support the structure (I) originally formulated by Englund.

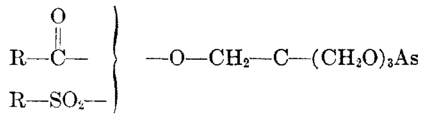


I



II

Esterification of I by the conventional methods outlined in the experimental section to produce the carboxylic or sulfonic acid esters III proceeded readily. The esters prepared are listed in Table I.



$$\left.\begin{matrix} R-\overset{O}{\overset{\|}{C}}- \\ R-SO_2- \end{matrix}\right\} -O-CH_2-C-(CH_2O)_3As$$

III

These esters and the arsenite I were not hygroscopic, but were hydrolyzed on contact with water. Because these esters were susceptible to hydrolysis, isolation was accomplished by evaporating the reaction mixture to dryness and then either extracting the ester into petroleum ether (Method B, Table I) or by adding cold methanol to remove the pyridine hydrochloride and leave the ester as a residue (Method C, Table I). Pentaerythritol acetate arsenite, however, was prepared from isopropenyl acetate and pentaerythritol arsenite (Method A, Table I), and the acetate was distilled directly from the reaction mixture.

As expected, the pentaerythritol arsenite esters hydrolyzed to produce the corresponding pentaerythritol monoesters. This hydrolysis was carried out efficiently by placing a methylene chloride solution of the arsenite ester on a short silica gel column and eluting the hydrolyzed product with methanol in methylene chloride. The pentaerythritol monoesters prepared in this way are listed in Table II.

Acetolysis of some of the arsenite esters III was carried out to produce the corresponding ester triacetate. This reaction proceeded readily on mixing the ester III, acetic anhydride, and a catalytic amount of sulfuric acid. In addition to pentaerythritol tetracetate, pentaerythritol tosylate triacetate, m.p. 70° and pentaerythritol benzoate triacetate, m.p. 95°, were prepared in this manner.

The nitrolysis of the arsenite esters to produce an organic acid ester of pentaerythritol trinitrate[4] also appeared to be a general reaction. Both pentaerythritol arsenite *p*-toluenesulfonate and pentaerythritol arsenite acetate were converted to the trinitrate esters on treatment with 90% nitric acid at 0°. The same nitration procedure

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[1] E. Berlow, R. H. Barth, and J. F. Snow, *The Pentaerythritols*, Reinhold Publishing Corporation, New York, N.Y., 1958, pp. 212–58.

[2] B. Englund, *J. prakt. Chem.*, **124**, 191 (1930).

[3] Ref. (1) p. 50.

[4] N. S. Marans, D. E. Elrick, and R. F. Preckel, *J. Am. Chem. Soc.*, **76**, 1304 (1954).