cyanuric chloride and the fluoro alcohol. Yields of 65–80% were obtained when 1,1,5-tri-H-perfluoropentanol or 1,1,7-tri-H-perfluoroheptanol were used, but low yields were obtained from the other fluoro alcohols, probably because of solubility differences.

The toluene–collidine method could be successfully applied to the synthesis of the bridged compound 2,2,-3,3-tetrafluoro-1,4-bis[2,4-bis(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine-6-oxy]butane from 2,2,3,3-tetrafluorobutane-1,4-diol and 2-chloro-4,6-bis(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine in a moderate yield. The result was somewhat unexpected since cyanuric chloride and 1,4-butanediol are reported to give tetrahydrofuran in the presence of aqueous sodium hydroxide.[6] None of the fluorine-substituted tetrahydrofuran derivative could be isolated from the reaction mixture in this work.

Fully chlorinated derivatives could be prepared by the ultraviolet-catalyzed chlorination of the fluoroalkoxy-*s*-triazines in carbon tetrachloride. The chlorinated derivatives were less stable than the unchlorinated compounds and could not be distilled. Although antimony fluorides have been used to fluorinate fluorine-substituted α-chloro ethers, no reaction occurred when the chlorinated fluoroalkoxy-*s*-triazines were treated with $SbCl_3$ and $SbCl_3F_2$, either in the absence of a solvent or in a nonreactive solvent such as *n*-decane or benzotrifluoride. Other solvents such as dimethyl sulfoxide and dimethylacetamide decomposed the chlorinated fluoroalkoxy-*s*-triazines.

Experimental

2,4,6-Tris(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine.—A stirred solution of 14.7 g. (0.080 mole) of cyanuric chloride in 100 ml. of toluene was treated sequentially with solutions of 83.6 g. (0.25 mole) of 1,1,7-tri-H-perfluoroheptanol in 130 ml. of toluene and 30.6 g. (0.25 mole) of *s*-collidine in 50 ml. of toluene. The time required for each addition was about 15 min. After the resulting mixture was refluxed for 2 hr., cooled, and filtered, 36.0 g. (calcd. 37.1 g.) of collidine hydrochloride was recovered by filtration. Evaporation of the solvent and distillation of the product through a 30-cm. vacuum-jacketed column gave 72.0 g. (84%) of 2,4,6-tris(1,1,7-H-perfluoroheptoxy)-*s*-triazine, b.p. 172–182° (0.04 mm.). After recrystallization from a 1:1 mixture of toluene and petroleum ether (b.p. 35–60°), 67.2 g. (78%) of the product, m.p. 54–55.5°, was obtained.

Anal. Calcd. for $C_{24}H_9F_{36}N_3O_3$: C, 26.90; H, 0.85; F, 63.85. Found: C, 26.59; H, 0.74; F, 63.63.

Diethyl ether was used as the solvent in one preparation of tris(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine; however, only 63% of the required collidine hydrochloride was isolated. Replacement of the ether with toluene and additional heating was required to precipitate the remaining collidine hydrochloride.

2,4-Bis(perfluorophenoxy)-6-(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine.—To a stirred solution of 48.0 g. (0.100 mole) of 2,4-dichloro-6-(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine in 100 ml. of ether was added a solution of 38.8 g. (0.210 mole) of pentafluorophenol in 80 ml. of diethyl ether, and the resulting mixture was treated with a solution of 25.4 g. (0.210 mole) of *s*-collidine in 60 ml. of ether. Each addition required about 15 min. The mixture was refluxed for 2 hr., cooled, and filtered to give 35.5 g. (calcd. 31.4 g.) of collidine hydrochloride. Evaporation of the ether and fractional distillation of the residue gave 69.0 g. (89%) of 2,4-bis(perfluorophenoxy)-6-(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine, b.p. 161–162° (0.07 mm.), $n^{30}D$ 1.4238.

Anal. Calcd. for $C_{22}H_3F_{22}N_3O_3$: C, 34.08; H, 0.39; F, 53.92. Found: C, 34.40; H, 0.57; F, 53.65.

2,4-Dichloro-6-(1,1,3-tri-H-perfluoropropoxy)-*s*-triazine.—A stirred solution of 184 g. (1.00 mole) of cyanuric chloride in 2250 ml. of diethyl ether was treated first with 131 g. (1.00 mole) of 1,1,3-tri-H-perfluoropropanol in 500 ml. of ether, and then with a solution of 121 g. (1.00 mole) of *s*-collidine in 200 ml. of ether. Both reagents were added in rapid drops. When the product was refluxed 2 hr., cooled, and filtered, 147 g. (calcd. 157 g.) of collidine hydrochloride was recovered. Evaporation of the solvent and distillation of the residue through a 30-cm. vacuum-jacketed column gave 195 g. (70%) of 2,4-dichloro-6-(1,1,3-tri-H-perfluoropropoxy)-*s*-triazine, b.p. 111–116° (5.6 mm.), $n^{25}D$ 1.4624. Redistillation gave 173 g. of the product boiling at 118° (9 mm.), $n^{27}D$ 1.4613.

Anal. Calcd. for $C_6H_3Cl_2F_4N_3O$: C, 25.73; H, 1.08; Cl, 25.32; F, 27.15. Found: C, 25.77; H, 1.35; Cl, 25.09; F, 27.09.

2,4-Bis(1,1,7-tri-H-perfluoroheptyloxy)-6-(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine.—A solution of 38.0 g. (0.10 mole) of 2,4-dichloro-6-(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine in 100 ml. of carbon tetrachloride was added to 66.4 g. (0.20 mole) of 1,1,7-tri-H-perfluoroheptanol dissolved in 100 ml. of 2 *N* sodium hydroxide solution and stirred and maintained at 0° for 2 hr. After the organic phase was separated and evaporated, the product distilled at 182–187° (0.3 mm.) and weighed 67.4 g. (69%), $n^{29}D$ 1.3595.

Anal. Calcd. for $C_{22}H_9F_{32}N_3O_3$: C, 27.20; H, 0.93; F, 62.60. Found: C, 27.51; H, 1.18; F, 62.88.

2,2,3,3-Tetrafluoro-1,4-bis[2,4-bis(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine-6-oxy]butane.—A stirred mixture of 3.2 g. (0.02 mole) of 2,2,3,3-tetrafluorobutane-1,4-diol and 23.0 g. (0.04 mole) of 2-chloro-4,6-bis(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine in 100 ml. of toluene was treated with a solution of 4.8 g. (0.04 mole) of *s*-collidine in 15 ml. of toluene, and the mixture was refluxed 2 hr. The product was cooled to 50–60° and filtered, and the solvent was evaporated from the filtrate. The residual oil crystallized on storage at 4°. Recrystallization from a 1:1 (v./v.) mixture of toluene and petroleum ether (b.p. 60–90°) gave 14.7 g. (59%) of the product melting at 99–103°. Two additional crystallizations gave 7.5 g. (30%) of the purified product, m.p. 105.5–106.5°.

Anal. Calcd. for $C_{30}H_{18}F_{36}N_6O_6$: C, 29.05; H, 1.30; F, 55.14. Found: C, 29.20; H, 1.18; F, 55.04.

2,4,6-Tris(1,1,7-trichloroperfluoroheptoxy)-*s*-triazine.—A solution of 21.4 g. (0.020 mole) of 2,4,6-tris(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine in 150 ml. of carbon tetrachloride at 50° was treated with chlorine under ultraviolet irradiation, the gas being introduced below the surface of the liquid at a rate of 2 bubbles/sec. for 72 hr. When the product was cooled to room temperature and filtered, 10.4 g. of crystals, m.p. 102.5–104.0°, was obtained. Additional cooling in an ice bath gave 13.8 g. of product, m.p. 107.5–108.5°, and evaporation of filtrate gave another 2.1 g. of crystals, m.p. 107–108.5°. The combined fractions (26.3 g.) represented a 96% yield. Recrystallization from carbon tetrachloride gave 24.3 g. (89%) of product, m.p. 105–106°. The n.m.r. spectrum indicated that the compound did not contain hydrogen.

Anal. Calcd. for $C_{24}Cl_9F_{36}N_3O_3$: C, 20.87; H, 0.00; Cl, 23.10; F, 49.52. Found: C, 20.80; H, 0.0; Cl, 23.24; F, 49.33.

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(6) A. J. Matuszko and M. S. Chang, *Chem. Ind.* (London), 882 (1963).

A Stable 1,4-Dihydronaphthalen-1,4-imine

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Previous attempts[1-3] to prepare 1,4-dihydronaphthalen-1,4-imines by the addition of benzyne to various

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(1) G. Wittig and W. Behnisch, *Ber.*, **91**, 2358 (1958).

(2) G. Wittig and B. Reichel, *ibid.*, **96**, 2851 (1963).

(3) E. Wolthuis, D. Vander Jagt, S. Mels, and A. De Boer, *J. Org. Chem.*, **30**, 190 (1965).

N-substituted pyrroles have yielded instead N-substituted 1- or 2-naphthylamines, apparently resulting from rearrangement of the unstable intermediate imines.

It has now been found that benzyne adds to N-benzyl-2,3,4,5-tetramethylpyrrole (1) to give the stable imine, 1,2,3,4-tetramethyl-1,4-(N-benzylimino)-1,4-dihydronaphthalene (2). Its preparation and some of its properties are described herewith.

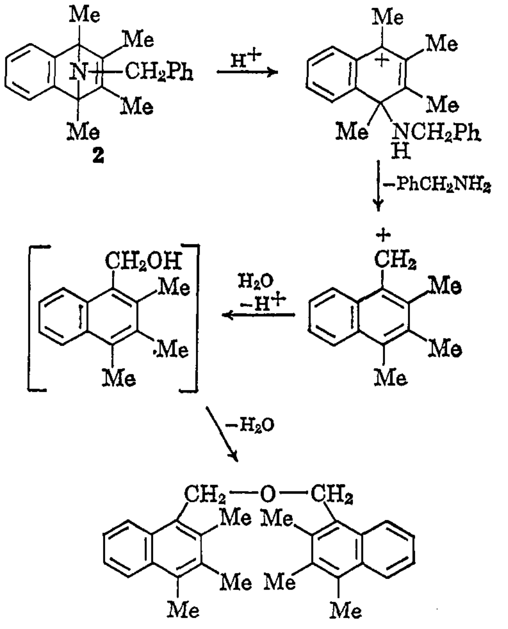
The pyrrole 1 was prepared in good yield, essentially by the method described earlier for similar compounds.[3] Its addition to benzyne proceeded smoothly, and the product imine was isolated without difficulty. Elementary analyses and molecular weight determinations indicated that the product is a 1:1 adduct of benzyne and the pyrrole. It is decidedly basic, and titration of it with standard perchloric acid[4] confirmed the expected molecular weight. It is soluble in cold, dilute acids, and when the acidic solution is made alkaline within a few minutes the original compound is reprecipitated in good yield and purity. However, if the acidic solution is boiled, a crystalline product forms almost at once, which proves to be bis[2,3,4-trimethylnaphthyl-(1)-methyl] ether.[5] The other product formed in this reaction is benzylamine which is isolated in nearly theoretical yield as its benzoyl derivative.

The reaction of the imine with acid is reminiscent of a similar one involving 1,2,3,4-tetramethyl-1,4-epoxy-1,4-dihydronaphthalene in methanol with hydrochloric acid[5] and suggested that the imine should react similarly. Indeed, reaction of 2 in methanol with a few drops of concentrated hydrochloric acid gives 1-(methoxymethyl)-2,3,4-trimethylnaphthalene[5] and benzylamine. Furthermore, reaction of 2 in methanol with dry hydrogen chloride gives 1-(chloromethyl)-2,3,4-trimethylnaphthalene.[5] These reactions indicate that the imine is an analog of the epoxides.

Spectral evidence also confirms the identity of imine 2. Its ultraviolet spectrum is definitely more like that of benzene than of naphthalene, indicating only one aromatic ring. Its infrared spectrum gives no evidence for the presence of the N-H bond, a fact which was confirmed by its resistance to acetylation. Its n.m.r. spectrum clearly shows the presence of two pairs of equivalent methyl groups, which rules out the possibility of other than a 1,4 addition of the pyrrole to the benzyne.

Two properties of this imine deserve special mention. Its great stability (except in acid media) is surprising, for it differs from those proven to be unstable only in the fact that it is more highly methylated. Furthermore, the addition of a little hydrochloric acid to the methanolic solution of the imine 2 causes a pronounced hypsochromic shift in the ultraviolet spectrum, after which neutralization of the acid with ammonium hydroxide restores the original imine spectrum. The hypsochromic shift is very likely due to protonation of the unshared pair of electrons on the nitrogen atom, although the usual type of interaction of these electrons with neighboring π electrons is impossible here. After saturating the isolated double bond, the product still shows the same spectral shift upon addition of acid, but to a lesser degree. This suggests that perhaps the nitrogen electron pair may serve as a bridge for interaction of the π electrons in the separate rings.

The following mechanism is suggested for the rupture of the imine, a route analogous to that given for the epoxides.[5]



Experimental[6,7]

N-Benzyl-2,3,4,5-tetramethylpyrrole (1).—3,4-Dimethyl-2,5-hexanedione (71.1 g.) was mixed with ligroin (125 ml., b.p. 100–115°) in a flask fitted with an agitator and a Barrett water trap. To the stirred mixture were added benzylamine (57 g.) and concentrated hydrochloric acid (4 drops). The mixture was refluxed 2 hr., during which time water (17 ml.) had collected in the trap. It was then distilled under vacuum, first to remove the solvent, and then to give 1 (90 g., 84%), b.p. 165–166° (13 mm.). An analytical sample was obtained by distillation at 141–141.5° (4 mm.): m.p. 21–21.5°; $n^{20}\text{D}$ 1.557; $\lambda_{\max}^{\text{MeOH}}$ mμ (log ϵ) 208 (4.07), 226 sh (3.79).

Anal. Calcd. for $C_{15}H_{19}N$ (213.3): N, 6.57. Found: N, 6.63.

1,2,3,4-Tetramethyl-1,4-(N-benzylimino)-1,4-dihydronaphthalene (2).—Magnesium turnings (2.7 g.) were added to a flask, which was then evacuated and filled with nitrogen to a positive pressure. There was added about 10% of a solution of *o*-bromofluorobenzene (17.5 g.) in THF (50 ml., freshly distilled over lithium aluminum hydride). After the reaction had started, there was added THF (20 ml.), followed by a solution of the pyrrole 1 (21.3 g.) in THF (25 ml.). Then the remaining *o*-bromofluorobenzene solution was added at reflux temperature during about 5 hr. The mixture was refluxed with stirring 2 hr. more and then 16 hr. without stirring. The solvent was removed under vacuum, the residue was extracted twice with hexane, and the hexane solution was cooled and filtered to give 2 (14.5 g., 50%). Recrystallization from hexane gave pure 2 (11.5 g.): m.p. 115.9–116.4°; $\lambda_{\max}^{\text{MeOH}}$ mμ (log ϵ) 208 (4.53), 253 (2.95), 260 (2.97), 266 (2.99), 274 (3.00), 282 (2.92); $\nu_{\max}^{\text{Nujol}}$ 1000–1200 cm.$^{-1}$ (C–N stretch). The n.m.r. spectrum showed sharp absorptions at 84 and 96 c.p.s., indicating two pairs of identical methyl groups. Cryoscopic molecular weight determinations in benzene gave 283. Perchloric acid titration[4] gave a molecular weight of 293.

Reaction of 2 with Aqueous Hydrochloric Acid.—One gram of 2 was dissolved in water (15 ml.) and concentrated hydrochloric acid (1 ml.). (Immediate neutralization of a sample of this solution gave 2.) The acid solution was heated, becoming cloudy

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[4] E. F. Hillenbrand and C. A. Pentz in "Organic Analysis," Vol. III, J. Mitchell, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 145.

[5] E. Wolthuis, B. Bossenbroek, G. DeWall, E. Geels, and A. Leegwater, *J. Org. Chem.*, **28**, 148 (1963).

[6] The authors thank Dr. G. Slomp and his associates at The Upjohn Co., Kalamazoo, Mich., for their assistance in obtaining and interpreting the n.m.r. spectra.

[7] Melting points are corrected. N.m.r. spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as internal standard, and the ultraviolet and infrared spectra were determined on Beckman DB and Perkin-Elmer 21 instruments, respectively.

at 60°, refluxed for 4 hr., and cooled overnight, and the precipitate (needles) was filtered and washed with dilute acid and then water and dried to give 0.620 g., m.p. 170–175°. Two recrystallizations from methanol gave a product, m.p. 188.5–189°. Mixture melting point and infrared and ultraviolet spectra proved it to be bis[2,3,4-trimethylnaphthyl-(1)-methyl] ether.[5] Benzoylation of the acidic filtrate gave 0.511 g., m.p. 105.8–106° (after recrystallization from ligroin), and a mixture melting point with an authentic sample proved it to be N-benzylbenzamide.

Reaction of 2 with Methanolic Hydrochloric Acid.—To a solution of 2 (0.520 g.) in methanol (5 ml.) was added concentrated hydrochloric acid (5 drops). The solution turned pink at once and was refluxed 4 hr., cooled, and poured into water containing excess sodium carbonate. The oily solid so obtained was extracted with hexane; the extract was washed neutral, dried over sodium sulfate, and evaporated to dryness; and the residue was extracted with water (10 ml.) containing concentrated hydrochloric acid (2 drops). The residue, insoluble in acid, weighed 0.150 g., m.p. 73–75°, and recrystallization from methanol gave the pure product, m.p. 76–76.5°, identified by mixture melting point and spectra to be 1-(methoxymethyl)-2,3,4-trimethylnaphthalene.[5] The acidic filtrate was made alkaline, giving 0.270 g. of a solid, m.p. 108–112°, which was recrystallized from hexane to give the starting material, 2, m.p. 115.5–116°. Benzylamine was identified in the filtrate by benzoylation.

Reaction of 2 in Methanol with Dry Hydrogen Chloride.—A solution of 2 (0.554 g.) in dry methanol (10 ml.) was saturated at 20° with HCl gas. The pink solution was evaporated to about 5 ml. and cooled to give crystals, which were filtered and washed with cold methanol to give 0.054 g., m.p. 93.5–94°, identified by infrared spectrum as 1-(chloromethyl)-2,3-4-trimethylnaphthalene.[5] Reaction of it with boiling methanol gave 1-(methoxymethyl)-2,3,4-trimethylnaphthalene.[5]

Ultraviolet Spectral Changes on Protonation of 2.—To a solution of 2 (2.71 mg.) in methanol (10 ml.) was added 3 M hydrochloric acid (1 drop), whereupon the spectrum showed $\lambda_{\max}^{\text{MeOH}}$ mμ (log ε) 252 (2.80) 258 (2.80), 262 sh (2.75), 267 sh (2.64), and 280 sh (2.21). Within 15 min. after the addition of the acid, the solution was neutralized with 4 *M* ammonium hydroxide (1 drop), after which the spectrum was that of 2.

A sample of 2 was hydrogenated in the Brown[2] Hydro-analyzer and found to absorb 1.05 moles of hydrogen/mole of 2. The product was isolated and gave the spectrum: $\lambda_{\max}^{\text{MeOH}}$ mμ (log ε) 205 (4.31), 256 sh (2.88), 261 (2.99), 267 (3.08), 274 (2.99). After acidification (as above), the spectrum showed: $\lambda_{\max}$ mμ (log ε) 210 (4.21), 260 sh (2.76), 263 (2.79), 270 (2.69). Upon neutralization, the solution again gave the original maxima.

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The Reaction of Lead Tetraacetate with Carbethoxyhydrazones[1,2]

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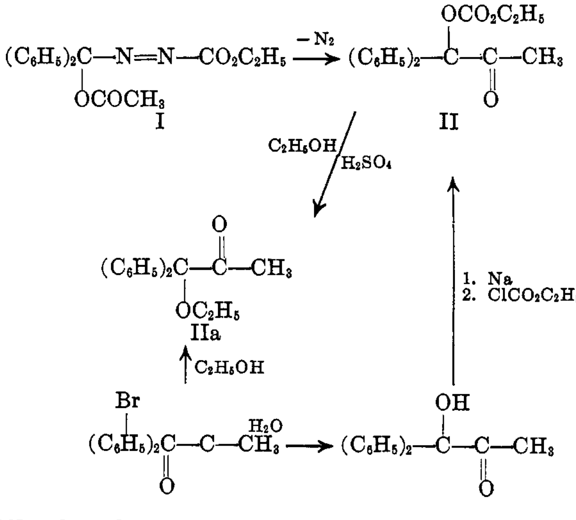
As part of a project designed to study azo and hydrazo aliphatic acid derivatives,[3] it appeared to be of interest to subject available carbethoxyhydrazones to treatment with lead tetraacetate. It was assumed that acetoxyazo esters, $R_2C(OCOCH_3)—N{=}N—CO_2C_2H_5$, would be obtained in high yields according to the reaction described by Iffland, Salisbury, and Schafer[4] for the oxidation of ketohydrazones.

When benzophenone carbethoxyhydrazone was caused to react with lead tetraacetate, a mixture of products resulted. This was separated to give the expected ethyl acetoxydiphenylmethylazocarboxylate (I) in 28% yield, an unknown oxygen-containing compound $C_{18}H_{18}O_4$ (II) in about 15% yield, and benzophenone. It was thought that acetic acid, formed during the reaction, had caused decomposition of the azo ester. Accordingly, the reaction was repeated in the presence of calcium oxide; however, there appeared to be no distinct advantage over the experiments conducted without the latter agent.

Analytical data suggested that II might be ethyl acetylbenzilate[5]; however, a mixture melting point determination and comparison of infrared and n.m.r. spectra of the compounds showed that they were similar but not identical. Alkaline hydrolysis of II produced benzhydrol and a small amount of an unidentified acidic material. Treatment of II with ethanol in the presence of sulfuric acid gave a product, IIa, which on heating with 18% hydrochloric acid was converted to a substance, IIb. An infrared spectrum of the latter showed hydroxyl and carbonyl absorption, and a positive test was obtained with 2,4-dinitrophenylhydrazine reagent. Compound II gave a material similar to IIb when heated with 18% hydrochloric acid. The product IIa was shown to be 1,1-diphenyl-1-ethoxy-2-propanone by analysis and comparison with an authentic sample prepared by ethanolysis of the known 1-bromo-1,1-diphenyl-2-propanone. This suggested that II is acetyldiphenylmethyl ethyl carbonate and was formed from the acetoxyazo ester I by a molecular rearrangement. The structure of II was confirmed by synthesis from the sodium derivative of 1,1-diphenyl-1-hydroxy-2-propanone and ethyl chloroformate.



Iffland and Davies[6] have described a similar rearrangement in which benzophenone 4,4-diethylsemicarbazone was transformed into 2-oxo-1,1-diphenyl-

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[1] This study was supported by Grant No. CA-04662 from the Cancer Chemotherapy National Service Center, National Cancer Institute, U. S. Public Health Service.

[2] Presented in part at the 15th Annual Kansas City Chemistry Conference of the American Chemical Society, Nov. 15, 1963.

[3] M. C. Chaco and Norman Rabjohn, *J. Org. Chem.*, **27**, 2765 (1962).

[4] D. C. Iffland, L. Salisbury, and W. R. Schafer, *J. Am. Chem. Soc.*, **83**, 747 (1961).

[5] Ethyl acetylbenzilate, m.p. 73–74°, was prepared by acetylation of ethyl benzilate. It was observed that ethyl acetylbenzilate undergoes solvolysis when heated with ethanol and sulfuric acid to give ethyl diphenylethoxyacetate, while acetylbenzilic acid under similar conditions affords diphenylethoxyacetic acid and a small amount of ethyl diphenylethoxyacetate.

[6] D. C. Iffland and T. M. Davies, *J. Am. Chem. Soc.*, **85**, 2182 (1963).