ester, m.p. 78–78.5°; $[\alpha]^{21}\text{D}$ −30.3°. Two other preparations of this ester following the methods of Page[2] and of Cataline[4] gave material melting at 75–76° and 74–75°, respectively. Crystallizations from acetone, ethanol or chloroform–methanol did not alter the melting point in any case. A sample of our material maintained at 75° for 100 hours melted over the range 75–85°. Another sample, maintained at 80° for 100 hours melted, after solidification, over the range 60–78°.

Our preparation would appear to be a hitherto unreported isomorphic modification of cholesteryl laurate.

Experimental[7]

Starting Materials.—Cholesterol (Amerchol), m.p. 141–143°; Lauric Acid (Eastman Kodak), m.p. 37°. The acid chloride gave quantitative yields of the amide, m.p. 99° (lit.[8] 98°) and anilide, m.p. 75° (lit.[8] 76°) when treated with ammonium hydroxide and aniline, respectively.

Cholesteryl Laurate.—A solution of 28 g. of cholesterol and 17.5 g. of lauroyl chloride in 25 cc. of pyridine was heated to boiling, and, after one minute, allowed to cool. The brown solid obtained on cooling was dissolved in ether, washed free of excess pyridine and acid and the ether dried over anhydrous sodium sulfate. Distillation of the ether left a tan solid, m.p. 73–76°. Three crystallizations from chloroform–methanol yielded 33 g. (80%) of white needles, m.p. 78–78.5°, $[\alpha]^{21}\text{D}$ −30.3° ($CHCl_3$).

Anal.[9] Calcd. for $C_{39}H_{68}O_2$: C, 82.33; H, 12.05. Found: C, 82.21; H, 11.99.

Cholesteryl Laurate.[2]—Lauric acid (4 g.) and cholesterol (2 g.) were heated in a stream of carbon dioxide at 200° for 3 hours. After removal of excess acid the ester was obtained as white needles from chloroform–methanol, m.p. 75–76°; $[\alpha]^{19}\text{D}$ −30.2° ($CHCl_3$). Mixed melting point with first preparation, 75–76°.

Cholesteryl Laurate.[4]—A solution of 5.8 g. of cholesterol, 3 g. of lauric acid and 0.13 g. of *p*-toluenesulfonic acid in 75 cc. of benzene was allowed to reflux, under constant water take-off, for 3 hours. After removal of all acidic material, the ester was crystallized from chloroform–methanol, m.p. 74–75°, $[\alpha]^{21}\text{D}$ −28.8° ($CHCl_3$). Mixed melting point with the initial preparation, 74–75°; mixed melting point with the second preparation, 75–76°.

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(7) All melting points corrected.

(8) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 223.

(9) Analysis by Mr. V. Tashinian of the microanalytical laboratory, University of California, Berkeley.

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Trifluoromethyl Substituted Biphenyls and Diphenyl Ethers

BY MOUSHY MARKARIAN

The recent interest in trifluoromethyl substituted biphenyls and diphenyl ethers[1,2] prompts us to report the syntheses of 3,3′-bis-(trifluoromethyl)-biphenyl, 4,4′-bis-(trifluoromethyl)-biphenyl, 3-trifluoromethyl diphenyl ether, 3-trifluoromethyl-4′-chlorodiphenyl ether, 3-trifluoromethyl 3′-ethyldiphenyl ether and 3-trifluoromethyl phenyl-α-naphthyl ether; the two bis-(trifluoromethyl)-biphenyls were prepared by coupling the appropriate Grignard reagent with either silver bromide[1] or cupric chloride.[3] For the preparation of 4,4′-bis-(trifluoromethyl)-biphenyl, the necessary starting material is *p*-bromobenzotrifluoride,[4] and we have developed a simple two-step preparation of this material. The *m*-bromobenzotrifluoride was obtained by the method of Simons and Ramler.[5]

The trifluoromethyl diphenyl ethers were all prepared by the method of Ullman and Sponagel.[6]

Experimental[7]

3,3′-Bis-(trifluoromethyl)-biphenyl.—*m*-Bromobenzotrifluoride (225 g.) was reacted with magnesium turnings (24.5 g.) and anhydrous cupric chloride (140 g.) in dry ether (750 cc.). After refluxing for two hours, the reaction mixture was poured onto ice and treated with excess concentrated hydrochloric acid to dissolve the copper chloride. The ether layer was washed with water and dilute sodium hydroxide and dried over anhydrous magnesium sulfate. The ether was removed and the residue was fractionated at 1 mm. pressure to yield 62 g. (42.7%) of colorless liquid; b.p. 79–80°; $n^{20}\text{D}$ 1.4899.

Anal. Calcd. for $C_{14}H_8F_6$: C, 57.92; H, 2.78. Found: C, 58.00, 57.88; H, 2.90, 2.78.

***p*-Bromobenzotribromide.**—Bromine (48 g.) was added dropwise to *p*-bromotoluene (17.1 g.) heated to 120–130° and illuminated with a 150-watt bulb. The temperature was gradually increased during the course of the addition and attained 210° when the bromine addition was completed. This final temperature was maintained another 10 minutes. The reaction mixture was then cooled and poured into an evaporating dish where it solidified to a crystalline mass; m.p. 72–76°; yield 38 g. (93%). Recrystallization from hexane raised the m.p. to 81–82°.

Anal. Calcd. for $C_7H_9Br_4$: C, 20.62; H, 0.99. Found: C, 20.71, 20.50; H, 1.00, 0.82.

***p*-Bromobenzotrifluoride.**—*p*-Bromobenzotribromide (175 g., 0.43 mole) and antimony trifluoride (89.4 g., 0.50 mole) were ground together in a mortar and placed in a 250-cc. flask equipped with a condenser for distillation. The mixture was heated with a free flame until reaction took place with distillation, and heating was maintained until distillation became negligible. The distillate and benzene extracts of the flask residue were steam distilled and then distilled at atmospheric pressure to yield 59 g. (60.9%) of *p*-bromobenzotrifluoride; b.p. 153–155°; $n^{25}\text{D}$ 1.4705.

4,4′-Bis-(trifluoromethyl)-biphenyl.—The Grignard reagent prepared from 6.2 g. of *p*-bromobenzotrifluoride was treated with 6.2 g. of anhydrous silver bromide and stirred overnight at room temperature. The ether solution was filtered, washed with water, and dilute sodium hydroxide and dried over anhydrous magnesium sulfate. The ether was removed to give 3 g. of solid, m.p. 75–85° which on recrystallization from methanol gave 1 g. (25%), m.p. 91–92°.

Anal. Calcd. for $C_{14}H_8F_6$: C, 57.92; H, 2.78; F, 39.30; mol. wt., 290. Found: C, 57.78, 57.90; H, 2.95, 2.72; F, 39.32, 39.53; mol. wt. (Rast), 310.

3-Trifluoromethyl Diphenyl Ether.—Phenol, 118 g. (1.25 moles) and 85% potassium hydroxide, 56 g. (0.85 mole) were placed in a one-liter three-neck flask equipped with stirrer, reflux condenser with Dean and Stark trap, and thermometer. Stirring was started and the mixture was heated to 140–150° until all of the potassium hydroxide had dissolved. The mixture was then cooled to 110° and 1 g. of copper powder was added, followed by 225 g. (1 mole) of *m*-bromobenzotrifluoride. The temperature of the reaction mixture was gradually raised until refluxing began with separation of water in the Dean and Stark trap. The water was periodically removed and the *m*-bromobenzotrifluoride returned to the reaction. As the reaction progressed, the temperature gradually rose to 190° with separation of potassium bromide and the amount of water separating became negligible. The reaction mixture was maintained at 190°

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(1) C. K. Bradsher and J. B. Bond, THIS JOURNAL, **71**, 2659 (1949).

(2) J. K. Wolfe, U. S. Patent 2,547,679.

(3) J. Krizewsky and E. E. Turner, *J. Chem. Soc.*, **115**, 559 (1919).

(4) For another preparation of *p*-bromobenzotrifluoride see R. G. Jones, THIS JOURNAL, **69**, 2346 (1947).

(5) J. H. Simons and E. O. Ramler, *ibid.*, **65**, 389 (1943).

(6) F. Ullman and P. Sponagel, *Ber.*, **38**, 2211 (1905).

(7) The microanalyses are by Dr. Carl Tiedcke.

for two hours, then cooled and poured into 1 liter of water containing 30 g. of sodium hydroxide. The mixture was steam distilled, the product separated from the aqueous layer and dried over anhydrous magnesium sulfate and redistilled at reduced pressure to obtain 184 g. (77.5%) of 3-trifluoromethyl diphenyl ether, b.p. 81° (1 mm.), $n^{20}D$ 1.5118.

Anal. Calcd. for $C_{13}H_9F_3O$: C, 65.53; H, 3.81. Found: C, 65.18, 65.04; H, 3.86, 3.98.

Three other trifluoromethyl substituted ethers were prepared as above.

3-Trifluoromethyl 4'-Chlorodiphenyl Ether.—From 169 g. (0.75 mole) of *m*-bromobenzotrifluoride and 121 g. (0.94 mole) of *p*-chlorophenol was obtained 75 g. (36.8%) of 3-trifluoromethyl 4'-chlorodiphenyl ether, b.p. 94–95° (1 mm.), $n^{20}D$ 1.5278.

Anal. Calcd. for $C_{13}H_8F_3ClO$: C, 57.30; H, 2.96. Found: C, 56.85, 57.04; H, 3.00, 3.10.

3-Trifluoromethyl 3'-Ethyldiphenyl Ether.—From 118 g. (0.525 mole) of *m*-bromobenzotrifluoride and 64 g. (0.525 mole) of *m*-ethylphenol was obtained 106 g. (76%) of 3-trifluoromethyl-3'-ethyl diphenyl ether, b.p. 89° (1 mm.), $n^{20}D$ 1.5100.

Anal. Calcd. for $C_{15}H_{13}F_3O$: C, 67.68; H, 4.92. Found: C, 67.32, 67.50; H, 5.16, 4.89.

3-Trifluoromethyl Phenyl-α-naphthyl Ether.—From 232 g. (1.03 moles) of *m*-bromobenzotrifluoride and 240 g. (1.87 moles) of α-naphthol was obtained 52.5 g. (17.7%) of 3-trifluoromethyl phenyl-α-naphthyl ether, b.p. 157–158° (3 mm.), $n^{20}D$ 1.5784, with recovery of half the *m*-bromobenzotrifluoride unchanged.

Anal. Calcd. for $C_{17}H_{11}F_3O$: C, 70.08; H, 3.85. Found: C, 70.65, 70.48; H, 3.85, 3.98.

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Internal Rotation. VII. The Energy Difference between the Rotational Isomers of Some Halogen Substituted Ethanes

BY F. E. MALHERBE[1] AND H. J. BERNSTEIN

Liquid 1,1,2-tribromoethane is considered to consist of different isomeric forms.[2] This view is supported by the fact that certain bands, *e.g.*, those at 1183 and 1001 cm.$^{-1}$ which are present in the infrared spectrum of the liquid are absent in the spectrum of the solid tribromoethane (see Table III). In the course of an investigation, by the dilute solution method,[3] of the temperature dependence of the intensity of bands belonging to different rotational isomers anomalous results were obtained, and it was in fact possible to obtain a spurious value for ΔH by investigating a pair of bands belonging to the same isomeric species. This apparent temperature dependence led us to reinvestigate 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane which had been done previously by the dilute solution method.[3] An attempt was made also to determine a value for the energy difference between the isomeric forms in liquid 1,1,2-trichloroethane, 1,1,2-tribromoethane and 1,1,2,2-tetrabromoethane.

Experimental

The infrared spectra were obtained on a Perkin–Elmer Model 12c infrared spectrometer with a Brown electronic recorder. Absorption bands at frequencies above 2000 cm.$^{-1}$ were recorded with a LiF prism, frequencies between 2000 and 660 cm.$^{-1}$ with a NaCl prism, frequencies between 660 and 420 cm.$^{-1}$ with a KBr prism and those below 420 cm.$^{-1}$ with a KRS-5 prism. In the region below 420 cm.$^{-1}$ the liquids only were investigated. The experimental technique and principles of the method have been described previously.[3] Here, a new furnace capable of more accurate temperature control, was used.

The 1,1,2,2-tetrachloroethane was an Eastman Kodak product, distilled through a Stedman column, of 40 theoretical plates, b.p. 146 ± 0.2° at 760 mm.

The 1,1,2,2-tetrabromoethane and 1,1,2-tribromoethane were also Eastman Kodak products, redistilled; b.p. 151 ± 0.2°, 188.4 ± 0.2°, respectively.

The 1,1,2-trichloroethane was a Carbide and Carbon Chemicals product redistilled; b.p. 113 ± 0.2° whereas the sample used in the earlier work[2] had been prepared by a well known method.[4]

Results

1,1,2,2-Tetrachloroethane.—Reinvestigation of the temperature dependence of the pairs of bands at 1279 and 1243 cm.$^{-1}$, respectively, which had been used in the previous work,[3] as well as their behavior on freezing the liquid, led to the conclusion that they belong to the same isomeric form. The apparent temperature dependence of the bands, giving the straight line of Fig. 13 in the earlier paper,[3] is due largely to underestimating the experimental error and perhaps, also to temperature effects which are being investigated in more detail at the present moment in this Laboratory. No suit-

TABLE I

INFRARED SPECTRA OF 1,1,2-TRICHLOROETHANE

Frequencies in cm.$^{-1}$; relative spectral densities in parentheses; (sh) indicates shoulder; frequencies of prominent bands in liquid spectrum which are absent in the solid spectrum are underlined

Liquid (0.025 mm. cell)	Solid (approx. 0.005 mm. layer)	Vapor (10 cm. cell, 100 mm.)
2998 (3)		2943 (3)
2873 (1)		2810 (1)
1430 (7)	1424 (3)	1437 (7)
1308 (5)	1305 (1)	1306 (5)
1264 (7)	1259 (2)	1260 (9)
1237 (5)		
1212 (9)	1212 (5)	1204 (10) doublet
1162 (3)	1162 (1)	1161 (3)
1124 (2)	1120 (1)	
1086 (sh)	1058 (1)	
1050 (3)	1050 (1)	1050 (3)
1010 (2)		
940 (sh)		941 (10)
933 (9)	932 (9)	932 (10)
890 (1)	887 (0)	890 (0)
875 (2)	873 (1)	881 (0)
857 (0)		
849 (0)		
785 (sh)	781 (sh)	796 (10)
777 (7)	770 (8)	787 (10)
730 (10)	727 (10)	736 (10)
700 (5)		
662 (7)	667 (8)	668 (10)
640 (3)	637 (sh)	
613 (0)	613 (0)	
586 (0)	586 (sh)	
569 (0)		
545 (sh)		
524 (3)		
(0.2 mm. cell)		
388 (6)		
330 (3)		

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[1] N. R. C. Post-doctorate Fellow 1950–1951.

[2] L. Kahovec and J. Wagner, *Z. physik. Chem.*, **B47**, 48 (1940).

[3] J. Powling and H. J. Bernstein, THIS JOURNAL, **73**, 1815 (1951).

[4] M. S. Kharasch and M. C. Brown, *ibid.*, **61**, 2142 (1939).