The main reaction mixture, after removal of precipitated sulfur, was washed with sodium bicarbonate solution and extracted with ether. Fractionation of the ether solution gave 56 g. of colorless liquid, with b.p. 126°, n^{20}_{D} 1.3852, d^{20}_{4} 0.978 and a molecular weight of 116. Ethyl carbonate is reported[7] to have b.p. 125.8°, n^{20}_{D} 1.3852, and d^{27}_{4} 0.9752 and has a calculated molecular weight of 118.13. The yield of ethyl carbonate was 93%.

Reaction of Ethoxydichloromethanesulfenyl Chloride with Alcohols.—Ethoxydichloromethanesulfenyl chloride, $\mathrm{C_2H_5\text{-}OCCl_2SCl}$ (II), was treated with methanol in the manner described above. From the reaction mixture, a small yield of colorless liquid with b.p. 105–106°, n^{20}_{D} 1.3790, d^{27}_{4} 1.003 and molecular weight of 104 was isolated. An authentic sample of ethyl methyl carbonate was prepared from methanol and ethyl chlorocarbonate, using pyridine to accept the hydrogen chloride liberated, and the carefully purified product had b.p. 107° (760 mm.), d^{25}_{4} 1.0068, d^{20}_{4} 1.0132, d^{0}_{4} 1.0363, n^{25}_{D} 1.3762 and n^{20}_{D} 1.3780. The calculated molecular weight of ethyl methyl carbonate is 104.1. The yield of ethyl methyl carbonate, based on the quantity of II taken, was less than 10%.

The low-boiling product of the reaction had a boiling point below −20° and a molecular weight of 51.0 indicating that it was methyl chloride rather than the corresponding ethyl compound; the yield of methyl chloride was 72%.

Again following the same procedures, II was treated with *n*-butyl alcohol. From the main reaction mixture a liquid was isolated with b.p. 59° (4 mm.), n^{20}_{D} 1.4116, d^{20}_{4} 0.9237 and molecular weight of 174.5. Butyl carbonate is reported[7] to have b.p. 207.5° (740 mm.), n^{20}_{D} 1.4117, d^{20}_{4} 0.9238 and has a calculated molecular weight of 174.24.

The more volatile product of the reaction had a b.p. of 11.3° and a molecular weight of 64.6. Ethyl chloride is reported to have b.p. 13° and has a calculated molecular weight of 64.52.

---

[7] P. N. Kogerman and J. Kranig, *Chem. Abs.*, **21**, 1729 (1927).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MAINE
ORONO, MAINE

---

t-Alkyl Borates

BY P. D. GEORGE AND J. R. LADD

RECEIVED OCTOBER 18, 1954

Considerable confusion exists concerning *t*-alkyl borates even though the picture on other borate esters is quite clear. The latter are prepared by reaction of hydroxyl compounds with boric oxide or with lower alkyl borates.[1–5]

$$6\mathrm{ROH} + \mathrm{B_2O_3} \rightleftarrows 2(\mathrm{RO})_3\mathrm{B} + 3\mathrm{H_2O}$$

$$3\mathrm{ROH} + (\mathrm{R'O})_3\mathrm{B} \rightleftarrows (\mathrm{RO})_3\mathrm{B} + 3\mathrm{R'OH}$$

The reactions are driven to completion by continuous removal of the water or lower alcohol formed. There is general agreement on the applicability of these methods to *n*-alkyl, *sec*-alkyl and aromatic borates, but the results with *t*-alkyl borates are conflicting.

Some investigators report that *t*-alkyl borates cannot be made by the alcoholysis of boric acid[4,5] or of *n*-alkyl borates.[5] Others report that they can be made by both methods but are too unstable to isolate.[3,6] Nevertheless distillable *t*-butyl borate has been obtained[7] by refluxing *t*-butyl alcohol, boric acid and benzene under an efficient fractional distillation column in order to continuously remove the water formed; other *t*-alkyl borates have been prepared similarly.[8]

We can confirm this recently reported synthesis because we had obtained the same *t*-butyl borate from the alternate synthesis involving alcoholysis of ethyl borate. *t*-Butyl borate was prepared readily in good yield by reaction of *t*-butyl alcohol, ethyl borate and a catalytic amount of sodium under conditions providing for continuous ethanol removal by efficient fractional distillation. Even though equimolar amounts of the starting materials were used, none of the intermediate ethyl *t*-butyl borates was found. The products were ethanol, unreacted ethyl borate and *t*-butyl borate, which was obtained in 45% yield. These results contrast markedly with those obtained upon alcoholysis of ethyl orthosilicate under analogous conditions; there *t*-butyltriethyl silicate was the major product.[9]

When the synthesis of *t*-butyl borate by the alcoholysis of boric acid appeared, we repeated it and obtained results comparable to those reported.[7] This method of preparation is more convenient than the ethyl borate alcoholysis. The latter is complicated by the proximity of the boiling points of ethyl and *t*-butyl alcohols and also by the availability of ethyl borate only as its ethanol azeotrope containing 30% borate.

t-Butyl borate appeared somewhat more hydrolytically stable than *n*- and *sec*-alkyl borates; however the compound hydrolyzed on exposure to atmospheric moisture. Moreover it was about 50% hydrolyzed on standing with distilled water for 24 hours, and it was 100% hydrolyzed on standing with 0.1 *N* HCl for 24 hours.[10] Alkyl borates are apparently more susceptible to hydrolysis than are the corresponding alkyl silicates.[11,12] This difference cannot be rationalized on the basis of electronegativity, inasmuch as boron is more electronegative than silicon. A more attractive explanation is found in the open sextet of the boron atom, which offers a coördination site for the unshared electron pair of the attacking water molecule.

Experimental

A reaction mixture consisting of 952 g. (6.5 moles) of ethyl borate, 518 g. (7.0 moles) of commercial *t*-butyl alcohol and

---

[1] W. J. Bannister, U. S. Patent 1,668,797, May 8, 1928; *C. A.*, **22**, 2172 (1928). See also J. R. Johnson and S. W. Tompkins, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 106.

[2] A. Dupire, *Compt. rend.*, **202**, 2086 (1936).

[3] H. Wuyts and A. Duquesne, *Bull. soc. chim. Belg.*, **48**, 77 (1939); *C. A.*, **33**, 7274 (1939).

[4] A. Scattergood, W. H. Miller and J. Gammon, Jr., THIS JOURNAL, **67**, 2150 (1945).

[5] L. H. Thomas, *J. Chem. Soc.*, 820 (1946)

[6] J. R. Anderson, K. G. O'Brien and F. H. Reuter, *J. Applied Chem.*, **2**, 241 (1952).

[7] S. B. Lippincott, U. S. Patent 2,642,453 (June 16, 1953).

[8] There was an earlier report that *t*-butyl borate had been obtained as an ordinary distillable liquid by reaction of *t*-butyl alcohol with boron triacetate—L. Kahovec, *Z. physik. Chem.*, **43B**, 109 (1939). Other workers[6] could not repeat this synthesis and neither could we.

[9] P. D. George and J. R. Ladd, THIS JOURNAL, **75**, 987 (1953).

[10] These results confirm the report[7] that *t*-butyl orthoborate is hydrolyzed easily. In reference 4 it is stated that diisopropylcarbinyl borate defied all attempts at hydrolysis even in alkaline solution at 100°; nevertheless in the same article there is reported for this compound a quantitative boron analysis made by titrating the boric acid liberated upon hydrolysis with standard sodium hydroxide solution in the presence of mannitol.

[11] C. S. Miner, Jr., L. A. Bryan, R. P. Holysz, Jr., and G. W. Pedlow, Jr., *Ind. Eng. Chem.*, **39**, 1368 (1947).

[12] R. Aelion, A. Loebel and F. Eirich, THIS JOURNAL, **72**, 5705 (1950).

0.5 g. of sodium[13] was subjected to careful fractional distillation in a column of approximately fifty theoretical plates over a period of several days. There was obtained 427 g. of distillate boiling principally at 78–79° and having $n^{20}D$ 1.366. The alcohol distillate deposited a white solid upon atmospheric exposure and therefore probably contained some ethyl borate. After the alcohol had been stripped from the reaction mixture the vapor temperature rose quickly to the boiling point of ethyl borate.

The distillation residue was freed of sodium alcoholate by rapid simple distillation at 100 mm. The crude product was fractionally distilled by E. M. Hadsell whereupon there were obtained two materials: 468 g., 3.2 moles, of ethyl borate, b.p. 120°, representing a 49% recovery of unreacted starting material; and 352 g., 1.5 moles, of *t*-butyl borate,[7] b.p. 101° at 74 mm., m.p. 18–19°, $n^{20}D$ 1.3879, representing a 45% yield based on unrecovered ethyl borate.

Anal. Calcd. for $C_{12}H_{27}O_3B$: B, 4.71. Found: B, 4.9, 4.9, 4.9, 4.8.

t-Butyl borate also was prepared by the alcoholysis of boric acid on a scale fourfold that reported.[7] There was obtained 1065 g., 58% yield of *t*-butyl borate which had b.p. 88–89° (53 mm.), $n^{20}D$ 1.3878 and an infrared spectrum (1R 4580) the same as that of the product from ethyl borate alcoholysis.

Upon exposure to atmospheric moisture for several hours *t*-butyl borate deposited a white solid, presumably boric acid. Some idea of the hydrolytic stability of the product may be gained from the method of analysis worked out by Dr. E. L. Simons. This simply involved allowing the compound to stand with an excess of 0.1 *N* HCl for about 24 hours and then potentiometrically titrating the boric acid formed. Only about 50% of the theoretical boric acid was found when the compound was allowed to stand with distilled water for 24 hours.

The infrared spectra of $(Me_3CO)_3B$ and of redistilled $(EtO)_3B$ were determined by C. A. Hirt with a Perkin-Elmer recording infrared spectrophotometer. The spectrum (1R 2309) of *t*-butyl borate showed well-defined, prominent bands at 3.39, 3.43, 3.49, 6.78, 6.87, 7.15, 7.21, 7.36, 7.45, 8.06, 8.45, 10.94, 11.04 and 13.10 μ. The spectrum (1R 2939) of ethyl borate showed well-defined, prominent bands at 3.36, 3.43, 3.53, 6.70, 6.96, 7.05, 7.27, 7.51, 7.78, 8.60, 9.07, 9.52, 11.21 and 12.37 μ.

---

[13] Small-scale runs made without sodium behaved capriciously. No ethanol was formed on refluxing *t*-butyl alcohol and ethyl borate (3.5:1 mole ratio) for several days through a fractional distillation column. On the other hand a similar run in a different column gave close to the theoretical amount of ethanol and about a 35% yield of *t*-butyl borate. It is unknown whether the negative result was due to poor fractionation or the positive result was due to accidental catalysis. Similar capricious behavior has been observed in the alcoholysis of ethyl silicate—D. F. Peppard, W. G. Brown and W. C. Johnson, THIS JOURNAL, **68**, 73 (1946).

RESEARCH LABORATORY
GENERAL ELECTRIC COMPANY
SCHENECTADY, NEW YORK

Fluorinated Amines

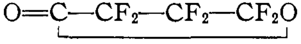
BY ALBERT L. HENNE AND JAY J. STEWART

RECEIVED JANUARY 20, 1954

The purpose of this work is the determination of the electronegative induction exerted by a CF_3 group on the amine function of a $CF_3(CH_2)_nNH_2$ series. We have observed for $CF_3(CH_2)_2NH_2$ a dissociation constant $K_B = 5 \times 10^{-6}$ and for $CF_3CH_2NH_2$ a value of 5×10^{-9}; for both unfluorinated propyl- and ethylamines we observed the accepted value 4.5×10^{-4}. A CF_3 group therefore affects the basicity of a NH_2 function adversely by a factor of 10^5 when separated by a single CH_2 group, and by a factor of only 10^2 when separated by two groups; this rapid decrease with distance characterizes induction.

It cannot be assumed that the basicity of the still unknown CF_3NH_2 can be estimated by any kind of extrapolation, because discontinuity is to be expected in $CF_3(CH_2)_nNH_2$ when n changes from 1 to 0. This is comparable to the discontinuity between benzylamine and aniline in the $C_6H_5(CH_2)_nNH_2$ series, or the break in the $CF_3(CH_2)_nH$ series where the protonic character of H increases with decreasing n, but disappears in $CF_3H (n = 0)$.

Degradative rearrangement of an amide (Hofmann hypohalite method) or an azide (Schmidt–Curtius reaction) were used to prepare $CF_3(CH_2)_2NH_2$ and $CF_3CH_2NH_2$. These degradations are known[1,2] not to be available for the synthesis of CF_3NH_2. The degradation of $C_3F_7CON_3$ gives a 76% yield of rearranged isocyanate C_3F_7NCO but no $C_3F_7NH_2$. This failure is not due to the rearrangement step but to the subsequent hydrolysis of the isocyanate; we believe that this hydrolysis does occur conventionally, but that the resulting $C_3F_7NH_2$ is at once hydrolyzed further with formation of a lower amide $C_2F_5CONH_2$, which we found in 10% yield in the degradation of $C_3F_7CON_3$ (in agreement with ref. 3), and regard this as a parallel to the hydrolysis of $O{=}C{-}CF_2{-}CF_2{-}CF_2O$ which does not yield $HO_2C(CF_2)_3OH$ but only $HO_2C(CF_2)_2CO_2H$.[4]



Experimental

All preparations started from $CF_3CH_2CH_2MgX$. The compound $CF_3CH_2CH_2Br$ can be made in 40% yield from $CCl_3CH_2CH_2Br$ and antimony fluoride but the reaction is complex and erratic and it is better to use the sequence $CCl_2{=}CHCH_3 \rightarrow CF_3CH_2CH_3 \rightarrow CF_3CH_2CH_2Cl$.[5,6] A conventional oxidation of the Grignard compound gave $CF_3CH_2CH_2OH$ in 50% yield, which a chromic oxidation transformed to $CF_3CH_2CO_2H$ in 80% yield. A conventional carbonation gave $CF_3(CH_2)_2CO_2H$ in 80% yield.[7] An attempted reaction with $ClNH_2$ failed to give $CF_3(CH_2)_2NH_2$.

Transformation of the acids to their chlorides was best with a 33% excess of PCl_5. The amides were obtained from them with a cold aqueous solution of ammonia kept saturated by a stream of NH_3 or with a chloroform solution of ammonia, both procedures being quite good.

The Hofmann Reaction.—The steps of the hypobromite degradation procedure[8] were standardized to ensure comparable results. Unfluorinated butyramide, $C_3H_7CONH_2$, gave 50% $C_3H_7NH_2{\cdot}HCl$, 53% CO_3, 37% $C_3H_7CO_2H$ and 47% NH_3Cl. Trifluorobutyramide, $CF_3CH_2CH_2CONH_2$, gave 35% $CF_3CH_2CH_2NH_2{\cdot}HCl$, 52% CO_2, 25% $CF_3CH_2CH_2CO_2H$, 33% NH_4Cl and some material boiling at 120–122°, $n^{20}D$ 1.4120 which could have been the intermediate $CF_3CH_2CH_2NCO$. It was concluded that the CF_3 group did not affect the rearrangement but might have slowed down the hydrolysis slightly. In contrast, trifluoropropionamide, $CF_3CH_2CONH_2$, gave a very poor yield (3%) of $CF_3CH_2NH_2{\cdot}HCl$, matched by a very small CO_2 evolution (2.5%) and there was a 27% recovery of unreacted amide, but no free acid. This was attributed to an over-riding loss of HF to the alkaline medium with formation of $CF_2{=}CHCONH_2$ and polymerization of this acrylic amide; in

---

[1] E. Gryszkiewicz-Trochimowski, H. Sporzynski and J. Wnuk. *Rec. trav. chim.*, **66**, 419 (1947).

[2] D. R. Husted and W. L. Kohlhase, THIS JOURNAL, **76**, 5141 (1954).

[3] A. H. Ahlbrecht and D. R. Husted, U. S. Patent 2,617,817 (1952); *C. A.*, **47**, 8774 (1953).

[4] M. Hauptschein. C. S. Stokes and A. V. Grosse, THIS JOURNAL, **74**, 1974 (1952).

[5] A. L. Henne and A. M. Whaley. *ibid.*, **64**, 1157 (1942).

[6] E. T. McBee, *ibid.*, **69**, 944 (1947).

[7] A. L. Henne and C. J. Fox, *ibid.*, **73**, 2323 (1951).

[8] K. R. S. Simon-Asher, *J. Chem. Soc.*, 2209 (1951).