in deuteriochloroform. All reactions were carried out under nitrogen in dry glassware. Microanalyses were performed by Microtech Laboratories, Skokie, Ill.

Addition-Alkylation.—In a typical experiment, ethyllithium (54 mmol) in benzene was added to a solution of anthracene (25 mmol) in tetrahydrofuran (125 ml) at 0°, and the resulting deep red color was discharged after 40 min by the addition of excess ethyl bromide. The product was partitioned between ether and water, dried over $MgSO_4$, and evaporated to provide crude IIb (95% by glpc[6]). Recrystallization from ethanol provided the analytical sample (Table I).

Alkylation of 9,10-Dihydroanthracene.—To a refluxing solution of 9,10-dihydroanthracene (3.6 g, 20 mmol) in ether (75 ml) and liquid ammonia (150 ml) in a Morton flask was added 31.3 ml of a 1.6 *M* solution of *n*-butyllithium (50 mmol) in hexane. The resulting dark red solution was stirred for 1 hr, then decolorized by the addition of ethyl bromide. Water (10 ml) was added, and the ammonia was allowed to evaporate. Work-up by extraction with ether provided crude IIb (86% by glpc[6]); the nmr spectrum of a recrystallized sample matched that of previously prepared IIb. Two other components of the crude product were characterized as IIIb (5%) and IVb (9%) by comparison of glpc retention times and nmr spectra with those of the authentic substances.

All other alkylations were carried out by essentially the same procedure.

II ($R = R' = C_6H_5CH_2$) proved exceptional in that it underwent decomposition on the glpc column (4-ft 2% Apiezon L) at 125° to furnish anthracene and bibenzyl. The latter were identified by glpc retention times and nmr spectra of samples trapped off the glpc column.

9,9,10-Trimethyl-9,10-dihydroanthracene (IVa).—Analogous methylation of IIa (10 mmol) in ether–ammonia with *n*-butyllithium (16 mmol) and excess methyl bromide afforded a white solid (2.17 g) consisting of IVa (90%) and IIa (9%) by glpc.[6] Recrystallization from ethanol provided IVa melting at 81–82.5°.

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.57; H, 8.20.

cis-**7,12-Dimethyl-7,12-dihydrobenz**[*a*]**anthracene** (VI).—Except for the use of tetrahydrofuran in place of ether, analogous conditions were employed for the methylation of 7,12-dihydrobenz[*a*]anthracene (5 g). The crude product, a viscous oil, crystallized upon chromatography on a column of neutral alumina. Recrystallization from ethanol provided VI, 2.24 g, mp 103.5–105° (lit.[2] mp 106–107°).

cis-**7,14-Dimethyl-7,14-dihydrodibenz**[*a,h*]**anthracene** (VII).—Methylation of 7,14-dihydrodibenz[*a,h*]anthracene in tetrahydrofuran–ammonia provided crude VII (isolated by extraction with ethyl acetate) in apparently quantitative yield (according to glpc on a 6-ft 1.5% OV-1 column at 250°). Recrystallization from ethyl acetate provided VII melting at 215–216.5° (lit.[2] mp 215–216.5°).

Nmr spectra.—All assigned structures were confirmed by nmr spectroscopy. The following summary of nmr data includes only compounds whose nmr spectra have not been previously reported.[2,3]

II ($R = i\text{-}C_3H_7$; $R' = CH_3$) showed 432 (m, 8, aryl), 244 (q, 1, $CHCH_3$, $J = 7$ Hz), 210 [d, 1, $CHCH(CH_3)_2$, $J = 7$ Hz], 95 (d, 3, CH_3, $J = 7$ Hz), and 55 cps (d, 6, CH_3, $J = 7$ Hz); the remaining methine proton appeared as a broad, weak band.

II ($R = n\text{-}C_4H_9$; $R' = CH_3$) showed 432 (m, 8, aryl), 243 (q, 1, $CHCH_3$, $J = 7$ Hz), 231 (t, 1, $CHCH_2$, $J = 7.5$ Hz), and 93 cps (d, 3, CH_3CH, $J = 7.5$ Hz); the remaining protons appear as a broad band in the aliphatic region.

II ($R = t\text{-}C_4H_9$; $R' = CH_3$) showed 440 (m, 8, aryl), 245 (q, 1, $CHCH_3$, $J = 6.5$ Hz), 224 (s, 1, CH), 104 (d, 3, CH_3CH, $J = 6.5$ Hz), and 55 cps (s, 9, CH_3).

II ($R = R' = n\text{-}C_4H_9$) showed 432 (m, 8, aryl) and 230 cps (t, 2, CH, $J = 7$ Hz); the remaining bands overlap.

II ($R = R' = C_6H_5CH_2$) showed 435 and 425 (m, 18, aryl), 253 (t, 2, CH, $J = 7$ Hz), and 179 cps (d, 4, CH_2, $J = 7$ Hz).

IVa showed 450 (m, 2, aryl), 436 (m, 6, aryl), 248 (q, 1, CH, $J = 7$ Hz), 105 (s, 3, CH_3), 95 (s, 3, CH_3), and 90 cps (d, 3, CH_3, $J = 7$ Hz).

Registry No.—II ($R = i\text{-}C_3H_7$; $R' = CH_3$), 21438-93-7; II ($R = n\text{-}C_4H_9$; $R' = CH_3$), 21438-94-8; II ($R = t\text{-}C_4H_9$; $R' = CH_3$), 21438-95-9; II ($R = n\text{-}C_4H_9$; $R' = n\text{-}C_4H_9$), 21438-96-0; II ($R = C_6H_5CH_2$; $R' = C_6H_5CH_2$), 21438-97-1; IVa, 14923-29-6.

Formation of Tri-*t*-butyl Orthoformate and *t*-Butyl Di-*t*-butoxyacetate in the Reactions of Chlorodifluoromethane and Dichlorofluoromethane with Potassium *t*-Butoxide[1]

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The reaction of dichlorofluoromethane with potassium *t*-butoxide in *t*-butyl alcohol solution yields a mixture of *cis*- and *trans*-1,2-di-*t*-butoxy-1,2-difluoroethylene and tri-*t*-butyl orthoformate. Chlorodifluoromethane yields the same products plus *t*-butyl difluoromethyl ether. In either case, if the reaction mixture is allowed to become acidic, *t*-butyl di-*t*-butoxyacetate may be formed, by solvolysis of the di-*t*-butoxydifluoroethylenes. The reactions are believed to be initiated by the formation of dihalomethylenes, which are transformed to *t*-butoxyfluoromethylene, from which the ortho ester and the dialkoxydifluoroethylenes are formed.

Cleaver has reported that the reaction of chlorodifluoromethane (not dichlorodifluoromethane, as stated in *Chemical Abstracts*) with the potassium salts of several secondary and tertiary alcohols yields 1,2-dialkoxy-1,2-difluoroethylenes and, in cases where secondary alkoxides are used, trialkyl orthoformates.[2]

$$CHClF_2 + ROK \longrightarrow ROCF{=}CFOR$$

Potassium *t*-butoxide gave a mixture of *cis* and *trans* isomers in about 25% yield, with no other products being noted. Potassium isopropoxide gave a smaller but unstated yield of 1,2-difluoro-1,2-diisopropoxyethylenes with the only other observed product being triisopropyl orthoformate. The difluorodialkoxyethylenes may be formed by the dimerization of intermediate alkoxyfluoromethylenes.[3] If so, they should also be formed, perhaps in higher yield, from dichlorofluoromethane, whose reaction with alkali-metal alkoxides passes almost entirely through the alkoxyfluoromethy-

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(1) Part XXVII in the series "Methylene Derivatives as Intermediates in Polar Reactions." For part XXVI, see J. Hine, R. B. Duke, and E. F. Glod, *J. Amer. Chem. Soc.*, **91**, 2316 (1969). This work was supported in part by National Science Foundation Grants GP-2002, GP-4445, and GP-7629.

(2) C. S. Cleaver, U. S. Patent 2,853,531 (1958); *Chem. Abstr.*, **53**, 5135*f* (1959).

(3) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, p 68.

lene stage,[4] unlike the analogous reactions of chlorodifluoromethane, where considerable amounts of alkyl difluoromethyl ethers are formed.[5,6] Most of the reactions in which alkoxyfluoromethylenes have been generated in the presence of alkoxide ions have been found to give trialkyl orthoformates.[4-6] Although no tri-*t*-alkyl orthoformate seems to be known, the reaction of dichlorofluoromethane with alkali-metal alkoxides has been found to give orthoformates in high yield.[4] It was therefore of interest to study the reactions of potassium *t*-butoxide with chlorodifluoromethane and dichlorofluoromethane.

Results

In the first runs on the reaction of dichlorofluoromethane with potassium *t*-butoxide in *t*-butyl alcohol, an excess of the haloform was used and the reaction mixture became acidic while the solvent was removed by distillation. The principal organic reaction product was a mixture of *cis*- and *trans*-1,2-di-*t*-butoxy-1,2-difluoroethylene, but smaller amounts of isobutylene and a higher boiling product identified as *t*-butyl di-*t*-butoxyacetate were also obtained.

When the reaction mixture was not allowed to become acidic no *t*-butyl di-*t*-butoxyacetate was obtained. A mixture of *cis*- and *trans*-1,2-di-*t*-butoxy-1,2-difluoroethylene was the principal product at potassium *t*-butoxide concentrations above about 0.1 M, but smaller amounts of a higher boiling product identified as tri-*t*-butyl orthoformate were also obtained. The singlet observed for this compound at τ 4.35 seemed at first to occur at too low a field for the methinyl proton of a trialkyl ortho ester. However, it was noted that the methinyl protons of trimethyl orthoformate, triethyl orthoformate, and triisopropyl orthoformate absorb at τ 5.15, 5.04, and 4.80, respectively. It therefore appears that increasing effective bulk of the alkyl group shifts the absorption of the methinyl proton of a trialkyl orthoformate to lower field.

In order to learn whether the *t*-butyl di-*t*-butoxyacetate arises by the alcoholysis of the 1,2-di-*t*-butoxy-1,2-difluoroethylenes, a solution of the latter compounds in *t*-butyl alcohol was refluxed. After an hour the only detectable product was a small amount of acid, but then the reaction mixture became acidic at an increasing rate and *t*-butyl di-*t*-butoxyacetate was formed.

In order to learn whether the 1,2-di-*t*-butoxy-1,2-difluoroethylenes could arise from 1,2-dichloro-1,2-difluoroethylenes, solutions of potassium *t*-butoxide and *cis*- and *trans*-1,2-dichloro-1,2-difluoroethylene were allowed to stand for longer times than those used in the reaction of dichlorofluoromethane with potassium *t*-butoxide. Titration and glpc showed that no significant amount of reaction occurred during these times.

The reaction of chlorodifluoromethane with potassium *t*-butoxide was found to yield the 1,2-di-*t*-butoxy-1,2-difluoroethylenes, tri-*t*-butyl orthoformate, and a colorless liquid that appeared to form an azeotrope with *t*-butyl alcohol. Analogy to other reactions in which alkyl difluoromethyl ethers have been formed from alkali metal alkoxide and chlorodifluoromethane[5,6] suggested that this compound was *t*-butyl difluoromethyl ether. This structure was confirmed by ir and pmr spectra, but, in view of the unstable nature of the compound and the previously observed tendency of sealed tubes of isopropyl difluoromethyl ether to explode,[5] no elemental analysis was run.

Discussion

It appears that in the preparation of orthoformates from haloforms and alkali metal alkoxides, dichlorofluoromethane is the haloform of choice. Haloforms that do not contain fluorine give methylene halides and the products of deoxideation[7] as significant by-products.[4] Haloforms with two fluorine atoms give large amounts of alkyl difluoromethyl ethers,[5,6] and fluoroform is relatively unreactive. Dichlorofluoromethane is the least expensive haloform that contains one fluorine atom and it is rather reactive toward alkali-metal alkoxides. Although the 1,2-di-*t*-butoxy-1,2-difluoroethylenes are the major products in the reaction with potassium *t*-butoxide, this reaction appears to be the only way in which a tri-*t*-alkyl orthoformate has ever been made.

It is possible that the 1,2-di-*t*-butoxy-1,2-difluoroethylenes are formed by the dimerization of *t*-butoxyfluoromethylene. We suggest that steric hindrance to reaction with *t*-butoxide ions and *t*-butyl alcohol causes the concentration of *t*-butoxyfluoromethylene to climb to considerably higher levels than those reached by primary and secondary alkoxyfluoromethylenes, and that these higher concentrations permit dimerization to become a major reaction.

The formation of *t*-butyl di-*t*-butoxyacetate from the di-*t*-butoxydifluoroethylenes in the presence of acid, for which several plausible alternative mechanisms can be written, may be the method of choice for the synthesis of derivatives of di-*t*-butoxyacetic acid in view of the fact that an alternative route that seems particularly promising, namely the reaction of esters of dichloroacetic acid with potassium *t*-butoxide, has been found to yield other products.[8]

Experimental Section

Formation of Tri-*t*-butyl Orthoformate from Dichlorofluoromethane and Potassium *t*-Butoxide.—Dichlorofluoromethane gas was introduced above the liquid level into a flask containing 3800 ml of 1.18 M potassium *t*-butoxide in *t*-butyl alcohol and equipped with a Dry Ice cooled condenser, gas collection apparatus, thermometer, and magnetic stirrer. A white precipitate of potassium chloride and potassium fluoride formed almost immediately. The reaction temperature was kept below 30° while 180 g (1.75 mol) of haloform was added over a period of 10 hr. The volume of the resultant solution, which was 0.06 M in base, was reduced to 500 ml by distillation at about 25 mm pressure. After 500 ml of pentane was added, the light brown reaction mixture was filtered through a sintered-glass funnel. A few pellets of potassium hydroxide were added to ensure basicity and the volume was reduced to 125 ml under vacuum. Distillation through a spinning-band column yielded 54.4 g (30%) of a mixture of *cis*- and *trans*-1,2-di-*t*-butoxy-1,2-difluoroethylenes, bp 24-26° (0.15 mm). The pmr and ir spectra and glpc retention times showed that these two components were the same as those in the 1,2-di-*t*-butoxy-1,2-difluoroethylene mixture prepared by the method of Cleaver. After two fractions of inter-

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(4) J. Hine, A. D. Ketley, and K. Tanabe, *J. Amer. Chem. Soc.*, **82**, 1398 (1960).

(5) J. Hine and K. Tanabe, *ibid.*, **79**, 2654 (1957); **80**, 3002 (1958).

(6) J. Hine and J. J. Porter, *ibid.*, **79**, 5493 (1957).

(7) P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959).

(8) W. E. Parham, F. C. Loew, and E. E. Schweizer, *J. Org. Chem.*, **24**, 1900 (1959).

mediate composition came a fraction of 12.3 g (3%) of tri-*t*-butyl orthoformate: bp 50–54° (0.8 mm); mp 25–26°; $n^{26}\mathrm{D}$ 1.4106; ir (neat) 1057 (broad), 2980, 1028, 1192, 1345, 1236, 2940, 1123, 1455, and 896 cm^{-1} in order of decreasing intensity; pmr (CCl_4) τ 4.35 [s, 1, $\mathbf{CH}(\mathrm{OBu}\text{-}t)_3$], 8.74 {s, 26.5, $\mathrm{CH[OC(\mathbf{CH}_3)_3]_3}$}; mass spectrum (70 eV) *m/e* (rel intensity) 231 (0.16), 217 (0.08), 175 (0.58), 159 (2.5), 145 (0.9), 137 (0.16), 113 (4.1), 103 (20), 89 (4.4), 58 (5.5), 57 (100), 43 (7.5), 42 (5.5), 41 (16), 39 (5.9). Early attempts to analyze this compound gave erratic results that seemed attributable to its hygroscopic character or perhaps to its instability. The following duplicate analysis was done on separate samples sealed under dry nitrogen.

Anal. Calcd for $C_{13}H_{28}O_3$: C, 67.20; H, 12.11; mol wt, 232.4. Found: C, 67.49, 67.77; H, 12.21, 12.08; mol wt, 227.

In another run, carried out using 800 ml of 0.93 *M* potassium *t*-butoxide, glpc analysis of the reaction mixture showed that the 1,2-di-*t*-butoxy-1,2-difluoroethylenes and tri-*t*-butyl orthoformate had been formed in respective yields of 81 and 4.5%, based on unrecovered haloform.

Reactions of Tri-*t*-butyl Orthoformate.—A sample of tri-*t*-butyl orthoformate that had been stored in a refrigerator over a couple of pellets of potassium hydroxide for 2 days was found to have undergone partial hydrolysis to yield *t*-butyl formate and *t*-butyl alcohol. Addition of a few drops of water caused the formation of increased amounts of these products, which were formed more rapidly and completely when an excess of dilute aqueous hydrofluoric acid was added to the ortho ester. When a sample of the ortho ester was kept at 95° for 5 hr, about 5% *t*-butyl alcohol and *t*-butyl formate was formed.

Formation of *t*-Butyl Di-*t*-butoxyacetate from Dichlorofluoromethane and Potassium *t*-Butoxide.—An excess (0.93 mol) of dichlorofluoromethane was allowed to react with 1.3 mol of potassium *t*-butoxide in 1300 ml of *t*-butyl alcohol using the procedure described in the preceding section. At the end of the reaction the neutral solution was heated to remove the solvent. When most of the solvent was removed, 1000 ml of water was added to dissolve the white solid in the reaction flask, and an acidic (pH <1) aqueous phase and an organic phase were produced. Distillation of the organic phase combined with ether extracts of the aqueous phase yielded the 1,2-di-*t*-butoxy-1,2-difluoroethylenes. The next fraction solidified in the condenser. It was identified as *t*-butyl di-*t*-butoxyacetate: mp 53–55°; ir (CCl_4) 1059, 1117, 1368, 1160 (broad), 1730 (ester C=O), 2985, 1765 (ester C=O), 970, 1026, 1255, 1307, 1393, 1481, 1460, 877, and 844 cm^{-1}; pmr (CCl_4) τ 5.18 (s, 0.93, methinyl H), 8.55 [s, 9, $\mathrm{CO_2C(\mathbf{CH}_3)_3}$], 8.78 {s, 18, $\mathrm{[(\mathbf{CH}_3)_3CO]_2C}$}; mass spectrum (70 eV) 245 (0.005), 217 (0.04), 204 (0.01), 189 (0.1), 159 (3.5), 131 (1.8), 115 (1.3), 113 (2), 103 (21), 59 (21), 57 (100), 41 (28), 29 (11), 15 (21).

Anal. Calcd for $C_{14}H_{28}O_4$: C, 64.58; H, 10.84; mol wt, 260.4. Found: C, 64.61, 64.80; H, 10.58, 10.72; mol wt, 263, 264.

Formation of *t*-Butyl Di-*t*-butoxyacetate from 1,2-Di-*t*-butoxy-1,2-difluoroethylenes.—A solution of 13 g (0.06 mol) of a mixture of *cis*- and *trans*-1,2-di-*t*-butoxy-1,2-difluoroethylene in 100 ml of *t*-butyl alcohol was refluxed for 1 hr and then found by ir and glpc analysis to contain no *t*-butyl di-*t*-butoxyacetate although the solution had become faintly acidic. After having been refluxed for another hour the solution was strongly acidic and contained an amount of ester that increased when the solution stood overnight. Treatment of the solution with aqueous sodium carbonate and ether extraction gave a stronger solution whose ir spectrum and glpc analysis showed clearly that *t*-butyl di-*t*-butoxyacetate was present.

Treatment of 1,2-Dichloro-1,2-difluoroethylenes with Potassium *t*-Butoxide.—Treatment of 1,2-difluoro-1,1,2,2-tetrachloroethane with zinc[9] yielded a mixture of 1,2-dichloro-1,2-difluoroethylenes that has been shown to contain roughly equal amounts of the *cis* and *trans* isomers.[10] When a solution of 0.19 *M* dichlorodifluoroethylenes (about 90% pure by glpc) and 0.13 *M* potassium *t*-butoxide in *t*-butyl alcohol was allowed to stand at about 25° for 11 hr, about 5% of the base was used up and a light yellow color had appeared. Glpc measurements on similar solutions showed no clearly discernible decrease in the concentration of dichlorodifluoroethylenes over a period of more than 24 hr.

Reaction of Chlorodifluoromethane with Potassium *t*-Butoxide.—Using the same apparatus as in the case of dichlorofluoromethane, 81 g (0.935 mol) of chlorodifluoromethane was added to 1000 ml of 1.56 *M* potassium *t*-butoxide in *t*-butyl alcohol at such a rate as to keep the reaction temperature between 50 and 60°. The resultant solution, which was still basic, was centrifuged to remove suspended white solid and distilled. The fraction of bp 60–80° could not be separated into pure components by distillation, but preparative glpc yielded a colorless liquid that decomposed with evolution of white fumes after it had been at nmr probe temperature (35°) for a few minutes. Solutions of the material were stable enough to permit measurements that gave evidence that it is *t*-butyl difluoromethyl ether: pmr τ 3.59 (t, 0.93, J = 77 Hz, $\mathrm{OC\mathbf{H}F_2}$), 8.55 [s, 9.0, $\mathrm{(\mathbf{CH}_3)_3C}$]; ir ($CS_2$) 1112, 1161, 1026, 1376, 1404, 3003, 1232, 1206, 1067, 1271, 1355, 915, 783, and 773 cm^{-1} in the order of decreasing intensity. Glpc measurements on some of the distilled fractions showed that at least 20 g (17%) of *t*-butyl difluoromethyl ether was present.

The ir spectrum of the gases collected during the reaction and distillation showed that chlorodifluoromethane and isobutylene were present.

In another run a 3% yield of tri-*t*-butyl orthoformate was obtained.

Registry No.—Tri-*t*-butyl orthoformate, 21372-83-8; *t*-butyl di-*t*-butoxyacetate, 21372-84-9; chlorodifluoromethane, 75-45-6; dichlorofluoromethane, 75-43-4; potassium *t*-butoxide, 865-47-4; *cis*-1,2-di-*t*-butoxy-1,2-difluoroethylene, 21449-72-9; *trans*-1,2-di-*t*-butoxy-1,2-difluoroethylene, 21449-73-0; *t*-butyl difluoromethyl ether, 21372-86-1.

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(9) E. G. Locke, W. R. Brode, and A. L. Henne, *J. Amer. Chem. Soc.*, **56**, 1726 (1934).

(10) N. C. Craig and D. A. Evans, *ibid.*, **87**, 4223 (1965).