

58 g. V and 5 g. FeCl_3 (B) at 24° give 8% of III; 40 g. V and 10 g. BiCl_3 (B) at 100° give 6% of III. *sec*-BuCl (50 g.), 50 g. pentane, 26 g. C_2H_4 , and 5 g. AlCl_3 (A) at -16° to -10° give 35% of 1-chloro-3-methyl-3-ethylpentane (?), b_8 51-2°, b_{700} 173-4°, n_D^{20} 1.4370, d_4^{20} 0.8863, *MR* 43.9 (calcd. 43.9). PrCl (75 g.), 12 g. C_2H_4 , and 6 g. AlCl_3 (A) at 2 to 6° give 5% of III; 50 g. *iso*-BuCl, 10 g. C_2H_4 , and 5 g. AlCl_3 (A) at -25° to -10° give 38% of II. Me_3CBr (VI) (80 g.) and 8 g. FeCl_3 (B) at 30° give 28% of $\text{Me}_3\text{CCH}_2\text{CH}_2\text{Br}$ (VII); 88 g. of VI and 4 g. BiCl_3 (B) at 70° give 23% of VII. VI (102 g.), 35 g. C_2H_4 , 50 g. pentane, and 3 g. AlCl_3 (B) at -23° to -17° give 40% of 1-bromo-3,3-dimethylpentane (VIII), b_{10} 51-2°, b_{760} 167-8°, n_D^{20} 1.4546, d_4^{20} 1.1497, *MR* 42.2 (calcd. 42.2); 100 g. VI with 8 g. FeCl_3 (B) at 40° or 10 g. BiCl_3 at 50° gives 25 or 12% of VIII. III yields 3,3-dimethyl-1-pentanol, b_{20} 78-9°, b_{745} 163-4°, n_D^{20} 1.4275, d_4^{20} 0.8320 (3,5-dinitrobenzoate, m , 50 -1°, whose 1-naphthylamine addn. *compd.* *m.* 114-15°). C. J. West

Synthesis and directed chlorination of 2,2-difluorobutane. Albert L. Henne and James B. Hinkamp. *J. Am. Chem. Soc.* 67, 1194-7(1945).—The chlorination of CF_3Et , Me_2CF_2 and $\text{MeCF}_2\text{CH}_2\text{Cl}$ is known to be strongly directed. To det. how far and in what direction the effect of a CF_2 group would extend, MeEtCF_2 (I) was chlorinated. I, f.p. -117.53° , b_{760} 30.92°, d_4^{20} 0.9159, n_D^{20} 1.3138, *MR* 20.33 (all b.p., d. and *n* under these conditions), was obtained in 51.3% yield from 70% com. $\text{MeCCl}:\text{CHMe}$ and HF (details given). I in sunlight in the presence of H_2O gives 2 parts of $\text{MeCF}_2\text{CHClMe}$ (II), f.p. -92.1° , b . 72.32°, d. 1.1259, n 1.3631, *MR* 25.16, and 3 parts of $\text{MeCF}_2\text{CH}_2\text{CH}_2\text{Cl}$ (III), f.p. -76.08° , b . 93.22°, d. 1.1552, n 1.3709, *MR* 25.21; no $\text{ClCH}_2\text{CF}_2\text{Et}$ was formed. II on further chlorination gave 2 parts of $\text{MeCF}_2\text{CCl}_2\text{Me}$ (IV), f.p. 43.66°, b . 89.84°, d_4^{20} 1.2393, n_D^{20} 1.3752, *MR* 30.12, and 1 part of $\text{MeCF}_2\text{CHClCH}_2\text{Cl}$ (V), b . 123.1°, d. 1.328, n 1.404, *MR* 30.0. III yielded only $\text{MeCF}_2\text{CH}_2\text{CHCl}_2$ (VI), f.p. -66.99° , b . 119.26°, d. 1.3138, n 1.4017, *MR* 30.19; a continuation of the chlorination yielded 7 parts of $\text{MeCF}_2\text{CH}_2\text{CCl}_3$ (VII), f.p. -29.5° , b . 139.15°, d. 1.4366, n 1.4245, *MR* 35.11, to 1 part of V. These results illustrate the extent to which the α -Me group is protected against Cl and confirm the strong tendency to accumulate the Cl atoms on the same C atom which has been noted in the propane series (C.A. 36, 4090). $\text{CH}_2\text{ClCF}_2\text{Et}$ (VIII), f.p. -78.96° , b . 82.72°, d. 1.1553, n 1.3685, *MR* 25.08, was obtained in 55% yield from $\text{CH}_2\text{ClCCl}_2\text{Et}$; chlorination of VIII yielded 4 parts of $\text{CH}_2\text{ClCF}_2\text{CH}_2\text{Cl}$ (IX), f.p. -28.7° , b . 142.28°, d. 1.3652, n 1.4153, *MR* 29.99, and 1 part of $\text{CH}_2\text{ClCF}_2\text{CHClMe}$, f.p. -60.5° , b . 115.67°, d. 1.3276, n 1.4025, *MR* 29.93; further chlorination (several weeks of exposure to brilliant sunlight at 60°) gave $\text{CCl}_3\text{CF}_2\text{CCl}_2\text{CCl}_3$, f.p. -8.42° , b_2 98°, d. 1.8990, n 1.5193, *MR* 59.15. II was obtained in 35% yield from $\text{MeCCl}_2\text{CHClMe}$, together with 31% of $\text{MeCF}_2\text{CHClMe}$. IX was obtained in 24% yield from $\text{CH}_2\text{ClCCl}_2\text{CHClMe}$, together with 53% of $\text{CH}_2\text{ClCF}_2\text{CHClMe}$; IX also results in 45% yield from the latter. V results in quant. yield by Cl addn. to $\text{MeCF}_2\text{CH}:\text{CH}_2$. $\text{Cl}_2\text{CHCF}_2\text{Et}$, f.p. -54.39° , b . 111.22°, d. 1.3113, n 1.3978, *MR* 29.99, results in 40% yield from $\text{CHCl}_2\text{CCl}_2\text{Et}$, together with 14% of $\text{Cl}_2\text{CHCF}_2\text{Et}$. VII yields $\text{MeCF}_2\text{CH}_2\text{CF}_2$, f.p. -35.01° , b . 40.14°, d. 1.2666, n 1.2824, *MR* 20.67. MeCF_2ClEt , f.p. -110.06° , b . 67.65°, d. 0.9982, n 1.3782, *MR* 25.55°. Cl reactivity tests show that α -Cl atoms are immobilized, β -Cl atoms are repressed, and γ -Cl atoms seem to be unaffected. C. J. West

Synthesis and directed chlorination of 1,1,1-trifluorobutane. Albert L. Henne and James B. Hinkamp. *J. Am. Chem. Soc.* 67, 1197-9(1945).—This study was to det. how far a CF_3 group would extend its influence. $\text{CHCl}:\text{CHEt}$ (I) was prepd. from PrCHO through Cl_2CHPr (39% yield) with boiling satd. KOH -BuOH in 64% yield; because the method could not be used with large quantities, tech. $\text{ClCH}_2\text{CHClEt}$ (II) was used. The reaction of II with 30% NaOH -EtOH was sufficiently exothermic to maintain itself and yielded 46% of I and 27% of $\text{CH}_2\text{Cl}:\text{CClEt}$. I with Cl_2 in the dark, at 10° gives 70-5% of Cl_2 -

CHCHClEt (III); in the presence of H_2O , the reaction is 4 times faster but the yield was approx. 55%. With aq. or alc. NaOH III gives 96% of I. I does not react with HF at room temp.; at elevated temps., CFCl_2Pr (IV) and CF_2ClPr (V) are formed. With 3 moles of I and 24 moles of HF at 65° , 33% of IV and 5.3% of V are formed, whereas at 100° 10.3% of IV and 49.6% of V result. Dropwise addn. of 196 g. of V to 180 g. KOH in 340 ml. boiling EtOH over a period of 3 hrs. gives 83.3% of CF_2CHClEt (VI); 1 mole of VI and 4 moles of HF, mixed at -80° and allowed to warm to room temp., gives 96-9% of CF_2Pr (VII); this is a highly exothermic reaction. IV with KOH -EtOH gives 90% of $\text{CFCl}:\text{CHEt}$ which, with HF at 65° for 8 hrs., gives V. VI, chlorinated in sunlight in the presence of H_2O , gives $\text{CF}_3\text{CH}_2\text{CHClMe}$ (VII) and $\text{CF}_3(\text{CH}_2)_2\text{Cl}$ (VIII) in the ratio of 4:5. Thus, as in previous cases, the group α to the fluorinated cluster resisted chlorination; the β and γ groups were affected in a manner which deviated but slightly from random chlorination, in favor of the β group. Further chlorination of VII yielded 8 parts of $\text{CF}_3\text{CH}_2\text{CCl}_2\text{Me}$ and 6 parts of $\text{CF}_3\text{CH}_2\text{CHClCHCl}_2$ and of VIII gave 2 parts of $\text{CF}_3\text{CH}_2\text{CH}_2\text{CHCl}_2$ (IX) and 1 part of $\text{CF}_3\text{CH}_2\text{CHClCH}_2\text{Cl}$. The predominating product on chlorinating IX was $\text{CF}_3\text{CH}_2\text{CH}_2\text{CCl}_3$. CFCl_2Pr , f.p. -112.4° , b_{700} 95.3°, d_4^{20} 1.1578, n_D^{20} 1.4007, *MR* 30.41 (in the following b.p., d., and *n* are for these conditions). CF_2ClPr , f.p. -119.39° , b . 56.03°, d. 1.0754, n 1.3462, *MR* 25.47. $\text{CFCl}:\text{CHEt}$, f.p. -144.9° , b . 54.4°, d. 1.0216, n 1.3851, *MR* 24.90. $\text{CF}_2:\text{CHEt}$, f.p. -164.95° , b . 3.71°, d_4^{20} 0.9284, n_D^{20} 1.3253, *MR* 19.97. CF_3Pr , f.p. -114.79° , b . 16.74°, d_4^{20} 1.0144, n_D^{20} 1.2921, *MR* 20.51. $\text{CF}_2\text{ClCHClEt}$, f.p. below -100° , b . 96.98°, d. 1.2715, n 1.3878, *MR* 30.24. CF_3CHClEt , f.p. below -100° , b . 58.3°, d. 1.1967, n 1.3369, *MR* 25.4. $\text{CF}_3\text{CH}_2\text{CHClMe}$, f.p. -79.24° , b . 65.63°, d. 1.2133, n 1.3433, *MR* 25.54; $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$, f.p. -67.25° , b . 86.60°, d. 1.2425, n 1.3505, *MR* 25.41. $\text{CF}_3\text{CH}_2\text{CCl}_2\text{Me}$, f.p. about -48° , b . 89.90°, d. 1.374, n 1.355, *MR* 30.6. $\text{CF}_3\text{CH}_2\text{CF}_2\text{Me}$, f.p. -35.01° , b . 40.14°, d. 1.2666, n 1.2824, *MR* 20.67. Reactivity tests indicated that both the α - and β -Cl atoms are immobilized by the CF_3 group and that the γ -Cl atom is only repressed. The influence of a CF_3 group, therefore, extends further than that of a

CF_2 group. C. J. West

Reaction of iodine and aluminum with ethers and alcohols. M. T. Dangyan. *J. Gen. Chem.* (U.S.S.R.) 11, 1215-17(1941); cf. C.A. 35, 5857⁹.— Et_2O mixed with Al and iodine yields EtI; similarly PhOEt yields 62.4% EtI and PhOH, while MeOPh gives 70% MeI and PhOH, and MeOH yields MeI and $\text{Al}(\text{OH})_3$. BuOH yields 70.9% BuI and $\text{Al}(\text{OH})_3$. The reactions are spontaneous and evolve considerable amts. of heat. G. M. Kosolapoff

Isomerization of alkyl phosphites. III. Synthesis of alkylphosphonic acids. Gennady M. Kosolapoff. *J. Am. Chem. Soc.* 67, 1180-2(1945); cf. C.A. 38, 5794⁹.—The following alkyl-substituted *di*-Et *alkanephosphonates*, $\text{RPO}(\text{OEt})_2$, were prepd. by the procedure outlined in Part I (C.A. 38, 951⁹): *hexane*, b_{17} 140-4°; *nonane*, b_{17} 177-86°; *decane*, b_{17} 186-93°; *dodecane*, b_3 165-75°; *tetradecane*, b_3 about 200°. Because of the long time required (up to 48 hrs.) at 150-60° to produce yields of 50% or less and the decomn. resulting from the distn. of the esters from the reaction product, this is not considered a satisfactory general synthetic method. Na di-Bu phosphite offers a satisfactory starting material because of its soly. in inert org. solvents (e.g., the lower petr. ether fractions) and the stability of such solns. on exposure to atm. moisture; the reactions with alkyl halides proceed readily at reflux temp. of the solvent, being complete in 3 to 6 hrs. A suspension of 1.15 g. of Na in 150 ml. of dry hexane or heptane was refluxed, treated with 9.7 g. of di-Bu phosphite during 20 or 30 min. and refluxed until the Na was dissolved (3 to 5 hrs.) and then treated with 0.05 mole of alkyl bromide during 30 to 45 min. and refluxed 5-6 hrs., the mixt. cooled, washed with H_2O , the org. layer sep'd., and the ester distd. *in vacuo*. *Di-Bu alkanephosphonates* (d_4^{20} and n_D^{20} are given): *ethane*, b_{17} 137-9°, d. 0.9623, n 1.4258; *butane*, b_{20} 160-2°, d. 0.9462, n 1.4302; *pentane*,