4.34 g. (0.026 mole) of silver acetate. The reaction flask was wrapped with aluminum foil and the mixture was stirred for 18 hr. at room temperature. The silver bromide was filtered and the filtrate was concentrated to about 40 ml. Ether was added and the layers were separated. The organic layer was dried ($MgSO_4$) and evaporated. Attempts to induce crystallization failed.

The viscous oil (8.9 g.) was dissolved in 10 ml. of ether and treated with a solution of 1.75 ml. of concentrated sulfuric acid and 2.37 g. of sodium dichromate dihydrate made up to 15 ml. with water according to the method of Brown and Garg.[14] The reaction temperature was maintained at 7–10° during the addition of the dichromate solution (20 min.). After stirring for 1 hr. between 10 and 20°, ether was added and the mixture was diluted with water. The aqueous layer was separated, extracted with 2–50-ml. portions of ether, and discarded. The combined organic layer was washed with a sodium bicarbonate solution and then with water. The ethereal solution was dried over magnesium sulfate and evaporated. Petroleum ether (b.p. 60–70°) was added to the residue and the crystalline product was collected by filtration, 4.45 g. (59.7%), m.p. 111–112° after recrystallization from a benzene–petroleum ether mixture.

Anal. Calcd. for $C_{21}H_{18}OSi$: C, 80.21; H, 5.77; Si, 8.93. Found: C, 80.13, 80.37; H, 5.71, 5.84; Si, 9.05, 9.14.

The infrared spectrum of the compound in carbon disulfide contained prominent bands at 3.3, 3.45, and 6.0, 9.0, and 13.07 μ, indicative of aromatic and aliphatic C–H, carbonyl group, the silicon–phenyl linkage, and *ortho* disubstitution, respectively. The n.m.r. spectrum of the ketone as a carbon tetrachloride solution showed two multiplets of five peaks each centered at τ 7.19 and 8.56, representing the protons at the 5-position (α to the carbonyl group) and 6-position, respectively, and two other multiplets at τ 1.82 and 2.26 for the aromatic proton on the benzo portion *ortho* to the carbonyl group[6] and the remainder of the aromatic protons.

Treatment of the ketone with an ethanolic solution of 2,4-dinitrophenylhydrazine gave the hydrazone as bright red flakes, m.p. 228–230° after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{27}H_{22}N_4O_4Si$: C, 65.57; H, 4.49; N, 11.33. Found: C, 65.55, 65.72; H, 4.43, 4.57; N, 11.29, 11.26.

The reported[15] melting points of the ketone and hydrazone are 127 and 240° dec., respectively. The melting point of each derivative was depressed when admixed with those above. The infrared spectra of the two ketones were quite different. That of the previously prepared sample[15] contained medium to strong bands at 7.47, 8.20, 8.53, 9.28–9.62 (broad), and 12.33 μ, which were not present in the spectrum of the ketone prepared in this investigation. The broad band at 9.28–9.62 μ may be attributed to the presence of an Si–O–Si or Si–O–C linkage.[16] The infrared spectra of the two hydrazones were similar, but not superimposable.

Reaction of 2:3-Benzo-4-bromo-1,1-diphenyl-1-silacyclohex-2-ene with Magnesium. Run 1.—A solution of 1.0 g. (0.00263 mole) of the bromo compound in 15 ml. of tetrahydrofuran was added dropwise to 0.1 g. (0.004 g.-atom) of magnesium and a crystal of iodine in 5 ml. of the same solvent. A reaction started immediately and, subsequent to complete addition, the mixture was refluxed for 2 hr. The reaction mixture was poured through a glass-wool plug into an ammonium chloride solution. Ether was added, the layers were separated, and the aqueous layer was extracted with ether. The combined organic layer was filtered to give 0.25 g. of a solid melting at 268–271°. The filtrate was dried and concentrated. An additional 0.11 g. of the high-melting solid was isolated. Further concentration of the filtrate gave a viscous yellow oil which could not be purified further.

The two solid fractions were combined and recrystallized from a benzene–petroleum ether (b.p. 60–70°) mixture to give 0.31 g. (39.2%) of fine needles, m.p. 271–273°. The infrared spectrum was similar to that of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene, showing absorption bands at 3.28, 3.44, 9.05, and 13.28 μ, characteristic of aromatic and aliphatic C–H, the silicon–phenyl linkage, and *ortho* disubstitution, respectively. The compound has been assigned the structure 4,4′-bi(2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene) (V).

Anal. Calcd. for $C_{42}H_{38}Si_2$: C, 84.23; H, 6.39; Si, 9.38; mol. wt., 599. Found: C, 84.61, 84.40; H, 6.43, 6.35; Si, 9.25; mol. wt. (benzene), 580.

Run 2.—The bromo compound (1.15 g., 0.00303 mole) was allowed to react with 0.1 g. (0.004 g.-atom) of magnesium in 20 ml. of tetrahydrofuran as described above, except that the mixture was refluxed for 1 hr. and then carbonated. No acidic products were produced. From the organic layer, there was obtained 0.22 g. (24.2%) of the solid isolated in run 1, m.p. 270–273°, and a viscous oil.

Acknowledgment.—This research was supported in part by the U. S. Air Force under Contract AF 33(616)-6463 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. The authors are grateful to Dr. Roy W. King for the determination and the assistance in interpreting the n.m.r. spectra.

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(14) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

(15) D. Wittenberg, P. B. Talukdar, and H. Gilman, *ibid.*, **82**, 3608 (1960).

(16) A. Lee Smith, *Spectrochim. Acta*, **16**, 87 (1960).

Oxidations with Oxygen Difluoride. II. Addition to Unsaturated Carbon

R. F. MERRITT AND J. K. RUFF

Redstone Arsenal Research Division, Rohm and Haas Company, Huntsville, Alabama

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Controlled oxidative fluorination of selected olefins and acetylenes has been demonstrated. Direct preparation of α-fluoro ketones, fluorohydrins, and α,α-difluoro ketones has been effected.

Following the initial preparation of oxygen difluoride (OF_2) by Lebeau and Damiens[1] in 1927, the investigation of the chemistry of this powerful oxidant was confined to various inorganic systems.[2] However, recent work[3] has shown that OF_2 oxidations of organic substrates can be controlled in the case of primary aliphatic amines. The facile amine oxidation,[3] which was rapid at −78°, suggested extension of similar techniques to study other Lewis base–OF_2 interactions.

It was found that certain olefins were sufficiently unreactive at −78° and controlled addition could be achieved. Acetylenes, however, were slightly less reactive at −78° and uptake of OF_2 proceeded at a convenient rate at −40°. In both cases, the products isolated contained a fluorine α to an oxygen atom, *e.g.*, α-fluoro ketones, α,α-difluoro ketones, and a fluorohydrin. Such products suggest direct addition of the elements of OF_2 across the double or triple bond followed by further reaction (decomposition) leading to observed compounds. Such direct addition of OF_2

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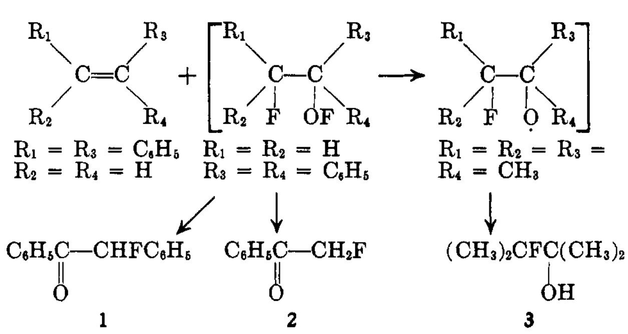
(1) P. Lebeau and A. Damiens, *Compt. rend.*, **185**, 652 (1927).

(2) See J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Supplement II, part I, Longmans, Green and Co., New York, N. Y., for a complete survey.

(3) R. F. Merritt and J. K. Ruff, *J. Am. Chem. Soc.*, **86**, 1392 (1964).

SCHEME I



to a double bond has been observed by Gatti.[4] Photoaddition of OF_2 to SO_3 was shown to produce FSO_2-OOF postulated as addition across the S–O double bond. The OF or hypofluorite group attached to carbon is unknown with the exception of trifluoromethyl hypofluorite (CF_3OF) prepared by Cady and Kellog.[5] This represents a rather special case in that decomposition to COF_2 (the only possible product) requires cleavage of the strong C–F bond. An alkyl hypofluorite would be expected to be much less stable as C–H and C–C bond cleavage is a lower energy process.[6] The formation of HF (−134 kcal./mole) provides additional strong driving force for decomposition. No hypofluorites were found among the products of the olefin or acetylene additions.

Results and Discussion

The general procedure employed with the low-temperature additions was to expose a cooled Freon 11 solution of the olefin or acetylene to subatmospheric pressures of OF_2. The progress of the reaction was followed by pressure-drop measurements with a manometer placed in the system.

The representative olefins chosen reacted smoothly at −78° within a short time (<2 hr.) forming the α-fluoro oxygenated derivatives shown in Scheme I.

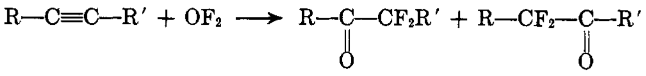
Tetramethylethylene rapidly consumed 1 equiv. of OF_2 within 1 hr. at −78°. The major product, 2-fluoro-3-hydroxybutane (**3**), is obtained consistently in yields of 65–70%. The fluorohydrin is extremely sensitive to moisture and complete conversion to pinacolone and HF is achieved by a brief exposure to air. Side products in varying small amounts were tetramethylethylene oxide and pinacolone, the latter probably arising from the hydrolysis of either the epoxide or the fluorohydrin. The source of the extra proton in the fluorohydrin is probably the unchanged tetramethylene whose 12 allylic protons are readily available, as well as traces of moisture and HF.

1,1-Diphenylethylene smoothly absorbed the OF_2 at −78° but more slowly (2.5 hr.) than the tetramethylethylene. The single significant product is ω-fluoroacetophenone (**2**) found in 66% yield. The major by-product, apart from a polymeric mass, was biphenyl.

cis-Stilbene was much more reactive than the *trans* isomer and was converted to α-fluoro-α-phenylacetophenone (**1**) as well as *cis*- and *trans*-α-fluorostilbenes. The yield of fluoro ketone was low (17%) since the majority of the product was an intractable polymeric mass. The *trans*-stilbene showed no reaction under the conditions necessary for complete consumption of the OF_2 by the *cis* isomer.

Butene-1 and propene-1 additions were uncontrollable and low-order detonations occurred upon mixing in every case. Styrene polymerized readily when exposed to the OF_2 at −78° and no monomeric products could be found. α,β-Unsaturated esters and nitriles such as methyl methacrylate and acrylonitrile are unreactive at −78° but polymerize readily at 0° and above. No monomeric adducts with OF_2 were found in the latter two cases.

The production of the α-fluoro ketones and fluorohydrin prompted a low temperature F^{19} n.m.r. investigation to ascertain the presence or absence of the expected hypofluorite group. The F^{19} n.m.r. spectrum of a sample of the crude reaction mixture from tetramethylethylene and OF_2 was taken at −78° immediately upon completion of the addition. The specimen was not warmed above −78° at any time prior to the recording of the spectrum. No fluorine signals other than those already observed in the final fluorohydrin were seen. The hypofluorite is either not an intermediate or undergoes rapid decomposition at −78°.



$$R{-}C{\equiv}C{-}R' + OF_2 \longrightarrow R{-}\underset{\underset{O}{\|}}{C}{-}CF_2R' + R{-}CF_2{-}\underset{\underset{O}{\|}}{C}{-}R'$$

	Yield, %	
$R = R' = C_6H_5$	82	...
$R = C_6H_5$; $R' = CH_3$	69	0
$R = CH_2CH_3$; $R' = CH_3$	27	42
$R = CH_2CH_3CH_3$; $R' = H$	33	...

The acetylenes examined reacted smoothly with OF_2 to produce α,α-difluoro ketones. All acetylenes were much less reactive than the corresponding olefins when treated with OF_2 in the same manner (Freon 11 at −78°). The addition could be made to proceed at a more convenient rate (22 hr.) by warming the acetylene–Freon mixture to −40°. However, the use of a 1:1 mixture of Freon 11 and diethyl ether enhanced the rate of addition and the rates become comparable at −78° with those of an olefin in only Freon 11 at −78°. The same α,α-difluoro ketones were formed at −40 and at −78°.

As α-fluorohypofluorites were the postulated intermediates in the olefin cases, the α-fluorovinyl hypofluorites would be the analogous product from acetylene additions. Such a group would possess marginal stability and rearrange with a fluorine shift to the observed difluoro ketones. In all cases, small (5–10%) amounts of acyl fluorides were formed. The origin of this group may lie in the addition of a second molecule of OF_2 to the adduct followed by cleavage of the α-alkoxy ketone. Scheme II outlines a possible course for this addition reaction.

The pentyne-2 addition mixture was examined at −78° by F^{19} n.m.r. The spectrum of the crude mixture, which had never been warmed above −78°, showed only the isomeric mixture of difluoro ketones and small amounts of acetyl and propionyl fluorides. No other types of fluorine signals were found which indicates that the reaction is complete at −78°.

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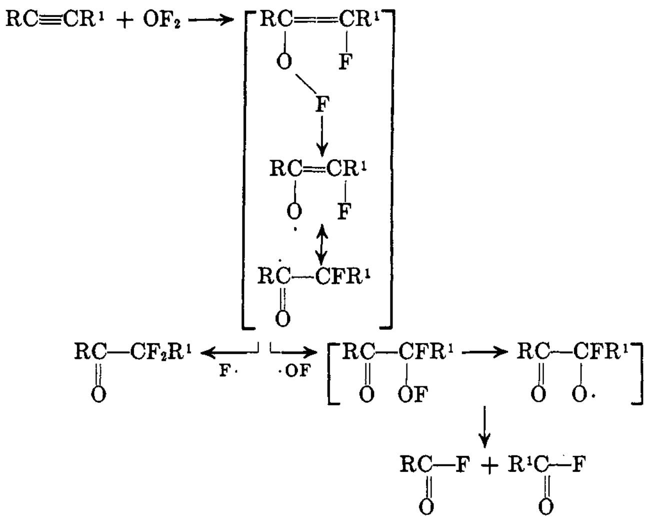
[4] R. Gatti, E. H. Starico, J. E. Sicre, and H. J. Shumacher, *Angew Chem.*, **75**, 137 (1963).

[5] K. B. Kellog and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

[6] The relative bond strengths follow: C–F −102 kcal./mole, C–C −80 kcal./mole, and C–H −99 kcal./mole (E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 37).

SCHEME II



Oxygen difluoride addition to unsaturated carbon has been shown to be rapid and controllable at low temperatures. The product formation can be generalized by postulating direct addition of the elements of OF_2 followed by further reaction of the energetic hypofluorite thus formed. The preparation of α,α-difluoro ketones from acetylenes possesses limited synthetic utility as they are difficult to prepare by other more standard methods.

Experimental

All melting points and boiling points are uncorrected. Infrared spectra were taken with a Perkin-Elmer Model 21 spectrophotometer. Proton n.m.r. spectra were recorded with a Varian Associates Model A-60 and F^{19} n.m.r. spectra with a Varian Associates Model HR-40 spectrometer. The spectra were taken with CCl_4 solvent unless otherwise indicated. Tetramethylsilane (TMS) was used as internal standard for the proton spectra and trifluoroacetic acid (TFA) for the fluorine spectra. Gas samples were analyzed routinely on a Consolidated Model 21-620 mass spectrometer. Vapor phase chromatograms were obtained with a Wilkens Model A-90-P instrument.

Materials.—The oxygen difluoride was purchased from Allied Chemical Company and used without further purification (<1% CO_2). The olefins and acetylenes were obtained from commercial sources and their physical constants compared with established values to ensure purity.

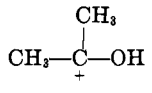
Apparatus.—The oxygen difluoride was stored in large-volume glass bulbs which were an integral part of a standard high-vacuum line. All mercury manometers were protected with a layer of degassed Kel-F KF-10[7] oil and stopcocks lubricated with Kel-F No. 90[7] grease. Other lubricants are *not* acceptable. The OF_2 can be stored in Pyrex indefinitely without decomposition if the above precautions are taken. Safety shields are to be used as OF_2 has proven somewhat treacherous.

The alkyl olefin–OF_2 additions were all performed in a similar manner except where product characteristics necessitated variation in work-up procedure. The case of tetramethylethylene given below is typical.

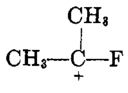
Tetramethylethylene–OF_2 Addition.—The title olefin (1.0 g., 12 mmoles) dissolved in 10 ml. of CCl_3F was slurried with 2.0 g. of NaF. The mixture was degassed and warmed to −78°, whereupon stirring was initiated and the OF_2 (12 mmoles) was admitted to the reactor. Within 2 hr. the OF_2 was completely consumed. The reaction mixture was again outgassed at −78° to ensure complete removal of the OF_2 and then warmed to 25° under nitrogen. Ether (10 ml.) was added and the sodium fluoride was removed by filtration. The ether and CCl_3F were slowly removed at 25° to leave 1.3 g. of crude yellow oil. Exposure of this oil to air at room temperature causes immediate darkening caused by elimination of HF. The oil was immediately diluted with 2 ml. of ether and analyzed by vapor phase chromatography (SF 96 at 80°). Three main products were indicated of which two were pinacolone (6% yield) and tetramethylene oxide (8% yield). These products were identified by a comparison of their infrared and n.m.r. spectra with those of authentic samples.

The third material, formed in 76% yield, was tetramethylethylene fluorohydrin, an unstable colorless liquid which rearranges to pinacolone and HF in the presence of acids, bases, or heat. The infrared spectrum contained bands for OH (2.77), C–CH_3 (7.26), and C–F (8.5–8.6 μ). The proton n.m.r. spectrum was a 6-proton singlet at δ 1.18 $[-\mathrm{O}-\overset{|}{\mathrm{C}}-(\mathrm{CH_3})_2]$ and a 6-proton doublet (J = 23 c.p.s.) centered at 1.33 $[-\mathrm{F}-\underset{|}{\overset{|}{\mathrm{C}}}-(\mathrm{CH_3})_2]$. The hydroxyl proton was found at δ 2.36. The fluorine n.m.r. spectrum consisted of a septet centered at +2887 c.p.s. from TFA and is indicative of fluorine split (J = 23 c.p.s.) by six equivalent adjacent protons.

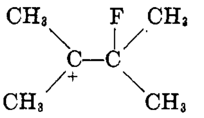
The mass spectrum exhibited no parent peak but the following definite fragments, among others, were found.



$m/e = 59$



$m/e = 61$



$m/e = 103$

Anal. Calcd. for $C_6H_{13}FO$: C, 59.97; H, 10.90. Found: C, 59.09; H, 10.81.

***cis*-Stilbene–OF_2 Addition.**—The *cis* olefin (4.5 g., 25 mmoles) consumed 22 mmoles of OF_2 at −78° within 3 hr. The usual work-up produced 5.01 g. of crude unstable oil which was immediately placed on a silica gel column and eluted with pentane–methylene chloride solvent mixture.

The first material appearing was *cis*-stilbene (0.49 g. or 2.7 mmoles recovered; 3 mmoles of OF_2 was also recovered.)

The second fraction was 0.75 g. (17.2% yield) of a mixture of *cis*- (one part) and *trans*-α-fluorostilbene (six parts), m.p. 90–91° (lit.[8] m.p. 93–94° for *trans*-α-fluorostilbene). The proton n.m.r. indicated a single nonaromatic proton (1.10 ratio) as a doublet centered at δ 5.54, with coupling constant J_{F-H} = 67 c.p.s. with the *trans* adjacent vinylic fluorine and J_{F-H} = 21 c.p.s. for the *cis*. The fluorine n.m.r. spectrum was also consistent with this formulation.

The next fraction, a solid, m.p. 43°, was assigned strucure α-phenyl-α-fluoroacetophenone. The weight of the fraction was 0.84 g. representing a yield of 18% based on OF_2 consumed. The infrared spectrum showed carbonyl absorption at 5.90 and C–F at 7.9 and 8.15 μ. The proton n.m.r. had a single nonaromatic proton (ratio 1:10) as a doublet (J_{F-H} = 51 c.p.s.) centered at δ 6.29. The fluorine spectrum possessed only a doublet centered at +4049 c.p.s. (TFA) with J_{F-H} = 51 c.p.s.

Anal. Calcd. for $C_{14}H_{11}FO$: C, 78.49; H, 5.18. Found: C, 78.11; H, 5.37.

An addition 2.5 g. of intractable tar was recovered from which nothing identifiable could be gleaned.

1,1-Diphenylethylene–OF_2 Addition.—The 1,1-diphenylethylene (4.5 g., 25 mmoles) consumed 22 mmoles of OF_2 at −78° within 4 hr. The usual work-up produced 5.75 g. of crude unstable oil which was immediately chromatographed on silica gel.

The first product eluted was 0.30 g. (9% yield) of biphenyl which was identified by comparison of infrared spectra with that of an authentic sample.

Following the biphenyl, 0.20 g. of starting 1,1-diphenylethylene was recovered.

The major product appeared as 2.0 g. (66% yield) of colorless oil, b.p. 41–52° (0.03 mm.), lit.[9] b.p. 65–70° (1 mm.), assigned as ω-fluoroacetophenone, which was formed in *ca.* 66% yield. The infrared spectrum confirmed the presence of carbonyl (5.85) and C–F (8.10 μ). The proton n.m.r. spectrum had two nonaromatic protons as a doublet centered at δ 8.5 with J_{F-H} = 48 c.p.s. The fluorine n.m.r. was a triplet centered at +5996 c.p.s. (TFA) with J_{F-H} = 47 c.p.s. The 2,4-dinitrophenylhydrazone (2,4-DNP) was prepared which had m.p. 223–224° dec. (lit.[9] m.p. 213–214°).

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(7) Minnesota Mining and Manufacturing Co.

(8) J. Borstein, M. R. Borden, F. Numes, and H. I. Tarlin, *J. Am. Chem. Soc.*, **85**, 1609 (1963).

(9) F. Bergmann and A. Kalmus, *ibid.*, **76**, 4137 (1954).

Diphenylacetylene (1.68 g., 10 mmoles) was dissolved in 25 ml. of Freon 11 (CCl_3F) and slurried with 2.0 g. of sodium fluoride. The mixture was thoroughly degassed and was equilibrated at −40°. The OF_2 was admitted to the reactor and 10 mmoles was consumed within 2 hr. The unchanged OF_2 was distilled off at −40° and the sodium fluoride was removed by filtration. Evaporation of the solvent produced 1.9 g. of yellow unstable oil with a very weak band at 5.49 (pH COF) and strong carbonyl absorption at 5.85, which agrees with the literature value[10] of 5.85 μ for α-phenyl-α,α-difluoroacetophenone. The 2,4-DNP prepared directly from this oil and recrystallized from ethanol had m.p. 181–182° (lit.[10] m.p. 180–181°).

Methylphenylacetylene (2.5 ml., 20 mmoles) was dissolved in a mixture of 5 ml. of Freon 11 and 5 ml. of diethyl ether. Sodium fluoride (2.0 g., 48 mmoles) was added and the entire mixture was thoroughly degassed. The OF_2 (20 mmoles) was passed into the reactor and work-up began at 50% OF_2 consumption. This required 70 min. at −78°. The excess OF_2 was removed and and the sodium fluoride was separated by filtration. The solvent was fractionated away and the pale yellow unstable oil was analyzed by vapor phase chromatography. The major product (81% yield, internal standard) is assigned the structure α-methyl-α,α-difluoroacetophenone and is accompanied by benzoyl fluoride (18%). The fluoro ketone had a carbonyl band at 5.85 μ and is therefore conjugated and analogous to α-phenyl-α,α-difluoroacetophenone mentioned above. The F^{19} n.m.r. spectrum was a quartet (J_{FH} = 20 c.p.s.) centered at +548 c.p.s. (TFA). The magnitude of the coupling constant is indicative of fluorine coupling with three equivalent protons on an adjacent carbon atom. The proton n.m.r. spectrum showed the nonaromatic protons as a triplet (J_{FH} = 20 c.p.s.) centered at δ 8.6 in a ratio of 3:5 with the aromatic protons.

Anal. Calcd. for $C_9H_8F_2O$: C, 63.53; H, 4.74. Found: C, 62.97; H, 5.02.

Pentyne-2 (3.4 g., 50 mmoles) was dissolved in 25 ml. of a 1:1 mixture of diethyl ether and Freon 11. Sodium fluoride (2.0 g.) was added and the solution was thoroughly degassed and equilibrated at −78°. The OF_2 (50 mmoles) was passed into the reactor and work-up began within 2 hr., (>90% consumption of OF_2). The unused OF_2 was distilled away and the sodium fluoride was separated by filtration. Distillation of the crude solution produced 4.2 g. (69% yield) of colorless liquid, b.p. 64–67° (756 mm.). Analysis by vapor phase chromatography (SF 96 at 52°) showed two products comprising 61 and 39% of the total. Both possessed carbonyl absorption at 5.71 μ ($CF_2C{=}O$) and represent the two possible isomeric difluoro ketones in a total yield of 69%. The proton n.m.r. spectrum of the 39% isomer showed a triplet (J_{FH} = 20 c.p.s.) centered at δ 1.68 and represents the ($O{=}C{-}CF_2CH_3$) group. The F^{19} n.m.r spectrum showed a quartet (J_{FH} = 20 c.p.s.) at +898 c.p.s. (TFA) thus identifying the 39% compound as 2,2-difluoropentanone-3. The 61% isomer is 3,3-difluoropentanone-2 and showed the fluorine as a triplet centered at +1238 (TFA) (J_{FH} = 16 c.p.s.).

Anal. Calcd. for $C_5H_8F_2O$: C, 49.18; H, 6.60. Found: C, 48.96; H, 6.34.

Pentyne-1 (3.4 g., 50 mmoles) was dissolved in 20 ml. of a 1:1 mixture of Freon 11 and diethyl ether. Sodium fluoride (2.0 g.) was added and the reaction mixture was thoroughly degassed and equilibrated at −78°. After the uptake of 50 mmoles of OF_2 the products were distilled under reduced pressure (25°) and the solution was concentrated. Analysis by vapor phase chromatography (SF 96 at 55°) indicated a single major product in 23% yield (internal standard) which had carbonyl absorption at 5.70 ($-CF_2C{=}O$), and C–F absorption at 8.1 and 9.0–9.5 μ. The proton n.m.r. spectrum showed a single proton as a triplet at δ 5.68 (J_{FH} = 54 c.p.s.) which is indicative of a ($O{=}C{-}CF_2H$) group. The fluorine n.m.r. spectrum was a doublet (J_{FH} = 52 c.p.s.) centered at +1950 c.p.s. (TFA). No evidence was found for the positional isomer, 2,2-difluoropentanal-1.

Anal. Calcd. for $C_5H_8F_2O$: C, 49.18; H, 6.60. Found: C, 49.28; H, 6.94.

Acknowledgment.—This work was sponsored under Army Ordnance Contract DA-01-021 ORD-11878. We are grateful to Mr. Jack Brooks for technical assistance and to Mrs. Carolyn Haney for n.m.r. spectra.

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[10] J. Bornstein and M. R. Borden, *Chem. Ind.* (London), 441 (1958).

Oxidations with Peroxytrifluoroacetic Acid–Boron Fluoride. IV.[1,2] Chloromesitylene

HAROLD HART, C. A. BUEHLER, A. J. WARING,

Department of Chemistry, Michigan State University, East Lansing, Michigan

AND SEYMOUR MEYERSON

Research and Development Department, American Oil Company, Whiting, Indiana

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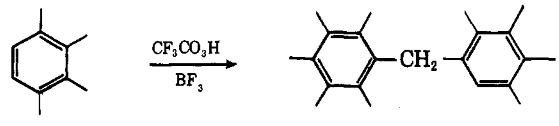
Oxidation of chloromesitylene with peroxytrifluoroacetic acid and boron fluoride gave, in addition to the expected chloromesitol, two diphenylmethane derivatives, 3,3′-dichloro-2,2′,4,4′,6,6′-hexamethyldiphenylmethane (VIII) and 4-(3′-chloro-2′,4′,6′-trimethylbenzyl)-3-chloro-2,6-xylenol (V), the latter being the principal reaction product. The structure of V was deduced largely from the mass-spectral fragmentation pattern and n.m.r. spectrum, and was confirmed by reduction to 4-(2′,4′,6′-trimethylbenzyl)-2,6-xylenol (VI), synthesized also by an independent route. Nitromesitylene gives an analogous oxidation product XI. The products are accounted for by the following reaction sequence: hydroxylation and further oxidation of one molecule of reactant to a benzylic ion, alkylation by this ion of a second molecule of reactant, debenzylation, and alkylation by the new benzylic ion of another molecule of reactant.

When prehnitene (I) was oxidized with peroxytrifluoroacetic acid and boron fluoride,[1a,c] a major product was 2,2′,3,3′,4,4′,5,5′-octamethyl diphenylmethane (II). It was suggested[1c] that II arose from alkylation of I with the appropriate tetramethylbenzyl cation; this, in turn, presumably was produced by debenzylation of III and IV, which were not isolated, but postulated as intermediates. 2,3,5- and 2,3,6-trimethylphenols, the other debenzylation products of III and IV, respec-



I II

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[1] For previous papers, see (a) C. A. Buehler and H. Hart, *J. Am. Chem. Soc.*, **85**, 2177 (1963); (b) A. J. Waring and H. Hart, *ibid.*, **86**, 1454 (1964); (c) H. Hart and C. A. Buehler, *J. Org. Chem.*, **29**, 2397 (1964).

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