REACTION OF TETRAFLUORODEHYDROBENZENE WITH AROMATIC HYDROCARBONS AND THEIR DERIVATIVES*

I. N. Vorozhtsov, N. G. Ivanova,
and V. A. Barkhash

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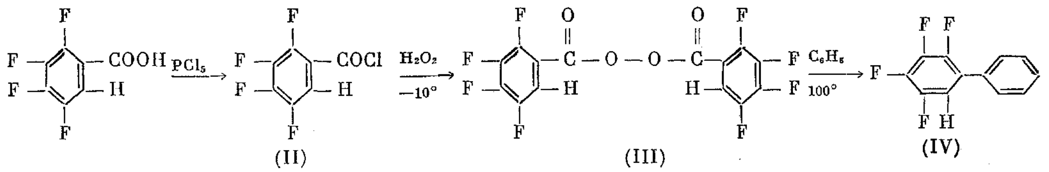
It was shown previously that a product of composition $C_{12}H_6F_4$ [1] is obtained when pentafluorophenylmagnesium chloride is heated in benzene in the presence of ethylene oxide, which evidently is the product of the addition of tetrafluorodehydrobenzene (formed from C_6F_5MgCl) to benzene. The compound $C_{12}H_6F_4$ was assigned the structure of 2,3,4,5-tetrafluorobiphenyl; later the structure of the biphenyl derivative was assigned by some American chemists to the product of the analogous reaction with toluene [2]. Recently [3], another structure, that of 5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene (I), was proposed for the compound $C_{12}H_6F_4$, on the basis that compound (I) absorbs 2 moles of hydrogen, and on pyrolysis gives 1,2,3,4-tetrafluoronaphthalene. Both of these transformations are impossible for the biphenyl derivative. That product (I) is not the biphenyl derivative was conclusively proved by us by the synthesis of 2,3,4,5-tetrafluorobiphenyl (IV), which differs from compound (I) in melting point and in the data of the infrared and ultraviolet spectra. The synthesis was carried out according to the scheme



However, the data given in [3] do not exclude still another structure for the addition product of C_6F_4 to benzene, and specifically, the structure of 1,2,3,4-tetrafluoro-9,12-dihydrodiphenylene (V). A compound of this formula should add 2 moles of hydrogen, and on pyrolysis should isomerize to the tetrafluorobenzocyclooctatetraene, which can then undergo cleavage to the tetrafluoronaphthalene and acetylene (cf. [4, 5]). We took the NMR spectrum of compound (I) (on a 100 MHz instrument), which disclosed the presence of two signals with centers at τ 5.1 (triplet, 2 protons) — nodal protons, and τ 3.6 (doublet of doublets, 4 protons) — vinyl protons; the character of the splitting and the values of the shifts could have been foreseen on the basis of the data for the NMR spectrum of barrelene [6]. The character of the spectrum fully corroborates structure (I), inasmuch as in compound (V) there are two kinds of nonequivalent vinyl protons. Besides this, the ultraviolet spectrum of compound (I) exhibits only weak absorption, with no well-defined maximum, in the 220-400 mμ region, which also contradicts structure (V), which contains the cyclohexadiene moiety with conjugated double bonds (Fig. 1).

From the still residue after the sublimation of compound (I) we were able to isolate still another product, which, based on the elemental analysis data and determination of the molecular weight, has the composition $C_{18}H_6F_8$, i.e., it is the addition product of two molecules of C_6F_4 to benzene. The product does not add hydrogen in the presence of PtO_2. We postulated that this product (VI) is formed by the diene synthesis reaction of the tetrafluorodehydrobenzene with compound (I); its structure is confirmed by the NMR spectrum, in which four signals are present: τ 6.66 (singlet, $1H^4$), τ 6.88 (triplet, $1H^1$), τ 7.05 (singlet, $2H^3$), and τ 8.21 (doublet, $2H^2$). In contrast to product (I), the ultraviolet spectrum of compound (VI) has an absorption maximum (λ_{max} 262 mμ, log ε 3,225), which is caused by the conjugation of the tetrafluorophenyl and cyclopropane rings in the structure of compound (VI); the ultraviolet spectra of compounds (VI) and phenylcyclopropane are similar (Fig. 2).

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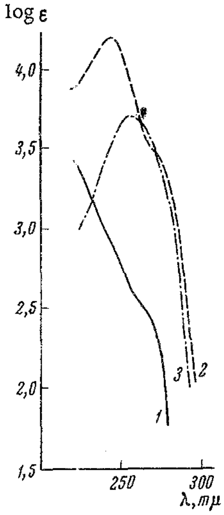
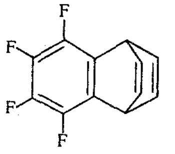
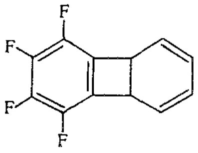


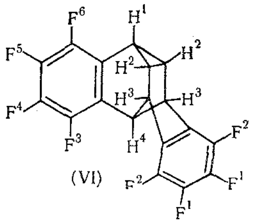
Fig. 1. Ultraviolet spectra in alcohol: 1) compound (I); 2) compound (IV); 3) 1,3-cyclohexadiene.



(I)

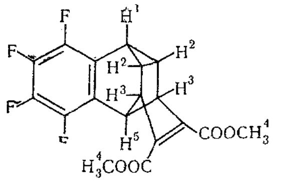


(V)

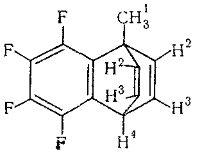


(VI)

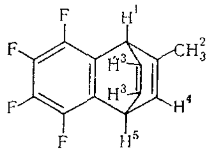
The formation of compound (VI) is apparently due to the peculiar partial conjugation of the 6 π-electrons in the barrelene portion of the (I) molecule (cf. [6]). It had been shown previously [7] that barrelene reacts by an analogous scheme with the dimethyl ester of acetylenedicarboxylic acid (VII). We also reacted compound (I) with ester (VII) and obtained adduct (VIII), the structure of which was proved by the NMR spectrum: τ 6.23 (singlet, $6H^4$), τ 6.35 (multiplet, H^1 and H^5), τ 7.38 (singlet, $2H^3$) and τ 7.92 (doublet, $2H^2$). The values of the chemical shifts of the signals and the character of the splitting are in good agreement with those for the adduct of barrelene with ester (VII) [7].



(VIII)



(IX)

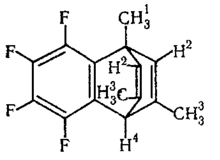


(X)

Contrary to [2], tetrafluorodehydrobenzene reacts with benzene homologs, also with the formation of tetrafluorobenzobicyclo[2.2.2]octatriene derivatives. With toluene we obtained a mixture of isomers of composition $C_{13}H_8F_4$, which was separated by GLC into a liquid (n_D^{22} 1.5042) and a solid (mp 37-39°) isomer, the structure of which was established by means of the NMR spectra. The NMR spectrum of the solid isomer has four signals: τ 3.6 (multiplet, $2H^3$), τ 3.8 (multiplet, $2H^2$), τ 5.2 (multiplet, $1H^4$), and τ 8.0 (doublet, $3H^1$). The NMR spectrum of the liquid isomer has five signals: τ 3.6 (doublet of doublets, $2H^3$), τ 4.1 (multiplet, $1H^4$), τ 5.2 and 5.4 (multiplets, $1H^5$ and $1H^1$), and τ 8.2 (doublet, $3H^2$). These data make it possible to assign the structure of 1-methyl- (IX) to the solid isomer, and the structure of 2-methyl-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene (X) to the liquid isomer.

When the reaction with mesitylene was run under analogous conditions we isolated in 33% yield a product of composition $C_{15}H_{12}F_4$, the structure of which, namely 1,3,10-trimethyl-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene (XI), was established by means of the NMR spectrum; the latter has four signals: τ 4.1 (multiplet, $2H^2$), τ 5.5 (multiplet, $1H^4$), τ 7.9 (doublet, $3H^1$), and τ 8.0 (doublet, $6H^3$). It is interesting to mention that tetrafluorodehydrobenzene does not react with hexamethylbenzene under our conditions, apparently because of steric hindrance. It was recently shown by Tatlow and co-workers [8] that the tetrafluorodehydrobenzene obtained from pentafluorophenyllithium reacts with durene to form the addition product, to which they assigned the structure of 2,3,9,10-tetramethyl-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]-octatriene.

The reaction of tetrafluorodehydrobenzene with anisole in the presence of ethylene oxide leads to a mixture of two products with mp 79-83 and 72-75° (4 : 1 ratio), which were separated by GLC. The compound with mp 79-83° has the composition $C_{13}H_8F_4O$, contains a OCH_3 group, and its structure, namely 1-methoxy-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene (XII), was established by means of the NMR spectrum, in which four signals are present: τ 3.6 (multiplet, $2H^2$), τ 3.8 (multiplet, $2H^3$), τ 5.3 (multiplet, $1H^4$), and τ 6.6 (doublet, $3H^1$). The compound with mp 72-75° has the composition $C_{12}H_6F_4O$, contains a $C=O$ group on the basis of the infrared spectrum, and adds 1 mole of hydrogen [compounds (I) and (IX)-(XII) add 2 moles of hydrogen in the presence of PtO_2]. On the basis of these data and the NMR spectrum we assigned the compound the structure of 2-keto-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octadiene (XIII). The NMR spectrum of ketone (XIII) has three multiplet signals, equal in area: τ 3.6 ($2H^2$), τ 5.6 (H^1 and H^4), and τ 8.1 ($2H^3$). The presence of a carbonyl group in compound (XIII) was confirmed by preparing the 2,4-dinitrophenylhydrazone. The formation of ketone (XIII) is apparently explained by the cleavage of the initially formed vinyl ether, isomeric with compound (XII).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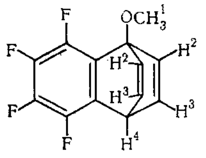
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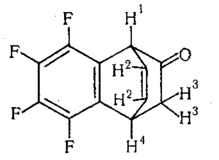
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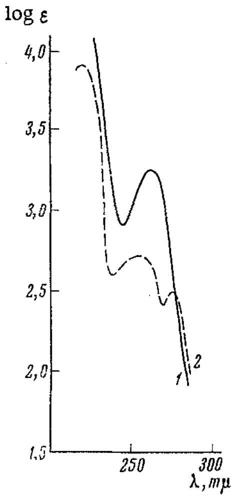

Fig. 2. Ultraviolet spectra in alcohol: 1) compound (VI); 2) phenylcyclopropane.

It should be mentioned that, in contrast to the data given in [3], under our conditions the yields of the addition products of tetrafluorodehydrobenzene are greatly dependent on whether the reaction is run in the presence of ethylene oxide or without it. When the reaction with benzene was run without the ethylene oxide (refluxing for 5 h) we obtained after distillation a mixture, which, based on the GLC data, was composed of 11 products, in which connection the chromatographic yield of compound (I) was a total of 11.6%. When the reaction was run under exactly the same conditions, but in the presence of ethylene oxide, then the distillate (based on the GLC data) consisted mainly of a mixture of compound (I), ethylene chlorohydrin and two isomeric alcohols of composition $C_8H_5F_5O$;* the yield of compound (I) was 35%. In the case of the reaction with toluene the yield of isomeric mixture (IX) and (X), without the ethylene oxide, and 24%, while in its presence the yield was 49%. In our opinion, ethylene oxide, forming a complex with the cleaved MgClF, facilitates a generation of tetrafluorodehydrobenzene.

The reaction of tetrafluorodehydrobenzene with aromatic hydrocarbons and their derivatives can apparently serve as a convenient method for the preparation of the very difficultly accessible derivatives of benzobarrelene (cf. [9]), which possess interesting chemical properties.

EXPERIMENTAL

The infrared spectra were taken on a UR-10 instrument for 5% solutions in CCl_4. The ultraviolet spectra were taken on an SFD-2 instrument, in alcohol, at a molar concentration of 10^{-4}, and a layer thickness of 0.5 cm. The F^{19} NMR spectra were taken on a JNM-3 instrument, at a frequency of 40 MHz, for approximately 30% solutions in tetrahydrofuran, using benzotrifluoride as the internal standard. The NMR spectra were taken on TsLA NMR 5535 (40 MHz) and JNM-3H (60 MHz) instruments for 20-25% solutions in CCl_4, using tetramethylsilane as the internal standard.

Reaction of Tetrafluorodehydrobenzene with Benzene. To a solution of C_6F_5MgCl, obtained from 42 g of C_6F_5Cl and 10.15 g of Mg, was added 120 ml of absolute benzene, the mixture was cooled to −15°, and a solution of 20 ml of ethylene oxide in 50 ml of absolute benzene, also cooled to −15°, was added. The temperature was raised slowly up to room temperature, and then the mixture was refluxed for 5 h. The mixture was decomposed with dilute HCl solution, and the aqueous layer was extracted with ether. After distilling off the solvents, and then the fraction with bp 36-40° (3 mm), the residue was cooled to give a precipitate, which was suction-filtered, purified by passage through an Al_2O_3 column [eluant-petroleum ether (bp 70-100°)], and then sublimed in a vacuum of 1-2 mm; here 15 g (32%) of compound (I), mp 71-72°, sublimed at a bath temperature of 40-50°, while 2.5 g (5%) of compound (VI), mp 174-175°, sublimed at a bath temperature of 130-135°. Found %: C 57.58, 57.41; H 1.85, 1.81; F 41.06, 41.09; mol. wt. 360. $C_{18}H_6F_8$. Calculated %: C 57.71; H 1.66; F 40.64; mol. wt. 374.2. Infrared spectrum (cm^{-1}): 1015 s (C—F), 1495 s, 1520 s (fluorinated aromatic ring), 3050 med (C—H in cyclopropane), 2990 med (C—H in cyclopentane). λ_{max} 262 mμ (log ε 3.225). The F^{19} NMR spectrum has four signals: 83.4 p.p.m. (doublet, 2 F^2), 88.5 p.p.m. (multiplet, F^3 and F^6), 97.4 p.p.m. (multiplet, 2 F^1 and F^4 or F^5), and 100.0 p.p.m. (triplet, F^4 or F^5).

Adduct (VIII) of Compound (I) and Dimethyl Ester of Acetylenedicarboxylic Acid (VII). A mixture of 1.13 g of compound (I) and 0.8 g of ester (VII) was heated at 100-110° for 14h. At the end of this time the reaction mixture was purified by thin-layer chromatography on Al_2O_3 plates (eluant—benzene). We obtained 0.5 g (25.8%) of adduct (VIII), mp 123-124.5° (from alcohol). Found %: C 58.87, 59.00; H 3.49, 3.52; F 20.36, 20.27. $C_{18}H_{12}F_4O_4$. Calculated %: C 58.70; H 3.26; F 20.65. In-

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* As was recently established, the main anomalous product formed in the reaction is α-pentafluorophenylethyl alcohol, containing β-pentafluorophenylethyl alcohol as impurity.

frared spectrum (cm^{-1}): 1510 s (fluorinated aromatic ring), 1618 med (C=C), 1730 s (C=O in esters), 2940 med (CH_3), 2990 med (CH). λ_{max} 238 mμ (shoulder, log ε 4.03).

1-Methyl-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene (IX) and 2-Methyl-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene (X). To a solution of C_6F_5MgCl, obtained from 10.5 g of C_6F_5Cl and 2.79 g of Mg, was added 20 ml of absolute toluene, the mixture was cooled to −15°, and a solution of 6.5 ml of ethylene oxide in 20 ml of absolute toluene was added. The running of the reaction and the workup were the same as in the experiment with benzene. An oil was obtained, which, based on the GLC data, contained 49% of a mixture of isomers (IX) and (X) in a 4 : 1 ratio. Fractional distillation gave a fraction with bp 110.5° (14 mm); n_D^{22} 1.4990. The elemental analysis data correspond to the composition $C_{13}H_8F_4$. The fraction was separated chromatographically (Apiezon L + polydiethylene glycol adipate/brick 10 : 100, column length 2 meters, temperature 178°, carrier gas He). Isomer (IX) has mp 37-39°. Found %: C 65.00, 64.76; H 3.41, 3.34; F 31.75, 31.87. $C_{13}H_8F_4$. Calculated%: C 64.98; H 3.36; F 31.63. Infrared spectrum (cm^{-1}): 1010 s (C—F), 1510 s (fluorinated aromatic ring), 1650 s (C=C), 2860 w, 2918 w, 2940 med, 2975 med (CH_3), 3080 med, 3000 med (olefinic C—H). Isomer (X) is a liquid with n_D^{22} 1.5042. Found %: C 64.88, 64.67; H 3.58, 3.57; F 31.43, 31.76. $C_{13}H_8F_4$. Calculated %: C 64.98; H 3.36; F 31.63. Infrared spectrum (cm^{-1}): 1490 s, 1510 s (fluorinated aromatic ring), 1645 med (C=C), 2985 med (CH_3), 3070 med, 2990 med (olefinic C—H).

1,3,10-Trimethyl-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene (XI). The reaction was run in the same manner as the preceding experiment. The starting quantities were: solution of C_6F_5MgCl from 10.58 g of C_6F_5Cl, 45 ml of dry mesitylene, and 6.5 ml of Al_2O_3. Fractional distillation gave compound (XI) in 33% yield, bp 123-129° (11 mm), mp 93-93.5° (sublimes in vacuo). Found %: C 67.43, 67.68; H 4.45, 4.44; F 28.57, 28.53. $C_{15}H_{12}F_4$. Calculated %: C 67.13; H 4.50; F 28.32. Infrared spectrum (cm^{-1}): 1500 s (fluorinated aromatic ring), 1680 s (C=C), 2890 w, 2860 w, 2915 med, 2935 med (CH_3), 3050 med (olefinic C—H).

Reaction of Tetrafluorodehydrobenzene with Anisole. The reaction was run in the same manner as the experiment with toluene. The starting quantities were: solution of C_6F_5MgCl from 31.4 g of C_6F_5Cl, 150 ml of dry anisole, and 19.5 ml of ethylene oxide. Fractional distillation gave a fraction with bp 132-140° (12 mm), which, based on the GLC data, consisted of a mixture of compounds (XII) and (XIII) (4 : 1). The fraction was separated chromatographically (polyethylene glycol adipate/brick 20 : 100, column length 2 meters, temperature 192°, carrier gas He). Compound (XII)has mp 79-83°. Found %: C 61.18, 61.17; H 2.98, 3.01; F 29.84, 29.72; OCH_3 12.16, 12.26. $C_{13}H_8F_4O$. Calculated %: C 60.94; H 3.14; F 29.67; OCH_3 12.11. Infrared spectrum (cm^{-1}): 1012 s (C—F), 1500 s (fluorinated aromatic ring), 1640 s (C=C), 2845 w, 2920 w, 2945 med (CH_3), 3000 med, 3065 med (olefinic C—H). Compound (XIII) has mp 72-75°. Found %: C 59.93, 59.75; H 2.68, 2.78; F 31.01, 31.59. $C_{12}H_6F_4O$. Calculated %: C 59.61; H 2.50; F 31.34. Infrared spectrum (cm^{-1}): 1510 s (fluorinated aromatic ring), 1645 s (C=C), 1768 s (C=O), 2860 w, 2932 med, 2970 med (CH_2), 3080 med (olefinic C—H). 2,4-Dinitrophenylhydrazone, mp 226-227.5° (from alcohol). Found %: C 51.50, 51.49; H 2.41, 2.26; F 17.60, 17.91; N 13.25, 13.36. $C_{18}H_{10}F_4N_4O_4$. Calculated %: C 51.21; H 2.42; F 18.00; N 13.24.

2,3,4,5-Tetrafluorobiphenyl (IV). A mixture of 5.5 g of 2,3,4,5-tetrafluorobenzoic acid (obtained from tetrafluorophthalic acid as described in [10]) and 15 g of PCl_5 was heated for 4 h at 150°, after which the unreacted PCl_5 was filtered, the $POCl_3$ was vacuum-distilled, and the residue was fractionally distilled. We obtained 3.7 g of compound (II) (61%), bp 65-66° (10 mm); $n_D^{21.5}$ 1.4772.

A mixture of 3.7 g of acid chloride (II) and 5.5 ml of 30% H_2O_2 solution was added at −10° to 7 ml of a 15% NaOH solution, and the mixture was stirred at this temperature for 1 h. The obtained precipitate was suction-filtered, washed with water, and dried in vacuo. We obtained 1.8 g of peroxide (III) (52.5%), mp 77-78.5° (from petroleum ether).

A mixture of 1.2 g of peroxide (III) and 6 ml of benzene was heated in an ampule for 72 h at 100-105°. The obtained precipitate was filtered, and the filtrate was passed through an Al_2O_3 column (eluant—benzene). We obtained 0.4 g of compound (IV) (57%), mp 65-66° (after two sublimations). Found %: C 63.26, 63.28; H 2.84, 2.70; F 33.49, 33.67. $C_{12}H_6F_4$. Calculated %: C 63.74; H 2.66; F 33.62. Infrared spectrum (cm^{-1}): 1010 s (C—F), 1500 s (fluorinated aromatic ring), 3025 w, 3050 med, 3080 med (C—H of aromatic ring). λ_{max} 242 mμ (log ε 4.166). The NMR spectrum has two signals (with a 5 : 1 ratio of the intensities): τ 2.77 (singlet, phenyl), τ 3.06 (multiplet, proton in a polyfluorinated ring).

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CONCLUSIONS

1. Tetrafluorodehydrobenzene, formed when pentafluorophenylmagnesium chloride is heated in the presence of ethylene oxide, reacts with aromatic hydrocarbons along the lines of the diene synthesis, with the formation of derivatives of 5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene.

2. The reaction product of tetrafluorodehydrobenzene with benzene, namely 5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene, gives adducts of the diene synthesis type with the dimethyl ester of acetylenedicarboxylic acid and tetrafluorodehydrobenzene.

3. The reaction of tetrafluorodehydrobenzene with toluene leads to a mixture of two isomers: 1-methyl- and 2-methyl-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene; the analogous reaction with mesitylene gave 1,3,10-trimethyl-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene.

4. The reaction of tetrafluorodehydrobenzene with anisole leads to a mixture of 1-methoxy-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octatriene and 2-keto-5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octadiene.

5. The synthesis of 2,3,4,5-tetrafluorobiphenyl was accomplished.

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