Rearrangement of 1,5,9-Cyclododecatriene with Polyphosphoric Acid

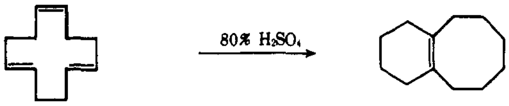
W. E. WELLMAN, M. C. BRENNEMAN, AND M. S. KONECKY

Chemicals Research Division, Esso Research and Engineering Company, Linden, New Jersey

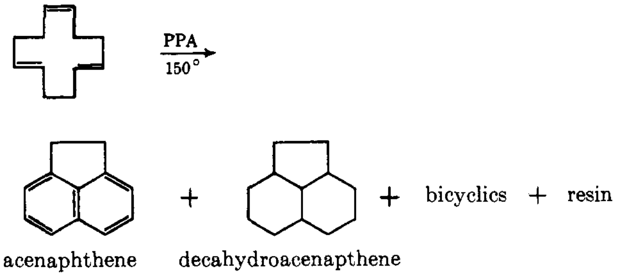
Received September 10, 1964

Treatment of *cis,trans,trans*-1,5,9-cyclododecatriene with excess polyphosphoric acid produced a mixture of hydrocarbons containing acenaphthene and decahydroacenaphthene. When a catalytic amount of polyphosphoric acid was used to effect the rearrangement of cyclododecatriene, the major product was octahydroacenaphthene. Several isomers were produced during the rearrangement, and they were separated and identified with the aid of preparative vapor phase chromatography.

The reaction of *cis,trans,trans*-1,5,9-cyclododecatriene (CDT) with 80% sulfuric acid has been shown as follows to produce a mixture of hydrocarbons containing $\Delta^{1,6}$-bicyclo[4.6.0]dodecene.[1] Another example of a transannular reaction of CDT has been furnished by Koch and Möller.[2] In this work, perhydroacenaphthene carboxylic acids were obtained from the reaction of CDT and carbon monoxide.



In the current work, a similar rearrangement of the carbon skeleton was observed when CDT was treated with an excess (8:1 wt. ratio) of polyphosphoric acid (PPA) at 150°. A very exothermic reaction occurred, and three types of reaction products were isolated. The major product, which constituted about 40–50% yield, was a high-boiling, clear, colorless liquid. Other products in minor amounts included a crystalline white solid, which was isolated in about 5% yield, and a low-melting resin in about 20–40% yield. Subsequent identification proved the solid to be acenaphthene and the liquid to be a mixture of compounds, including decahydroacenaphthene as the major component. The reaction is complex, however, as indicated by the presence of minor amounts of other rearrangement products, some of which appear to have bicyclic structures. Thus, the over-all equation can be written as follows. It appears that in the main reaction CDT was rearranged to a fused carbocyclic intermediate which subsequently underwent a disproportionation reaction to give the aromatic hydrocarbon, acenaphthene, and the completely saturated hydrocarbon, decahydroacenaphthene. The ability of polyphosphoric acid to promote rearrangement and aromatization has been demonstrated previously for heterocyclic systems.[3,4]



The distribution of products for the present reaction is dependent upon the amount of PPA present. When PPA was present in excess, the reaction products obtained with PPA–CDT ratios of 8:1, 5:1, and 3:1 were essentially identical. However, when the amount of PPA was reduced to a catalytic level, *i.e.*, a 1:10 ratio of acid–CDT, the product was considerably different. In this latter case, the major product was a mixture of octahydroacenaphthene isomers, and no measurable amount of acenaphthene or decahydroacenaphthene was produced. Also, the amount of resin and bicyclics was diminished. The lower concentration of polyphosphoric acid is sufficient to catalyze the skeletal rearrangement of CDT, but apparently insufficient to effect the disproportionation of the intermediate to acenaphthene and decahydroacenaphthene.

A more convenient procedure for synthesizing octahydroacenaphthene was developed which incorporates a solid catalyst, consisting of polyphosphoric acid impregnated on kieselguhr (Universal Oil Products #2 polymerization catalyst), in place of polyphosphoric acid. The reaction product was essentially identical with that obtained from the 1:10 (PPA–CDT) reaction, with octahydroacenaphthene the main component. However, isolation of the reaction product was greatly simplified when the solid catalyst was used, since the catalyst could be removed easily by filtration. This technique obviated a tedious extraction of the hydrocarbon product from aqueous phosphoric acid in which stable emulsions were formed. The rearrangement reaction was further improved when a solvent, such as xylene, was used. The solvent improved the yield of rearranged product to about 90% and helped to dissipate the heat of reaction. The rearrangement results are summarized in Table I.

Structure Proof

The proof of structure for the decahydroacenaphthene isomers was complicated by the lack of pure primary standards, making it necessary to synthesize and identify the pure isomers. For this purpose, acenaphthene was exhaustively hydrogenated over Raney nickel at 200°. Analysis of the reduced product by means of v.p.c. showed four peaks corresponding to four isomers which were subsequently isolated by preparative v.p.c. Each of these four isomers gave a negative potassium permanganate test, an indication of complete reduction of partially hydrogenated intermediates, and an elemental analysis which agreed with the theoretical value for decahydroacenaphthene. Further, the infrared spectra, consistent with the decahydroacenaphthene structure, are well defined and easily dis-

---

(1) E. T. Niles and H. R. Snyder, *J. Org. Chem.*, **26**, 330 (1961).
(2) H. Koch and K. E. Möller, *Angew. Chem.*, **73**, 240 (1961).
(3) H. R. Snyder and F. X. Werber, *J. Am. Chem. Soc.*, **72**, 2962 (1950).
(4) H. R. Snyder and M. S. Konecky, *ibid.*, **80**, 4388 (1958).

Table I

Rearrangement Results

	Reaction products, % yield				
PPA–CDT[a]	Acenaphthene	Decahydroacenaphthene	Octahydroacenaphthene	Resin	Unidentified
8:1	5	20	. .	29	20
3:1	4	24	. .	29	24
1:10	. . .	. .	73	12	Trace
U.O.P.[b]	. . .	. .	84	12	Trace
U.O.P.[b,c]	. . .	. .	87	9	Trace

[a] Weight ratio of polyphosphoric acid to 1,5,9-cyclododecatriene. [b] Universal Oil Products #2 polymerization catalyst, consisting of polyphosphoric acid impregnated on kieselguhr, was used in place of liquid polyphosphoric acid. [c] A solvent, xylene, was used in this reaction.

tinguishable for each isomer in the fingerprint region. The infrared scans for the fingerprint region for each of these isomers are reproduced in Figure 1. Finally, the four compounds had similar mass spectral cracking patterns which were also consistent with the decahydroacenaphthene structure. The patterns showed major parent ions at 164 and major fragment masses at 136, 135, and 121.

Thus, the four isomers of decahydroacenaphthene produced by the exhaustive reduction of acenaphthene were characterized and used as reference compounds and shall hereafter be referred to as DHAN I, II, III, and IV, based on their relative v.p.c. retention times.

Products from the Reaction in Excess Polyphosphoric Acid.—The products were essentially identical for all the runs in which an excess of polyphosphoric acid was used. In each case, the reaction product was extracted with ether, followed by a wash of the ether layer with aqueous sodium hydroxide and water. After evaporation of the ether, the product was distilled, yielding a colorless liquid distillate and a low-melting resin. Toward the end of the distillation a small amount of liquid, which subsequently solidified, was separated as an overhead fraction and was identified as acenaphthene. Identification was accomplished by means of the infrared spectrum and a mixture melting point determination with authentic acenaphthene.

The distillate was a complex mixture containing seven components. The major component, which constituted about 50% of the mixture, was isolated by preparative v.p.c. and identified as DHAN III, based on the comparison of its v.p.c. retention time, infrared spectrum, and mass spectral pattern with those of the authentic reference isomer.

None of the other six minor components were identified. Attempts to separate these materials by v.p.c. were unsuccessful. Although the mass spectrum of the mixture showed major parent masses at 164 and 166, the cracking pattern and the infrared spectrum showed no trace of any of the other DHAN isomers. Hydrogenation changed the mixture very little. One minor v.p.c. peak disappeared with a concurrent increase in DHAN III; thus, this component must have been an unsaturate with the acenaphthene skeletal structure. The remaining five components, however, appeared to be unaffected by the hydrogenation. Possibly these components, with masses 166 or 164, are bicyclics or tricyclics with skeletal structures differing from DHAN.

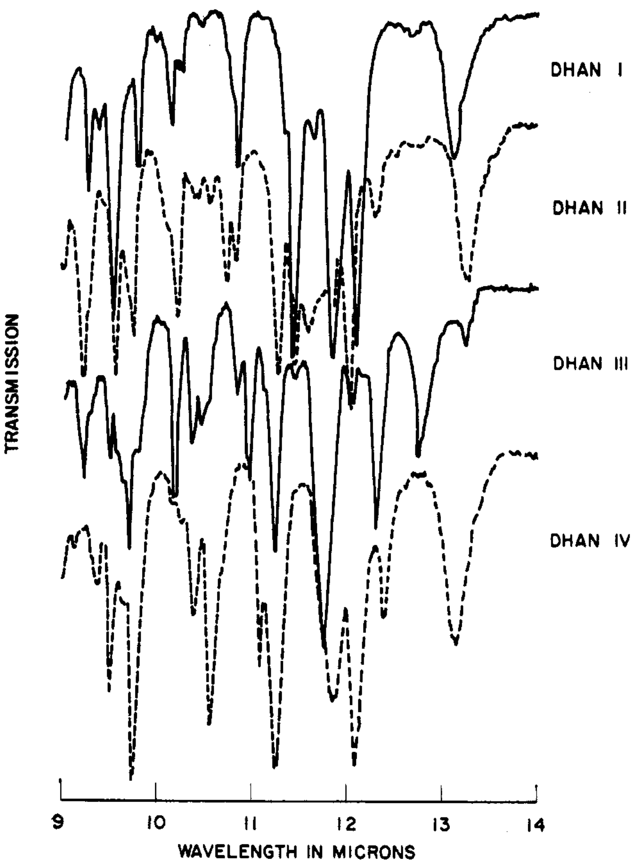


Figure 1.—Infrared spectra of decahydroacenaphthene isomers.

Products from the Reaction with Catalytic Amounts of Phosphoric Acid.—A different product was obtained when CDT was rearranged with catalytic amounts of polyphosphoric acid or polyphosphoric acid impregnated on kieselguhr. Under these conditions the organic phase of the reaction product, which was separated and distilled, comprised a colorless liquid and a small amount of resin. No acenaphthene was detected or isolated.

A sample of the distillate from a typical run, which was characterized by v.p.c., showed one large peak (65%), one medium peak (15%), and three smaller peaks (total 20%). Based upon retention times it was apparent that decahydroacenaphthene was not present in this mixture. One of the smaller peaks coincided in retention time with that of CDT and, therefore, appeared to be starting material. The two major components, which accounted for 80% of the total mixture, were isolated by preparative v.p.c. Each was characterized by a positive permanganate test for unsaturation, and a major parent mass at m/e 162. Thus, if the compounds were shown to possess the acenaphthene skeletal structure, they would have to be isomers of octahydroacenaphthene.

Therefore, the entire liquid distillate from the reaction mixture was hydrogenated yielding a five-component mixture which was separated by preparative v.p.c. Four of the components were positively identified as DHAN isomers based on a comparison of their v.p.c. retention times, infrared spectra, and mass spectral patterns with those of the reference compounds. The relative amounts were DHAN I 15%, II 20%, III 30%, and IV 22%. The other component was identified as cyclododecane by comparison with an authentic sample. Apparently the cyclododecane was produced by hydrogenation of the small amount of unreacted CDT.

These hydrogenation results indeed established that the original reaction mixture was predominently composed of materials with the acenaphthene skeletal structure, at least two of which (the major components) had a molecular weight of 162. Thus, these materials were necessarily isomers of octahydroacenaphthene. The two minor components which were not isolated had the same skeletal structure, but an undetermined molecular weight. Therefore, they could be other isomers of octahydroacenaphthene, or less saturated compounds of the same skeletal structure.

No attempt was made to locate the exact position of the double bonds in the octahydroacenaphthene isomers. However, the appearance of infrared absorption bands in the 5.8–5.9-μ region indicates that the unsaturation is probably of the $R_1R_2C{=}CR_3H$ or $R_1R_2C{=}CR_3R_4$ type.

Experimental

All melting points and boiling points are uncorrected. The melting points were taken on a Fisher-Johns melting point apparatus. Infrared spectra were determined using a Baird double-beam spectrophotometer. N.m.r. spectra were determined with a Varian Associates A-60 spectrometer. Vapor phase chromatographic analyses were carried out on a Perkin-Elmer Model 154-D vapor fractometer. Elemental analyses were performed by the Analytical Research Division of Esso Research and Engineering Co. The CDT used in the experiments was *cis,trans,trans*-1,5,9-cyclododecatriene supplied by the Enjay Chemical Co.

Preparation of Decahydroacenaphthene Isomers.—A solution of 80 g. of acenaphthene in 300 ml. of absolute ethanol was hydrogenated over 5 g. of Raney nickel for 20 hr. at 230° and 3000-p.s.i.g. hydrogen pressure. After the hydrogenation was complete, the solution was cooled, the catalyst was removed by filtration, and the filtrate was distilled *in vacuo*, yielding 73 g. (80%) of a clear, colorless liquid.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.92; H, 12.31.

The product contained four components which were separated by preparative v.p.c.[6] and designated DHAN I, II, III, and IV based on their relative retention times. Each component gave a negative permanganate test, showed a parent mass at *m/e* 164, and had major fragment ions at 136, 135, and 121. The infrared spectra are shown in Figure 1.

Rearrangement of CDT with Polyphosphoric Acid (8:1 Ratio).—To 32.8 g. (0.2 mole) of 1,5,9-cyclododecatriene was added 260 g. of polyphosphoric acid (Victor Chemical). This mixture was vigorously stirred and heated at 140–160° for 5 hr. At the end of this time, the warm melt was poured into 400 ml. of water and allowed to cool to room temperature. The organic layer was taken up in 400 ml. of ether, and the solution was filtered to remove a small amount of suspended gum. Then the ether solution was washed with water, 10% sodium hydroxide solution, water, and saturated sodium chloride solution. After drying over $MgSO_4$, the solution was filtered, and the ether was removed *in vacuo*. About 13.2 g. (40%) of a clear, colorless liquid was collected in fractions overhead (b.p. 40–47° at 0.1 mm.) leaving 9.4 g. (29%) of a green, low-melting resin in the pot. The liquid in the last overhead fraction subsequently solidified to a white solid (1.6 g., 5%) which, after recrystallization from petroleum ether, was identified as acenaphthene by means of infrared spectra and mixture melting points (m.p. 93–95°, lit. m.p. 95°).

Anal. Calcd. for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.43; H, 6.62.

Analysis of the liquid product by v.p.c.[5] revealed at least one major component (*ca.* 50%) and six minor components. The major component was isolated by preparative v.p.c.[6] and was identified as DHAN III by comparison of its v.p.c. retention time, infrared spectrum, and mass spectral pattern with those of the reference material.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.71, H, 12.35.

Hydrogenation of Rearranged Product.—The liquid rearrangement product from the preceding run was hydrogenated over Raney nickel for 6 hr. at 200° with a negligible amount of hydrogen uptake. The product showed one less v.p.c. peak,[5] and an increase in content of DHAN III to about 60%. The infrared spectrum showed no evidence of DHAN I, II, or IV.

Rearrangement of CDT with Polyphosphoric Acid (3:1 Ratio).—Into a 3-l., 4-necked flask equipped with a condenser, thermometer, stirrer, and dropping funnel was weighed 1800 g. of polyphosphoric acid. The acid was heated to 150°, and 590 g. (3.6 moles) of CDT was added over a 1-hr. period. The reaction mixture was stirred vigorously while the temperature was maintained at 140–160° for 3 hr. after the addition was completed. Then the mixture was cooled to 100° and poured onto 2 kg. of ice. The mixture was allowed to warm to room temperature and was filtered to remove a small amount of green gum which was suspended. The aqueous layer was separated from the organic layer and extracted with six successive 150-ml. portions of petroleum ether (b.p. 40–60°). The petroleum ether fractions were added to the organic layer, and this solution was washed three times with 150 ml. of water, once with 150 ml. of 10% NaOH solution, three times with 150 ml. of water, and once with 150 ml. of saturated NaCl solution. The ether solution was then dried over anhydrous $MgSO_4$ and filtered, and the petroleum ether was stripped off on a rotary evaporator. The liquid residue was distilled *in vacuo*, yielding 288 g. (48%) of a light yellow liquid (b.p. 98–106° at 6 mm.), 24 g. (4%) of a pale yellow solid (b.p. 150° at 9 mm.), and 174 g. (29%) of a dark green, low-melting resin. On the basis of v.p.c. analysis, infrared spectra, and mass spectral patterns, the products and product distribution were essentially identical with those obtained when CDT was rearranged withan eightfold excess of polyphosphoric acid.

Rearrangement of CDT with Polyphosphoric Acid (1:10 Ratio).—Into a 1-l. flask equipped with a stirrer, condenser, thermometer, and dropping funnel was placed 39 g. of polyphosphoric acid. The acid was stirred vigorously and heated to 150° while 390 g. of CDT was added over a 30-min. period. After the temperature was held at 150° an additional 4 hr., the reaction mixture was allowed to cool, and two phases separated. The upper organic phase was decanted, filtered, and distilled *in vacuo*, yielding 289 g. (73%) of a clear liquid (b.p. 102–107° at 6.4 mm.) and 47 g. (12%) of a dark brown resin. The liquid was analyzed.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.60; H, 11.40.

Analysis of the liquid *via* v.p.c.[5] showed four components in addition to about 3% unreacted CDT. The two major components, which comprised 80% of the total mixture, were isolated by preparative v.p.c.[6] Each of these compounds gave a positive permanganate test, had a major parent mass at *m/e* 162, and had an infrared absorption at 5.9 μ.

Hydrogenation of Rearranged (1:10) Product.—The liquid product from the preceding run (1:10 ratio) was hydrogenated over Raney nickel for 6 hr. at 200°. The product of the reduction contained five components which were separated by preparative v.p.c. Four of the components were positively identified as DHAN isomers by comparison of their v.p.c. retention times, infrared spectra, and mass spectral patterns with those of the reference compounds. The fifth component was identified as cyclododecane by comparison with an authentic sample. The relative amounts of the DHAN isomers were I 15%, II 20%, III 30%, and IV 22%.

Rearrangement of CDT with U.O.P. Catalyst.—Into a 500-ml. 4-necked flask equipped with stirrer, condenser, and thermometer were weighed 325 g. (2 moles) of CDT and 55 g. of crushed Universal Oil Products #2 polymerization catalyst (polyphosphoric acid impregnated on kieselguhr). The heterogeneous reaction mixture was vigorously stirred and heated at 150° for 3 hr.[7] Then the reaction mixture was cooled to 90° and filtered through a small amount of Hyflo Super-Cel on a Büchner funnel. The filter cake was rinsed with 30 ml. of *n*-pentane, the pentane was evaporated, and the organic material extracted from the filter

---

[5] Analysis was performed with a Perkin-Elmer 2-m. Q-column (20% Apiezon L on Chromasorb) operated at 200°.

[6] The isolation was accomplished with a modified Perkin-Elmer fractometer containing a 3 m. × 1 in. Q-column (20% Apiezon L on Chromasorb) operated at 200°.

[7] Caution must be taken when the temperature approaches 140° since the reaction is exothermic and can become uncontrolled (it may be necessary to remove the heat source and cool).

aid was combined with the main filtrate. The filtrate was distilled *in vacuo*, yielding 273 g. (84%) of a clear, colorless liquid (b.p. 102–106° at 7.0 mm.). The residue left in the distillation pot was a dark brown, low-melting resin which weighed 38.7 g. (11.8%).

The predominant products were isomers of octahydroacenaphthene and, on the basis of v.p.c. data, the product distribution was almost identical with that obtained when CDT was rearranged with catalytic amounts of polyphosphoric acid. The two major components, which were isolated by preparative v.p.c., were identical with the octahydroacenaphthene isomers from the preceding example. The comparison was made with v.p.c. retention times, infrared spectra, and mass spectral patterns.

Rearrangement of CDT with U.O.P. Catalyst in a Xylene Solvent System.—To 325 g. of (2 moles) CDT was added 110 g. of crushed Universal Oil Products polymerization catalyst and 250 ml. of xylene. The heterogeneous mixture was stirred vigorously and heated to 150°, at which temperature it was maintained 2 hr.[8] After the reaction was completed, the mixture was cooled to 90° and filtered through a layer of Hyflo Super-Cel. The filter cake was washed with xylene and the washings and the filtrate was combined and distilled *in vacuo*. About 281 g. (86.5%) of a clear, colorless liquid was distilled overhead, leaving a residue of 29 g. (9%) of brown, tarry polymeric bottoms. The product distribution was similar to that of the preceding examples where no solvent was used. The octahydroacenaphthene was isolated and identified as above.

Acknowledgment.—The authors wish to thank Dr. Paul Tschampel for his valuable assistance.

---

[8] In this case, there was no tendency for the reaction to become uncontrolled.

Fluoro Olefins. XII. The Reaction of Allylmagnesium Bromide with Fluoro Olefins[1,2]

Paul Tarrant and James Heyes

Department of Chemistry, The University of Florida, Gainesville, Florida

Received December 18, 1964

The reaction of fluoro olefins with allylic Grignard reagents generally gives good yields of allylfluoroethylenes. Crotonylmagnesium bromide gives exclusively the α-methallylethylene; a mechanism is offered to explain this behavior. Tetrafluoroethylene reacts abnormally with allylmagnesium bromide to give 1-bromo-1,2-difluoro-1,4-pentadiene as the chief product.

Although the reactions between fluoro olefins and organometallic alkyls, aryls, and acetylenes have been widely investigated,[3–7] there has been little mention of the reactions with olefinic organometallic compounds. The reactions between various fluoro olefins and trifluorovinyllithium were unsuccessful,[8,9] although the reaction between triethyltrifluorovinylsilane and vinyl- and allyllithium gave good yields of the substituted dienes $(C_2H_5)_3SiCF{=}CF{-}CH{=}CH_2$ and $(C_2H_5)_3SiCF{=}CFCH_2CH{=}CH_2$.[10] In order to prepare fluorine-containing dienes, *unsym*-dichlorodifluoroethylene was allowed to react with both vinylmagnesium chloride and vinyllithium under varying conditions; however, the Grignard reagent did not react, and the vinyllithium gave only a tar. The latter reaction might have given the diene $CH_2{=}CHCF{=}CCl_2$ which polymerized immediately. The isolation of $(C_2H_5)_3SiCF{=}CFCH{=}CH_2$ mentioned above would have been possible as the bulky silane grouping would prevent immediate polymerization.

In a further effort to prepare a fluoro diolefin the reaction between allylmagnesium bromide and olefins containing the trifluorovinyl group was investigated. In general, a reasonable yield of the allyl-substituted fluoro olefin was formed.

$$CH_2{=}CHCH_2MgBr + CF_2{=}CFX \longrightarrow CH_2{=}CHCH_2CF{=}CFX$$

The products of these reactions are shown in Table I. The reactions were carried out using equimolar amounts of the fluoro olefin and the Grignard reagent in diethyl ether solution. The yield of the diolefin was not altered when an excess of the Grignard was used.

Table I

Allylmagnesium Bromide and Fluoro Olefins

Olefin	Product	Yield, %
(1) $CF_2{=}CF_2$	I, $CH_2{=}CHCH_2CF{=}CFBr$	30
	II, $CH_2{=}CHCH_2CF{=}CFCH_2CH{=}CH_2$	10
(2) $CF_2{=}CF_2$[a]	III, $CH_2{=}CHCH_2CF{=}CFCl$	7
	II, $CH_2{=}CHCH_2CF{=}CFCH_2CH{=}CH_2$	15
$CF_2{=}CFCl$	III, $CH_2{=}CHCH_2CF{=}CFCl$	50
$CF_2{=}CFBr$	I, $CH_2{=}CHCH_2CF{=}CFBr$	30
$CF_2{=}CCl_2$	IV, $CH_2{=}CHCH_2CF{=}CCl_2$	40
$CF_2{=}CFCF_3$	V, $CH_2{=}CHCH_2CF{=}CFCF_3$	38
$\underbrace{CF_2CF_2CF{=}CF}$	[b]	
$CF_2{=}CFCH{=}CH_2$	VI, $CH_2{=}CHCH_2CF{=}CFCH{=}CH_2$[c]	30

[a] Reacted with allylmagnesium chloride. [b] Tar formed immediately at −78°. [c] Polymerizes on standing.

The reaction with tetrafluoroethylene gave none of the expected monoallyl derivative, although a low yield of the disubstituted compound II was formed: the main product was 1-bromo-1,2-difluoro-1,4-pentadiene (I).

$$CH_2{=}CHCH_2MgBr + CF_2{=}CF_2 \longrightarrow \underset{\text{I}}{CH_2{=}CHCH_2CF{=}CFBr} + \underset{\text{II}}{[CH_2{=}CHCH_2CF]_2{=}}$$

It is unlikely that the bromide ion as such attacks tetrafluoroethylene as the reaction of anhydrous magnesium bromide with neither tetrafluoroethylene nor 1,1,2-trifluoro-1,4-pentadiene, in diethyl ether, led to a bromine-containing product. It is more likely that the Grignard reagent itself brominated the fluoro olefin. No reaction took place between 1,1,2-trifluoro-1,4-pentadiene and allylmagnesium bromide. These re-

---

[1] Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[2] Part XI: P. Tarrant and D. E. O'Connor, *J. Org. Chem.*, **29**, 2012 (1964).

[3] P. Tarrant and D. A. Warner, *J. Am. Chem. Soc.*, **76**, 1624 (1954).

[4] T. F. McGrath and R. Levine, *ibid.*, **77**, 4168 (1955).

[5] S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

[6] J. D. Park and R. Fontanelli, *ibid.*, **28**, 259 (1963).

[7] P. Tarrant, J. Savory, and E. S. Iglehart, *ibid.*, **29**, 2009 (1964).

[8] P. Tarrant, P. Johncock, and J. Savory, *ibid.*, **28**, 839 (1963).

[9] P. Tarrant and A. C. Wright, unpublished work.

[10] D. Seyferth and T. Wada, *Inorg. Chem.*, **1**, 78 (1962).