

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Diels-Alder Reactions with Fluorine-containing Olefins

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The Diels-Alder reactions of five fluorine-containing dienophiles with cyclopentadiene, butadiene and anthracene have been investigated. An adduct was obtained in all cases except in the reaction between allyl fluoride and butadiene. Qualitatively, the relative order of reactivity was found to be: $\text{CF}_2\text{CF}=\text{CF}_2 > \text{C}_2\text{F}_5\text{CH}=\text{CH}_2 > \text{CF}_3\text{CH}=\text{CH}_2 > \text{CH}_2\text{FCH}=\text{CH}_2 > \text{CF}_3\text{C}(\text{CH}_3)=\text{CH}_2$.

Discussion

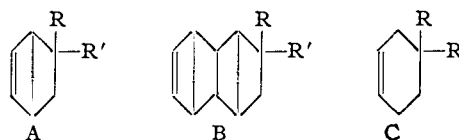
The Diels-Alder reactions of allyl chloride and bromide,² vinyl chloride, 1,2-dichloroethylene and trichloroethylene³ have been carried out with cyclopentadiene. More recently it has been shown that 1,2-dibromoethylene and 1,3-dichloropropene can be used as dienophiles⁴; *cis*- and *trans*-dichloroethylene have been condensed with anthracene.⁵ Unsubstituted olefins, e.g., ethylene and propylene react with cyclopentadiene and cyclohexadiene at high temperature and under pressure.⁶ In view of the polarization of the double bond by the strong electron-withdrawing effect of fluorine atoms,⁷ fluorine-containing olefins should be expected to act as dienophiles regardless of whether the reaction proceeds by an ionic mechanism⁸ or involves an intermediate molecular complex.⁹

In order to determine the influence of fluorine atoms in dienophiles, allyl fluoride, 3,3,3-trifluoropropene, perfluoropropene, 3,3,4,4,4-pentafluoro-1-butene and 2-methyl-3,3,3-trifluoropropene were treated with butadiene, cyclopentadiene and anthracene. Each of the fluorine-containing olefins reacts with cyclopentadiene at 135 and at 190°. Under comparable conditions, the yields of adducts were similar and in the range of 60–70%, except with allyl fluoride (27%) and 2-methyl-3,3,3-trifluoropropene (25%). In the case of allyl fluoride, the single fluorine atom probably exerts insufficient polarization on the double bond, while the reactivity of 2-methyl-3,3,3-trifluoropropene may be reduced both by polar and steric effects. The results obtained with butadiene are similar to those with cyclopentadiene. Perfluoropropene gave the highest yield, 2-methyl-3,3,3-trifluoropropene the lowest (15%), while allyl fluoride failed to give an adduct under the conditions employed.

The reactions of the olefins with anthracene show more pronounced temperature effects. Allyl fluoride and perfluoropropene gave adducts at 110°; 3,3,3-trifluoropropene, perfluoropropene and 3,3,4,4,4-pentafluoro-1-butene react at 200° to give

adducts in 84–98% yield. 2-Methyl-3,3,3-trifluoropropene can be added to anthracene at 200° in 57% yield.

The adducts A from 3,3,3-trifluoropropene, 3,3,4,4,4-pentafluoro-1-butene and 2-methyl-3,3,3-trifluoropropene with cyclopentadiene were accompanied by small amounts of bis-adducts, assumed to have the structure B.

R = H, CF₃, C₂F₅; R' = H, CH₃

The adducts, A and C from cyclopentadiene and butadiene, respectively, were converted to dibromides by means of bromine in carbon tetrachloride for identification purposes. The olefins were regenerated by debromination with zinc and ethanol. This procedure was utilized also to separate 4-pentafluoroethylcyclohexene and 4-methyl-4-trifluoromethylcyclohexene from the accompanying butadiene dimer, vinylcyclohexene.

The structures of the adducts A are further supported by the infrared absorption spectra which contain characteristic bands at 7.14–10.0 μ (C–F), 5.97–6.11 μ (CH=CH), 3.23–3.5 μ (C–H)¹⁰ and a strong band at 13.8–14.0 μ, observed in bicyclo[2.2.1]heptenes such as bornylene,¹¹ norbornylene, dehydronorborneol, 5-carboxylbicyclo[2.2.1]-2-heptene, 5-chlorobicyclo[2.2.1]-2-heptene and 5-bromobicyclo[2.2.1]-2-heptene.¹² The infrared spectra of the dibromides from the adducts C have two bands at 9.95–10.53 μ and 9.47–10.00 μ which are characteristic of cyclohexane derivatives.¹³

The anthracene adducts have been established as 9,10-adducts by means of their ultraviolet absorption spectra^{14,15}; all the compounds exhibited three maxima at 252, 264 and 272 mμ with log ε's of 3.0–4.0.

Experimental¹⁶

Preparation of the Olefins. Allyl Fluoride.—Allyl fluoride, b.p. –3°, was prepared in 30% yield from allyl bromide and

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(16) All temperatures are uncorrected; the melting points were determined with a Fisher-Johns melting point apparatus. Carbon, hydrogen and bromine analyses by H. Galbraith, Knoxville, Tenn., and Mrs. C. S. T. Yeh of this Department. Fluorine analyses by Clark Microanalytical Laboratory, University of Illinois, Urbana, Ill.

TABLE I
 CYCLOPENTADIENE ADDUCTS

Com- pound	From olefin	Ratio C ₅ H ₆ Olefin	Temp., °C.	Time, hr.	Yield, % ^b	B.p., °C.	n _D ²⁰	Carbon, %		Hydrogen, %		Fluorine, %	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
I	CFH ₂ CH=CH ₂	1.0	135 ^a	60	27	66 ^f	1.4548	76.19	76.13	8.73	8.78	15.08	15.82
II	CF ₃ CH=CH ₂	1.0	135	60	65	119	1.4051	59.25	59.17	5.56	5.50	35.19	34.87
		0.8	190	24	57 ^c								
III	C ₂ F ₅ CH=CH ₂	1.0	135	60	66	130	1.3853	50.99	51.17	4.25	4.36	44.76	44.59
		0.8	190	24	60 ^d								
IV	CF ₃ CF=CF ₂	1.0	135	60	69	141	1.3741	44.44	44.48	2.78	2.87	52.78	52.38
		0.8	190	24	66								
V	CF ₃ C(CH ₃)=CH ₂	1.0	135	60	22	136	1.4168	61.36	31.58	6.25	6.24	32.40	32.22
		0.8	170	168	25 ^e								

^a Allyl fluoride is unstable at higher temperatures. ^b Yield based on unrecovered olefin. ^c A 2% yield of bis-adduct was obtained, b.p. 95–96° (10 mm.), n_D²⁰ 1.4733. *Anal.* Calcd. for C₁₃H₁₅F₃: C, 68.60; H, 6.16. Found: C, 69.06; H, 5.76. ^d A 4% yield of bis-adduct was obtained, b.p. 99–100° (10 mm.), n_D²⁰ 1.4488. *Anal.* Calcd. for C₁₁H₁₃F₅: C, 59.60; H, 5.38. Found: C, 59.65; H, 5.58. ^e A 7% yield of bis-adduct was obtained, m.p. 66.5°. *Anal.* Calcd. for C₁₄H₁₇F₃: C, 69.30; H, 7.01. Found: C, 69.18; H, 7.19. ^f At 55 mm.

 TABLE II
 BUTADIENE ADDUCTS^a

Compounds	From olefin	Yield, % ^b	B.p., °C.	n _D ²⁰	Carbon, %		Hydrogen, %		Fluorine, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
VI	CF ₃ CH=CH ₂	35	104	1.3856	56.00	56.01	6.00	6.20	38.00	37.54
VII	C ₂ F ₅ CH=CH ₂	38	119 ^c	1.3725	48.00	47.80	4.50	4.71	47.50	45.22
VIII	CF ₃ CF=CF ₂	64	97	1.3430	41.18	41.39	2.94	2.94	55.88	56.05
IX	CF ₃ C(CH ₃)=CH ₂	15	122	1.3989	58.54	58.57	6.71	6.82	34.76	33.43

^a The reactions were carried out by heating for 24 hours at 180° with a molar ratio of 0.9 for butadiene and olefin. ^b Yield based on unrecovered olefin. ^c The pure product was obtained free of vinylcyclohexane by debrominating the purified dibromo compound.

 TABLE III
 ANTHRACENE ADDUCTS

Olefin	Ratio C ₁₄ H ₁₀ Olefin	Temp., °C.	Time, hr.	Yield, % ^a	M.p., °C.	Carbon, %		Hydrogen, %		Fluorine, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
CFH ₂ CH=CH ₂	0.21	110	24	75	115–116	85.71	85.91	6.30	6.23	7.99	8.30
CF ₃ CH=CH ₂	.47	200	20	83	122–123	74.45	74.42	4.74	4.83	20.81	20.46
C ₂ F ₅ CH=CH ₂	.41	200	20	86	74–75	66.67	66.35	4.01	3.99	29.32	28.95
		110	24	76	143–144	62.20	62.20	3.05	3.05	34.75	33.95
CF ₃ CF=CF ₂	.75	150	24	95							
		.32	200	20	97						
		.28	200	20	56	106	75.00	75.00	5.21	5.20	19.79
CF ₃ C(CH ₃)=CH ₂	.75	110	24	<1							

^a Yield based on unrecovered anthracene.

potassium fluoride by the method Hoffmann¹⁷ used to prepare 1,6-difluorohexane and was characterized by formation of the dibromide.¹⁸

3,3,3-Trifluoropropene.—3,3,3-Trifluoropropene was prepared in a new fashion by the pyrolysis at 490 ± 10° of 1,1,1-trifluoro-2-propyl acetate. The reaction product was rectified from a low temperature column and, of the 67.4 g. of acetate used, 7.4 g. was recovered unchanged. The yield of 3,3,3-trifluoropropene was 30 g. (81%), b.p. –24° (lit. b.p. –24°,¹⁹ –22°²⁰); it was characterized as the dibromide.²⁰

2-Methyl-3,3,3-trifluoropropene.—2-Methyl-3,3,3-trifluoropropene was prepared by the reaction of ethyl trifluoroacetate and methylmagnesium iodide followed by dehydration of the product, 2-methyl-1,1,1-trifluoro-2-propanol, with phosphorus pentoxide, according to the procedure of Low.²¹

3,3,4,4,4-Pentafluoro-1-butene.—3,3,4,4,4-Pentafluoro-1-butene was prepared from 3,3,4,4,4-pentafluoro-2-butanol by the method of McBee, Higgins and Pierce.²²

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Perfluoropropene.—Perfluoropropene was prepared from the sodium salt of perfluorobutyric acid.²³

Diels-Alder Reactions.—A typical experiment of each series of Diels-Alder reactions is described to illustrate the method. The data for all of the experiments are summarized in Tables I, II and III.

With Cyclopentadiene.—Perfluoropropene (22.5 g., 0.15 mole), cyclopentadiene (9.9 g., 0.15 mole) and hydroquinone (0.2 g.) were heated in a Carius tube at 135° for 60 hours. Four grams of perfluoropropene was recovered. The adduct (18.4 g., 69%) was distilled from the remaining mixture, b.p. 141°, n_D²⁰ 1.3741.

Bis-adducts were isolated in some cases when the reactions were carried out at a higher temperature (190°).

With Butadiene.—A mixture of 22.5 g. (0.15 mole) of perfluoropropene, butadiene (7.29 g., 0.135 mole) and hydroquinone (0.2 g.) was heated in a Carius tube at 180° for 24 hours. The reaction mixture contained 6.5 g. of unchanged perfluoropropene. The yellow reaction mixture was distilled to give 14.1 g. (64%) of adduct, b.p. 97°, n_D²⁰ 1.3430.

Allyl fluoride failed to react with butadiene. Various reaction conditions, such as longer reaction time (24–96 hr.) lower reaction temperatures (75–150°) and the use of solvents (ethanol, xylene and acetic acid), failed to effect the reaction. In some cases, decomposition of allyl fluoride and polymerization of butadiene were observed.

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TABLE IV
 BROMINATION PRODUCTS FROM THE ADDUCTS

From compound	Yield, %	B. p. °C.	Mm.	n_D^{20}	Carbon, %		Hydrogen, %		Fluorine, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
I ^a	52	121-123	3	1.15524	33.56	33.61	3.84	3.86	55.94	55.97
II	85	119	10	1.5013	29.75	29.58	2.79	2.87	49.68	49.70
III	85	121-122	10	1.4711	29.04	29.18	2.42	2.44	43.01	42.92
IV	89	92-93	10	1.4580	25.53	25.60	1.60	1.64	42.55	42.36
V	53	126-128	10	1.5037	32.14	31.87	3.27	3.32	47.62	47.69
VI	97	91	10	1.4871	27.17	27.17	2.90	2.99	51.61	51.50
VII	84	95	10	1.4606	26.67	26.78	2.50	2.91	44.44	44.59
VIII	91	89	10	1.4343	23.08	23.08	1.65	1.60	43.96	43.81
IX	73	110	10	1.4896	29.63	29.82	3.40	3.49	49.38	49.29

^a There also was obtained from this reaction mixture a compound resulting from the loss of HBr from the dibromide, b.p. 93-94° (10 mm.), n_D^{20} 1.5100. Anal. Calcd. for C₈H₇FBr: C, 46.83; H, 4.88; F, 39.02. Found: C, 46.50; H, 5.35; F, 39.32.

With Anthracene.—3,3,3-Trifluoropropene (8 g., 0.083 mole), anthracene (7 g., 0.039 mole) and benzene (25 g.) were heated in a sealed tube at 200° for 20 hours. Two and four-tenth grams of 3,3,3-trifluoropropene was recovered by distillation at room temperature and 3.5 g. of anthracene was recovered by filtration. Evaporation under vacuum of the remaining benzene solution and recrystallization of the crude product from aqueous ethanol gave 4.5 g. (83.5%) of the adduct, m.p. 122-123°.

Bromination of the Adducts.—The general method of preparation of the dibromides of the bicyclo[2.2.1]-heptenes and cyclohexenes is illustrated by the following example: A solution of 5,6,6-trifluoro-5-trifluoromethylbicyclo[2.2.1]-2-heptene (21.6 g., 0.1 mole) in carbon tetrachloride (15 ml.) was placed in a 100-ml., 3-necked flask fitted with a reflux condenser, a stirrer and a dropping funnel. The flask was cooled in a Dry Ice-trichloroethylene bath maintained at -20 to -10°. A solution of 16 g. (0.1 mole) of bromine in 15 ml. of carbon tetrachloride was added slowly. After the addition was complete, the reaction mixture was brought to room temperature and stirred for one hour. The excess bromine was then removed by shaking with sodium bisulfite solution. The organic layer was separated, washed with water, dried over calcium chloride and distilled under reduced pressure. The 1,2-dibromo-5,6,6-trifluoro-5-trifluoromethylbicyclo[2.2.1]heptane (33.5 g., 89%) boiled at 92-93° (10 mm.), n_D^{20} 1.4580.

The yields and physical properties of the dibromides are listed in Table IV. A monobromo compound was obtained in the bromination of 5-fluoromethylbicyclo[2.2.1]-2-heptene.

Debromination Procedure.—A mixture of 1,2-dibromo-4-pentafluoroethylcyclohexane (12.3 g., 0.03 mole), zinc dust (6.5 g., 0.1 g. atom) and 50 ml. of absolute ethanol was refluxed for 24 hours. The solution was decanted from the metal, diluted with water and acidified with 10% sulfuric acid. The organic layer was separated. The aqueous portion was extracted twice with ether. The ether extracts were combined with the organic layer, washed with brine and dried over anhydrous magnesium sulfate. Distillation gave 3.7 g. (54%) of 4-pentafluoroethylcyclohexene, b.p. 119°, n_D^{20} 1.3725.

Absorption Spectra.—Ultraviolet absorption spectra were determined with a Cary recording spectrophotometer in 95% ethanol at a concentration of 3.3×10^{-4} mole per liter. The infrared spectra were obtained for the pure liquids with a Perkin-Elmer model 21 recording spectrometer in capillary cells of 0.0125 to 0.0325 mm. thickness.

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The Reactions of Perfluoronitriles with Grignard Reagents¹

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Straight chain alkyl and phenyl Grignard reagents react with perfluoroaceto-, propio-, and butyronitriles to give the expected ketones. The reaction of isopropylmagnesium bromide with heptafluorobutyronitrile yields heptafluorobutyraldehyde unless a reverse addition technique is used. *t*-Butylmagnesium chloride and heptafluorobutyronitrile react to give the exchange products, trimethylacetone and heptafluoropropylmagnesium chloride.

Discussion

Jones² has described the reaction of trifluoroacetonitrile with benzylmagnesium chloride; subsequent work by Nes and Burger³ elucidated the structure of the original product to be *o*-methyltrifluoroacetophenone. In an attempt to extend the reaction to other Grignard reagents with fluorine-containing nitriles a general method has been developed for the preparation of perfluoro-

alkyl alkyl ketones and perfluoroalkyl aryl ketones. No evidence was obtained that migration of the perfluoroaryl group took place as indicated by Nes and Burger.³

The results of the reaction of several Grignard reagents with trifluoroacetonitrile, pentafluoropropionitrile and heptafluorobutyronitrile are in Tables I and II. The main competing reaction was the aldol condensation of the resulting ketones, presumably catalyzed by the Grignard reagent.⁴ With methylmagnesium iodide this condensation was the main reaction, and no simple ketone was obtained.

(1) This paper represents part of a thesis submitted by D. D. Meyer to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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