The crude product was dissolved in 150 ml of THF and treated with 50 ml of 30% $HClO_4$. After stirring for 8 hr, the solution was neutralized with 10% NaOH, diluted with brine, and extracted twice with ether. The combined ether extracts were dried and the solvent was evaporated. Liquid products were purified by bulb-to-bulb distillation; solids were recrystallized from hexane or benzene–hexane solution.

Cis Hydroxylation.[22]—To 20 mmol of the olefin, dissolved in *ca.* 100 ml of ethanol and stirred at −20°, was added over a period of 20 min a solution of potassium permanganate (2.12 g, 13.4 mmol) and magnesium sulfate (1.5 g, 12.5 mmol) in *ca.* 200 ml of water. The mixture was immediately filtered through Celite, and the cake was washed with methanol and ether. The filtrate was concentrated, diluted with brine, and extracted several times with ether. The combined extracts were dried and the solvent was evaporated. Chromatography on silica gel (5% ether in hexane) gave the substantially pure diol, which was distilled (bulb to bulb) or recrystallized as necessary.

Physical constants and selected nmr data for compounds prepared by these methods are summarized in Table II. Nmr signals not given in Table II were fully consistent with the assigned structures.

Hydride Reduction of α-Ketols. General Procedure.—Into a dry nitrogen-flushed test tube, containing a magnetic spin ball and fitted with a septum cap, was injected 1.5 mmol of hydride solution. After cooling to −78°, the ketol (0.5 mmol in 0.5 ml of toluene) was added slowly with stirring. After 4 hr, the cold bath was removed and stirring was continued at room temperature for 18 to 20 hr. The reaction was quenched by the cautious addition of 3 ml of water, sufficient 6 *N* HCl to dissolve the gelatinous precipitate was added, and the mixture was extracted three times with 15-ml portions of ether. The combined extracts were dried and the solvent was evaporated. The residue was heated briefly under vacuum to drive off any unreacted ketol; the product diol thus obtained was *ca.* 95% pure.

(22) M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 315 (1949).

Registry No.—**1**, 37160-77-3; **2**, 6986-70-5; **3**, 7737-47-5; **4**, 3155-01-9; **5**, 37160-81-9; **6**, 6196-59-4; *erythro*-**7**, 37163-97-6; *threo*-**7**, 37163-98-7; *erythro*-**8**, 6702-10-9; *threo*-**8**, 6464-40-0; *erythro*-**9**, 23646-57-3; *threo*-**9**, 23646-58-4; *erythro*-**10**, 37164-02-6; *threo*-**10**, 37164-03-7; *erythro*-**11**, 37164-04-8; *threo*-**11**, 37164-05-9; *erythro*-**12**, 37164-06-0; *threo*-**12**, 37164-07-1; TIBA, 100-99-2; DIBAH, 1191-15-7; $LiAlH_4$, 16853-85-3; $LiAl(OMe)_3H$, 12076-93-6; REDAL, 21608-56-0; AlH_3, 7784-21-6; $LiAl(t\text{-}AuO)_3H$, 17476-04-9.

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Stereochemistry of the Diels–Alder Reaction. V. Fluorinated Trans-Olefinic Acids and Derivatives with Cyclopentadiene

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The Diels–Alder reactions of a series of fluorinated *trans*-crotonic acids, esters, amides, an acid chloride, and an aldehyde with cyclopentadiene at 25° are discussed. The endo–exo ratios were determined by gas chromatographic and/or infrared analyses. The fluoroalkyl groups in all cases dominated the stereochemical course of the reactions, and in one series of crotonic acids the endo–exo ratios correlated very well with the inductive effects (σ_I) of these groups.

Two of the previous papers[1,2] in this series dealt with the Diels–Alder reactions of *trans*-4,4,4-trifluorocrotonic acid with various dienes. A third paper[3] examined the stereochemistry of the reaction of cyclopentadiene with several other *trans*-β-perfluoroalkylcrotonic acids. Olefins with fluorines in varying numbers and positions have also been studied with cyclopentadiene, butadiene, and anthracene.[4,5] In this paper we describe the stereochemistry of the products from the reactions of cyclopentadiene with a series of *trans*-β-fluoroalkyl-α,β-unsaturated acids, amides, esters, etc.

A list of dienophiles that were prepared for this study is given in Table I. The acids were prepared *via* hydrolysis of the corresponding esters, which in turn were prepared by means of the Knoevenagel reaction as generally described in previous papers.[6] Only one ester, ethyl 4-fluorocrotonate (**3**), was prepared differently owing to the fact that 2-fluoroethanal is relatively inaccessible. Numerous attempts to fluorinate methyl and ethyl 4-bromocrotonate using sodium, potassium, lithium, and silver fluorides under various conditions afforded only 7.5% of **3** as the best yield.[7]

All the dienophiles were assigned the trans configuration mainly on the basis of infrared absorption at *ca.* 5.95 and 10.30 μ, which is diagnostic for a trans system.[8] Proton magnetic resonance spectra for these compounds were very complex due to ^1H–^{19}F coupling.

Diels–Alder Reactions.—The dienophiles listed in Table I were stirred for 16–18 hr with a slight excess of cyclopentadiene at 25° in a constant-temperature

* Requests for information and reprints should be sent to this author at The Children's Hospital Research Foundation, Elland Ave. and Bethesda, Cincinnati, Ohio 45229.

(1) E. T. McBee, C. G. Hsu, and C. W. Roberts, *J. Amer. Chem. Soc.*, **78**, 3389 (1956).

(2) E. T. McBee, C. W. Roberts, and C. G. Hsu, *ibid.*, **78**, 3393 (1956).

(3) H. P. Braendlin, A. Z. Zielinski, and E. T. McBee, *ibid.*, **84**, 2109 (1962).

(4) H. P. Braendlin, G. A. Grindahl, Y. S. Kim, and E. T. McBee, *ibid.*, **84**, 2112 (1962).

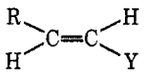
(5) E. T. McBee, C. G. Hsu, O. R. Pierce, and C. W. Roberts, *ibid.*, **77**, 915 (1955).

(6) (a) E. T. McBee, Y. S. Kim, and H. B. Braendlin, *ibid.*, **84**, 3154 (1962); (b) A. Z. Zielinski, E. T. McBee, and H. P. Braendlin, *Rocz. Chem.*, **37**, 905 (1963).

(7) (a) D. R. Bennett, K. S. Andersen, M. V. Anderson, Jr., D. N. Robertson, and M. B. Chenoweth, *J. Pharmacol. Exp. Ther.*, **122**, 489 (1958). (b) A 16% yield of ethyl 4-fluorocrotonate was obtained from 1-chloro-3-fluoropropan-2-ol by E. D. Bergmann, S. Cohen, and I. Shahak, *J. Chem. Soc.*, 3448 (1961). See also F. L. Pattison and B. C. Saunders, *J. Chem. Soc.*, 2745 (1949).

(8) (a) L. F. Hatch and S. S. Nesbitt, *J. Amer. Chem. Soc.*, **72**, 727 (1950); (b) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1956.

TABLE I
PREPARATION AND PROPERTIES OF DIENOPHILES



Compd	R	Y	Yield, %	Bp, °C (mm)[a]	n^{20}D or mp, °C	Ref
1	CH_3	CO_2H	*b*	81 (13)	71.4–71.7	*i*
2	CH_2F	CO_2H	7.5		88–90	*j*
3	CHF_2	CO_2H	36[c]	73–74 (3)	59–60.5	
4	CF_3	CO_2H	22[d]	68–69	55–56	*l*
5	C_2F_5	CO_2H	49[c]	73–76 (11)	43–44	*k*
6	*n*-C_3F_7	CO_2H	84[e]	83–85 (12)	46.5–48	*l*
7	CF_3	CO_2Et	25[d]	115	1.3597	*l*
8	C_2F_5	CO_2Et	44[c]	125	1.3480	*k*
9	*n*-C_3F_7	CO_2Et	54[c]	140–141	1.3442	*l*
10	*n*-C_7F_{15}	CO_2Et	39[c]	104 (20)	1.3369	*m*
11	*n*-C_3F_7	CO_2Me	46[c]	126–127	1.3386[f]	*n*
12	*n*-C_3H_7	COCl	68	107–108	1.3482	*o*
13	*n*-C_3F_7	CHO	60[g]	80–81	1.3324	
14	*n*-C_3F_7	$CONH_2$	88		95–96	
15	*n*-C_3F_7	$CONHCH_3$	40		42–43	*p*
16	*n*-C_3H_7	$CONHC_6H_5$	75		130.5–131.5	*l*
17	*n*-C_3F_7	CH_2OH	70[h]	80–81 (37)	1.3363	*q*

[a] At atmospheric pressure unless stated otherwise. [b] Can be purchased from a number of sources. [c] Overall yield from aldehyde (Knoevenagel reaction). [d] Yield from trifluoroacetic acid (ref *l*). [e] Yield from **9**. [f] At 19°. [g] Yield from **17**. [h] Yield from 4,4,5,5,-6,6,6-heptafluoro-2-iodo-2-hexen-1-ol. A mixture of cis and trans isomers was obtained. [i] W. M. Gearhart, "Kirk–Othmer Encyclopedia of Chemistry and Technology," 2nd ed, Vol. 6, 1965, p 464. [j] Reference 7. [k] Reference 6b. [l] E. T. McBee, O. R. Pierce, and D. D. Smith, *J. Amer. Chem. Soc.*, **76**, 3722 (1954). [m] E. T. McBee, C. W. Roberts, and C. Wilson, Jr., *ibid.*, **79**, 2323 (1957). [n] H. Albrecht and S. Smith, British Patent 904,263. [o] R. Filler, *J. Amer. Chem. Soc.*, **76**, 1376 (1954). [p] E. T. McBee, C. W. Roberts, and C. W. Wilson, Jr., *ibid.*, **81**, 1719 (1961). [q] J. D. Park, F. E. Rodgers, and J. R. Lacher, *J. Org. Chem.*, **26**, 2089 (1961).

bath.[9] The amides **14–16** reacted very slowly, but only the alcohol **17** failed to react at all. The yields and physical properties of the adducts are summarized in Table II.

Many methods exist for the determination of the configuration of a Diels–Alder adduct from cyclopentadiene and an unsaturated acid. The older techniques are based on the assumption that only the endo carboxyl group can interact with the double bond to form a lactone. These methods have the inherent drawback that they involve isolation procedures which can often lead to inaccurate product ratios. In addition, skeletal rearrangments are known, and certain exo acids have been observed to yield lactones.[10] Thus, while bromo- and iodolactonizations were used in this work to separate the endo from the exo adducts, gas–liquid chromatography (glpc) and infrared spectroscopy were used to determine the isomer ratios.[11] Since the methyl esters of **18**, **19**, and **20** were separable by glpc, the endo–exo ratios of the acids were determined from the glpc analyses of these esters. For the remaining adducts the general procedure followed was to first prepare authentic samples of endo and exo alcohols (**34–37**). This was accomplished through the lithium aluminum hydride reduction of the corresponding acids, which had been previously separated *via* iodolactonization. Glpc analyses demonstrated clearly that the endo acids quantitatively gave only endo alcohols, and likewise with the cis isomer. The compounds **21–30** were then reduced with lithium aluminum hydride, and the ratios of the resulting endo and exo alcohols were determined.

Since the amides **31–33** could not be reduced directly to the corresponding alcohols, quantitative infrared analysis was the only method used to determine the isomer ratios of these adducts. In the case of compound **23**, this analytical technique gave an endo–exo ratio of 3.6:1.0, which agreed well with the value of 3.76:1.00 obtained by glpc analysis.

Discussion

From the data given in Table II, it is readily apparent that fluorine substituents dominate the stereochemical course of the Diels–Alder reactions.[12a] For instance, the introduction of a single fluorine caused a complete reversal in the endo–exo ratio of **19** compared to that of **18**. Further insertion of fluorines caused additional changes in this ratio which correlate surprisingly well with the inductive effects (σ_I's of the R groups) of the substituents, as shown in Figure 1.[12b]

Many theories, hypotheses, and rationalizations have been proposed during the past 30 years to explain

(9) The effect of temperature on the ratio of stereoisomeric adducts can be fairly large.[10] In this study the reaction of cyclopentadiene with **9** at 25° gave a C_3F_7 endo–exo ratio of 5.06:1.00, whereas at 0° the ratio was 6.40:1.00.

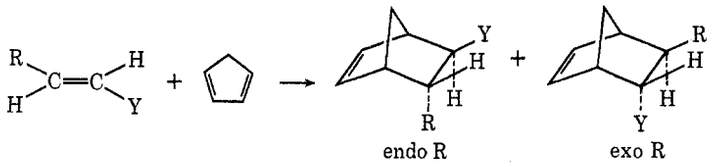
(10) (a) K. Adler, G. Stein, F. Buddenbrock, W. Eckardt, W. Frercks, and S. Schneider, *Justus Liebigs Ann. Chem.*, **514**, 1 (1934); (b) R. B. Woodward and H. J. Baer, *J. Amer. Chem. Soc.*, **70**, 1161 (1948); (c) S. Beckman, R. Schaber, and R. Bamberger, *Ber.*, **87**, 997 (1954); (d) C. D. Ver Nooy and C. S. Rondestvedt, Jr., *J. Amer. Chem. Soc.*, **77**, 3583 (1955); (e) J. A. Berson and A. Remanick, *ibid.*, **83**, 4947 (1961).

(11) Some of the values given in this paper differ from previously reported endo–exo ratios that were determined by bromolactonization and hydration.[3]

(12) (a) Chlorine and bromine substituents are apparently also very effective. Ethyl 4-chlorocrotonate and ethyl 4-bromocrotonate gave 78 and 73.5% endo (CH_2X) respectively when treated with cyclopentadiene; however, the conditions used were more drastic (170° for 7 hr). H. Christol, A. Donche, and F. Plénat, *Bull. Soc. Chem. Fr.*, 1315 (1966). (b) The Hammett σ_I values for CH_3 (−0.07), CH_2F (0.12), CHF_2 (0.29), and CF_3 (0.39) were taken from W. Sheppard, *Tetrahedron*, **27**, 945 (1971), and that of C_2F_5 (0.41) was obtained from W. Sheppard, *Trans. N. Y. Acad. Sci.*, **29**, 700 (1967). No value for the *n*-perfluoropropyl group is available.

Table II

Preparation and Properties of Diels–Alder Adducts



Compd[n]	R	Y	Yield, %	% endo R	endo R/exo R	Bp, °C (mm)	n_D or mp, °C
18	CH_3	CO_2H		37.4[a]	0.59	106–110 (3)	93–95[b]
19	CH_2F	CO_2H		63.0	1.70		Oil[c]
20	CHF_2	CO_2H	98.6	70.3	2.36	105–106 (1.5)	65–83[d]
21	CF_3	CO_2H	99	73.7	2.80	104–105 (2.5)	67–73[e]
22	C_2F_5	CO_2H	93	74.5	2.92	110–111 (1.8)	37–38[f]
23	n-C_3F_7	CO_2H	97	79.0	3.76	115–122 (2.5)[g]	54–71[h]
24	CF_3	CO_2Et	93	77.9	3.52	58–60 (1.3)	1.4250 (21)
25	C_2F_5	CO_2Et	96	81.7	4.46	78–79 (6.9)	1.4063 (20)
26	n-C_3F_7	CO_2Et	94	83.3	5.06	69–70 (2)	1.3960 (20)
27	n-C_7F_{15}	CO_2Et	88	84.3	5.37	85–87 (0.7)	1.3730 (20)
28	n-C_3F_7	CO_2Me	93	82.8	4.81	98–99 (21)	1.3950 (21)
29	n-C_3F_7	COCl	92	67.5	2.08	82–83 (11)	1.4087 (18)
30	n-C_3F_7	CHO	89	76.6	3.28	83–84 (19)	1.3963 (20)
31	n-C_3F_7	$CONH_2$	40.5[i]	>95	>19		104–107
32	n-C_3F_7	$CONHCH_3$	61[i]	>95	>19		82–83
33	n-C_3F_7	$CONHC_6H_5$	82.5[i,j]	>95	>19		94–98
34	n-C_3F_7	CH_2OH				104–108 (19)[k]	1.4043 (21)[k]
35	CF_3	CH_2OH					1.4402 (17.5)
36	C_2F_5	CH_2OH					1.4201 (17.5)[l]
37	n-C_7F_{15}	CH_2OH					34–49[m]

[a] Lit. 38.6%; ref 17b. [b] Lit. mp 95°: G. Komppa and S. Beckmann, *Justus Liebigs Ann. Chem.*, **523**, 68 (1936). [c] Benzylthiouronium salt, mp 144–145°. [d] **20n** (endo), mp 97–99°. [e] **21n**, mp 93.5–94° (ref 1); **21x** (exo), mp 118.5–119.5°. [f] **22n**, mp 53–54°. [g] Reference 3. [h] **23n**, mp 77–78°; **23x**, mp 82–83°. [i] Per cent conversion. [j] Reaction time was 70 hr. [k] Lit. bp 118° (21 nm), $n^{20}D$ 1.4030: ref 4. [l] α-Naphthylurethane derivative mp 106–108°. [m] Isomers were separated by preparative glpc on a 20% Carbowax 20 M column; **37n**, mp 58–60°; **37x**, mp 40.5–42°. [n] Satisfactory analytical data were reported for all new compounds listed in the table.

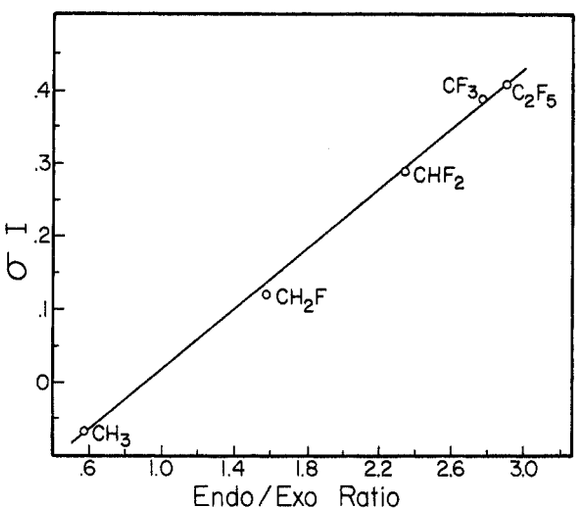


Figure 1.—Plot of the endo/exo ratios of compounds **18–22** *vs.* the Hammett σ_I values of the R groups.

the preference for endo addition.[13,14] We will simply explain the stereochemical results given in Table II as due to secondary attractive forces between nonbonding centers, and suggest that these forces, and consequently the endo-directive ability of small alkyl groups, parallel the electron inductive effects of these groups.[15] Lack of sufficient σ values prevented any attempt to similarly correlate quantitatively the esters **24–27**, but the same trend is also apparent in this series. This latter series also demonstrates the relatively small role which steric hindrance apparently plays in determining the endo–exo ratio. The per cent *endo*-C_7F_{15} (**27**) was determined to be only slightly larger than that found for the C_3F_7 group (**26**), but then the inductive effects of these two groups are probably only slightly different also. Steric requirements, on the other hand, continually increase in going down the series, but there seems to be little evidence here that these demands are forcing the larger perfluoroalkyl groups into the less hindered exo position.

No simple correlation could be obtained between the endo–exo ratios of compounds **23**, **26**, and **28–30** and the σ_I's and σ_R's of the various carboxyl functions. The endo-directive abilities parallel the electronegativity of these substituents, namely COCl > CHO = CO_2H > CO_2R > $CONR_2$. This same order has been reported for para-substituted *trans*-cinnamic acids, esters, etc.[16] The CH_2OH group would probably fit at the end of this list, but **17** does not react with the

(13) (a) K. Alder, W. Günyl, and K. Wolff, *Ber.*, **93**, 809 (1960); (b) Y. Kobuke, T. Fueno, and J. Furukawa, *J. Amer. Chem. Soc.*, **92**, 6548 (1970).

(14) K. N. Houk, *Tetrahedron Lett.*, 2621 (1970), and references cited therein.

(15) A multiple linear regression analysis using both σ_I and σ_R values was also run on compounds **18–22**. [See M. Charton, *J. Org. Chem.*, **31**, 3745 (1966)]. A correlation coefficient of 0.9994 was obtained with the values of α = 1.423, β = 6.210, and h = 1.625, but the very small σ_R values for these substituents make such a correlation almost meaningless. A correlation coefficient of 0.9964 was obtained with the σ_I values alone.

(16) C. S. Rondestvedt, Jr., and C. D. Ver Nooy, *J. Amer. Chem. Soc.*, **77**, 4878 (1955).

electron-rich cyclopentadiene under the same conditions used for the other dienophiles.

Experimental Section

Ethyl 4-Fluorocrotonate. A.—Ethyl 4-bromocrotonate (9.7 g, 0.05 mol) was treated under nitrogen with freshly prepared silver monofluoride (12.8 g, 0.1 mol) in 50 ml of ether and refluxed for 8 hr. Distillation gave 0.46 g (7%) of ethyl 4-fluorocrotonate, bp 53–56° (15 mm). Glpc indicated that this material was about 85% pure.

B.—When the same reaction was carried out with THF as the solvent, the yield was 5%.

C.—The ester was also added slowly to an equal amount of powdered silver monofluoride cooled in a water bath. When the vigorous reaction subsided another portion of AgF was added. The reaction mixture was poured into a slurry of NaF in pentane. Distillation gave a 7.5% yield of ethyl 4-fluorocrotonate which was *ca.* 90% pure.

D.—Potassium fluoride in ethylene glycol gave trace amounts of product. Sodium fluoride in THF and in acetone did not react. Solvents such as *N*-methylpyrrolidinone caused decomposition of the esters.

***trans*-4-Fluorocrotonic Acid (2).**—Ethyl-4-fluorocrotonate (2.3 g, 7 mmol) was saponified by adding 10 ml of 20% NaOH dropwise and heating at 70°. After 1 hr the solution was homogeneous and after acidification and extraction with ether an oil was isolated. Sublimation (60°, 1 mm) gave 1.37 g (75%) of **2**, mp 88–90°.

Anal. Calcd for $C_4H_5FO_2$: C, 46.15; H, 4.84. Found: C, 46.52; H, 4.82.

3-Hydroxy-4,4-difluorobutyric Acid (Knoevenagel Procedure).—Difluoroacetaldehyde (13.0 g, 0.16 mol) was distilled into a 100-ml flask with 17.7 g (0.17 mol) of malonic acid, 40 ml of pyridine, and 0.3 ml of piperidine. After the carbon dioxide evolution ceased, the solvent was stripped off. Distillation of the residue afforded 15.5 g (69%) of 3-hydroxy-4,4-difluorobutyric acid, bp 93–96° (12 mm). The distillate turned to a glass on standing.

Ethyl 3-Hydroxy-4,4-difluorobutanoate (Reformatsky Procedure).—Difluoroacetaldehyde (22 g, 0.275 mol) and ethyl bromoacetate (47.0 g, 0.28 mol) were placed in a dropping funnel. Approximately one-half of this solution was added to 18 g (0.28 g-atom) of zinc dust in freshly distilled benzene. The mixture was refluxed until reaction began (a light green color appeared). The remainder of the solution was then added slowly, and enough heat was supplied to maintain reflux for an additional 1 hr. Distillation afforded 19.8 g (48%) of ethyl 3-hydroxy-4,4-difluorobutanoate, bp 95–97° (35 mm), $n^{20}D$ 1.4016.

Anal. Calcd for $C_6H_{10}F_2O_3$: C, 42.63; H, 6.56; F, 22.48. Found: C, 43.10; H, 6.18; F, 22.95.

Ethyl *trans*-4,4-Difluorocrotonate.—Ethyl 3-hydroxy-4,4-difluorobutanoate (17 g, 0.1 mol) was poured over excess P_2O_5 and heated for 1 hr at 60°. After distillation 12 g (80%) of ethyl *trans*-4,4-difluorocrotonate was collected, bp 65° (35 mm), $n^{20}D$ 1.3945.

Anal. Calcd for $C_6H_8F_2O_2$: C, 48.01; H, 5.47; F, 25.17. Found: C, 48.14; H, 5.50; F, 25.18.

***trans*-4,4-Difluorocrotonic Acid (3).**—Ethyl 4,4-difluorocrotonate (7.5 g, 0.05 mol) and 20 ml of 10% sodium hydroxide were stirred and heated until a homogeneous solution was obtained. After the usual work-up 5.0 g (82%) of **3** was obtained, bp 73–74° (3 mm), mp 59–60.5°. The ir spectrum showed absorption at 10.25 μ characteristic of a trans olefin. In addition **3** was converted with diazomethane to the methyl ester and glpc showed at most only a trace of the cis isomer.

***trans*-4,4,5,5,6,6,6-Heptafluoro-2-hexenal (13).**—To 90 g (1 mol) of "active" manganese dioxide in 300 ml of pentane was added in one portion 9.00 g (39.8 mmol) of **17**. After stirring for 4 hr the reaction mixture was filtered, and the filtrate was fractionally distilled. Thus, 5.34 g (60%) of **13** was obtained: uv max (hexane) 213 mμ (log ϵ 3.35); nmr ($CDCl_3$) δ 6.63 (complex multiplet, 2) and 9.62 (complex multiplet, 1).

Anal. Calcd for $C_6H_3F_7O$: C, 32.16; H, 1.35. Found: C, 32.12; H, 1.35.

***trans*-4,4,5,5,6,6,6-Heptafluoro-2-hexenamide (14).**—To 11 ml of ice-cold concentrated ammonium hydroxide was slowly added 5.3 g (20.5 mmol) of **12**. The white precipitate was filtered, washed, and recrystallized from hexane–chloroform (4:1). Isolated in this manner was 4.32 g (88%) of **14**, uv max (EtOH) 209 mμ (log ϵ 3.53), 229 (3.43).

Anal. Calcd for $C_6H_4F_7NO$: C, 30.14; H, 1.69; F, 55.62; N, 5.86. Found: C, 30.17; H, 1.70; F, 55.25; N, 5.91.

General Procedure for the Preparation and Isolation of the Diels–Alder Adducts.—A slight molar excess of freshly distilled cyclopentadiene was added over a period of 5–10 min to the various dienophiles. The reaction was then stirred for 16–18 hr at 25°. Distillation *in vacuo* yielded the pure adducts except with the amide adducts where column chromatography was used.

Lithium Aluminum Hydride Reduction of the Diels–Alder Adducts. General Procedure.—To 3.2–9.3 mmol of the Diels–Alder adduct in 40 ml of absolute ether was added over a 30-min period under nitrogen a slurry of $LiAlH_4$ (3.4–9.5 mmol) in 30 ml of ether. The reaction was kept at 0° during the addition and for 30 min thereafter. The mixture was then gently refluxed for 2–3 hr, after which 95% ethanol was slowly added to decompose the excess $LiAlH_4$. The reaction mixture was then poured onto a slurry of concentrated H_2SO_4 (10 ml) and 200 g of crushed ice. The organic layer was separated, filtered, and dried and the ether was evaporated. The yield of the bicyclic alcohol was determined either by actual isolation or by the use of *N*-undecane as an internal standard and comparison of glpc peak heights with mixtures of known compositions. The endo–exo isomer ratios were determined by direct comparison of the relative peak areas with a K & E compensating planimeter, and reproducibility was found to be $\pm 2\%$.

Analysis of Amide Adducts. General Procedure.—The uv extinction coefficients of a series of standard solutions of the amide dienophiles were found to obey Beer's law in the range 10^{-5}–10^{-4} *M*. Consequently, quantitiative uv analysis was used to determine the amount of unreacted dienophile in the crude Diels–Alder adducts of the amides.

The exo–endo-isomer distributions were determined by quantitative ir analysis. Pure exo amides were easily prepared from the exo acid **23n**. An endo-rich sample was obtained from **29** enabling artificial mixtures to be prepared.

Iodolactonization of 3-Heptafluoropropylbicyclo[2.2.1]hept-5-ene-2-carboxylic Acid (23).—A sample of **23** (18.38 g, 0.060 mol) was dissolved in 60 ml of CH_3OH and almost neutralized with 6 *N* NaOH. The solution was then treated with 100 ml of 5% $NaHCO_3$ and the volume was adjusted to 520 ml with water. After treatment with 40 ml of iodine stock solution,[18d] the mixture was allowed to stand for 2 hr at 0° and then it was extracted with two 75-ml portions of ether. The combined ether fractions were washed successively with 1% sodium thiosulfate and water. After evaporation of the ether, the residue was dried over $CaSO_4$ *in vacuo* to give 4.70 g of crude iodolactone. This material was chromatographed (alumina, benzene) and recrystallized from hexane, mp 46–48°.

Anal. Calcd for $C_{11}H_8F_7IO_2$: C, 30.58; H, 1.87; F, 30.78; I, 29.37. Found: C, 30.60; H, 2.03; F, 31.00; I, 29.40.

Isolation of 3-*endo*-Heptafluoropropylbicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic Acid (23n).—The aqueous fraction from the above iodolactonization was treated with 1% sodium thiosulfate and dilute HCl, respectively. Crude **23n** precipitated and was filtered *in vacuo* from the ice-cold solution. Recrystallization from hexane at Dry Ice temperature gave 10.6 g (57%) of **23n**: mp 77–78°; ir (Nujol) 3.42 (s), 5.81 (s), 6.84 (s), 7.24 (m), 7.38 (m), 7.50 (m), 7.71 (m), 7.84 (m), 7.95 (m), 8.09 (s), 8.20 (s), 8.37 (m), 8.48 (s), 8.90 (m), 8.96 (m), 9.17 (m), 10.76 (m), 13.51 (m), 13.74 (s), 14.58 μ (m).

3-*exo*-Heptafluoropropylbicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic Acid (23x).—To 1.20 g (2.77 mmol) of the iodolactone prepared above was added 1.00 g (0.0155 g-atom) of powdered zinc in 10 ml of glacial acetic acid. The mixture was stirred for 69 hr at 23° and then filtered. Dilute sodium hydroxide was added and the mixture was ether extracted. The ether yielded 0.06 g of unreacted iodolactone. When the aqueous layer was acidified with 6 *N* HCl, **23x** precipitated. Sublimation at 50° (0.5 mm) gave 0.61 g (75%) of **23x**, mp 77–83°. After two recrystallizations from hexane the melting point was 82–83°; mixture melting point with **23n** (25%) was 52–73°; ir (Nujol) 3.40–3.50 (s), 5.84 (s), 7.03 (m), 7.30 (m), 7.45 (s), 7.53 (s), 7.78 (s), 7.89 (s), 8.04–8.65 (vs), 8.89 (s), 9.00 (s), 9.10 (s), 10.10 (m), 10.27 (m), 10.84 (m), 10.96 (m), 11.59 (m), 13.75 (s), 14.10 (s), 14.61 (s).

Registry No.—2, 37759-72-1; 3, 37759-73-2; 4, 406-94-0; 5, 37759-75-4; 6, 37759-76-5; 7, 25597-16-4; 8, 37759-78-7; 9, 37759-79-8; 10, 37759-80-1; 11, 37759-81-2; 12, 37759-82-3; 13, 37759-83-4; 17, 37759-84-5; 15, 37759-85-6; 16, 37759-86-7; *cis*-17, 37759-87-8; *trans*-17, 37759-88-9; *endo*-19 benzylthiouronium, 37746-47-7; *exo*-19 benzylthiouronium, 37746-48-8; *endo*-20, 37746-49-9; *exo*-20, 37705-54-7; *endo*-21, 37746-50-2; *exo*-21, 37746-51-3; *endo*-22, 37746-52-4; *exo*-22, 37746-53-5; *endo*-23, 37746-54-6; *exo*-23, 37746-55-7; *endo*-24, 37746-56-8; *exo*-24, 37746-57-9; *endo*-25, 37746-58-0; *exo*-25, 37746-59-1; *endo*-26, 37746-60-4; *exo*-26, 37746-61-5; *endo*-27, 37705-55-8; *exo*-27, 37705-56-9; *endo*-28, 37746-62-6; *exo*-28, 37746-63-7; *endo*-29, 37746-64-8; *exo*-29, 37746-65-9; *endo*-30, 37746-66-0; *exo*-30, 37746-67-1; *endo*-31, 37746-68-2; *exo*-31, 37746-69-3; *endo*-32, 37746-70-6; *exo*-32, 37746-71-7; *endo*-33, 37746-72-8; *exo*-33, 37746-73-9; *endo*-35, 37746-74-0; *exo*-35, 37746-75-1; *endo*-36 α-naphthylurethane, 37705-57-0; *exo*-36 α-naphthylurethane, 37746-76-2; *endo*-37, 37705-58-1; *exo*-37, 37705-59-2; cyclopentadiene, 542-92-7; ethyl 4-fluorocrotonate, 37746-77-3; ethyl 4-bromocrotonate, 37746-78-4; 3-hydroxy-4,4-difluorobutyric acid, 37746-79-5; difluoroacetaldehyde, 430-69-3; ethyl 3-hydroxy-4,4-difluorobutanoate, 37746-81-9; ethyl *trans*-4,4-difluorocrotonate, 37746-82-0.

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Stereochemistry of Asymmetric Silicon. XXII. Preparation and Properties of Optically Active Perfluorophenyl Compounds[1,2]

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The synthesis and resolution of two new optically active organosilicon systems has been achieved. These are α-naphthylperfluorophenylmethylsilanes, α-NpPh$_F$MeSi*X, and phenylmethylpentafluorophenylsilanes, PhMePh$_F$Si*X. Synthesis and resolution of these compounds is of special significance for organosilicon stereochemistry and reaction mechanisms because of the highly electron-withdrawing polar effect of the pentafluorophenyl group. The available data relating to the magnitude of the electron-withdrawing effect of the C_6F_5 group indicate that it approximates Br.

Since the electronegativity of the pentafluorophenyl group is approximately equal to that of Br[3] and is much greater than that of other "nonreactive" substituents previously bonded to asymmetric silicon,[4-7] it was of considerable interest to undertake the preparation and study of optically active compounds containing this group, in order to determine whether its presence would change the stereochemical course of substitution reactions at asymmetric silicon. The synthetic methods for preparation of C_6F_5MgBr[8,9] and C_6F_5Li[10,11] have been well established, and the coupling of either of these organometallic reagents with the appropriate chlorosilane has been shown to yield compounds containing the pentafluorophenyl group bonded to silicon.[12] The synthesis and properties of optically active perfluorophenylsilicon compounds is discussed in the next section.

(1) For the preceding paper in this series, see L. H. Sommer, K. T. Rosborough, and J. McLick, *J. Amer. Chem. Soc.*, **94**, 4217 (1972).

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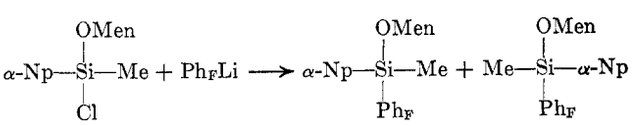
(12) For a recent paper containing pertinent earlier references, see A. J. Oliver and W. A. G. Grahm, *J. Organometal. Chem.*, **19**, 17 (1969).

Optically Active Perfluorophenylsilicon Compounds.—Two new monofunctional triorganosilicon systems incorporating the pentafluorophenyl group have been prepared by two methods and these are discussed below.

Reaction of α-naphthylmagnesium bromide with methyltrimethoxysilane gave a 68% yield of α-naphthylmethyldimethoxysilane, α-NpMeSi(OMe)$_2$, bp 118–119° (1.0 mm). Lithium aluminum hydride reduction of α-NpMeSi(OMe)$_2$ in refluxing ether gave an 88% yield of α-naphthylmethylsilane, α-NpMeSiH$_2$, bp 77–79° (0.35 mm). This substance was treated with chlorine in CCl_4 to give predominantly α-naphthylmethylchlorosilane, α-NpMeSiHCl. It is interesting that the electron-withdrawing effect of chlorine in α-NpMeClSiH is sufficient to prevent the substitution of chlorine for the remaining hydrogen atom. Without purification, α-NpMeSiHCl was then mixed with (−)-menthol in pentane to give a 78% yield of α-naphthylmethyl-(−)-menthoxysilane, bp 118° (0.13 mm). α-NpMeSi(H)-(−)-OMen was then treated with chlorine to give α-naphthylmethyl-(−)-menthoxychlorosilane. Without purification, α-NpMeClSi-(−)-OMen was



treated with a previously prepared solution of pentafluorophenyllithium at −78° in ether (or tetrahydrofuran) to give a 69% yield of the desired diastereomeric mixture of (±)-α-naphthylmethylpentafluorophenyl-(−)-menthoxysilane, bp 160–164° (0.1 mm).