benzoyl peroxide at 100° gave comparable results, and quantitative rearrangement was also obtained when C_3F_6 was replaced by CF_2=CFCl and the mixture exposed to sunlight. Substitution of $(CF_3CO)_2O$ for the olefin or exposure of the N-bromoimide alone to sunlight gave a little free bromine but recovery of most of the bromoimide, with no rearranged product.

Because of the extreme reactivity of the acyl isocyanate, it was identified by indirect methods, as follows.

A small sample of the isocyanate was allowed to stand 2 weeks in an ether solution of benzyl alcohol. Evaporation of the solvent left a solid which on recrystallization from cyclohexane melted at 76.5 to 78.5°.

Anal. Calcd. for $BrC_{12}F_6H_8NO_3$: C, 35.2; H, 2.0; N, 3.4. Found: C, 35.7; H, 2.3; N, 3.0.

The white solid formed on reaction of the acyl isocyanate with water, after washing and recrystallization from benzene, melted at 98 to 100°.

Anal. Calcd. for $BrC_4F_6H_2NO$: Br, 29.2; N, 5.1. Found: Br, 26.9[14]; N, 5.0.

Acknowledgments.—The authors are indebted to Dr. Wallace Brey for interpretation of the n.m.r. spectra, and to Dr. Henry C. Brown for a comparison infrared spectrum of 2,5-bis-(trifluoromethyl)-oxadiazole.

[14] Although the bromine value for this compound is low, it is felt that the complete body of evidence strongly supports the proposed structure for the rearranged product.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Stereochemistry of the Diels–Alder Reaction. III. Fluorinated *trans*-Olefinic Acids as Dienophiles

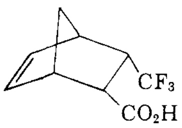
BY H. P. BRAENDLIN, A. Z. ZIELINSKI[1] AND E. T. MCBEE

RECEIVED JUNE 29, 1961

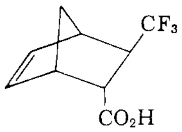
Adducts between cyclopentadiene and acids of the general formula *trans*-R_fCH=$CHCO_2H$ were prepared. Bromination in chloroform was shown to be a good adduct isomer determination method, revealing a consistent carboxy-*exo* to carboxy-*endo* relationship of 2:1. In some instances of adduct hydration, skeletal rearrangement was observed.

The steric course of the Diels–Alder reaction between a cyclic conjugated diene and a dienophile was stipulated by Alder and Stein to result in the product with maximum overlap of double bonds.[2] This was extended by Alder and Windemuth to include the formation of products wherein maximum overlap of unshared electron pairs is observed.[3] Thus, dienophiles carrying an electronegative substituent near the olefinic linkage were said to react with cyclic conjugated dienes to give predominantly the adduct with the substituent in the *endo* position of close proximity to the double bond formed by the diene portion of the molecule. However, exceptions to this rule are being observed with increasing frequency. Not only have *cis*-α,β-disubstituted ethylenes, such as maleic anhydride, been known for some time to give both *endo* and *exo* products,[3,4] but also in *trans*-olefin addition both substituents have been found to vie for the *endo* position to give mixed adducts.[5] In most cases of such mixed addition of *trans*-α,β-disubstituted ethylenes to a cyclic conjugated diene both substituents carried double bonds, *i.e.*, two π-electron systems were in competition. Recently, however, also *trans* substituents lacking π-electrons, such as trifluoromethyl[5e] and halogen,[5f] have been observed to exert considerable *endo* direction. Finally, studies with acrylic compounds[5f,6] have revealed that, at least in these systems, two α-substituents can compete with each other for the *endo* position even if one substituent is not electronegative. Thus, acrylonitrile, acrylamide and methacrylic compounds give cyclopentadiene adducts with large percentages of the isomers having hydrogen or methyl *endo*.

Since the mechanism of the Diels–Alder reaction is still obscure, the driving forces behind these anomalies are also unexplained. It is possible that the behaviors of the three groups of ethylenic dienophiles, *cis*- and *trans*-α,β- and α,α-disubstituted ethylenes, differ essentially. Whereas α-methyl may compete with α-carboxy for the *endo* position, *trans*-β-methyl appears to be unable to do so: *trans*-crotonyl chloride adds to cyclopentadiene with the methyl group exclusively *exo*[7]; *trans*-4,4,4-trifluorocrotonic acid, on the other hand, gives an adduct mixture (I) which was indicated to have a carboxy-*exo* (Ia) to carboxy-*endo* (Ib) ratio of 2:1.[5e]



Ia



Ib

It has now been found that this ratio is not only reproducible but applies also to cyclopentadiene adducts of other fluorinated acids of the formula R_fCH=$CHCO_2H$. The compounds C_3F_7CH=C-

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[2] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[3] K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938).

[4] (a) A. Wassermann, *J. Chem. Soc.*, 1511 (1935); 612 (1942); *Trans. Faraday Soc.*, **34**, 128 (1938); **35**, 841 (1939); (b) K. Alder, *et al.*, *Ann.*, **525**, 247 (1936); **566**, 1, 58 (1950); (c) H. Kwart and I. Burchuk, *J. Am. Chem. Soc.*, **74**, 3094 (1952); (d) D. Craig, *et al.*, *ibid.*, **73**, 4889 (1951); **76**, 4060 (1954); (e) J. A. Berson, *et al.*, *ibid.*, **75**, 1721 (1953); **78**, 6049 (1956).

[5] (a) C. S. Rondestvedt and J. C. Wygant, *J. Org. Chem.*, **17**, 975 (1952); *J. Am. Chem. Soc.*, **73**, 5785 (1951); (b) C. D. VerNooy and C. S. Rondestvedt, *ibid.*, **77**, 3583 (1955); C. S. Rondestvedt and C. D. VerNooy, *ibid.*, **77**, 4878 (1955); (d) F. Winternits, M. Mousseron and G. Rouzier, *Bull. soc. chim. France*, 170 (1955); (e) E. T. McBee, C. G. Hsu and C. W. Roberts, *J. Am. Chem. Soc.*, **78**, 3389 (1956); (f) K. Alder, R. Hartmann and W. Roth, *Ann.*, **613**, 6 (1958).

[6] (a) J. S. Meek and W. B. Trapp, *J. Am. Chem. Soc.*, **79**, 3909 (1957); (b) W. R. Boehme, E. Schipper, W. G. Scharpf and J. Nichols, *ibid.*, **80**, 5488 (1958); (c) K. Alder, K. Heimbach and R. Reubke, *Ber.*, **91**, 1516 (1958); (d) M. Schwarz and M. Maienthal, *J. Org. Chem.*, **25**, 499 (1960); (e) J. A. Berson, *et al.*, *J. Am. Chem. Soc.*, **82**, 5501 (1960); *Tetrahedron Letters*, **No. 4**, 131 (1961).

[7] K. Alder and G. Stein, *Ann.*, **514**, 197 (1934).

TABLE I

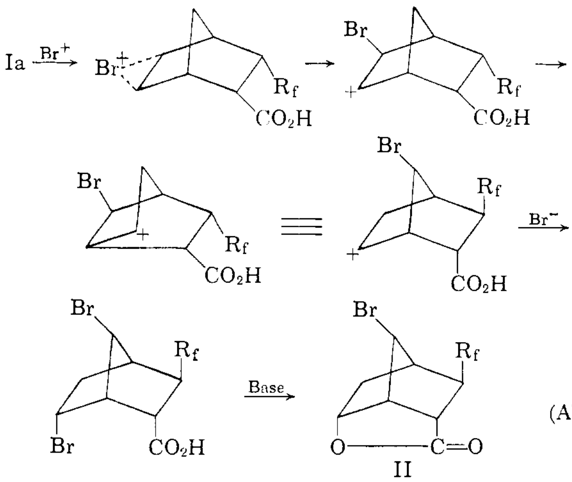
DIELS–ALDER ADDUCTS BETWEEN CYCLOPENTADIENE AND ACIDS *trans*-$R_fCH{=}CHCO_2H$

R_f	B.p. °C.	B.p. Mm.	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Fluorine, % Calcd.	Fluorine, % Found
CF_3	104–105	2.5	69–71[a]						
C_3F_7	115–122	2.5	46.5	43.15	42.96	2.96	3.00	43.44	43.69
C_5F_{11}	124–137	2	42–44	38.44	38.74	2.24	2.53	51.44	51.42
C_7F_{15}	146–166	2.5	81.5–82.5	35.59	35.84	1.79	2.11	56.30	56.00

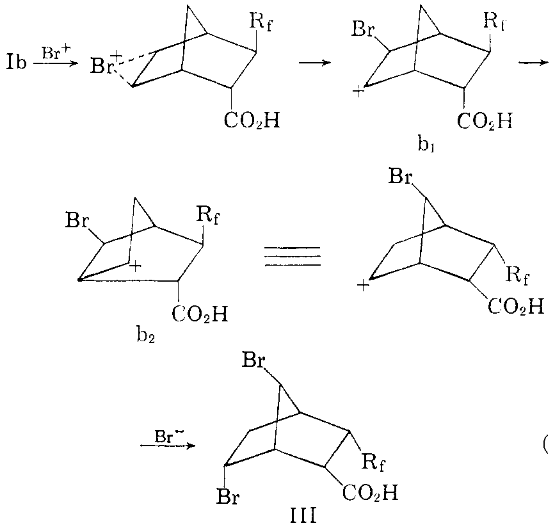
[a] McBee and co-workers[5e] report m.p. 60–70°.

HCO_2H, $C_5F_{11}CH{=}CHCO_2H$ and $C_7F_{15}CH{=}CHCO_2H$, all having *trans* configuration as established by infrared spectroscopy and vapor phase chromatographic purity, were prepared and added to cyclopentadiene (Table I). Although the acids underwent reaction readily and quantitatively, a distinct decrease in reaction rate was observed, though not measured, with increasing perfluoroalkyl chain length. This was ascribed to increasing steric hindrance exerted toward attack on the β-carbon atom by the nucleophilic diene. The assumption that true Diels–Alder addition takes place between cyclopentadiene and the unsaturated acids employed is valid: results described in the following paper carry evidence that no 1,2-additions occurred.

Of the methods most frequently used in determining the carboxy *exo–endo* relationship in the Diels–Alder adduct mixtures, hydration[7,8] and bromolactonization (bromination in base)[5b,e] are known to be accompanied by skeletal rearrangement reactions and are, therefore, unsuitable for exact isomer determination. Of the two reportedly good methods for distinguishing between *trans*-olefin adduct isomers, iodolactonization[5c] and bromination,[5d,e] the latter was chosen since it had already been successfully employed with one fluorinated species.[5e] A carboxy-*exo* adduct should on bromination in a neutral solvent and subsequent treatment with base yield a dibromoacid, and the *endo* isomer a bromolactone. However, skeletal rearrangements are conceivable under these conditions. For instance, an *exo* adduct could rearrange according to A to yield a bromolactone (II). Similarly, a rearrangement type B involving an *endo* adduct could yield a non-vicinal dibromide (III). Neither rearrangement occurs in these reactions. Debromination with zinc of a dibromoacid derived from the adduct mixture I gave a pure acid[5e] which had properties different from I and which was quantitatively rebrominated to the starting material. Hence, partial rearrangement can be excluded. Total rearrangement of both Ia and Ib, which would reverse the *exo–endo* ratio, is without precedence and can, moreover, be excluded in the case A and hence generally: the bromolactone IV obtained on bromolactonization, identical to the lactone obtained on bromination and subsequent lactonization, gave 45% of the corresponding epoxyacid V.[5e] Compound II is not capable of epoxidation. Furthermore, although theoretically possible, debromination of III to Ib with rearrangement is highly unlikely.[9]



(A)



(B)

Therefore, the ratios of dibromoacid to bromolactone (Table II) reflect the ratios of carboxy-*exo* to carboxy-*endo* in the adduct mixtures. The CF_3– and C_3F_7– substituted adducts, prepared under closely similar reaction conditions, have the same *exo–endo* relationship of 2:1. The reason for this consistency is unknown, and mechanistic concepts must await further study. It appears that any steric effect possibly exerted by the larger C_3F_7– group is obscured by other, more powerful, driving forces in the steric control of this type of reaction. A significant thermal rearrangement is unlikely, since neither purification (40° and 140°: see also Table II, last two lines) nor bromination (0° and 60°) at different temperatures changed the ratio to any appreciable degree. This implies

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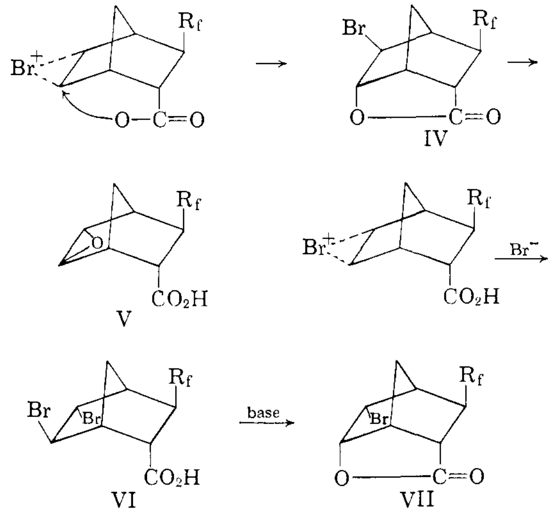
(8) (a) O Aschan, *Ber.*, **61**, 38 (1928); (b) K. Alder, F. W. Chambers and W. Trimborn, *Ann.*, **566**, 27 (1950); (c) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **70**, 1161 (1948).

(9) J. A. Berson, *ibid.*, **76**, 4069 (1954).

that the retrogressive step to the addenda is very slow and/or that thermodynamic equilibrium effects play minor roles. At present, experiments are being carried out to establish kinetic control in this type of reaction.

It is generally agreed that bromonium ion attack on bicycloheptenes occurs *exo*, *i.e.*, by the path of least steric hindrance. Furthermore, although in some instances *cis* addition has been observed,[10,11] for example, on catalysis by light,[11] *trans* bromination is the rule.[4d,9,11–13] In our experiments, product properties did not change when brominating in the dark, which appears to ensure ionic and therefore *trans* addition. However, this is incompatible with the fact that bromolactonization and bromination with subsequent lactonization yield the same lactone (IV), whose structure was indicated by epoxidation to V. Since *trans* bromination and subsequent conversion could reasonably take place only *via* VI, resulting in VII which is isomeric to IV, either an unprecedented *cis* epoxidation, VII → V, or *cis* bromination occurred.



The results obtained on hydration of the Diels–Alder adduct mixtures (Table II) are evidence of skeletal rearrangement reactions. The hydroxyacid to lactone ratio is a low 1.2 in the case of the CF_3–derivative but reproduces a 2:1 relationship in the mixtures carrying longer-chain perfluoroalkyl substituents. The high CF_3–lactone content is ascribed to a rearrangement of *exo* adduct similar to the rearrangement type A, which was suggested for such reactions.[5e,8] The hydroxyacid to lactone ratio increase with increasing hydration temperature, insignificant with CF_3 but substantial with C_3F_7, is attributed to a rearrangement similar to B, *i.e.*, conversion of carboxy-*endo* to carboxy-*exo*. Of interest is the dependence of these hydration effects on both the nature of the fluorinated substituent and on the temperature.

TABLE II

HYDRATION OF DIELS–ALDER ADDUCT MIXTURES

Perfluoroalkyl group	Amounts hydrated, g.	Initial temp., °C.	Reaction time, hr.	Hydroxyacid, %	Lactone, %	Ratio H/L
CF_3	4.23[a]	25	29	50	43	1.16
CF_3	2.14[a]	45	27	52	43	1.24
C_3F_7	5.59[a]	25	44	65	31	2.10
C_3F_7	7.10[a]	45	23	67	26	2.58
C_3F_7	41.64[a]	45	45	70	27	2.59
C_5F_{11}	4.28[a]	25	87	62	30	2.07
C_7F_{15}	3.95[a]	25	186	62	31	2.00
C_7F_{15}	4.10[b]	25	163	65	31	2.10

[a] Adduct purified by distillation. [b] Adduct purified by crystallization.

The possibility of other types of rearrangement cannot be ignored. In particular, the failure to recrystallize the hydroxyacids, obtained on hydration, to sharply melting substances (Table III) is noteworthy. This may be inherent in the type of compound, but contrasts with the properties observed in a similar (brominated) hydroxyacid.[5e] The presence of hydroxyacid isomers due to rearrangements different from A and B, but not necessarily affecting carboxy-*exo* or -*endo* configuration, is indicated. However, isomer separation and the investigation of such rearrangement reactions are reserved for subsequent study.

Experimental[14]

Perfluorocapronaldehyde.—The aldehyde was prepared, according to the procedure described by Pierce and Kane,[15] by addition of the corresponding perfluoroacid to cold lithium aluminum hydride; yield 49.4%, b.p. 78°, $n^{20}D$ 1.2838.

Anal. Calcd. for C_6HOF_{11}: C, 24.17; H, 0.39; F, 70.12. Found: C, 24.21; H, 0.22; F, 70.00.

Ethyl 3-Hydroxy-4,4,5,5,6,6,7,7,8,8,8-undecafluorooctanoate.—The ester was prepared according to the Reformatsky procedure described by McBee, Pierce and Smith[16]; yield 63.7%, b.p. 106–109° (8.5 mm.), m.p. 41.5–42.5°.

Anal. Calcd. for $C_{10}H_9O_3F_{11}$: C, 31.10; H, 2.35; F, 54.12. Found: C, 31.04; H, 2.48; F, 54.12.

Ethyl *trans*-4,4,5,5,6,6,7,7,8,8,8-Undecafluoroöct-2-enoate.—The above ester was dehydrated with phosphoric anhydride according to the procedure described by McBee, *et al.*,[16] with short initial warming; yield 74.8%, b.p. 126–129° (67 mm.), $n^{20}D$ 1.3408.

Anal. Calcd. for $C_{10}H_7O_2F_{11}$: C, 32.62; H, 1.92; F, 56.77. Found: C, 32.62; H, 2.20; F, 56.71.

***trans*-4,4,5,5,6,6,7,7,8,8,8-Undecafluoroöct-2-enoic Acid.**—The above ester was hydrolyzed by refluxing with aqueous sodium hydroxide according to McBee, *et al.*[16]; yield 82.6%, b.p. 114–147° (17 mm.), m.p. 64.5–65.5°.

Anal. Calcd. for $C_8H_3O_2F_{11}$: C, 28.25; H, 0.89; F, 61.45. Found: C, 28.40; H, 0.93; F, 61.16.

***trans*-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluorodec-2-enoic Acid.**—The corresponding olefinic ester[16] was hydrolyzed as described above; yield 87.7%, b.p. 134–136° (11 mm.), m.p. 90–91°.

Anal. Calcd. for $C_{10}H_3O_2F_{15}$: C, 27.29; H, 0.70; F, 64.74. Found: C, 27.40; H, 0.65; F, 65.01.

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(10) J. A. Berson and R. Swidler, *J. Am. Chem. Soc.*, **76**, 4060 (1954).

(11) J. A. Berson, *ibid.*, **76**, 5448 (1954).

(12) K. Alder and G. Stein, *Ann.*, **504**, 247 (1933), and other publications.

(13) H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, **75**, 3356 (1953); **76**, 4072, 4078.

(14) All melting points and boiling points are uncorrected. Analyses were performed by Dr. C. S. Yeh, Purdue University. Infrared spectra were obtained by Mrs. W. Dilling, Purdue University, on a Perkin-Elmer model 21 spectrophotometer. Vapor phase chromatograms were determined with a Perkin-Elmer model 154 Vapor Fractometer.

(15) O. R. Pierce and T. Kane, *J. Am. Chem. Soc.*, **76**, 300 (1954).

(16) E. T. McBee, O. R. Pierce and D. D. Smith, *ibid.*, **76**, 3722 (1954).

TABLE III

PHYSICAL PROPERTIES OF HYDRATION PRODUCTS

R	B.p., °C.	Mm.	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Fluorine, % Calcd.	Fluorine, % Found
				Lactones					
C_3F_7	128–129	3	42.5–43	43.15	43.45	2.96	3.21	43.44	43.16
C_5F_{11}			65–65.5	38.44	38.20	2.24	2.40	51.44	51.75
C_7F_{15}			99–101	35.59	35.87	1.79	1.99	56.30	56.25
				Hydroxyacids					
C_3F_7	161–182	4	92–96	40.70	40.96	3.42	3.76	41.02	40.82
C_5F_{11}			106–110	36.80	36.91	2.61	2.52	49.28	49.01
C_7F_{15}			127–130	34.36	34.16	2.12	2.12	54.36	54.40

Purity and *trans* configuration was established for each olefinic acid by vapor phase chromatography and infrared spectroscopy, respectively.

Cyclopentadiene.—Dicyclopentadiene was cracked at its normal boiling point, and the monomer was purified by fractionation through a 3 cm. × 10 cm. glass helices packed column. Redistillation through a short column gave pure diene, b.p. 40–41°, $n^{20}D$ 1.4410, which was collected in a chilled receiver and used immediately.

Diels–Alder Reaction between Acids *trans*-$R_fCH{=}CHCO_2H$ and Cyclopentadiene. General Procedure.—Freshly distilled cyclopentadiene (0.2 mole) was added to the fluorinated olefinic acid (0.2 mole), in a flask fitted with a Dry Ice condenser, at a rate governed by the initial evolution of heat. The vigorousness of the initial reaction decreased with increasing perfluoroalkyl chain length. After standing for 18 hours at room temperature (with heating to reflux in the cases of the C_5F_{11}– and C_7F_{15}–derivatives), the semi-solid mixture was distilled under vacuum to give a quantitative yield of the adduct mixture. The latter crystallized on standing. For physical properties see Table I.

Bromination of the Diels-Alder Adduct Mixtures (Table II). (a) **The $C_3F_7CH{=}CHCO_2H$ Adduct in Cold Chloroform.**—Freshly distilled bromine (3.62 g., 0.023 mole) in 40 ml. of chloroform was added slowly at 0° to 7.0 g. (0.023 mole) of the cyclopentadiene–hexafluorohexenoic acid adduct mixture in 100 ml. of chloroform. The resulting solution was stirred for 6 hours at that temperature and was allowed to warm to room temperature over a period of 2 hours. After washing with 200 ml. of 10% aqueous sodium carbonate and drying over sodium sulfate, chloroform was evaporated to give 2.86 g. (33%) of the lactone; after recrystallization from pentane, m.p. 67–68°.

Anal. Calcd. for $C_{11}H_8O_2BrF_7$: C, 34.29; H, 2.08; F, 34.55. Found: C, 34.67; H, 2.18; F, 34.70.

The basic solution was acidified with 10% sulfuric acid and extracted exhaustively with ether. After drying over sodium sulfate and removal of ether, the residue crystallized to give 6.94 g. (66%) of the dibromoacid; after recrystallization from heptane, m.p. 133–134°.

Anal. Calcd. for $C_{11}H_9O_2Br_2F_7$: C, 28.34; H, 2.43; F, 34.33. Found: C, 28.16; H, 2.37; F, 34.33.

(b) **The $CF_3CH{=}CHCO_2H$ Adduct in Refluxing Chloroform.**—The adduct mixture (2.5 g., 0.012 mole) was dissolved in 100 ml. of chloroform in a 200-ml. flask, fitted with condenser and dropping funnel, and covered with aluminum foil. To the refluxing solution, 2 g. (0.012 mole) of bromine in 25 ml. of chloroform was added dropwise over a period of 3 hours. After a total reaction time of 6 hours, the mixture was worked up as under (a) to give 33% lactone, m.p. 70–72°, and 66% dibromoacid, m.p. 162–163°. (McBee, *et al.*[6] report the same physical properties.)

Hydration of the Diels-Alder Adduct Mixtures. General Procedure.—The adduct mixture and 85% sulfuric acid (10 ml. for each gram of adduct) were stirred at room temperature for a given period of time. In some instances an initial temperature of 45° was employed for 2 hours, with subsequent reaction at room temperature. On dilution with ice-water to double the reaction volume, the aqueous mixture was continuously extracted with ether for 48 hours. The ether extract was shaken with two 100-ml. portions of a 10% sodium carbonate solution. The ethereal layer was dried over magnesium sulfate, and the ether was removed to yield crude lactone. Pure lactone was obtained by distillation or crystallization. The basic solution was acidified with sulfuric acid, and the aqueous mixture was continuously extracted with ether for 48 hours. Drying and removal of ether yielded crude hydroxyacid. On standing, crystals of analytically pure product were obtained. With the C_3F_7– derivative, unsuccessful attempts were made at recrystallization from ether–pentane, acetone–water and cyclohexene. In each instance, the hydroxyacid separated as a highly viscous, glass-like, material. Attempted purification by chromatography on alumina or silica gel was equally unsuccessful. For amounts of material used, initial temperatures and yields, see Table III. For physical properties of lactones and hydroxyacids, see Table IV.

Acknowledgment.—The financial support of the Westinghouse Electric Corporation is gratefully acknowledged.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Stereochemistry of the Diels–Alder Reaction. IV. Adducts between Cyclopentadiene and Fluorinated Olefins[1]

BY H. P. BRAENDLIN, G. A. GRINDAHL, Y. S. KIM AND E. T. MCBEE

RECEIVED JUNE 29, 1961

The addition products between cyclopentadiene and hexafluoropropene, and *trans*-heptafluorohexenoic acid, respectively, have been identified by chemical means as the Diels–Alder adducts. The syntheses of 6,6,7-trifluoro-7-trifluoromethylbicyclo[3.2.0]heptane and of 7-heptafluoropropylbicyclo[3.2.0]heptane derivatives are described.

Addition reactions between olefins and conjugated dienes have been known for some time. Generally, moreover, such addition occurs in 1,4-fashion across the diene system; this is well known as the Diels–Alder reaction.[2] However, 1,2-addition reactions to conjugated dienes have

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(1) From portions of the theses submitted by George A. Grindahl and You Sun Kim to the Graduate School of Purdue University, in partial fulfillment of the requirements for the degrees of Master of Science and Doctor of Philosophy, respectively.

(2) (a) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937). (b) K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938).