TABLE III

PHYSICAL PROPERTIES OF HYDRATION PRODUCTS

| R | B.p., °C. | Mm. | M.p., °C. | Carbon, % |  | Hydrogen, % |  | Fluorine, % |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Calcd. | Found | Calcd. | Found | Calcd. | 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 semisolid 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.

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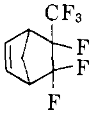
[1] From portions of the theses submitted by George A. Grindahl and You Sun Kim to the Graduate School of Purdue University, in partial fulfillment of the requirements for the degrees of Master of Science and Doctor of Philosophy, respectively.

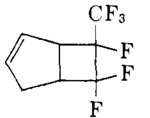
[2] (a) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937), (b) K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938).

also been observed, notably with ketenes[3] and tetrafluoroethylene, the latter undergoing both modes of addition.[4] This behavior forced a reexamination of the products between cyclopentadiene and other fluorine-containing olefins, such as perfluoropropene[5] and, in particular, *trans*-$\beta$-perfluoroalkyl-$\alpha,\beta$-unsaturated acids.[6]

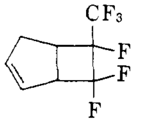
Compounds Ia, b and c are possible structures representing the cyclopentadiene–perfluoropropene adduct. Each isomer, furthermore, can exist with the trifluoromethyl group in the *endo* as well as the *exo* position, making a total of six possible isomers.



Ia

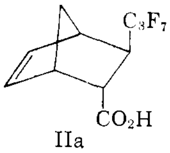


Ib

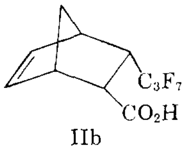


Ic

Addition of the *trans* unsaturated acids to the diene resulted in mixtures to which the carboxy-*endo* and -*exo* Diels–Alder structures, *e.g.*, IIa and IIb were assigned.[6] *exo*-Acid formation was reasoned to arise from the competitive *endo* affinity of the perfluoroalkyl group, in accordance with Alder's modified rule[2b] of maximum overlap of unshared electron pairs as driving force in the steric course of addition between cyclic conjugated dienes and dienophiles. Before continuing the study of addition with fluorinated *trans* unsaturates of this type, however, the occurrence of true Diels–Alder addition had to be verified. Although there is no precedence of 1,2-addition of olefinic acids to conjugated dienes, it could conceivably occur with the fluorinated species to give either mixed 1,2-adduct isomers or a mixture of 1,4- and 1,2-adducts. $\beta$-Perfluoroalkyl-$\alpha,\beta$-unsaturated acids have a remarkable polarity with a considerably electropositive $\beta$-carbon atom,[7] and the possibility of such a factor altering the normal course of the reaction was not to be ignored.



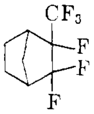
IIa



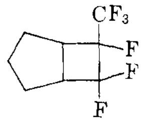
IIb

Structural elucidation of I and II could not be achieved by spectroscopic means[8]; also, degradation and hydrolysis of I failed to give the desired information. However, successful comparative results were obtained on independent syntheses of isomer derivatives of I and II, in analogy to the structural proof offered by Smith and coworkers[3] for the cyclopentadiene–diphenyl ketene adduct.

The vapor phase chromatogram of crude I recorded only one sharp peak, revealing the presence of only one component. Thus, in contrast to tetrafluoroethylene, hexafluoropropene did not exhibit the tendency for mixed addition. Moreover, when the reactants were present in equimolar amounts, yield was quantitative (v.p.c.), although mechanical losses were incurred in subsequent purification. Catalytic hydrogenation of I gave III; addition of hexafluoropropene to cyclopentene gave IV, with both possible isomers ($CF_3$ *endo* and *exo*) in nearly equal amounts. Comparison of physical properties revealed III to be different from IV (Table I). Hence, III could not have arisen from Ib or Ic, since hydrogenation of either should have yielded one of the isomers of IV. The only possible structure for the hexafluoropropene–cyclopentadiene adduct is therefore the Diels–Alder formulation Ia.[9] This is supported by the fact that bromination of I with N-bromosuccinimide failed. Compound Ib or Ic should undergo this type of bromination readily, whereas Ia, wherein the allylic positions are bridgeheads, is expected to be reluctant to free radical attack.

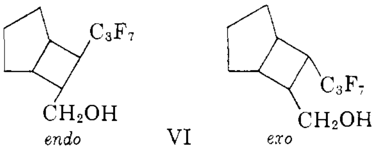


III

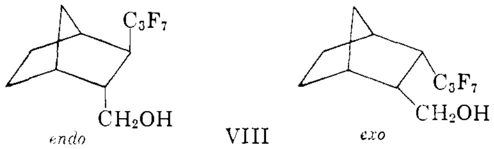


IV

A similar procedure was employed in the structural elucidation of II. Addition of ethyl *trans*-4,4,5,5,6,6,6-heptafluorohexenoate to cyclopentene gave V which was shown by vapor phase chromatography to consist of two compounds in 5:1 ratio. Compound V, undoubtedly an *endo–exo* isomer mixture, was then reduced to the carbinol mixture VI. The physical properties of VI were different from those of the carbinol mixture VIII which was obtained on lithium aluminum hydride reduction of II, followed by catalytic hydrogenation of the intermediate VII (Table II). In conclusion, the only possible structures for VII and VIII, and hence II, are Diels–Alder formulations.



VI



VIII

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[3] L. I. Smith, C. L. Agre, R. M. Leekely and W. W. Pritchard, *J. Am. Chem. Soc.*, **61**, 7 (1939).

[4] (a) D. D. Coffman, P. L. Barrick, R. C. Cramer and M. S, Raasch, *ibid.*, **71**, 490 (1949); (b) J. J. Drysdale, W. W. Gilbert, H. K. Sinclair and W. H. Sharkey, *ibid.*, **80**, 3672 (1958).

[5] E. T. McBee, C. G. Hsu, O. R. Pierce and C. W. Roberts, *ibid.*, **77**, 915 (1949).

[6] (a) E. T. McBee, C. G. Hsu and C. W. Roberts, *ibid.*, **78**, 3389 (1956); (b) H. P. Braendlin, A. Z. Zielinski and E. T. McBee, *ibid.*, **84**, 2109 (1962).

[7] (a) E. T. McBee, O. R. Pierce and D. D. Smith, *ibid.*, **76**, 3722, 3725 (1954); (b) E. T. McBee, C. W. Roberts and G. Wilson, Jr., *ibid.*, **79**, 2323 (1957).

[8] No definite infrared spectral assignments could be made, and nuclear magnetic resonance spectra were ambiguous because of extensive spin–spin splitting between non-equivalent groups and atoms.

[9] The formation of only one of the two possible configurational isomers of Ia ($CF_3$ *endo* or *exo*) is significant; configurational elucidation is at present being attempted.

Table I

| | B.p., °C. | $n^{20}D$ | Retention time, min.[a] |
|---|---|---|---|
| 5,5,6-Trifluoro-6-trifluoromethylbicyclo[2.2.1]-hept-2-ene (I) | 140–140.5 | 1.3740 | |
| 2,2,3-Trifluoro-3-trifluoromethylbicyclo[2.2.1]-heptane (III) | 150 | 1.3720 | 1.80 |
| 6,6,7-Trifluoro-7-trifluoromethylbicyclo[3.2.0]-heptane (*endo* + *exo*, IV) | 131 | 1.3650 | 1.38, 1.50 |

[a] Perkin–Elmer C column, temperature 130°, 16 p.s.i., helium as carrier gas.

Table II

| | B.p., | | $n^{20}D$ | Retention time, min.[a] |
|---|---|---|---|---|
| | °C. | Mm. | | |
| Ethyl 3-heptafluoropropylbicyclo[3.2.0]heptane-2-carboxylate (V) | 93–94 | 4 | 1.3870 | 4.00, 4.80[10]<br>5:1 |
| 3-Heptafluoropropylbicyclo-[3.2.0]heptane-2-carbinol (VI) | 134–135 | 65 | 1.3930 | 2.60[10] |
| 3-Heptafluoropropylbicyclo-[2.2.1]hept-5-ene-2-carbinol (VII) | 118 | 21 | 1.4030 | 3.05[10] |
| 3-Heptafluoropropylbicyclo-[2.2.1]heptane-2-carbinol (VIII) | 90 | 1 | 1.4010 | 3.20[10] |

[a] Perkin–Elmer Q column, temperature 280°, sensitivity 8, flow rate 4.5, helium as carrier gas.

## Experimental[11]

**Starting Materials.**—Cyclopentadiene was obtained on depolymerization of commercial dicyclopentadiene by distillation through a Kornblum head and redistillation through a short column; b.p. 40–43°, $n^{20}D$ 1.4407.

Hexafluoropropene, obtained through the courtesy of the E. I. du Pont de Nemours Co., was not purified, the gas, b.p. −29°, being used directly from the transport cylinder.

Heptafluorobutyraldehyde and ethyl *trans*-4,4,5,5,6,6,6-heptafluorohexenoate were prepared by the procedures of Pierce and Kane[12] and McBee and co-workers,[7a] respectively. The heptafluorohexenoic acid–cyclopentadiene adduct II was prepared according to the procedure of McBee and co-workers.[6b]

**5,5,6-Trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene (I).**—Freshly distilled cyclopentadiene (17.1 g., 0.26 mole) and hydroquinone (1.8 g.), were placed in a 600 × 19 × 25 mm. Carius tube, and the tube was chilled to −78° in a Dry Ice–trichloroethylene-bath, while protecting the contents of the tube with a Drierite drying tube during the cooling procedure. Hexafluoropropene (38.6 g., 0.26 mole) was condensed into the tube, and the latter was sealed at −78°, placed in a combustion furnace and, after being allowed to warm up to room temperature, it was heated to 150–160° for 72 hours (caution). The tube was then removed from the furnace, cooled to −78° and opened. While warming to room temperature, the tube was vented through a Dry Ice trap to recover any unreacted perfluoropropene. Examination of the crude reaction mixture, obtained in quantitative yield, by vapor phase chromatography revealed the presence of only one compound. During the suction filtration used to remove hydroquinone, 5.0 g. of the filtrate was lost, probably due to volatilization. Fractionation of the filtrate yielded 41.2 g. (76%) of colorless I.

*Anal.* Calcd. for $C_8H_6F_6$: C, 44.44; H, 2.78; F, 52.78. Found: C, 44.48; H, 2.87; F, 52.38.

**2,2,3-Trifluoro-3-trifluoromethylbicyclo[2,2,1]heptane (III).**—A solution of I (21.6 g., 0.1 mole) in 100 ml. of absolute ethanol was treated with hydrogen and Raney nickel in a Parr hydrogenator under a pressure of 53 p.s.i. for 3 hours. Hydrogen pressure drop indicated a quantitative uptake of hydrogen by the olefin (a calibration run was made with cyclohexene). Removal of the Raney nickel by filtration through a sintered glass filter funnel and fractionation of the filtrate gave 16 g. (68%) of III.

*Anal.* Calcd. for $C_8H_8F_6$: C, 44.03; H, 3.70; F, 52.27. Found: C, 44.38; H, 3.71; F, 51.90.

**6,6,7-Trifluoro-7-trifluoromethylbicyclo[3.2.0]heptane (IV).**—A 100-ml. stainless steel autoclave equipped with a Magna-Dash stirrer was evacuated to 0.5 mm. pressure and cooled to −78° in a Dry Ice–trichloroethylene-bath. Hexafluoropropene (51.5 g., 0.33 mole) and cyclopentene (22.5 g., 0.33 mole) were condensed into the autoclave through a valve with the exclusion of air. After heating to 300° under an autogenous pressure of 2000 p.s.i. for 12 hours, the autoclave was cooled to room temperature and vented through a series of refrigerated traps (0°, −78°, −195°); 38.9 g. of $C_3F_6$ was recovered. Fractionation of the residue yielded 12.4 g. (68%) of the adduct IV.

*Anal.* Calcd. for $C_8H_2F_6$: C, 44.03; H, 3.70; F, 52.27. Found: C, 44.11; H, 3.94; F, 52.04.

Previous runs in which pressures of 500 p.s.i. and 670 p.s.i. were developed failed to yield any addition compound.

**Ethyl 3-Heptafluoropropylbicyclo[3.2.0]heptane-2-carboxylate (V).**—Ethyl hexafluorohexenoate (23 g., 0.09 mole) and 30 g. (0.44 mole) of cyclopentene were placed in a 100-ml. autoclave equipped with Magna-Dash stirrer. The mixture was stirred under nitrogen pressure (2000 p.s.i.) at 250° for 33 hours. After cooling, the autoclave content was washed out with ether, and the ether solution was dried over anhydrous magnesium sulfate. Distillation gave 26 g. of cyclopentene and 13 g. of unreacted ester. Further distillation under reduced pressure gave 1.3 g. of V.

*Anal.* Calcd. for $C_{13}H_{15}O_2F_7$: C, 46.42; H, 4.46; F, 39.58. Found: C, 46.42; H, 4.70; F, 39.80.

**3-Heptafluoropropylbicyclo[3.2.0]heptane-2-carbinol (VI).**—A solution of V (2.6 g., 0.008 mole) in 50 ml. of anhydrous ether was added dropwise over a period of 10 minutes with stirring and cooling to 6 g. of lithium aluminum hydride in 30 ml. of anhydrous ether. The reaction mixture was then refluxed for 18 hours under stirring, whereupon it was hydrolyzed with 95% ethanol and dilute sulfuric acid. After separating the ether layer, the aqueous layer was extracted with ether, and the combined ethereal solution was dried over anhydrous magnesium sulfate. The ether was removed and the residue distilled to give 1.8 g. (19%) of VI.

*Anal.* Calcd. for $C_{11}H_{13}OF_7$: C, 44.89; H, 4.42; F, 45.24. Found: C, 44.98; H, 4.58; F, 45.00.

**3-Heptafluoropropylbicyclo[2.2.1]hept-5-ene-2-carbinol (VII).**—A suspension of 6 g. of lithium aluminum hydride in 50 ml. of anhydrous ether was added dropwise over a period of 20 minutes to a solution of 23.7 g. (0.08 mole) of II in 30 ml. of anhydrous ether, with stirring and cooling to 0°. The mixture was refluxed gently for 6 hours and hydrolyzed with 95% ethanol and dilute sulfuric acid. Purification as described above and distillation gave 9.2 g. (85%) of VII.

*Anal.* Calcd. for $C_{11}H_{11}OF_7$: C, 45.21; H, 3.76; F, 45.55. Found: C, 45.20; H, 3.88; F, 45.48.

**3-Heptafluoropropylbicyclo[2.2.1]heptane-2-carbinol (VIII).**—Absolute ethanol (150 ml.), 11 g. (0.04 mole) of VII, 0.2 g. of platinum oxide and 150 ml. of absolute ethanol were placed in a Parr hydrogenator, and the reaction bottle was flushed twice with dry hydrogen. After shaking the mixture under a hydrogen pressure of 50 p.s.i. for 24 hours at 30°, the platinum oxide was filtered off

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(10) Reduction to the carbinols was carried out for the purpose of easier identification, since vapor phase chromatographic resolution of the corresponding acids or esters, with the exception of V, could not be achieved. In all three instances, only single carbinol peaks were obtained on the vapor phase chromatograms. However, each peak carried a tail indicative of the presence of isomers. The possibility of total loss of one isomer could be excluded when lithium aluminum hydride reduction of II, containing at least 26% of the *endo* adduct,[6b] gave 85% of VII.

(11) All boiling points are uncorrected. Analyses were performed by Dr. C. S. Yeh, Purdue University. The infrared spectra were obtained by Mrs. W. Dilling, Purdue University, on a Perkin–Elmer model 21 spectrophotometer. The vapor phase chromatograms were determined with a Perkin–Elmer model 154 Vapor Fractometer.

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

and the alcohol removed from the filtrate. The residue was distilled to give 5.6 g. (51%) of the desired VIII.

*Anal.* Calcd. for $C_{11}H_{13}OF_7$: C, 44.89; H, 4.42; F, 45.24. Found: C, 45.06; H, 4.70; F, 45.39.

**Acknowledgment.**—The financial support of the Hooker Chemical Corporation is gratefully acknowledged.

[CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY,[1a] UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

# Primordial Organic Chemistry. I. Compounds Resulting from Electron Irradiation of $C^{14}H_4$

BY CHRISTOF PALM[1b] AND MELVIN CALVIN

RECEIVED OCTOBER 25, 1961

$C^{14}$-Labeled methane, together with a number of other presumed primordial gases of the earth's atmosphere, has been subjected to electron bombardments. The products formed have been examined by paper chromatography, ion exchange chromatography, mass spectrometry and ultraviolet light spectrophotometry. A number of minor molecules have been specifically identified, and urea has been found as a major component in the absence of added phosphine; the formation of urea is inhibited by added phosphine. Most of the products can be accounted for as discrete molecules, even though they are as yet unidentified.

## Introduction

We have extended our experiments with ionizing irradiation (5 Mev. electrons from a linear accelerator) on supposed primitive gas mixtures, containing certain compounds of carbon, hydrogen, oxygen and nitrogen.[2-4]

Chemical evolution has been suggested as the process preceding biological evolution.[3-6] Although little is known with certainty about the atmosphere of primitive earth, it is generally assumed that reducing atmospheric conditions prevailed at that time.[7a,b] Aqueous $CO_2$-containing ferrous ion and hydrogen was irradiated with accelerated $\alpha$-particles in 1951.[2a,8] Mixtures of $CH_4$, $NH_3$, $H_2O$ and $H_2$ were sparked in 1953.[9a,b] The results have given rise to further experiments and more factual basis for discussions of chemical evolution. Not only have mixtures of simple gases like $H_2$, $CH_4$, CO, $CO_2$, $NH_3$ and $H_2O$ been exposed to varied sources of energy[10] but also some more "evolved" compounds which had been found or were assumed to be involved in these first experiments.

Beta emission, notably from potassium-40, might have contributed a small part to the over-all spectrum of available energy sources four to five billion years ago.[11] Its connection with the possibly catalyzing mineral surfaces make it particularly interesting. Electron irradiation also proves to be a convenient energy source. So far, only two brief mentions of electron irradiation for this purpose exist.[12] The reasons for irradiation of $H_2$, $CH_4$, $NH_3$ and $H_2O$ rather than $CO_2$, $N_2$, and $H_2O$ shall not be discussed here beyond the assumption of $H_2$ in the primitive atmosphere. It should be emphasized, however, that the irradiations presented here can only help to understand chemical evolution, not necessarily reproduce it.

The number of identified compounds formed by primordial chemistry is still very limited. They account for only a small fraction of all the organic matter produced in these experiments. The large variety of reactions and compounds has truly been a limitation in this chemistry of products derived largely from $CH_4$, $H_2$, $NH_3$, $H_2O$ and energy. Too few compounds are formed in amounts easily susceptible to ordinary analysis. For this reason, the use of carbon-14 labeled $CH_4$ is stressed here as it will allow more detailed analysis of the fate of carbon.

The formation of amino acids has been well established in primordial chemistry.[9a,b,13-16] One of the main incentives of the present work has been to contribute to the discussion on the still unsolved problem of how readily heterocyclic bases, *i.e.*, purines and pyrimidines, might be formed in such systems. So far, none of these have been reported to be found in reactions involving compounds of complexity no greater than $H_2$, $CH_4$, $H_2O$, and $NH_3$ ($N_2$, CO, $CO_2$).[17] It was only during the progress of the present investigations that evidence appeared that by heating a concentrated aqueous

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(1) (a) The preparation of this paper was sponsored by the U. S. Atomic Energy Commission. (b) Permanent address: Laboratory of Inorganic Chemistry, University of Munich, Munich, Germany.

(2) (a) W. M. Garrison, *et al.*, *Science*, **114**, 461 (1951); (b) C. Palm and M. Calvin, in University of California Radiation Laboratory Report, UCRL-9519, Jan. 31, 1961, p. 30.

(3) M. Calvin, *Ann. Intern. Med.*, **54**, 954 (1961).

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