Table I. Photoinitiated Halogenations of 1:1 Neopentane–Methylene Chloride Mixtures

	yields[a]				
halogenating agent	CO_2	neo-$C_5H_{11}X$	$CHCl_2X$	selectivity[b]	accountability[c]
$AcOBr/Br_2$[e]	77[d]	7	14	12	98
$AcOCl/Cl_2$[e]	66	14	28	12	96
AcOBr, $Cl_2C{=}CH_2$[f]	100	0	0		100
AcOCl, $Cl_2C{=}CH_2$[f]	98	0	0		98

[a] Yields determined by GC and expressed as percentages based on starting hypohalite. [b] Selectivity calculated from the molar ratio ($CHCl_2X$/neo-$C_5H_{11}X$) times (12 neopentane hydrogens/2 CH_2Cl_2 hydrogens) to account for the statistical factor. [c] (mmol of CO_2 + mmol of halogenated product/mmol of AcOX)100. [d] Yield of methyl bromide was 75%; yield of acetic acid was 25%. [e] 10^{-3} M. [f] 0.1 M.

pentane/methylene chloride mixtures were used. Typically these reactions (tungsten lamp irradiation, 2–3 h for 100% conversion, −78 °C, CCl_3F solvent, 0.2 M AcOBr, 10^{-3} M Br_2, 1 M neo-C_5H_{12}, and 1 M CH_2Cl_2) give CO_2 (77% yield), bromination products (21%), and acetic acid (25%). This appears to be the first report of a noncage reaction of acetoxy radical. The ratio of bromodichloromethane to neopentyl bromide is 2 ± 0.3.

In the absence of acetyl hypobromite, attempts at photobromination failed under the above conditions using various concentrations of Br_2; there was no bromination.

The same reaction conditions using acetyl hypochlorite give similar results in the presence of 10^{-3} M chlorine—66% CO_2 and 40% chlorination products. The ratio of chloroform to neopentyl chloride is 2 ± 0.3. Chlorine alone under these conditions produces neopentyl chloride exclusively; the reaction of Cl· with CH_2Cl_2 is not a significant pathway in this competition.

$AcOBr/Br_2$ under the above reaction conditions brominates 1-bromobutane—68% CO_2 and 32% halogenation products, equal amounts of 1,1-dibromobutane (11%), 1,2-dibromobutane (11%), and 1,3-dibromobutane (11%) are obtained; 1,4-dibromobutane is not produced. Bromine atom chains, if they operated at these low temperatures, would produce almost exclusively 1,2-dibromobutane (by extrapolation from higher temperatures).[6a] Little discrimination between C-2 and C-3 is a characteristic of radicals such as succinimidyl,[1] Cl·,[6b] and *t*-BuO·.[6c]

It is remarkable that in the above experiments there is no halogenation of substrates if free halogen is scavenged. Experiments in which vinylidiene chloride (0.1 M) was employed as scavenger for the halogens, all other experimental details being the same, resulted in quantitative Hundsdiecker reactions, without detectable attack on neopentane, methylene chloride, or 1-bromobutane.

The possibility that chain carriers other than acetoxy are participating must be considered: Bromine atoms do not react at −78 °C. Chlorine atoms are excluded because they show a totally different selectivity. Methyl radicals are the intermediates in the Hundsdiecker, and yet there is no halogenation of substrate. This leaves acetoxy radicals as the probable intermediate, a conclusion which is supported by observing the same selectivity for both AcOBr and AcOCl.

A reasonable hypothesis is that two different types of acetoxy are produced, one, produced in the presence of halogens, which abstracts hydrogen atoms beyond the cage with low selectivity and the other, produced in halogen-scavenged systems, which undergoes decarboxylation too rapidly for noncage encounters. The latter type of behavior had been predicted for the $^2A_1$ σ state on the grounds that $^2A_1$ correlates with ground-state CO_2.[7] The acetoxy which accounts for hydrogen atom abstraction can be assigned the $^2B_2$ σ state or the $^2A_2$ π state;[7–9] neither of these correlates with ground-state CO_2, and thus it is possible for them to escape the cage and engage in relatively nondiscriminate hydrogen atom abstractions. For convenience, the notation π is given to the hydrogen atom abstracting species and σ to the other acetoxy ($^2A_1$). The σ state ($^2A_1$) would result from attack of $CH_3\cdot$ on CH_3CO_2X and the π state (hydrogen atom abstracting intermediate) from attack of halogen atom on CH_3CO_2X.

$$\begin{array}{ll}
\sigma & CH_3\cdot + CH_3CO_2X \rightarrow CH_3X + \sigma\text{-}CH_3CO_2\cdot \\
 & \sigma\text{-}CH_3CO_2\cdot \rightarrow CH_3\cdot + CO_2 \\
\hline\hline
\pi & X\cdot + CH_3CO_2X \rightarrow X_2 + \pi\text{-}CH_3CO_2\cdot \\
 & \pi\text{-}CH_3CO_2\cdot + RH \rightarrow CH_3CO_2H + R\cdot \\
 & R\cdot + X_2 \rightarrow RX + X\cdot
\end{array}$$

$$\begin{array}{l}
\pi\text{-}CH_3CO_2\cdot \rightarrow \sigma\text{-}CH_3CO_2\cdot \text{ and/or} \\
\qquad\qquad R\cdot + CH_3CO_2X \rightarrow RX + \sigma\text{-}CH_3CO_2\cdot
\end{array}$$

The calculations concerned with carboxylate radicals lead to no single conclusion about the ordering of the states;[7–9] they have been done at too simple a level. It is hoped that suitable calculations will become available in the future. We expect that experiments which are in progress will provide an experimental basis for energy sorting the acetoxy states.

Acknowledgment. Support of this research by the National Science Foundation under Grant CHE-7810049 is gratefully acknowledged.

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Chiral Aggregation Phenomena. 2. Evidence for Partial "Two-Dimensional Resolution" in a Chiral Monolayer

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We wish to report the results of a novel attempt to resolve a racemic monolayer film of a chiral surfactant spread on an aqueous subphase by seeding with crystals of one of the enantiomers. Although the investigation of monolayers at the gas-liquid interface is a well-studied and currently active field,[1] there have been relatively few reports of stereochemical phenomena in films cast from chiral surfactants.[2] In the course of comparing the surface properties of racemic *N*-α-methylbenzylstearamide with those of its two pure enantiomers,[3] we noted a considerably higher surface free energy for the racemic films on aqueous sulfuric acid subphases than for comparable films of the enantiomers. This was manifested both in terms of higher surface pressures at

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[‡] These results and experimental conditions are described more fully in the doctoral thesis of Orlean Thompson, Department of Chemistry, University of Pittsburgh, 1980.

(1) Several excellent texts which review this field are: (a) Gaines, G. L. "Insoluble Monolayers at Liquid-Gas Interfaces", Wiley: New York, 1966. (b) Adam, N. K. "The Physics and Chemistry of Surfaces", 3rd ed.; Oxford University Press: London, 1941. (c) Davies, J. T.; Rideal, E. K. "Interfacial Phenomena", 2nd ed.; Academic Press: New York, 1963. (d) Adamson, A. W. "Physical Chemistry of Surfaces", 3rd ed.; Wiley-Interscience: New York, 1976. (e) Cadenhead, D. A. In "Chemistry and Physics of Interfaces, II"; Ross, S., Ed.; American Chemical Society: Washington, D.C., 1971, p 28. (f) Gershfeld, N. L. *Annu. Rev. Phys. Chem.* **1976**, *27*, 349–368. This is an excellent recent review of the field, and subjects some commonly held assumptions to close scrutiny. (g) Goddard, E. D. *Adv. Chem. Ser.* **1975**, *No. 144*, 1.

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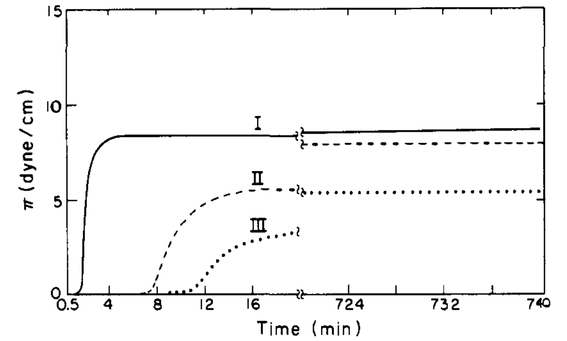

Figure 1. Equilibrium spreading pressures (ESP). Crystals of racemate (I,—), 1:1 *R*-(+)/*S*-(−) mixture (II, - - -), and(*S*)-(−)-stearamide (III, ···) on 10 N H_2SO_4 at 25 °C.

equivalent surface areas for films compressed on a Langmuir film balance and also by greater relative static surface tension lowering as measured by the du Noüy tensiometer. A larger driving force for expansion by the racemic film has been observed consistently in many experiments which we shall report in detail[4,14] elsewhere.

The lower surface pressure of the enantiomeric film suggests the possibility of resolving a compressed racemic film through seeding with pure enantiomeric crystals if the film is in a metastable condition analogous to a solution which is supersaturated with respect to the enantiomers.[5] One may also imagine the possibility of spontaneous two-dimensional resolution if, in fact, highly organized "crystalline" monolayers follow the behavior pattern seen occasionally for three-dimensional crystals. Such a case of spontaneous "unmixing" might be as uncommon for monolayers as it is for crystals. However, it offers a very simple (and previously unrecognized) alternative to the many kinds of prebiotic chiral environments[6] which have been proposed for the asymmetric synthesis of the first optically active biopolymers. If spontaneous resolution had occurred in some film patches of the "primordial oil slick",[6] the stage would have been set to provide stereoselectivity for a condensation reaction which would otherwise have resulted in racemic products.

Evidence that formation of a mixed racemic monolayer may be inhibited *kinetically* is shown in Figure 1 where equilibrium spreading pressures (ESP) were determined for films spread from three highly purified crystalline samples of *N*-α-methylbenzylstearamide. Curve I represents the rapid attainment of the ESP at about 8 dyn/cm when crystals of pure racemic amide are placed on the surface of a 10 N solution of highly purified aqueous sulfuric acid in the trough of an automated Langmuir film balance.[4,14] Film pressure was exerted against a floating Teflon barrier and registered with a torsion balance capable of reading to the nearest 0.005 dyn/cm. The surface area and temperature (25 °C) were maintained constant during the experiment.

Curve III was generated from a pure crystal of the *S*-(−) isomer, and an identical curve was generated from crystals of its antipode. Obviously, the enantiomers spread more slowly and gave a lower final film pressure than did the racemate. This is consistent with their behavior in Π-A isotherms and surface tension comparisons.[3] Intermolecular forces appear to be stronger in the enantiomeric crystals and compressed monolayers than in those of the racemate. Support for this claim is also found in the lower rates of solution and lower equilibrium solubilities of the enantiomers (0.3657 mg/mL) in hexane compared to the racemate (1.0084 mg/mL) and in the lower heat of fusion of the latter based on differential scanning calorimetry (DSC).

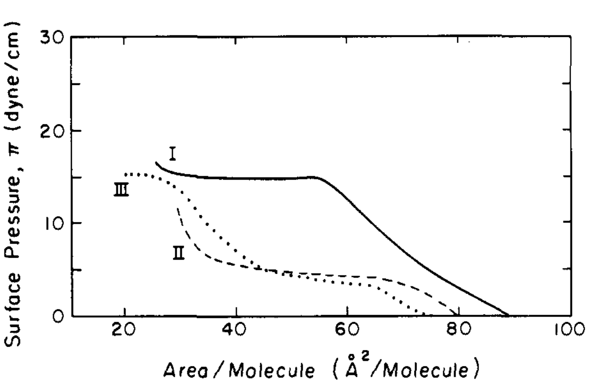

Figure 2. Force–area curves of stearamide films on 6 N H_2SO_4 at 25 °C. (I) Natural racemate; (II) enantiomeric stearamide; (III) mixture of solutions of enantiomers on the surface in 1:1 ratio.

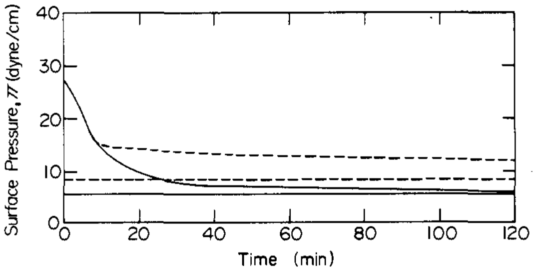

Figure 3. Seeding racemic steramide film after compression to 45 Å²/molecule on 10 N H_2SO_4 at 25 °C. (- - -) Seeding with racemic stearamide crystals; (—) seeding with *R*-(+) crystals. Horizontal lines represent ESP for racemic (- - -) and enantiomeric (—) stearamides.

Curve II of Figure 1 was generated from a mixture of fine crystals of the (*R*)-(+)- and (*S*)-(−)-stearamides. This mixture of enantiomeric crystals differs from those of the true racemate used to produce the film for curve I, which is a racemic compound as shown by X-ray powder diffraction diagrams[7] and DSC thermograms.[8] Thus, a racemic film produced by molecules escaping from equal quantities of small *R*-(+) and *S*-(−) crystals is relatively slow to reach the same surface energy as a racemic film spread from crystals of the pure racemate.

Similar differences in rates of mixing of antipodes to form a racemic film were also found in the absence of crystals—for films spread from dilute hexane solutions. Figure 2 compares the force–area curves for these films of the stearamide spread under identical conditions.[9] Curve I was determined for a film spread from a solution of the racemate. Curve II was determined with films cast from solutions of either enantiomer. The film for curve III was spread by spotting similar volumes of solutions of both enantiomers on the surface until the total surface concentration of amide was equal to that for the films of racemate or enantiomer referred to above.[10] The remarkable inhibition of mixing rate in initially compressed films is clear from comparison of curve III with curves I and II. Thus, the kinetic obstacles to the mixing of enantiomer molecules in the monolayer to produce a racemic film are demonstrated both for films spread from crystals and from solution. Since films of racemate and enantiomers were spread

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(7) We are indebted to Professor Richard Butera for guidance in the operation of the Diano X-ray diffractometer.

(8) DSC thermograms were obtained with a Perkin-Elmer DSC-1B instrument which was available to us through the generosity of Professor J. H. Magill in the Department of Metallurgical and Materials Engineering.

(9) The standard technique for spreading films from a highly purified hexane solution used a microsyringe to place droplets at about 50 spots on the aqueous surface at 25 ± 0.2°. The droplets were distributed as evenly as possible over the surface, and this spreading operation required 1–2 min. After the film stood 20 min to allow for solvent evaporation it was steadily compressed at a usual rate of 7.2 Å²/molecule/min with the motor-driven barrier of the film balance.

(10) In this experiment, two microsyringes were employed. First, 25 droplets of one enantiomer solution were placed as far apart as possible on the surface in about 30 s. Then, an equal volume of the solution of its anipode was spread in the same way.

at equal areas per molecule for each of these comparisons, the inherent cratic entropy difference of $R \ln 2^5$ between the racemic and enantiomeric forms should make a constant contribution to the differences in the final equilibrium states of the films.[11] How this factor affects rates of mixing in these experiments is not clear to us.

On the strength of the above experiments, the resolution of a racemic film was approached by seeding with pure crystals of either enantiomer. The racemic film was spread on 10 N H_2SO_4 from a dilute hexane solution. After the usual 20 min for solvent evaporation was allowed, the barrier drive was started, and the film was compressed to 28 dyn/cm. The dashed curve in Figure 3 shows the surface pressure decrease caused by seeding the compressed film with pure racemic crystals. After 1.5 h the surface pressure had decreased nearly to the ESP of the racemic film.

The experiment was now repeated by compressing a freshly spread racemic film, but this time crystals of pure *R*-(+) enantiomer were sprinkled on the surface. The solid curve of Figure 3 shows *the rapid decrease of surface pressure to a point well below the ESP of the racemic film* and approaching that of a pure enantiomeric film.

These results imply the deposition of *R*-(+) molecules on the added crystals, leaving a partially resolved film which was composed of predominantly *S*-(−) molecules. Equivalent results were obtained by seeding with *S*-(−) crystals which would leave predominantly an *R*-(+) film. We have already presented evidence above that the free energy of enantiomer crystals is lower compared to liquid or film states than are racemic crystals.

We have tried repeatedly to detect unseeded spontaneous resolution by leaving racemic films under compression for periods of 20 h, the present limit for maintaining reasonably constant conditions. In no case have we been able to detect a spontaneous decrease in surface pressure which could not be attributed to leaks or other artifacts.

Resolution of racemates from bulk solution by seeding with enantiomers is only possible in cases, such as the present one, where the racemic crystals are more soluble than those of the enantiomer.[5] Since this is not the usual case, out study of the present situation may have been fortuitous, or the balance of forces which govern resolution from monolayers is somewhat different from those that normally apply to bulk solution.[12] It is possible that accessibility to many metastable polymorphic states, as is common for long chain surfactants, would facilitate resolutions from monolayers under conditions less favorable to normal more compact molecules. These possibilities bear on the potential relevance of these experiments to spontaneous generation of prebiotic chiral environments.

In a control experiment where a compressed *R*-(+) film was seeded with *R*-(+) crystals, the final pressure approached the ESP for a film spread from *R*-(+) crystals, whereas seeding with *S*-(−) crystals gave a final pressure approaching the ESP of a racemic film. Seeding with stearic acid, a totally different but related surfactant, produced no change in surface pressure.

To the best of our knowledge, there is no precedent for these experiments and hence no way of judging the generality of the results. With relation to the "origin of life question", it must remain as inherently speculative but permissive evidence for one possible type of chiral environment.

Acknowledgment. This work was supported by NSF Grant CHE-7622369 and NIH Grant GM-20386. The invaluable contributions of Dr. Martin Stewart and Jean Chao for the preparation and purification of materials and of Dr. Barbara Kinzig for design of the film balance and for many helpful discussions are gratefully appreciated.

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[11] A referee has pointed out that the observed difference in equilibrium surface pressure between racemate and enantiomers at 70 Å^2/molecule is almost exactly the 4 dyn/cm attributable to this entropy factor.

[12] We are indebted to Professor Ernest Eliel for drawing this to our attention.

Octafluorocyclooctatetraene Transition-Metal Chemistry: 1,2-η and 1,2,3,6-η Complexes of Iron and Platinum

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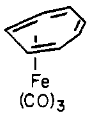
Cyclooctatetraene (COT)[1] has occupied a prominent place in the historical development of organometallic chemistry.[2] It is a versatile ligand which has exhibited a flexible hapticity in its modes of bonding to transition metals, lanthanides, and actinides.[1,2] Moreover, the elucidation of the nature of metallotropic rearrangements in COT complexes, particularly in Fe(COT)(CO)$_3$ (**1**), occupied the attention of many leading research groups for a number of years.[2] Fluorocarbon organometallics have often proved to be more stable thermally and to exhibit different bonding modes from their hydrocarbon analogues.[3] This communication reports examples of 1,2-η complexes of octafluorocyclooctatetraene (OFCOT, **2**)[4] with iron(0) and platinum(0). These undergo intramolecular oxidative addition reactions, with formation of a metal–carbon σ bond, to afford 1,2,3,6-η bonded complexes.



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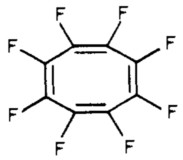

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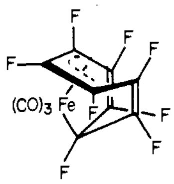

3

Reaction of OFCOT with excess $Fe_2(CO)_9$ in refluxing hexane afforded the pale yellow, sublimable complex **3** as air-stable crystals. The structure of **3** has been established (−30 °C) by single-crystal X-ray diffraction techniques to be that shown in Figure 1.[5]

The coordination geometry around Fe may be described either as (a) trigonal bipyramidal (if the allyl ligand is considered to

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[†] Alfred P. Sloan Research Fellow, 1980–1982.

[1] For a review of cyclooctatetraene and its derivatives, see: Fray, G. I.; Saxton, R. G. "The Chemistry of Cyclooctatetraene and its Derivatives"; Cambridge University Press: Cambridge, 1978.

[2] The organometallic chemistry of cyclooctatetraene is reviewed in ref 1 and in: Deganello, G. "Transition Metal Complexes of Cyclic Polyolefins"; Academic Press: New York, 1979.

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[5] Complex **3** (38%): mp 126–127.5 °C; ν_{CO}(benzene) 2105, 2060, $\nu_{C=C}$ 1745 cm^{-1}; ^{19}F NMR (1:1 $CDCl_3/C_6H_6$) (chemical shift in ppm upfield from internal $CFCl_3$; relative intensity) δ 113.0 (2 F), 127.9 (3 F), 161.9 (2 F), 170.4 (1 F). Crystals of **3** are orthorhombic, *Pnma*, $a = 10.432$ (2), $b = 13.262$ (2), $c = 8.599$ (2) Å; $Z = 4$. The structure was solved by heavy atom methods and refined by full-matrix least-squares procedures to final agreement factors $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.025$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_0|^2]^{1/2} = 0.031$, using 1598 reflections with $I \geq 2.0\sigma(I)$.[6] The molecule is located on the crystallographic mirror plane and thus has rigorous C_s symmetry, with the iron, one carbonyl, the ση carbon, and the central carbon of the η^3-allyl carbon, and the central carbon of the η^3-allyl group in the mirror plane. Selected bond lengths (Å): Fe–C1 = 2.078 (1), Fe–C2 = 2.071 (1), Fe–C5 = 2.059 (2), C1–C2 = 1.424 (1), C2–C3 = 1.475 (2), C3–C4 = 1.318 (2), C4–C5 = 1.487 (1). Selected bond angles (deg): C5–Fe–C9 = 177.5 (1), C1–Fe–C5 = 95.7 (1), C1–Fe–C9 = 86.4 (1), C10–Fe–C10′ = 98.4 (1), C10–Fe–C2 = 92.1 (1), C10–Fe–C1 = 130.8 (1), C10–Fe–C2′ = 163.9 (1).

[6] Experimental procedures are essentially as previously delineated: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* **1976**, *A32*, 381–386.