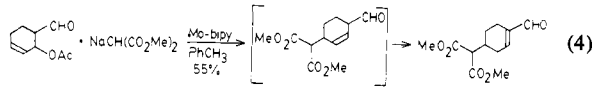
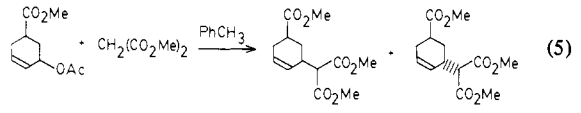
a new catalyst in DME, i.e., $Mo(DME)(CO)_4$.[14] DME, being a strong σ-donating ligand like bpy, shows a similar selectivity pattern. Use of *O,N*-bis(trimethylsilyl)acetamide as the base to generate the nucleophile in lieu of sodium hydride and a noteworthy improvement in the regioselectivity (cf. entry 7a,b in the table) from 85:15 (tertiary to primary) to 96:4. The source of this effect may derive from this base acting as a ligand toward molybdenum.

Chemo- and regioselectivity are highlighted in the successful alkylation of 3-acetoxy-4-carboxaldehydocyclohex-1-ene (eq 4)



(4)

in which the polar group directs the incoming nucleophile to the more distal carbon.[15] This example also illustrates the preference for alkylation over elimination. While the stereochemistry of the reaction could not be discerned in this case due to the migration of the double bond, it could be determined in the case of 3-acetoxy-5-carbomethoxycyclohex-1-ene (eq 5). The Mo(bpy)



(5)

base			
NaH	Mo(bpy)	85	15
NaH	Mo(c)	50	50
O TMS | $CH_3C{=}NTMs$	Mo(c)	>95	<5

catalyst gives predominantly the same product that derives from the corresponding palladium reaction when NaH is used as base. Strikingly, the Mo(c) catalyst produces a 1:1 ratio of the *E* and *Z* isomers under the above conditions but only the product of net retention when *O,N*-bis(trimethylsilyl)acetamide is used as base. While a double retention or a double inversion accounts for formation of the product of net retention, the latter appears most reasonable. Following the reaction by VPC as well as a control experiment reveals that the mixed stereochemistry does not result from isomerization of the starting acetate. While the source of this stereochemical result remains to be elucidated,[16] the ability to change the stereochemical course of the reaction by ligand variation should prove useful.

Allylic alkylation catalyzed by molybdenum forms a useful and frequently complementary alternative to the palladium-catalyzed reaction. For example, regioselectivity appears more sensitive to ligand variation in the case of Mo. Higher selectivity for attack at a primary vs. secondary carbon of a π-allyl fragment occurs with Mo. It also appears that more flexibility in stereocontrol may exist. On the other hand, these reactions require higher temperatures and longer times. More thorough evaluation of this Mo chemistry will be required to delineate its full potential.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs. We thank the NSERC of Canada for a graduate fellowship for M.L.

Registry No. 3, 1830-92-8; **4** (R = H), 74036-93-4; **4** (R = CH_3), 82352-40-7; **5**, 82352-41-8; (*E*)-**6**, 72444-93-0; (*Z*)-**6**, 60729-61-5; **7**, 60729-63-7; 6-formyl-2-cyclohexenyl acetate, 61088-60-6; 4-(dimethoxycarbonylmethyl)-1-cyclohexenecarboxaldehyde, 82352-42-9; methyl *cis*-α,5-dimethoxycarbonyl-3-cyclohex-1-eneacetate, 64841-68-5; methyl *trans*-α,5-dimethoxycarbonyl-3-cyclohex-1-eneacetate, 74545-66-7; 2-propenyl acetate, 591-87-7; 2-butenyl acetate, 628-08-0; 3-phenyl-2-propenyl acetate, 103-54-8; 2-methylenecyclohexyl acetate, 53723-50-5; 1-(cyclopentenyl)ethyl acetate, 74545-46-3; 3,7-dimethyl-2,6-octadienyl acetate, 16409-44-2; 1-ethenyl-1,5-dimethyl-4-hexenyl acetate, 115-95-7; methyl 1-(2-propenyl)-2-oxocyclopentanecarboxylate, 74036-93-4; methyl 1-(2-butenyl)-2-oxocyclopentanecarboxylate, 82352-40-7; methyl 1-(1-methyl-2-propenyl)-2-oxocyclopentanecarboxylate, 82352-41-8; methyl 1-(3-phenyl-2-propenyl)-2-oxocyclopentanecarboxylate, 82352-43-0; methyl 1-(1-phenyl-2-propenyl)-2-oxocyclopentanecarboxylate, 82352-44-1; methyl 1-(1-cyclohexenylmethyl)-2-oxocyclopentanecarboxylate, 82352-45-2; methyl 3-cyclopropenyl-2-methoxycarbonylbutanoate, 74545-48-5; methyl 2-(2-ethylidenecyclohexyl)-2-methoxycarbonylacetate, 82352-46-3; $NaCH(CO_2CH_3)_2$, 18424-76-5; Mo(bpy), 15668-64-1; Mo(c), 13939-06-5; Mo(pc), 15444-66-3.

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(16) Three rationales can account for this observation: (1) competing retention and inversion pathways in the oxidative addition; (2) competing retention and inversion pathways in the reductive elimination; (3) loss of stereochemistry in the intermediate π-allyl complex.

Structure of a Photodimer Determined by Natural-Abundance ^{13}C–^{13}C Coupling

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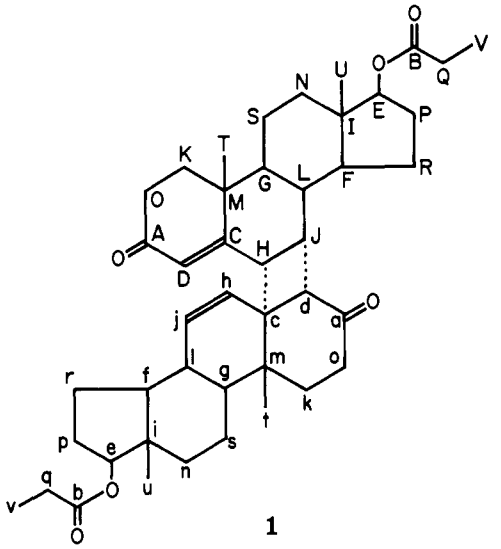
Photodimerization of $\Delta^{4,6}$-diene-3-keto steroids[1,2] has been shown to involve cyclobutane formation between the α,β double bond of one monomer unit and the γ,δ double bond of the second, giving a single product in essentially quantitative conversion. Unfortunately it has not proved possible to make a clear-cut distinction between the head-to-tail (formula **1**) and the opposite



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head-to-head structures. A theoretical treatment of this problem[3] concluded that the head-to-tail isomer should be preferred because of the calculated dipolar character of the reactive excited state. Over the years, a variety of attempts has failed to distinguish these two possibilities.[4-8] These methods include attempts to bridge across the two halves in 17-hydroxy derivatives,[4] measurements of dipole moments,[5] conventional NMR spectroscopy, attempts at dimerization in the solid state so that topochemical considerations of monomer crystal packing could be applied,[6] and x-ray

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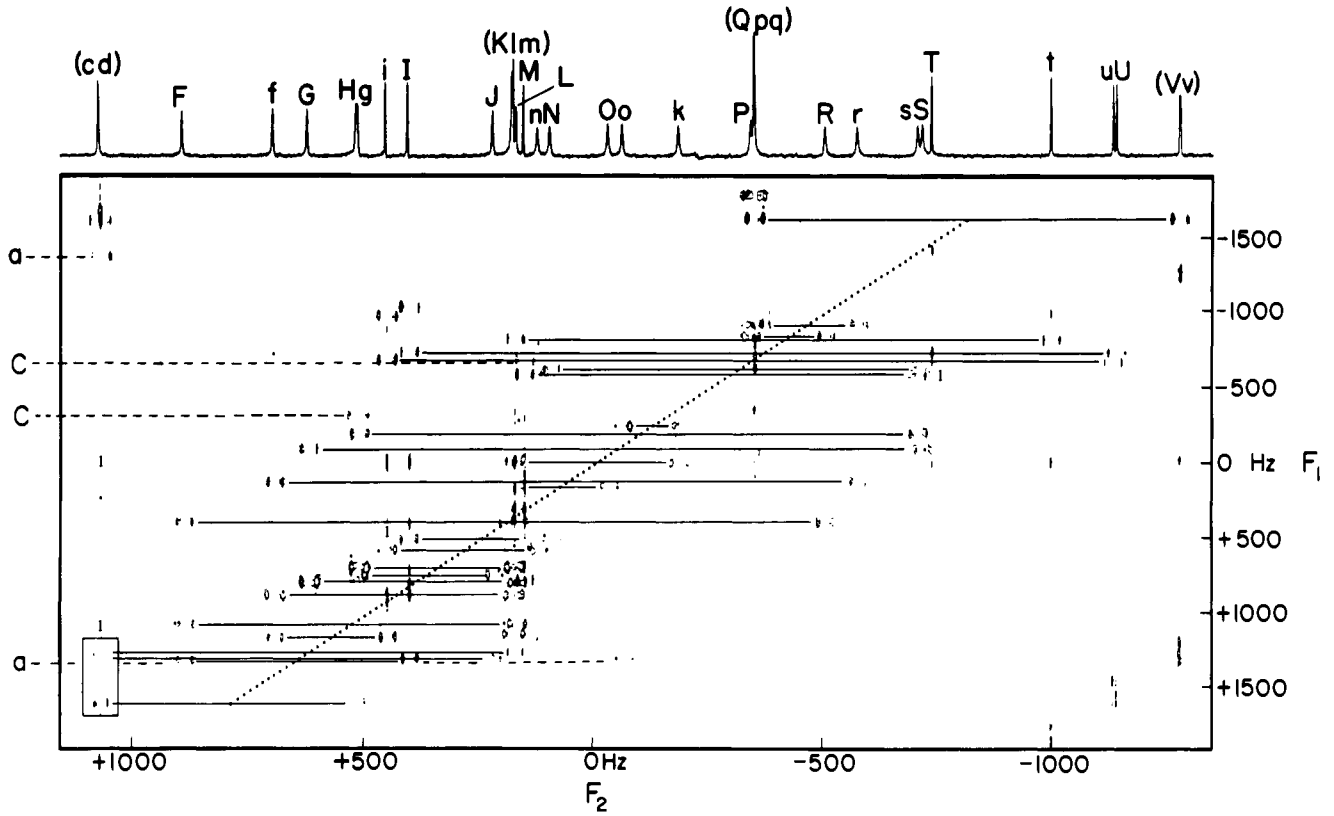

Figure 1. Two-dimensional intensity contour map used to determine the connectivity of the photodimer by observation of direct ^{13}C–^{13}C couplings. The conventional proton-decoupled ^{13}C spectrum runs along the top of the diagram. Coupled pairs of ^{13}C sites generate four-line AB or AX subspectra (joined by the horizontal bars). A few sites are coupled to low-field resonances (a and C, for example) outside the frequency range of this chart. The small rectangular region at the bottom left is enlarged and reproduced in Figure 2.

studies of a dibromo diester.[7] A recent x-ray diffraction study of the dimer of cholesta-4,6-diene-3-one was thwarted by the fact that the unit cell contained two molecules of the dimer.[8]

We now report the successful resolution of this problem by determining the connectivity of the carbon framework directly by double-quantum NMR.[9] The problem is to determine whether the structure illustrated by the dotted lines in formula **1** (head-to-tail) or the opposite head-to-head arrangement with c bound to J and d bound to H. Provided that the ^{13}C NMR spectrum is properly assigned, direct observation of natural abundance ^{13}C–^{13}C coupling should decide this issue unequivocally.

The proton-decoupled ^{13}C spectrum of the dimer (0.84 g in 2 mL of $CDCl_3$) consists of a crowded high-field region (top of Figure 1) and a few well-resolved resonances at low field. The first step is to determine the number of protons directly attached to each carbon site by recording the two-dimensional J spectrum.[10] This complements the information obtained from the double-quantum spectrum. A clean spectrum of the ^{13}C satellites is obtained by suppressing the strong signals from isolated ^{13}C spins, exploiting the special phase properties of double-quantum coherence.[11-13] The double-quantum coherence is allowed to precess during the variable evolution period of a two-dimensional Fourier transform experiment[14,15] and its frequency determined indirectly. This provides a direct identification of the two ^{13}C resonances coupled by $^1J_{CC}$ since the double-quantum frequency is equal to the sum of the two chemical shifts.[16,17]

Figure 1 shows a contour map of the resulting two-dimensional ^{13}C spectrum, obtained after 15 h of data accumulation on a Varian XL-200 spectrometer. Because of data storage limitations, only the crowded high-field region has been recorded. The spectrum is a superposition of several AB or AX subspectra from directly bound ^{13}C nuclei, each subspectrum having an F_1 coordinate determined by the appropriate ^{13}C shifts, and its midpoint on the dotted diagonal.[17] Subspectra involving a low-field resonance have been aliased in the F_1 dimension and only the high-field part is detected, although the other chemical shift value can be calculated from the double-quantum frequency.

These results give the assignment, allowing the carbon sites of formula **1** to be labeled A–V (upper monomer unit) in order of increasing shielding. Corresponding sites in the lower unit are labeled a–v. The four-membered ring HJcd is the critical part of the structure. Unfortunately the key resonances from sites c and d are degenerate in frequency. Resonance a is readily identified as the only carbonyl coupled to a triplet (o) and either a doublet (d) or a singlet (c). Resonance C must be the quaternary sp^2 carbon since it is directly connected to a triplet (H) and a singlet (M). Resonance H is connected to J and either c or d. This ambiguity is the stumbling block to a straightforward solution of problem.

Fortunately there is a simple modification of the experiment that allows us to circumvent the difficulty. Sites c and d may be distinguished on the grounds that c is a quaternary carbon whereas d is a methine. The entire two-dimensional experiment was repeated in a mode that suppressed all protonated carbon resonances, leaving only quaternary resonances. A delay $(2J_{CH})^{-1}$ was introduced between the last radiofrequency pulse and the start

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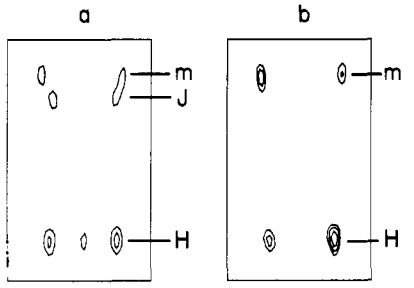

Figure 2. A small region of the intensity contour map of Figure 1 showing the doublets from sites c and d which are coupled to sites m, J, and H at higher fields. The frequencies of the resonances from sites c and d are degenerate, so the connectivity pattern remains ambiguous in spectrum a. However in spectrum b resonances from proton-bearing sites have been suppressed, leaving only the quaternary site c, establishing its connectivity to m and H but not J.

of data acquisition, during which the proton decoupler was switched off, allowing ^{13}C magnetization vectors from all proton-bearing sites to precess into antiparallel alignments, giving zero net signal when the proton decoupler is switched on again.[18,19]

The small region of the contour map corresponding to the chemical shifts of site c and d is enlarged in Figure 2. In the regular spectrum (a) ambiguity remains, but the spectrum (b) from quaternary sites shows that c is coupled to H but not to J. Hence the head-to-tail structure is confirmed.

With the details of the connectivity known, a tentative assignment of the stereochemistry can be proposed.[20] The question of why a single dimer is formed in a photochemically reversible reaction occurring in homogeneous solution remains unanswered.[21]

Registry No. 1, 82902-61-2.

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Formation and Enhanced Stability of Fluoroalkyl Bilayer Membranes

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Contribution No. 665
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It has been established that the bilayer membrane is formed from totally synthetic amphiphiles.[1] These amphiphiles are composed of cationic, anionic, nonionic, or zwitterionic head groups and of double-chain alkyl groups[2] or single-chain units with rigid segments[3] as hydrophobic moieties. Thus, the bilayer formation can be considered as a general physicochemical phenomenon observed for a large variety of amphiphiles, although these bilayer-forming compounds have been limited to hydrocarbon amphiphiles. Fluorocarbon amphiphiles are known to show surfactant behavior quite different from that of the corresponding hydrocarbon amphiphiles such as low surface tension,[4] limited miscibility with hydrocarbon micelles,[5] and formation of giant micelles.[6,7]

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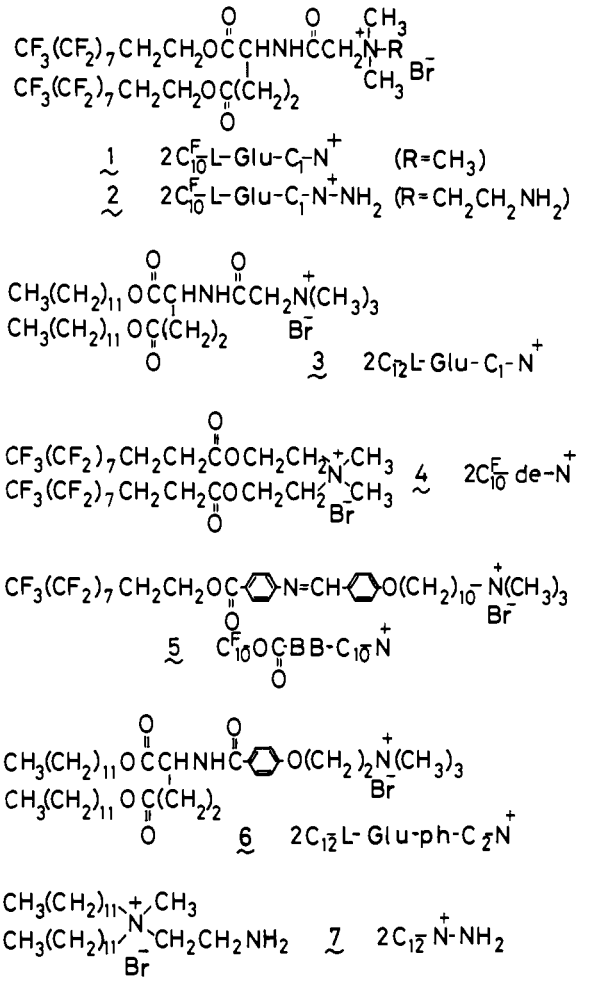
Chart I



Therefore, if bilayer membranes of fluorocarbon amphiphiles are prepared, they would show interesting characteristics that combine organized assemblage of the bilayer membrane and peculiar physicochemical properties of fluorocarbon compounds. We describe in this communication the first examples of fluoroalkyl bilayer membranes.[8]

More than 20 fluoroalkyl amphiphiles have been newly synthesized in these laboratories.[9] Their aggregation characteristics in water are in general similar to those of the hydrocarbon counterparts. For example, a well-sonicated aqueous solution of $2C_{10}^{F}$-L-Glu-C_1-N^+ (**1**, Chart I) gives single- and double-walled vesicles with diameter of 500–2000 Å (Figure 1),[10] and a solution of the hydrocarbon counterpart, $2C_{12}$-L-Glu-C_1-N^+ (**3**) contains small, multiwalled bilayer vesicles. Amphiphile **4** gave multiwalled vesicles. We showed previously that amphiphiles derived from

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(8) Similar attempts are being done at the University of Mainz, Germany: Ringsdorf, H., personal communication.
(9) The fluoroalkyl amphiphiles were synthesized from *1H,1H,2H,2H*-perfluorodecanol or *2H,2H,3H,3H*-perfluoroundecanoic acid (Ugine Kuhlmann) by the procedures used for preparation of the corresponding hydrocarbon amphiphiles, and the final products were identified by thin-layer chromatography, NMR spectroscopy, and elemental analysis; Okahata, Y.; Yasunami, S., unpublished results from these laboratories.
(10) The formation of the vesicle structure was confirmed by trapping experiments which had been used for hydrocarbon vesicles.[11] For this purpose, aqueous dispersions of **1** were prepared in the presence of water-soluble amines (D-glucosamine and ethanolamine) and separated from untrapped amines by gel chromatography (Sephadex G-50). Trapped amines were detected by reaction with excess fluorescamine. Trapping of fluorescent riboflavin was also ascertained.
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