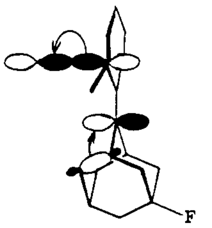
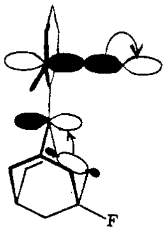
of the epimeric alcohols **5** via cation **7** were measured separately but under identical conditions by means of ^1H NMR; the rate of growth of the vinyl proton signal of **9** was monitored, with the proton signal of added methylene chloride as the standard. The contrast between the two is easily visible in Figure 1; the *E* alcohol forms the olefins 43 times faster than the *Z* isomer does. Thus, the face selection observed in the reactions of **2** has been reversed by an overall factor of roughly 10^4.

It should be noted that (*E*)- and (*Z*)-**5** would be enantiomers but for the presence of the 5-fluoro substituent. That is to say, the rates would be identical in the unsubstituted alcohols; hence, the observed rate ratio must be attributed to the fluorine atom. We can conceive of no explanation for this reversal other than that based on the change in symmetry of the orbital being vacated, when the ionization processes of isomers **2** are compared with those of isomers **5**. In both cases, the mechanism of the directive effect is the induction by the fluorine atom, which differentiates the vicinal carbon–carbon bonds flanking C_2. The possibility that our observation is related to the stability or basicity of the initial alcohols seems remote, as we have to date not encountered any instance in which 5-fluoro substitution led to substantial deviations from 50/50 *equilibrium* populations of epimers. Thus, when a 50/50 mixture of (*E*)- and (*Z*)-5-fluoroadamantan-2-ols is treated with various amounts of Eu(fod)$_3$, the NMR signals undergo virtually identical shifts, so that such an explanation is ruled out as the basis of the rate ratio for (*E*)- and (*Z*)-**2**.



E-5



Z-5

If our present interpretation is correct, it will be of interest to study whether similar reversals of stereochemistry are characteristic of the vinylogs of the host of solvolysis substrates in which σ,[10] σ–π,[11] and π[12] assistance have been claimed. Similarly, the question arises whether and to what extent the capture of nucleophiles by carbonyl compounds,[6] the attack of electrophiles on olefins,[13] and pericyclic reactions[14,15] will reverse stereochemistry when vinylogs are considered. Examples may already be in the literature; we regard Smith's observation of anti cuprate methylation to 5-methoxy-2-cyclopentenone as one possibility.[16]

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Supplementary Material Available: Details of the preparation of compounds **3–6** and **9** and listings of their ^{13}C NMR signals and the shift reagent results of (*E*)-**6** (7 pages). Ordering information is given on any current masthead page.

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Synthesis of Benzene from Methane over a Ni(111) Catalyst

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We report the synthesis of C_6H_6 from CH_4 over a Ni(111) catalyst under ultrahigh vacuum (UHV) conditions. The gas phase hydrocarbon selectivity of this synthesis for benzene production is 100%. This is the first observation of a reaction of CH_4 to form a gas-phase, higher hydrocarbon over a metallic catalyst at the low pressures ($<10^{-4}$ Torr) commensurate with a UHV environment. Since CH_4 is normally unreactive under these conditions, this synthesis is effected by molecular beam techniques to activate CH_4 via a new mechanism: collision-induced dissociative chemisorption.[1,2] A monolayer of CH_4 physisorbed on Ni(111) at 47 K is exposed to a beam of Kr atoms. The collision of the incident Kr with the physisorbed CH_4 distorts the CH_4 from its tetrahedral configuration, thereby lowering the barrier to dissociation into an adsorbed methyl radical and an adsorbed hydrogen atom. As the surface temperature is raised to 230 K, all the adsorbed CH_3 dissociates to CH and the CH recombines to form adsorbed C_2H_2[3] via a mechanism established and discussed elsewhere.[4] Some of the C_2H_2 trimerizes to adsorbed C_6H_6,[5,6] and at 410 K and 425 K, respectively, the atomically adsorbed hydrogen desorbs as H_2 and some of the chemisorbed C_6H_6 desorbs. The progress of this reaction is monitored, and the adsorbed intermediates are identified by high-resolution electron energy loss spectroscopy. The gas-phase products are detected mass spectrometrically in a thermal desorption experiment.

The key to benzene formation is the attainment of a sufficiently high C_2H_2 coverage to allow C_2H_2 to trimerize without having to diffuse over a large area. In separate studies using C_2H_2 as the initial reactant,[6] C_2H_2 below 0.1 monolayer (ML) dehydrogenates at 440 K without undergoing the trimerization to and desorption as C_6H_6 which takes place at temperatures as low as 300 K for a C_2H_2 saturation coverage of 0.25 ML. Therefore, to effect trimerization at the lower surface temperatures where there is no C_2H_2 dehydrogenation, the C_2H_2 coverage must be high. The difficulty with the attainment of high C_2H_2 coverage is that the three adsorbed hydrogen atoms produced from the dissociative chemisorption of each CH_4 molecule block sites for the dissociation of additional CH_4. The hydrogen must be removed by maintaining the surface at a sufficiently high temperature to desorb it. Unfortunately, temperatures above 395 K also result in partial dehydrogenation of the C_6H_6 product to C_6H_5 or C_6H_4.[6] The following procedure, carried out in an apparatus described previously,[1c,2] is designed to achieve a high C_2H_2 coverage by providing sites for CH_4 dissociation while minimizing the dehydrogenation of the C_6H_6 product.

The Ni(111) crystal is maintained at 47 K in an ambient atmosphere of 3.5×10^{-6} Torr of CH_4. Under these conditions,

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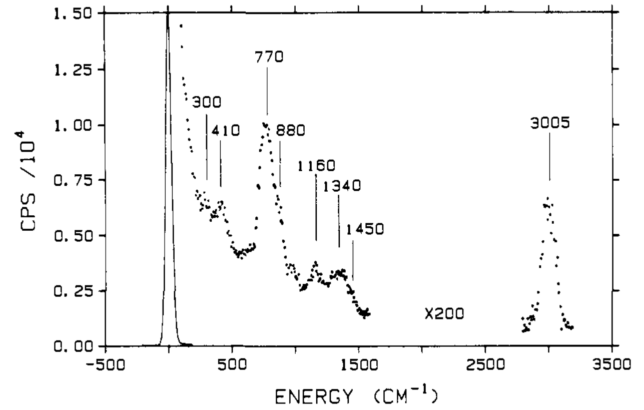

Figure 1. High-resolution electron energy loss spectrum of adsorbed layer after procedure described in text. The spectrum was measured 8° away from the specular angle at an incident electron energy of 3.5 V with $\Delta E = 50$ cm^{-1} and at a surface temperature of 40 K. The features marked are assigned to modes of C_6H_6: 3005 cm^{-1} to ν_1, ν_5, ν_{12}, and ν_{15}; 1450 cm^{-1} to ν_{13}; 1340 cm^{-1} to ν_9; 1160 cm^{-1} to ν_{10} and ν_{17}; 880 cm^{-1} to ν_2, 770 cm^{-1} to ν_4; 410 cm^{-1} to ν_{20}; 300 cm^{-1} to the Ni-C_6H_6 mode.

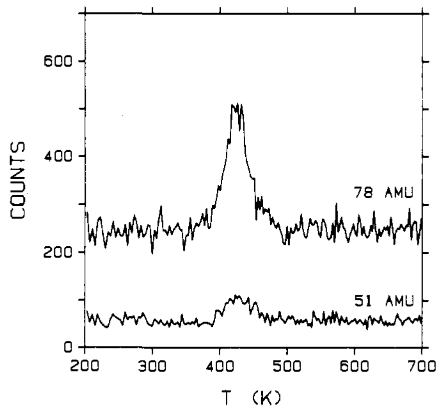

Figure 2. Thermal desorption spectrum from adsorbed layer prepared as described in text. The relative partial pressures at masses 78 and 51 are plotted as a function of crystal temperature. Mass 51 is a fragment ion from the cracking of C_6H_6 after electron-impact ionization. Benzene desorbs at 425 K for a heating rate of 17 K s^{-1}.

a saturated layer of physisorbed CH_4 (0.33 CH_4/Ni) is maintained.[1,2] A monoenergetic Kr beam with a translational energy of 88 kcal/mol, produced by the high-pressure expansion of a 0.3% mixture of Kr in He from a nozzle at 898 K, impinges on the CH_4-covered surface at normal incidence for 45 s. At this energy, the Kr flux is 5×10^{14} cm^{-2} s^{-1} and the cross section for CH_4 dissociation by collision with Kr is 1.9 Å^2 in the limit of zero chemisorbed carbon coverage. After the ambient CH_4 is pumped away, the crystal is heated to and held at 395 K for 30 s, which results in the thermal desorption of all the unreacted CH_4, the recombinative desorption of H_2, and formation of C_2H_2. The C_2H_2 coverage is increased to 0.25 ML by repeating this procedure 12 times. As the C_2H_2 coverage nears 0.25 ML, adsorbed benzene forms and partially desorbs during the annealing to 395 K. Figure 1 shows a vibrational spectrum, measured at 40 K, of the adsorbed layer after this sequence. The majority of the loss features are assigned to the vibrational modes of molecular C_6H_6, as indicated in the figure caption. This spectrum is very similar to one measured after adsorption of 0.14 ML of C_6H_6 on Ni(111) and annealing to 395 K[6] and to one measured in a previous study of the reactions of C_2H_2 on Ni(111).[5] The features that are not attributable to C_6H_6, 1250 cm^{-1}, 970 cm^{-1}, and 650 cm^{-1}, are assigned to modes of C_4 species, C_8 species, or partially dehydrogenated benzene. The crystal, with the adsorbed layer so prepared, is now heated at 17 K s^{-1} while the ambient pressure of masses 78 and 51 is monitored with the mass spectrometer. The resulting thermal desorption spectra are shown in Figure 2. The fragmentation pattern observed for the reaction product is that of benzene. No desorption of other hydrocarbons is detected. The desorption yield of 0.2 ± 0.04%, which is calculated from the thermal desorption spectrum, is a lower limit because as much as 85% of the C_6H_6 formed has already desorbed during the multiple annealings to 395 K. The upper limit for the desorption yield is estimated as 1.5%. The remaining adsorbed benzene and hydrocarbon fragments dehydrogenate as the temperature is increased above 425 K via a mechanism described elsewhere[6] and ultimately dissolve as carbon into the bulk of Ni. These data show conclusively that C_6H_6 is produced from CH_4 on a Ni(111) surface and desorbs at 425 K. These data also provide mechanistic information useful to the possible extrapolation of this synthesis from molecular beam-UHV environments to more practical conditions.

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Registry No. C_6H_6, 71-43-2; CH_4, 74-82-8; Ni, 7440-02-0.

Telluroaldehydes and Telluroketones

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Studies on the chemistry of organic molecules containing the tellurocarbonyl group have been rather scarce because of the lability of the carbon-tellurium double bond.[1] Telluroesters and -amides, stabilized by resonance delocalization of oxygen and nitrogen lone-pair electrons onto tellurium, and stable tellurocarbonyl compounds coordinated to the transition metals have been reported since 1979,[2-5] whereas generation of "free" telluroaldehydes and -ketones[6] has not been known hitherto and therefore remains a challenge for synthesis. Recently we have described simple and convenient methods for selenoaldehyde[7] and selenoketone[8] generations, in which bis(trimethylsilyl) selenide

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