87462-49-5; **9**-DME·C_6H_6, 87462-52-0; **10**·DME, 87462-54-2; **11**, 87462-55-3; **12**, 87462-56-4; **13**, 87462-57-5; **14**, 87462-58-6.

Supplementary Material Available: Six tables of preparative, analytical, ^1H, ^{13}C, and ^{31}P NMR, and ESR data plus tables of final fractional atomic coordinates, thermal parameters, bond distances, angles, and observed and calculated structure factors for **2**, **7**, and **9**, (151 pages). Ordering information is given on any current masthead page.

Regiospecific Trapping of Radicals from Cyclization Reactions. Cyclic Nitriles via Isocyanide Trapping

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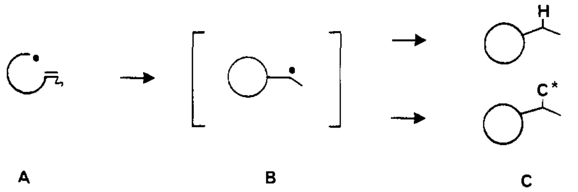
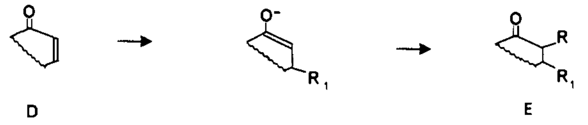
Received July 22, 1983

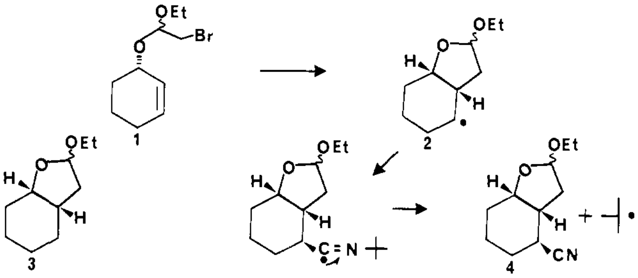
We report here the successful regiospecific intermolecular trapping of a radical arising from a cyclization reaction with a functional carbon species C*.[1] The general process is illustrated by A → C.



Such a process might do for free radical reactions what has proved so valuable in carbanion chemistry, namely, the net addition of two unrelated substituents to adjacent positions of a carbon–carbon double bond. The latter process, D → E, which requires an electron-deficient double bond (e.g., an α,β-unsaturated ketone), has become an important method for the control of regiochemistry in the years since various domains of its usefulness were first demonstrated.[2]



A particularly attractive reagent for the B → C transformation could be *tert*-butyl isocyanide, which should lead to the transfer of the chemically versatile cyano group with the ejection of a presumably innocuous *tert*-butyl radical (cf. **1** → **4**).



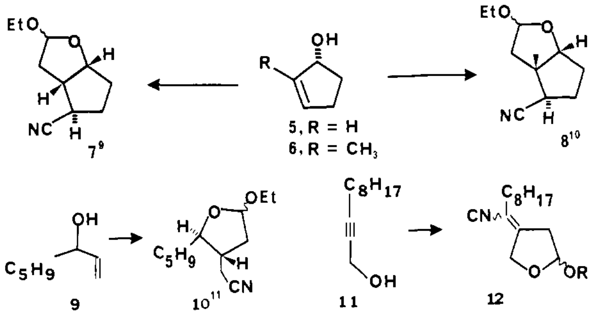
Preliminary experiments showed that addition of *tert*-butyl isocyanide to the tributyltin hydride medium previously used for the cyclization of **1** to **3**[3] simply gave the usual bicyclic acetal **3** but no trapping. This result did show, however, that bromine abstraction from **1** by tin radicals is considerably faster than the rate of their known[4] addition to isocyanides.

Trapping of the intermediate radical **2** by isocyanide might be effective with a tin radical precursor (e.g., hexaphenylditin) having no tin–hydrogen bonds. In that situation, the rate of the reaction of radical **2** with excess isocyanide[5] might well be higher than the rate of hydrogen transfer to **2** from various species in the reaction medium.[6]

We now describe the successful implementation of this scheme. Cyclizations were conducted by photolyzing a 0.05–0.1 M solution of bromo acetal[3] and 1 mol equiv of hexaphenylditin in benzene containing 20 equiv of *tert*-butyl isocyanide. The yields of the desired nitriles were ca. 60%.

In a typical experiment, a mixture of 39 mg of *1*, 110 mg of hexaphenylditin, and 260 mg of *tert*-butyl isocyanide in 2 mL of degassed benzene was stirred under argon (warming to ~50 °C to dissolve the tin compound). Irradiation with a 450-W medium-pressure Hanovia lamp was conducted for ~8 h.[7] Removal of benzene, separation of most of the hexaphenylditin after addition of ether, and chromatography (silica gel; 10% ethyl acetate–petroleum ether) gave the cyano bicyclic ether **4** in ~58% yield.[8]

Some of the two-step transformations of unsaturated alcohols that were carried out in the same manner are illustrated below (in all cases the first step is mixed bromo acetal formation).



We note that trapping is successful with a variety of radical

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(1) We have previously demonstrated regiospecific *intramolecular* trapping of a radical from the cyclization of bromo acetals: Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3720. Somewhat related to the present work is the external transfer of an allyl group in a radical cyclization reaction: Pereyre, M. *J. Organomet. Chem.* **1975**, *96*, 225. For an excellent review of radical cyclizations by intramolecular addition, see: Surzur, J. M. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982; Vol. 2.

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(7) The reaction was conducted in a quartz flask (photolysis was also effective but slower in Pyrex). The water–cooled lamp kept the solution at ~40 °C. A film, presumably a polymer of diphenyltin, slowly deposited on the walls, drastically reducing the irradiation efficiency. The reaction could be brought to completion by periodic solvent addition, which made available new, UV-transparent surfaces.

(8) The structures of the trapped nitriles are based (a) on the structures of their precursors, (b) on their NMR spectra, and (c) on the presence of the cyano absorption at 2240 ± 10 cm^{-1} (2225 cm^{-1} for **12**). Isomer ratios could be determined from the ^1H and ^{13}C NMR spectra and capillary GC of the corresponding lactones (Jones oxidation). The ^{13}C spectrum of the cyanolactone from **4** showed that the cyano substituent was, introduced with greater than 8:1 selectivity (>20:1 by capillary GC), presumably β as shown.

(9) In 62% yield. Corresponding lactone (one isomer by capillary GC) NMR δ ($CDCl_3$) 2.42 (1 H, dd, $J = 2.5, 18.5$ Hz) and 2.93 (1 H, dd, $J = 10, 18.5$ Hz, $CH_2C(=O)$); IR 1760, 2230 cm^{-1}.

(10) In 65% yield, as a mixture (6:1) of **8** with its cyano epimer. The ratio of the two isomers follows from NMR integration of the angular methyl peaks in the derived lactones: δ (C_6D_6) major 0.69, minor 0.55. The structures of the isomers were proved by correlation with authentic lactonic nitriles made from the corresponding known lactonic acids (Akhrem, A. A.; Titov, Y. A. "Total Steroid Synthesis"; Plenum Press: New York, 1970; p 305).

(11) In 61% yield. The corresponding lactone was, as expected, very largely one isomer (cf. ref 3) as judged by capillary GC and from the clean pair of doublets of doublets at δ (C_6D_6) 1.53 ($J = 8, 17.5$ Hz), 1.96 ($J = 8.5, 17.5$ Hz) for the α methylene hydrogens.

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types; primary (**10**), secondary (**4**, **7**, **8**), and vinylic (**12**), and that the stereochemistry of the cyano center is determined by the relative ease of access to the cyclized radical.

Even at this early stage it seems clear that the process of radical cyclization–trapping will prove synthetically valuable.

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

Registry No. 1, 85710-98-1; **4** (isomer 1), 87453-49-4; **4** (isomer 2), 87453-62-1; **4** (cyanolactone), 87453-59-6; **5**, 3212-60-0; **5** (bromoacetal), 87453-50-7; **6**, 3718-58-9; **6** (bromoacetal), 87453-51-8; **7**, 87453-52-9; **7** (cyanolactone), 87453-60-9; **8**, 87453-53-0; **9**, 87453-54-1; **9** (bromoacetal), 87453-55-2; **10**, 87453-56-3; **10** (cyanolactone), 87453-61-0; **11**, 34683-71-1; **11** (bromoacetal), 87453-57-4; **12**, 87453-58-5; *tert*-butyl isocyanide, 7188-38-7; hexaphenylditin, 1064-10-4; bromoacetaldehyde, 17157-48-1.

Catalytic Chemistry of Palladium Surfaces under Ultrahigh Vacuum Conditions

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Received July 25, 1983

Reaction steps that may ensue after the chemisorption of a hydrocarbon on a transition-metal surface are thermodynamically a sensitive function of temperature and pressure. Low temperatures and high H_2 pressures, for example, favor C–H bond formation. The unusual conditions employed for some surface science studies, i.e., ultralow pressure and surface coverages of a monolayer or less, are not optimal for hydrogenation (C–H bond formation), addition, and oligomerization reactions. These involve bimolecular reaction steps, which are not favored by low surface coverages (particularly if mobility of surface species is low). Also, the probability of hydrogenation is low because the thermodynamic activity of chemisorbed hydrogen atoms is low at pressures of 10^{-10}–10^{-11} torr. Hence, the typical ultrahigh vacuum–low temperature reaction course for chemisorbed hydrocarbons is dehydrogenation[1-8] although there are well-established exceptions such as the hydrogenation of acetylene chemisorbed on Pt(111) to form Pt(111)–CCH_3.[9-11]

Recently, we have found[12,13] that palladium surfaces under ultrahigh vacuum conditions exhibit a chemistry demonstrably different from those of nickel and platinum. Specifically, acetylene trimerizes to form benzene on the low Miller index planes of palladium.[13,14] Other reactions compete with the trimerization but benzene formation is the major reaction at least on the Pd(111) surface at near saturation coverages provided that acetylene is initially adsorbed at low temperatures, <-100 °C (with these conditions, the conversion was $\sim$25%, whereas benzene formation was a minor reaction at 25 °C). The presence of sulfur on the surface substantially increased the conversion to benzene. Benzene formation in these reactions is presumably acetylene trimerization, a reaction not commonly observed for metallic catalysts but is common[15] to metal coordination catalysts. Interestingly, toluene could be generated as the major product by heating a mixture of propyne and acetylene chemisorbed on Pd(111): the ratio of toluene to benzene was 3:1 from a Pd(111)–propyne–acetylene state formed by chemisorbing (at -120 °C) propyne first. We have also detected significant benzene formation on heating Pd(111)–propyne (Figure 1, supplementary material) and Pd(111)–trimethylsilylacetylene although these reactions are complex and the benzene yields are 10% or less. Use of ^{13}C-labeled propyne molecules may reveal the genesis of benzene in this complex reaction.

Pyridine was formed from acetylene and hydrogen cyanide on Pd(111) in yields of approximately 10%. The acetylene and the hydrogen cyanide were coadsorbed at -110 °C, and then the crystal was heated. Pyridine desorbed at $\sim$100 °C, the characteristic desorption temperature for Pd(111)–NC_5H_5. Attempts to hydrogenate pyridine on this surface were unsuccessful.

On Pd(111) or Pd(100), we have demonstrated the following hydrogenation reactions: acetylene to ethylene (50%), ethylene to ethane (25%), benzene to cyclohexane (5%), and norbornadiene to norbornane (5–10%) as well as olefin formation from propyne, 2-butyne, and 2-pentyne. The typical experimental protocol comprised (i) adsorption of hydrogen (or deuterium) and then adsorption of the hydrocarbon at -130 °C and (ii) the thermal desorption experiment with a heating rate of $\sim$25 °C s^{-1}. Appearance of the hydrogenated product was at $\sim$0 °C (C_2D_4 from $C_2D_2 + D_2$ on Pd(111)), 25 °C (C_2D_6 from $D_2 + C_2D_4$ on Pd(100)), 25 °C (c-C_6D_{12} on Pd(110)), and 10 °C (norbornane on Pd(111)). These temperatures for the appearance of the alkanes are very similar and in the case of ethane and cyclohexane substantially exceed the characteristic desorption temperatures of these alkanes on Pd(111). Hence the onset of rapid hydrogenation in these UHV systems is about at 0–25 °C for these palladium surfaces. In the $C_2H_2 + D_2$ reaction, the major product was $C_2H_2D_2$ (Figures 2 and 3, supplementary material).

Hydrogenation of acetonitrile to ethylamine was also demonstrated. Cochemisorption of D_2 and CD_3CN at 25 °C (Pd(100)) followed by the thermal desorption experiment gave $\sim$5% conversion of CD_3CN to $C_2D_5ND_2$ which desorbed at $\sim$80 °C (Figure 4, supplementary material).

Hydrosilation reactions with acetylene were effected on Pd(111) with conversions of 10–20%. In these experiments, the adsorption was effected at -110 °C with either $(CH_3)_3SiH$ (Figure 5, supplementary material) or $(CH_3)_2SiHCl$ as the silane reagent. Critical to the high conversions (for UHV conditions) was adsorption of the acetylene before the silane (reverse order of addition with respect to hydrogenation reactions). The vinylsilane products, $(CH_3)_3SiCH{=}CH_2$ and $(CH_3)_2SiCl(CH{=}CH_2)$ desorbed from Pd(111) at $\sim$50 °C. Conversions in these reactions were increased by a factor of $\sim$5 using a Pd(111)–P surface ($\sim$0.5 monolayer).

The contrast between palladium and its two congeners in UHV catalytic chemistry is sharp. Hydrogenation of benzene could not be demonstrated on Ni(111) under conditions identical with the above-described palladium chemistry, and hydrogenation of acetylene gave only trace conversions to ethylene. Analogous negative results were observed relative to acetylene conversion to benzene and hydrogenation of acetonitrile to ethylamine. The Pt(111) chemistry was identical with that of Ni(111) with only

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