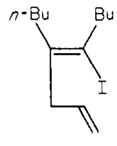
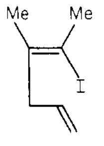
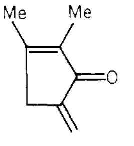


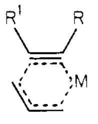
4b



4c



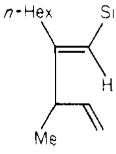
3b



7

attention to bimetallic systems and have found that treatment of 5-decyne with diallylzinc and I_2ZrCp_2,[1] generated in situ from Cl_2ZrCp_2 and NaI, smoothly provides, after iodinolysis, **4b**[8] (*Z*/*E* = 94/6)[9] in 84% yield. Likewise, 2-butyne is converted into **4c**[8] (*Z*/*E* = 80/20)[9] in 92% yield. As expected, conversion of **4c** into methylenomycin B (**3b**) proceeds in 51% yield under the same reaction conditions as those for the preparation of **3a**: bp 60 °C (0.1 mm); IR (neat) 1690 (s), 1665 (m), 1630 (s), 1330 (s), 1030 (s), 930 (m), 800 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.74 (s, 3 H), 2.05 (s, 3 H), 3.05 (bs, 2 H), 5.30 (d, J = 1 Hz, 1 H), 6.00 (d, J = 1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 8.23, 16.64, 36.97, 114.85, 138.23, 141.78, 164.02, 196.04.

The necessity for I_2ZrCp_2 in the above allylmetalation suggested to us that, unlike the known allylmetalation reactions that are believed to proceed via six-centered transition states **7**, this reaction might proceed via a four-centered transition state, as might be suggested for the previously reported Zr-promoted carbometalation reactions.[1,3] To probe this point, the regioselectivity of the two allylzincation reactions herein reported were examined. The reaction of 1-(trimethylsilyl)-1-octyne with crotylzinc chloride, generated in situ by treatment of crotylmagnesium chloride with $ZnCl_2$, followed by protonolysis produced **8**[8] (*E*/*Z* = 90/10)[9] in 68% yield with no indication for the formation of its regioisomer **9**. On the other hand, the reaction of 5-decyne with dicrotylzinc in the presence of I_2ZrCp_2, generated as described earlier, followed by protonolysis gave **10**[8] in 92% yield as an essentially single isomer, with no indication for the formation of its regioisomer **11**. These two reactions must proceed via different paths, and the results are consistent with the notion that the former may proceed via **7**, while the latter may involve a four-centered transition state. Our attempts to react 1-(trimethylsilyl)-1-octyne with either isoprenylzinc chloride or diisoprenylzinc did not produce cleanly the desired products.



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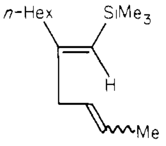

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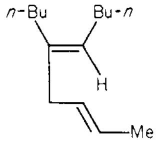

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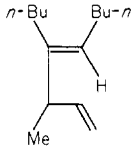

11

The results described herein not only expand the scope of controlled carbometalation of alkynes but also demonstrate a novel and potentially attactive approach to the synthesis of carbocycles via carbometalation.

Acknowledgment. We thank the National Science Foundation, the National Institutes of Health, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support.

Supplementary Material Available: Experimental findings for **4a-c**, **5**, **6a**, **8**, and **10** (2 pages). Ordering information is given on any current masthead page.

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(15) **Note Added in Proof**: Professor G. Molander of the University of Colorado has informed us of their study of allylmetalation of alkynylsilanes.

Synthesis and Molecular Structures of Homoleptic Dicyclohexylphosphide Complexes of the Early Transition Metals

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Received July 21, 1983

We report the isolation of homoleptic dicyclohexylphosphide complexes, $M_x(PCy_2)_y$, for 10 of the 12 early transition metals. These are the first well-characterized examples[1-4,20] of a potentially large class of compounds, analogous to the well-known[5] diorganoamide complexes $M_x(NR_2)_y$. The unusual structures of the new complexes result from the bulky PCy_2 ligand, metal-phosphorus multiple bonding, and, for the anionic derivatives, strong phosphorus-lithium interactions.

Addition of a tetrahydrofuran (THF) solution of $LiPCy_2$[6] to a solution or suspension of a transition-metal halide THF adduct[7] at -80 °C[8] produces the complexes **1-10** (Table I, supplementary material). **1-9** are isolated as crystalline solids by hexane extraction of the evaporated reaction residue, addition of 1,2-dimethoxyethane (DME), and cooling to -30 °C. Complex **10** is insoluble in hexane or benzene and is separated from LiBr by fractional crystallization from DME at -30 °C. Four classes of compounds are distinguishable:

[Li(DME)][M(PCy$_2$)$_5$] (1, M = Zr; 2, M = Hf). The molecular structure of $\mathbf{2}\cdot C_6H_6$ in Figure 1A was determined by X-ray diffraction.[9] The distorted trigonal-bipyramidal geometry about hafnium has Hf-P bond distances[10,11] and phosphorus geometries[12] consistent with the valence bond representation shown. An 18-e^- configuration is attained by participation of the P(4) lone pair in a three-center, two-electron Hf-P-Li bond. The tight binding

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[1] Early reports by Issleib, et al., include the reactions of $LiPCy_2$ with $MCl_3{\cdot}3THF$ (M = Ti, V, Cr)[2] and $MnBr_2$[3]; the products are misformulated as monomeric TiP_2, VP_3, CrP_3, and $Li[MnP_3]$ species, where P = PCy_2.

[2] Issleib, K.; Wenschuh, E. *Chem. Ber.* **1964**, *97*, 715-720.

[3] Issleib, K.; Wenschuh, E.; Frohlich, H.-O. *Z. Naturforsch.* **1962**, *176*, 778-779.

[4] Monomeric THF adducts of tris(di-*tert*-butylphosphide) complexes of several lanthanides have been reported: Schumann, H.; Frisch, G.-M. *Z. Naturforsch.* **1979**, *34b*, 748-749.

[5] Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Ellis Horwood: Chichester, 1980; Chapter 8.

[6] Isolated as a yellow solid from *n*-BuLi and $HPCy_2$ in diethyl ether. Modified after: Issleib, K.; Tzschach, A. *Chem. Ber.* **1959**, *92*, 1118-1126.

[7] M = Ti, Zr, Hf, V, Nb: Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135-139. M = Cr: Herwig, W.; Zeiss, H. H. *J. Org. Chem.* **1958**, *23*, 1404. M = Mo: Dilworth, J. R.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1983**, 397-398. M = W: Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430-1431. M = Mn: Hosseiny, A.; McAuliffe, C. A.; Minten, K.; Parrott, M. J.; Pritchard, R.; James, J. *Inorg. Chim. Acta* **1980**, *39*, 227-231. M = Re: Allen, E. A.; Johnson, N. P.; Rosevear, D. T.; Wilkinson, W. *J. Chem. Soc. A* **1969**, 788-791.

[8] Low-temperature, dropwise addition suppresses reduction of the transition metal with concomitant formation of P_2Cy_4.

[9] Crystal data for $\mathbf{2}\cdot C_6H_6$ grown from benzene-DME: $C_{70}H_{126}HfLiO_2P_5$, M_r = 1340.08, monoclinic, space group $P2_1/n$ (No. 14), a = 19.215 (2) Å, b = 19.922 (3) Å, c = 18.821 (2) Å, β = 90.171 (1)°, V = 7205 (3) Å^3, Z = 4, ρ(calcd) = 1.24 g cm^{-1}; T = -100 °C. On the basis of refinement of 677 variables (Hf, P, O, and non-benzene C's with anisotropic thermal parameters) using 7971 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, R = 0.036, R_w = 0.038. Full details will be published separately (see also supplementary material).

[10] Relevant bond distances: Hf-P(1) = 2.533 (1), Hf-P(2) = 2.475 (1), Hf-P(3) = 2.504 (1), Hf-P(4) = 2.639 (1), Hf-P(5) = 2.712 (1), P(4)-Li = 2.653 (8), P(5)-Li = 2.579 (8) Å.

[11] Cf. Hf-P = 2.682 (1), Hf $\leftrightharpoons$ P = 2.488 (1) Å in $(\eta\text{-}C_5H_5)_2Hf(PEt_2)_2$: Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049-1051.

[12] Displacement of Hf atom from the PC_2 plane: P(1) = 0.634, P(2) = 0.095, P(3) = 0.647, P(4) = 1.185, P(5) = 2.058 Å.

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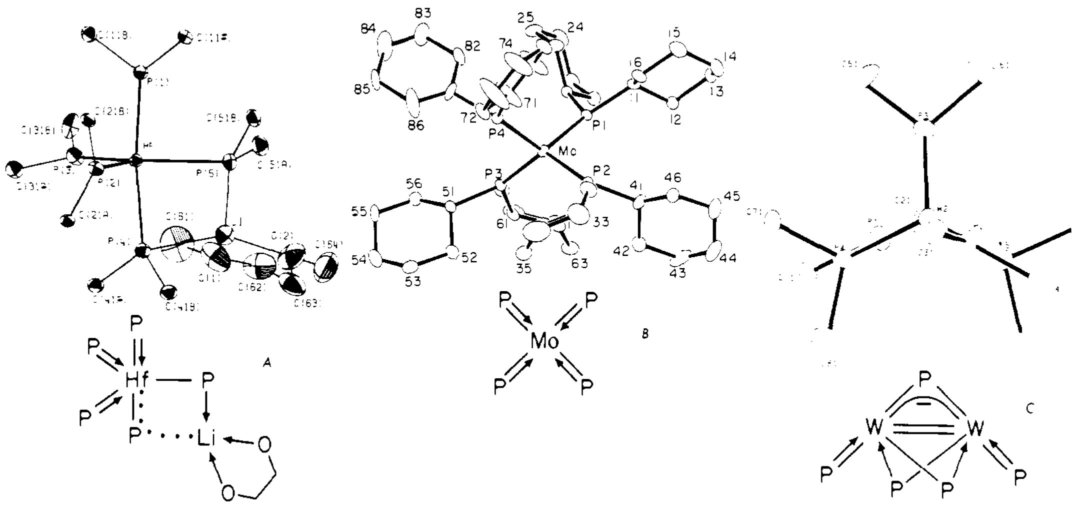
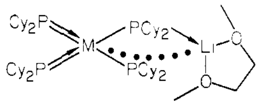


Figure 1. Molecular structures and valence bond representations of **2** (A), **7** (B), and **9** (C). All hydrogen atoms and, for **2** and **9**, all carbons (except C_α) of cyclohexyl rings are omitted for clarity. **9** is viewed down the W–W bond.

of the $[Li(DME)]^+$ fragment by the "polyphosphine" anion persists in solution at low temperatures as shown by ^1H, ^{13}C, and ^{31}P NMR spectroscopy (Tables III–V, supplementary material). For example, the $^{31}P\{^1H\}$ NMR spectrum of **2** at 25 °C consists of a broad singlet, indicative of five equivalent PCy_2 ligands. At −100 °C, three broad resonances with relative intensities of 1:2:2 are observed; the limiting low-temperature spectrum has not yet been obtained.

Reduction of **1** with lithium naphthalenide in THF produces $LiPCy_2$ and a thermally stable Zr(III) complex, tentatively identified as $[Li(THF)_n][Zr(PCy_2)_4]$ (**11**) by its ESR spectrum (Table VI, supplementary material). This complex is analogous to **3**–**5** discussed below.

$[Li(DME)_n][M(PCy_2)_4]$ (n = 1: 3, M = Ti; 4, M = V; 5, M = Re. n = 2: 6, M = Nb). Detailed molecular structures of **3**–**6** have not yet been determined. We propose the structure below for **3**–**5**, since it is consistent with the ESR spectral data for **3**



and allows the Re(III) center in **5** to achieve an 18-e⁻ configuration. The ESR spectrum of **3** in pentane at 25 °C consists of a binomial quintet, indicating fast exchange between terminal and Li-bound PCy_2 ligands. At −100 °C, the exchange is quenched, and the hyperfine splittings suggest the asymmetric coordination of the $[Li(DME)]^+$ fragment by the polyphosphine anion shown.

Compounds **5** and **6** are probably not four-coordinate in good donor solvents; diamagnetic **5** equilibrates with a purple, paramagnetic adduct in THF or DME, and **6** is stable in solution only in these solvents. Slow liberation ($t_{1/2} \approx 2$ h at 25 °C in C_6D_6) of 2 equiv of $HPCy_2$ and 2 equiv of DME/Nb produces an incompletely characterized, paramagnetic Nb complex.

Oxidation of **3**, **4**, and **6** with $[(\eta\text{-}C_5H_5)_2Fe][BF_4]$ in DME at 25 °C affords the thermally unstable compounds $M(PCy_2)_4$ (**12**, M = Ti; **13**, M = V; **14**, M = Nb), identified by their ESR (**13** and **14**) or ^{31}P NMR spectra (**12**). These spectral data are consistent with the distorted tetrahedral structure found for **7**.

$Mo(PCy_2)_4$ (7). The molecular structure[13] of **7** shown in Figure 1B consists of a distorted tetrahedral (local D_{2d}) MoP_4 coordination sphere with short (avg. 2.265(2) Å) Mo–P double bonds, two large P–Mo–P angles (P(1)–Mo–P(4) = 121.3 (1)° and P(2)–Mo–P(3) = 124.9 (1)°), and nearly planar $MoPC_2$ units. The bonding in **7** is analogous to that discussed previously for $Mo(NMe_2)_4$[14] and $Mo(t\text{-}BuS)_4$.[15]

$[Li(DME)_n][M_2(PCy_2)_5]$ (n = 3: 8, M = Cr; 9, M = W. n = 1: 10, M = Mn). The crystal structure[16] of **9**·DME·C_6H_6 is composed of discrete $[Li(DME)_3]^+$ cations and $[W_2(PCy_2)_5]^-$ anions. The distorted confacial bitetrahedral structure of the anion contains three bridging and two terminal PCy_2 ligands and a W–W double bond.[17,18] The alignment of the PC_2 trigonal planes of the double-bonded, terminal PCy_2 ligands with two of the W–P–W bridge planes shown in Figure 1C accounts for the 1:2:2 $^{31}P\{^1H\}$ NMR spectrum observed for **9** in THF at −80 °C (Table V, supplementary material). At 80 °C in DME, two resonances with a 3:2 ratio are observed; NMR spectra of **9** in noncoordinating solvents are more complicated due to strong P–Li interactions. The paramagnetism of **8** (μ_{eff} = 3.7 μ_B/Cr_2 dimer) presumably reflects the decreased strength of the metal–metal interaction (cf. $M_2Cl_9^{3-}$, M = Cr, Mo, W[19]).

The paramagnetic d^5 complex **10** ($\mu_{eff} \approx 2.0$ μ_B/Mn) has different solubility properties than **1**–**9** and is probably oligomeric.

The ligating properties of the new transition-metal-containing polyphosphines **1**–**10** are presently under investigation.

Acknowledgment. We thank the following persons for skilled technical assistance in the following areas: Synthesis, S. A. Hill, D. W. Reutter, K. H. Richmond, and W. M. Gray; X-ray, L. F. Lardear; NMR, G. Watunya, J. D. Center, and N. R. Dando and Drs. D. C. Roe, P. J. Domaille, and D. W. Ovenall; ESR, D. J. Jones and J. T. Seningen.

Registry No. 1, 87462-35-9; **2**·C_6H_6, 87462-38-2; **3**, 87462-40-6; 4, 87462-42-8; **5**, 87462-44-0; **6**, 87462-46-2; 7, 87462-47-3; **8**·$(DME)_3$,

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(13) Crystal data for 7 grown from benzene/DME: $C_{48}H_{88}MoP_4$; M_r = 885.07, triclinic, space group $P\bar{1}$ (No. 2), a = 14.786 (4) Å, b = 18.790 (4) Å, c = 10.025 (2) Å, α = 102.24 (2), β = 109.44 (2), γ = 85.47 (2)°, V = 2567 Å^3, Z = 2, ρ(calcd) = 1.145 g cm^{-1}; T = −100 °C. On the basis of refinement of 478 variables (all non-hydrogen atoms with anisotropic thermal parameters) using 5606 unique reflections with $F_o^2 > 2\sigma(F_o^2)$, R = 0.052, R_w = 0.059. See supplemental material for full details.

(14) Chisholm, M. H.; Cotton, F. A.; Extine, M. W. *Inorg. Chem.* **1978**, *17*, 1329–1332.

(15) Otsuka, S.; Kamata, M.; Hirotsu, K; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3011–3014.

(16) Crystal data for **9**·DME·C_6H_6 grown from benzene–DME: $C_{79}H_{153}LiO_8P_5W_2$, M_r = 1760.60, monoclinic, $P2_1/n$, a = 20.593 (3) Å, b = 24.307 (3) Å, c = 18.253 (2) Å, β = 96.75 (1)°; V = 9073 Å^3, Z = 4; ρ(calcd) = 1.289 g cm^{-1}, T = −100 °C. On the basis of isotropic–anisotropic refinement of 809 variables using 7333 unique reflections with $F_o^2 > 2\sigma(F_o^2)$, R = 0.064, R_w = 0.062. Full details will be published separately (see also supplementary material).

(17) Relevant bond distances: W–W = 2.5505 (9), W(1)–P(1) = 2.346 (4), W(1)–P(3) = 2.377 (4), W(1)–P(4) = 2.473 (4), W(1)–P(5) = 2.381 (4), W(2)–P(2) = 2.345 (4), W(2)–P(3) = 2.387 (4), W(2)–P(4) = 2.379 (4), W(2)–P(5) = 2.469 (4) Å.

(18) A theoretical study of the bonding and fluxionality of **9** is in progress in this department by F. A. Van-Catledge.

(19) Saillant, R.; Wentworth, R. A. D. *Inorg. Chem.* **1969**, *8*, 1226–1229.

(20) **Note Added in Proof**: The synthesis and molecular structure of $Mo_2(P\text{-}t\text{-}Bu_2)_4$ has recently appeared: Jones, R. A.; Lasch, J. G.; Norman, N. C.; Whittlesey, B. R.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 6184–6185.

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, ^{1}H, ^{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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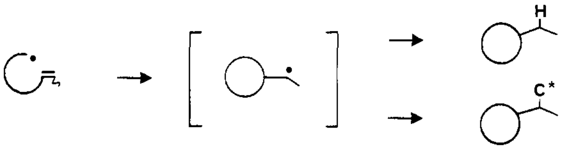
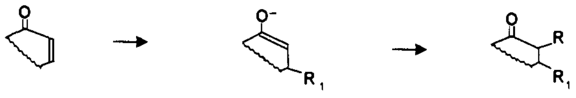
Received July 22, 1983

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.



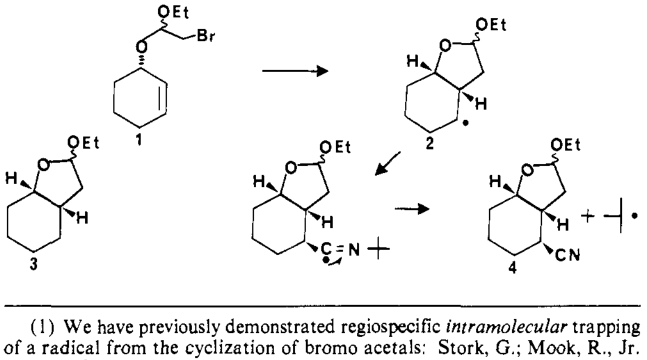
A B C

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]



D E

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**).



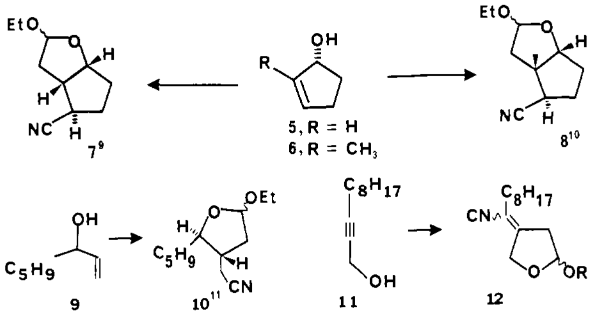
Preliminary experiments showed that addition of *tert*-butyl isocyanide to the tributyltin hydride medium previously used for the cyclization of **1** to **3**[3] simply gave the usual bicyclic acetal **3** but no trapping. This result did show, however, that bromine abstraction from **1** by tin radicals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

[2] (a) Stork, G.; Rosen, P.; Goldman, N. L. *J. Am. Chem. Soc.* **1961**, *83*, 2965. Stork, G.; Rosen P.; Goldman, N. L.; Coombs, R. V.; Tsuji, J. *Ibid.* **1965**, *87*, 275. Stork, G.; Hudrlik, P. F. *Ibid.* **1968**, *90*, 4464. Stork, G. *Pure Appl. Chem.* **1968**, *17*, 383. (b) Stork, G.; D'Angelo J. *J. Am. Chem. Soc.* **1974**, *96*, 7114. Stork, G. Isobe, M. *Ibid.* **1975**, *97*, 6260. (c) Stork, G.; Ganem, B. *Ibid.* **1973**, *95*, 6152. Stork, G.; Singh J. *Ibid.* **1974**, *96*, 6181.

[3] Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741.

[4] Saegusa, T.; Kobayashi, S.; Ito, Y.; Yasuda, N. *J. Am. Chem. Soc.* **1968**, *90*, 4182.

[5] Blum, P. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1313.

[6] Cyanogen, cyanogen bromide, and alkyl cyanoformates (but not isocyanides) have been used for cyanation of carbon-centered radicals: Tanner, D. D.; Bunce, N. J. *J. Am. Chem. Soc.* **1969**, *91*, 3028. Tanner, D. D.; Rahimi, P. M. *J. Org. Chem.* **1979**, *44*, 1674. Tanner, D. D.; Lycan, G.; Bunce, N. J. *Can. J. Chem.* **1970**, *48*, 1492.

[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 ^{1}H 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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