enophilic attack, since the hydrogen atom at the cyanohydrin carbon in **1a**,**b** is being abstracted, affording (*E*)-**4** via structure A and (*Z*)-**4** via structure A′. Steric congestion is minimized by placing the bulky silyloxy substituent as far away from the reaction center as is feasible, so that structure A is preferred over A′ on the basis of energy. Consequently, for **1b** (R = *t*-Bu) the diastereomeric ratio is significantly higher than for **1a** (R = Me), i.e., dr > 99:1 vs. dr = 96:4 (Scheme I), as would be expected on steric grounds. However, in structure B the chiral cyanohydrin center is remote from singlet oxygen in the enophilic attack and conformational flexibility is responsible for the lower diastereoselectivity observed with **2a**,**b** (Cram-type stereocontrol). Indeed, whether **2a** (R = Me) or **2b** (R = *t*-Bu) are used, the dr values are within experimental error (Scheme I).

It is important to emphasize that the cis effect[5] is responsible for the observed diastereoselectivity in the photooxygenation of the silyl cyanohydrins **1a**,**b** and **2a**,**b**. Such stereoelectronic factors should prove useful in controlling the stereochemistry of singlet oxygen reactions, particularly in the synthetic application of diastereoselective oxygen functionalization.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 172), the Fonds der Chemischen Industrie, the Stiftung Volkswagenwerk, and A. v. Humboldt Stiftung for generous financial support, Petra Seufert for technical assistance, and Dr. Dieter Scheutzow for spectral services (NMR).

Waldemar Adam,* Luiz H. Catalani,[1] Axel Griesbeck
Institut für Organische Chemie
der Universität Würzburg, Am Hubland
D-8700 Würzburg, FRG
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Cobalt-Mediated [2 + 2 + 2]Cycloadditions of Alkynes to the Pyrrole 2,3-Double Bond: A Novel Construction of Fused Dihydroindoles

Summary: Auxiliary η^5-CpCo mediates the [2 + 2 + 2]-cycloaddition of alkynes to the pyrrole 2,3-double bond, furnishing complexed fused dihydroindoles.

Sir: Pyrrole is a pivotal structural unit in nature, in synthetic organic chemistry, and in medicinally active compounds.[1] Its double bonds, particularly when vinyl-substituted, have been utilized in cycloaddition reactions leading to fused heterocycles.[1,2] We report that η^5-CpCo mediates a novel transformation of the pyrrole ring: the [2 + 2 + 2]cycloaddition of its 2,3-double bond to alkynes to generate the new 3a,7a-dihydroindole nucleus as incorporated in a variety of tri- and tetracyclic diene complexes. After those in indole,[3] our observations provide the second example of the incorporation of aromatic double bonds into cobalt-mediated cycloadditions,[4] involving a considerably more challenging substrate and pointing to a significantly larger scope of the reaction than previously anticipated.

The starting materials **1** were prepared in one step from pyrrole by adaptations of the literature procedures using known alkynoyl chlorides or iodoalkynes[3] (Table I).

The results presented in Table II were obtained under identical conditions to provide comparative data (unless noted otherwise): 1 equiv of **1**, 1.2 equiv of $CpCo(CO)_2$, 5 equiv of monoalkyne (added slowly by syringe pump at 23 °C). The solvent used was toluene, and the solution was irradiated with a Sylvania 300-W tungsten halogen slide projector lamp over the 10–15 h reaction time.

The cocyclizations of **1** shown in Table II give reproducible results; however, the reaction conditions are unoptimized. Thus, as shown in Table III, the chemo- and stereoselectivity of the reaction, as well as the yields of products can vary with changes in temperature, the nature of the cobalt auxiliary, and concentration of substrates. We have also noted temperature effects on the regioselectivity when unsymmetrically substituted cocyclization partners are used.[9] Because of the time-consuming nature of optimization, we have only carried it out for **1a** (92%). The results indicate that virtually quantitative yields might be attainable by fine-tuning conditions.

Some additional comments are in order concerning our results. (1) Stereochemical assignments were made by analogy to related systems utilizing the effects of the magnetic anisotropy of cobalt in ^1H NMR spectroscopy.[4] Further confirmation of regiochemistry was obtained by desilylation of some complexes with tetrabutylammonium fluoride and ^1H NMR analysis of the products. (2) The diastereomeric cobalt diene complexes shown in Table II were inseparable by chromatography or crystallization. However, their diastereomeric relationship was proven by oxidative demetalation to provide a single product. The product ratios appear to be of kinetic origin, equilibration being absent under the reaction conditions (110 °C). (3) Oxidative demetalation of the complexes in Table II can be accomplished either to the free diene or to the aromatized indole system, depending on conditions. The latter can be chosen to exactly meet the electronic requirements of the specific system by electrochemical methods. Thus, for example, **2a** and **3a** show an irreversible oxidation wave in cyclic voltammetry at +0.25V (vs. Ag/Ag^+, THF, 23 °C). In practical terms, complexes **2** and **3** will liberate their ligands as the diene by treatment with 1 equiv of Ce^{4+} (as ceric ammonium nitrate) or Hg^{2+} (as mercuric acetate) in CH_3CN and/or THF at temperatures ranging from −78 to

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[5] N-Alkynoylated pyrroles were prepared by treatment of the alkynoyl chloride with *N*-lithiopyrrole in THF at −78 °C.

[6] Formed by exposure of 5-iodopentyne to *N*-potassiopyrrole in Me_2SO at 23 °C.

[7] All new compounds gave satisfactory analytical and/or spectral data.

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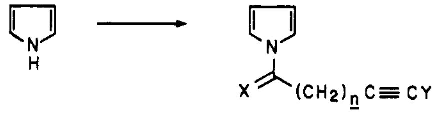
Table I. Synthesis of Cyclization Precursors 1

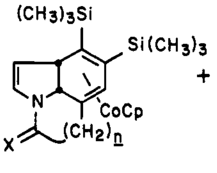
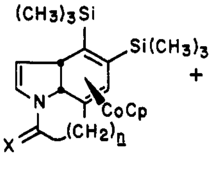
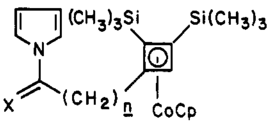
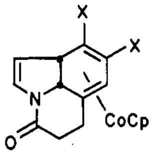
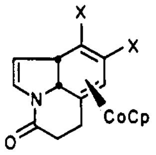
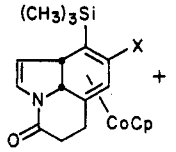
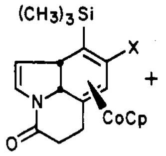
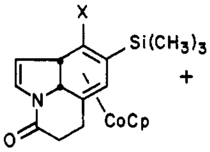
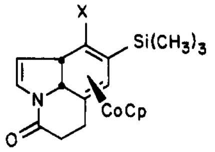
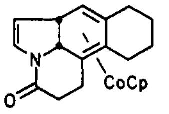
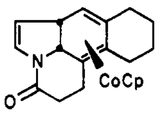


1

	1					
	X	Y	*n*	yield, %	mp or bp (mm), °C	method ref
1a	O	H	2	93	28–30	5
1b	O	H	3	74	42–44	5
1c	O	H	4	94	53–55	5
1d	H_2	H	2	51	160 (1)	6
1e	O	$(CH_2)_4C\equiv CH$	2	70	>250 (0.3)[a]	5

[a] Kugelrohr distillation.

Table II. Results of the Inter- and Intramolecular Cyclizations of 1[7]

starting material	cocyclization partner	products (% yield)			
1c–d	$(CH_3)_3SiC\equiv CSi(CH_3)_3$				
		2a (38) 2b (23) 2c (0) 2d (56)[a]	3a (10) 3b (3) 3c (0) 3d (0)	4a (0) 4b (0) 4c (11) 4d (0)	
1a	XC≡CX				
	X = CH_2CH_3	5a (19)	6a (6)		
	X = CO_2CH_3	5a′ (61)	6a′ (0)		
1a	$XC\equiv CSi(CH_3)_3$				
	X = CO_2CH_3	7a (20)	8a (0)	9a (19)	10a (0)
	X = OCH_3	7a′ (24)	8a′ (12)	9a′ (4)	10a′ (2)
1e					
		11e (39)[b]	12e (7)		

[a] This run was carried out at −78 °C. [b] 1–2 mmol of 1e in 30 mL of irradiated toluene containing 1.2 equiv of $CpCo(CO)_2$ at 23 °C.

0 °C or as the aromatized indole with 6–8 equiv of Ce^{4+} in good to excellent yields. The sequence cyclization–oxidation provides access to the novel 3a,7a-dihydroindole nucleus and also consitutes a new indole synthesis. (4) Further confirmation of the kinetic control over the cyclization is found in the recomplexation of the free ligand from **2a** and **3a** [$CpCo(CH_2{=}CH_2)_2$,[8] 23 °C] which gave exclusively **2a** in quantitative yield. (5) The employment of $CpCo(CH_2{=}CH_2)_2$ appears clearly advantageous (Table III) in these and some other[9] cyclizations allowing for reaction temperatures as low as −78 °C. Even at these temperatures, ^1H NMR monitoring does not permit the detection of any intermediates, demonstrating the extraordinary facility with which these processes occur. (6) The cyclization of **1c** failed, at least under the standard conditions (Table II), indicating some limitations of the method. (7) The cooligomerization of **1d** shows that electronic activation of the aromatic ring is not necessary for the reaction to be successful. (8) Finally, a dramatic example of how the cobalt auxiliary controls the reactivity of the substrates is provided by the formation of **5a′** in the complete absence of the reported products of the thermal reaction of pyrrole with dimethyl butynedioate.[1,2i]

In short, this work opens up new powerful synthetic avenues in polyheterocycle construction and suggests possible extensions to other heteroaromatics and perhaps carboaromatics.

Note Added in Proof: The structure of **5a′** has been

Table III. Effect of Reaction Conditions on the Cocyclizations of 1a

$$1a + (CH_3)_3SiC{\equiv}CSi(CH_3)_3 \xrightarrow{CpCo(L)_2,\ h\nu} 2a + 3a + 4a$$

L	$(CH_3)_3SiC{\equiv}CSi(CH_3)_3$, equiv	temp, °C	yield, %		
C_2H_4	solvent	134	37	0	58
CO	solvent	134	25	0	49
CO	15	110	10	0	17
C_2H_4	solvent	25	74	18	0
CO	solvent	25	51	13	0
CO	5	25	38	10	0
C_2H_4	5	0	40	13	0
C_2H_4	5	-78	35	0	0

confirmed by X-ray analysis.

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Supplementary Material Available: Mp, bp, spectral, and analytical data on 25 new compounds, general experimental procedures employing $CpCoL_2$ (L = CO or $CH_2{=}CH_2$), and optimized procedure for the preparation of **2a** and **3a** (12 pages). Ordering information is given on any current masthead page.

George S. Sheppard, K. Peter C. Vollhardt*
Department of Chemistry
University of California, Berkeley
and the Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

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Free Radical Reactions of Organomercury Halides with Alkenes and Alkynes[1]

Summary: Substituted acetylenes or electronegatively monosubstituted ethylenes react with *t*-BuHgCl in photostimulated free radical chain processes in PhH or Me_2SO to form $R^1C(t\text{-}Bu){=}C(HgCl)R^2$ (R^1, R^2 = H, Ph; H, COMe; EtO_2C, Ph; EtO_2C, EtO_2C) or $t\text{-}BuCH_2CH(HgCl)E$ (E = $(EtO)_2PO$, $PhSO_2$, $p\text{-}O_2NC_6H_4$, $SiPh_3$). Reduction by BH_4^- or cleavage by I_2 forms $R^1C(t\text{-}Bu){=}CHR^2$ and $t\text{-}BuCH_2CH_2E$ or $R^1C(t\text{-}Bu){=}C(I)R^2$ and $t\text{-}BuCH_2CH(I)E$.

Sir: We have previously reported the photostimulated free radical chain reaction of alylmercury halides with substituted alkenes[2] and alkynes[3] occurring by an addition–elimination mechanism with retention of configuration for Q = I or HgCl (eq 1).[4,5] Alkenes that are effective traps

$$RHgCl + R'CH{=}CHQ \xrightarrow[\substack{Q\,=\,Bu_3Sn,\ PhS,\\ PhSO_2,\ I,\ HgCl\\ R'\,=\,Ph,\ Cl,\ MeO_2C}]{h\nu} R'CH{=}CHR \qquad (1)$$

for alkyl radicals but that are not susceptible to such addition–elimination processes can also react cleanly with RHgCl by chain or nonchain processes. Chain reactions occur when the radical formed by addition of R• to the alkene is either a good donor (D•) or acceptor (A•) (reactions 2 and 3).

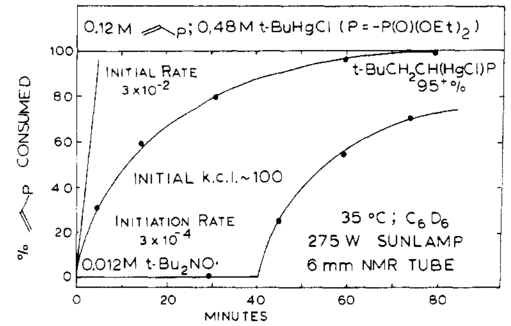

Figure 1. Measurement of initial kinetic chain length in PhH at 35–40 °C determined by ^1H NMR. In Me_2SO the rates are ~20% faster with the same inhibition period. Reactions in Me_2SO are considerably faster than in PhH at the latter stages of the reaction; the build-up of the terminating HgCl may be more important in PhH than in Me_2SO.

Table I. Reaction Products from $R^1C{\equiv}CR^{2}$[a]

R^1, R^2	kinetic chain length[b]	products (%)[c]	
		t-BuC(R^1)=C(R^2)H	t-BuC(R^1)=C(I)R^2
H, Ph	15 (Me_2SO); 10 (PhH)	63	41
H, COMe	25 (Me_2SO); 15 (PhH)	90[d]	85
EtO_2C, Ph		72	94
EtO_2C, CO_2Et		97	96

[a] Reaction of 3 equiv of *t*-BuHgCl for 1–2 h with 0.2–0.4 mmol of alkyne in 2.5 mL of Me_2SO or PhH with irradiation from a 275-W sunlamp at 35–40 °C. [b] $[PhC{\equiv}CH]_0$ = 0.166 M; $[MeC(O)C{\equiv}CH]_0$ = 0.137 M. [c] Mixtures of *E* and *Z* isomers.[9] [d] $t\text{-}BuCH{=}CHCH(OH)CH_3$ (70%), $t\text{-}BuCH{=}CHCOCH_3$ (20%).

$$RHgCl + D\cdot \rightarrow D^+ + R\cdot + Hg^0 + Cl^- \qquad (2)$$

$$RHgCl + A\cdot \rightarrow AHgCl + R\cdot \qquad (3)$$

Competition reactions of excesses of *t*-BuHgCl and *n*-BuHgCl with $Me_2C{=}NO_2^-$, $PhCH{=}CHSnBu_3$, PhSSPh, or $CH_2{=}CHP(O)(OEt)_2$ (VP) give a 3°/1° relative reactivity of >200, >200, >300, and >1000, respectively, where the chain-carrying radicals are either D• ($RCMe_2NO_2^{\bullet-}$, $Bu_3Sn^\bullet$) or A• ($PhS^\bullet$, $RCH_2\dot{C}HP(O)(OEt)_2$) and kinetic chain lengths measured by $(t\text{-}Bu)_2NO\cdot$ inhibition are 50, 40, 400, and 116, respectively. The high 3°/1° reactivity requires that reactions 2 and 3 are one-step processes.[6] *Such high 3°/1° reactivities appear to be characteristics of dissociative electron transfer processes*, or perhaps, in the case of reaction 3, of a process with extensive electron shift in the transition state.[7]

Photostimulated reactions of RHgCl with VP, $CH_2{=}CHSO_2Ph$, or $CH_2{=}CHC_6H_4NO_2\text{-}p$ in PhH or Me_2SO proceed by chain reactions in which the consumption of the alkene is drastically retarded by the presence of $(t\text{-}Bu)_2NO^\bullet$ (Figure 1). An initial kinetic chain length (kcl) of 95 (C_6D_6) and 116 ($Me_2SO\text{-}d_6$) is calculated for reaction 4 under the concentrations and conditions employed. In

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[5] Similar substitutions are observed for allyl iodides, sulfides, sulfones, or stannanes and for alkenyloxystannnes.

[6] The reaction of RHgCl with BH_4^- involves the intermediates RHgH, RHg•, R• (Russell, G. A.; Guo, D. *Tetrahedron Lett.* **1984**, *25*, 5239). Relative reactivities of *t*-BuHgH and *n*-BuHgH toward the adduct radicals from reactive alkenes such as $CH_2{=}C(Cl)CN$ or $CH_2{=}CHCO_2Et$ are ~1:1.

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