COBALT-MEDIATED ALKYLATION OF SILOXY FURANS

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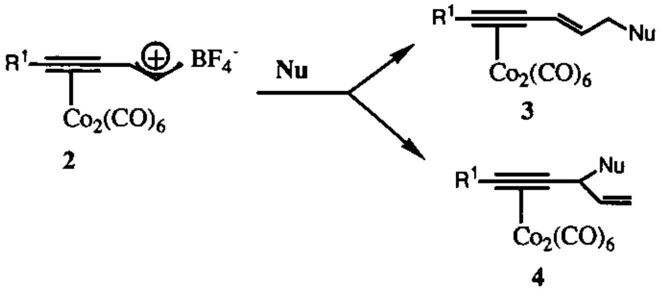
Abstract - Dicobalt hexacarbonyl complexes of propargylium and α-vinylpropargylium cations couple efficiently.with 2-trimethylsilyloxyfuran (**5**), 4-trimethylsilyloxy-2-benzyloxymethylfuran (**15**) and 2-trimethylsilyl-3-trimethylsilyloxy-4-ethylbenzo[*b*]furan (**20**) to produce the corresponding complexed furan derivatives in good yields. A convenient procedure for introducing the 2,4-enyne moiety regio- and stereoselectively into the above heterocycles using this methodology is described.

The discovery of propargylium dicobalt-hexacarbonyl complexes, $[(RC{\equiv}CCR_2)Co_2(CO)_6]BF_4$ (**1**), and subsequent investigations of their reactivity[1] have provided a convenient and rather general method for the formation of carbon-carbon bonds. A very important feature of these coupling reactions is the absence of allenic byproducts. This represents a great improvement in regioselectivity as compared to that generally observed with coupling reactions of conventional propargyl synthons.[2] The reactivity of the parent propargyl cobalt complexes (**1**) has been studied with a variety of carbon-centered nucleophiles including electron rich aromatics, β-dicarbonyls, ketones and enol derivatives, allylsilanes, metal hydrides, and alkyl-metals such as trialkyl- and alkynyl-aluminum derivatives.[2] The product metal complexes are oxidatively demetalated under mild conditions and the derived acetylenes can be conveniently transformed to cyclopentenones, a process which has been applied to the synthesis of natural products.[3,4]

The vinylogous complexes (**2**) were also investigated briefly by our group. Carbon nucleophiles (anisole, allylsilanes, isopropenyl acetate), as shown in Scheme 1, were found to react with these species at the allyl terminus remote from the organometallic substituent and with complete E-stereoselectivity to produce (**3**) exclusively.[5] However, with alcohols as nucleophiles attack at the internal carbon predominated. The full synthetic scope and the factors controlling regioselectivity, however, were not thoroughly investigated.

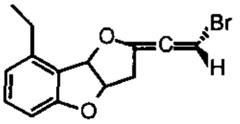
Scheme 1



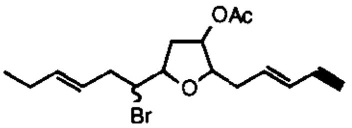
Nu: anisole, allylsilanes, isopropenyl acetate, alcohols

The potential utilization of complexes (**1**) and (**2**) as alkylating agents for heterocyclic compounds has received little attention. In an early study Pauson and coworkers[6] allowed the parent propargylium cation complexes (**1**) to react with thiophene, furan and some derivatives. Furan was found to undergo dialkylation whereas thiophene underwent monoalkylation. The yields of the the alkylated heterocycles were good.

In recent years an increasing number of natural products which incorporate the 2,4-pentenyne moiety have been discovered. Included among these are variously substituted tetrahydrofurans and tetrahydropyrans represented by marine natural products such as kumausyne[7] and isodactylyne[8] (below). The potential for using the α-vinyl derivatives such as **2** as agents for introducing the en-yne side chain via reactions with reactive heterocycles appeared to us to be an attractive synthetic method. We also envisioned expanded opportunities for use of the parent propargyl complexes (**1**) as alkylating agents for heterocycles. In continuing our efforts to explore and to exploit the reactivity of the propargylic and the α-vinylpropargylic cationic salts, we have selected three electron rich heterocycles, 2-*trimethylsilyloxyfuran* (**5**), 4-trimethylsilyloxy-2-benzyloxymethyl-2*H*-furan (**15**) and 2-trimethylsilyl-3-trimethylsilyloxy-4-ethylbenzo[*b*]furan (**20**) for examination of their coupling reactions with complexes (**1**) and (**2**). As a result of these efforts several alkylated butenolides have been synthesized as well as 2,4-pentenyne derivatives which are attractive intermediates for the synthesis of the marine natural products kumausyne and panacene.



Panacene



Kumausyne

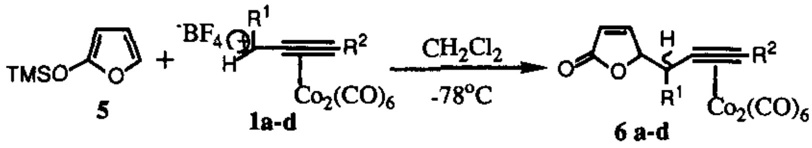
RESULTS AND DISCUSSION

Our interest in the synthesis of substituted butenolides was based on several different considerations. First, it served our main objective to expand the range of heterocyclic reaction partners to include substituted furans. Also we were interested in the regioselectivity of attack on the requisite 2-trimethylsiloxyfuran (**5**), C-3 vs C-5. Finally, a large variety of natural products (e.g. deer, whiskey and cognac lactones) could be made from the alkylated intermediates.[9]

In order to test the reactivity of the heterocycle (**5**) with the cationic complexes, we combined the propynylium cation complex (**1a**) with furan (**5**) at -45 °C in CH_2Cl_2; the reaction was complete within 10 min as judged by tlc monitoring (eq. 1). After work-up and chromatographic purification, the product (**6a**) was isolated in 72% yield as a brick red solid. The presence of key resonances in the ^1H nmr spectrum at 6.10 ppm (complexed acetylenic H), 3.34-3.15 ppm (diastereotopic protons adjacent to the methine (H-5)) and olefinic resonances at 7.55 and 6.22 ppm ($J = 5.7$ Hz) indicated that alkylation had in fact occurred at C-5. Satisfactory elemental analysis and the mass spectrum confirmed the composition of **6a** . Complete characterizational data is provided in Table 1.

Table 1. Preparation and Properties of Dicobalt Hexacarbonyl Complexes of 2(3*H*)-Furanones

Cmpd	*R*[1]	*R*[2]	*Yield (%)*	*mp (°C)*	*Molecular Formula*	*Ms(12eV m/e (%)*	*^{1}H (Nmr) δ, J (Hz)*
6a	H	H	72	56-57	$C_{13}H_6O_8Co_2$ (408)	380 (M^+-28, 19.2), 268 (100)	7.55 (dd, J=1.8, 5.7 Hz, 1 H); 6.22 (dd, J=1.8, 5.7 Hz, 1 H); 6.10 (s, 1 H); 5.15 (m, 1 H); 3.34 (dd, J=3.7, 15.8 Hz, 1 H); 3.15 (dd, J=9.3, 15.8 Hz, 1 H)
6b	H	Me	78	55-55	$C_{14}H_8O_8Co_2$ (422)	394 (M^+-28, 21.3), 310 (100)	7.56 (dd, J=1.8, 5.7 Hz, 1 H); 6.23 (dd, J=1.8, 5.7 Hz, 1 H); 5.16 (m, 1 H); 3.33 (dd, J=3.7, 15.8 Hz, 1 H); 3.06 (dd, 9.3, 15.8 Hz, 1H); 2.71 (s, 3H)
6c	H	Et	70	72-73	$C_{15}H_{10}O_8Co_2$ (436)	408 (M^+-28, 5.9), 87 (100)	7.55 (dd, J=1.8, 5.7 Hz, 1 H); 6.22 (dd, J=1.8, 5.7 Hz, 1 H); 5.16 (m, 1 H); 3.31 (dd,J=3.7,15 Hz,1 H); 3.06 (dd, J=9.3, 15 Hz, 1 H); 2.92(m, 2 H); 1.30 (t, J=7.5 Hz, 3 H)
6d	H	n-Pr	65	oil	$C_{18}H_{16}O_8Co_2$ (478)	---------------	7.55 (dd, J=1.5, 5.7 Hz, 1 H); 6.25 (dd,J=1.8, 5.7 Hz, 1 H); 5.15 (m, 1 H) 3.30 (dd, J=3.7, 15.9 Hz, 1 H); 3.05 (dd, J=9.3, 15.8 Hz, 1 H); 2.85 (m, 2 H); 1.51 (m,6 H); 0.95 (t, J=7.5 Hz, 3 H)
9	vinyl	H	56	oil	$C_{15}H_8O_8Co_2$ (434)	406 (M^+-28, 6), 220 (100)	7.43 (dd, J=1.5, 5.7 Hz, 1 H); 6.63 (dd, J=1.5,15.0 Hz, 1 H); 6.15 (s, 1 H); 6.13 (dd, J=1.8, 5.7 Hz, 1 H); 6.0 (dt, J=7.5, 15.0 Hz, 1 H); 5.13 (m, 1 H); 2.64 (m, 2 H)
10	"	"	19	oil	"	406 (M^+-28, 21), 321.8 (100)	7.45 (dd, J=1.5, 5.7 Hz, 1 H); 6.21 (dd, J=1.8, 5.7 Hz, 1 H); 6.14 (s, 1 H); 5.7 (dt, J=10, 17 Hz, 1 H); 5.25 (m, 2 H); 5.18 (m,1H); 3.8 (dd, J=3.3, 9.2 Hz, 1 H)



(1)

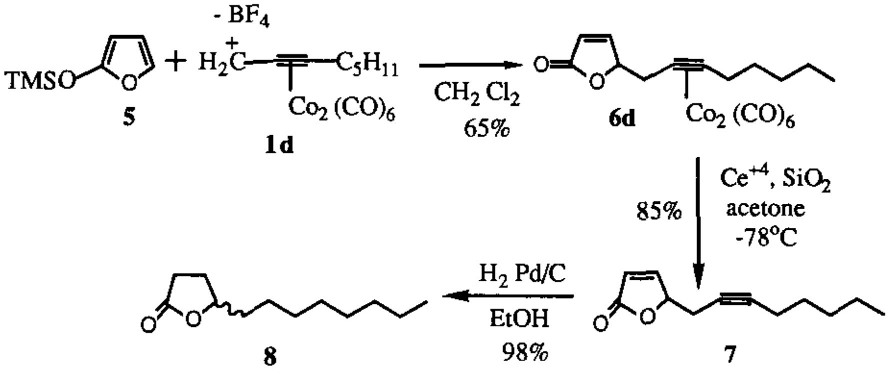
a: $R^1 = R^2 = H$; **b**: $R^1 = H$, $R^2 = CH_3$; **c**: $R^1 = H$, $R^2 = CH_2CH_3$; **d**: $R^1 = H$, $R^2 = CH_2CH_2CH_3$

The preparation of butynyl derivative (**6b**) was accomplished in the same general manner as above for **6a** combining **1b** with **5** (eq. 1). The resulting bright red solid (mp 54-55°C) was obtained in 78% yield after chromatography. The nmr spectrum exhibited of **6b** featured two multiplets at 3.33 and 3.06 ppm corresponding to the pair of diastereotopic methylene protons coupled to the methine proton (H-5), a singlet at 2.71 ppm for the methyl group on the complexed acetylene, and olefinic resonances at 7.56 and 6.23 ppm. Mass spectral fragmentation and elemental analysis again supported the structural assignment.

An *n*-pentyl side chain is found in the natural product Cognac lactone (tetrahydro-4-methyl-5-pentylfuran-2-one), a compound that is used in the flavoring of Cognac.[10] To further illustrate the generality of the alkylation reaction, the synthesis of compound (**6c**) was effected according to eq. 1. Compound (**6c**) was isolated in 70% yield (mp 72-73 °C) after chromatographic purification. The nmr spectrum was definitive with multiplets at 3.31 and 3.06 (from the diastereotopic methylene protons) and the two olefinic proton resonances at 7.55 and 6.22 ppm (J= 5.9 Hz).

In order to demonstrate the practical utilization of this chemistry we undertook a short total synthesis of *rac*-tetrahydrofuran-5-octyl-2-one (**8**), a natural product found in the pygidial glands of the bettles *Bledius mandibularis* and *B. spectabilis*. This compound is also found in several food aromas and has been used in perfumery and flavor mixtures.[11] Our synthesis (Scheme 2) started with the preparation of hexacarbonyl-(μ-[5-(2-octynyl)-5*H*-furan-2-one]-dicobalt (*Co-Co*) (**6d**) which was obtained in 65% yield as a dark red oil from the corresponding salt (**1d**) and the heterocycle (**5**) using the same conditions that were applied above. The structure assigned to **6d** was supported by ir absorptions at 2100, 2040 and 2020 cm^{-1} (M-CO), 1750 cm^{-1} (lactone C=O) and 1160-1040 cm^{-1} (C-O stretch); and by

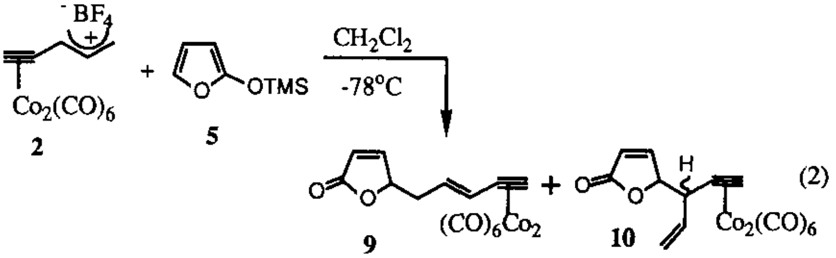
Scheme 2



^{1}H nmr absorptions at 5.15 (m, H-5), 3.3 and 3.1 ppm (multiplets, diastereotopic methylene protons), and the olefinic resonances at 7.55 and 6.25 ppm. Oxidative-demetallation of **6d** was performed in a medium consisting of acetone, ceric ammonium nitrate and silica gel at -78°C. After isolation, the intermediate acetylenic furanone (without purification) was hydrogenated over Pd/C, affording furanone (**8**) as a pleasant smelling oil in nearly quantitative yield. The overall yield from the alkylation for the sequence was 57%. It is interesting to note that the intermediate acetylenic butenolide possesed no significant odor.

A variety of means exist to synthesize substituted butenolides.[12] We offer the present method of alkylating siloxyfurans as a facile, efficient and potentially quite general route to substituted butenolides which can be subsequently transformed chemoselectively by a variety of reagents. Consistent with our observations of regioselective attack at the 5-position of (**5**), Boukouvalas and coworkers found that **5** reacts regioselectively at the 5-position with a variety of alkyl halides in the presence of silver salts.[13] Another group led by Casiraghi[14] also demonstrated that 2-trimethylsiloxyfuran underwent vinylogous aldol reactions selectively at the 5-position when allowed to react with aldehydes.

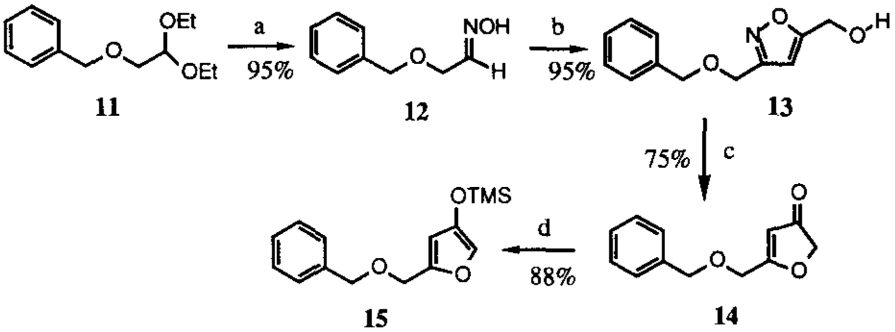
As noted earlier numerous naturally occurring oxygen heterocycles contain the 2,4-enyne moiety as part of their structure. Furthermore, these compounds exhibit a number of significant physiological properties.[15] These facts prompted our efforts to synthesize a few substituted butenolides such as **9** . As shown in eq. 2, the α-vinyl salt (**2**) was treated with furan (**5**) in methylene chloride at -78°C; typically, the reaction was over within 5 min as indicated by tlc (pentane/ether 2:1). After work-up and purification *via* chromatography, two products were obtained as dark red oils in 56% **9** and 19% **10** yield. The products result from exclusive reaction at the 4-position of the furan but alternative attack on the allyl terminii of **2** .



Compound (**9**) was characterized by an nmr multiplet at 2.64 ppm (diastereotopic methylene protons), olefinic resonances of the en-yne unit at 6.63 and 5.97 ppm with J=16.2 Hz indicative of a trans stereochemistry, and the other expected resonances. The mass spectrum of **10** demonstrated it to be isomeric with **9** but its ^{1}H nmr spectrum was distinctly different with a double doublet at 5.26 ppm (for H-5), an ABX vinylic resonance pattern at 5.20 and 5.18 ppm, a doublet of doublets (J=3.3, 9.2 Hz) at 3.90 ppm (H-6), and two resonances at 7.45 (H-4) and 6.21 (H-3) ppm (J=5.7 Hz) for the butenolide olefinic protons. A peak of 406 (M^+-28, 21.4) was observed in the mass spectrum. Interestingly, **10** appears to be formed as a single diastereomer. Presently we have no explanation for the incomplete regioselectivity observed with siloxyfuran (**5**) (in comparison with previously examined carbon nucleophiles). The result may indicate reversibility in the alkylation step, as inferred in reactions of **2** with alcohols[5] and siloxyfuran (**15**) (*vide infra*).

To further investigate the stereo- and regio-selective aspects of the vinylogous cationic complex (**2**), we sought an appropriately substituted furan (**15**) which when coupled with **2** would provide an intermediate (e.g. (**16**)) which could be further elaborated to the furanoid marine natural product kumausyne. Our approach to 2,4-disubstituted furan (**15**) (Scheme 3) started from the sodium salt of benzyl alcohol and its substitution reaction with 1,1-diethoxy-2-bromoethane in the presence of a catalytic amount of tetrabutylammonium iodide. From this reaction the benzyloxyacetaldehyde diethyl acetal (**11**) was obtained in 65% yield; its structure was confirmed spectroscopically. The acetal (**11**) was hydrolyzed in the presence of acidic Amberlyst resin in aqueous acetone. The resulting aldehyde was obtained in nearly quantitative yield after workup. Aldehyde (**11**) was then converted to the corresponding oxime (**12**) using hydroxylamine in aqueous ethanol in 95% yield. We also noticed that the acetal on a longer reaction time was also converted directly to the oxime under the same conditions. The oxime was converted to the isoxazole (**13**) by treatment with NBS at -20°C in DMF and subsequently with a mixture of triethylamine and propargyl alcohol. The resulting isoxazole was obtained in 95% yield. The nmr spectrum of **13** exhibited a resonance for H-4 at 6.33 ppm. The ir and mass spectra were confirmatory.

Scheme 3



Reagents: (a) $NH_2OH{\cdot}HCl$, $EtOH/H_2O$, 48 h; (b) NBS, $HC{\equiv}CCH_2OH$, Et_3N/Et_2O, 40°C; (c) Ra Ni/HOAc, H_2;
(d) LDA/THF, -78°C, TmsCl

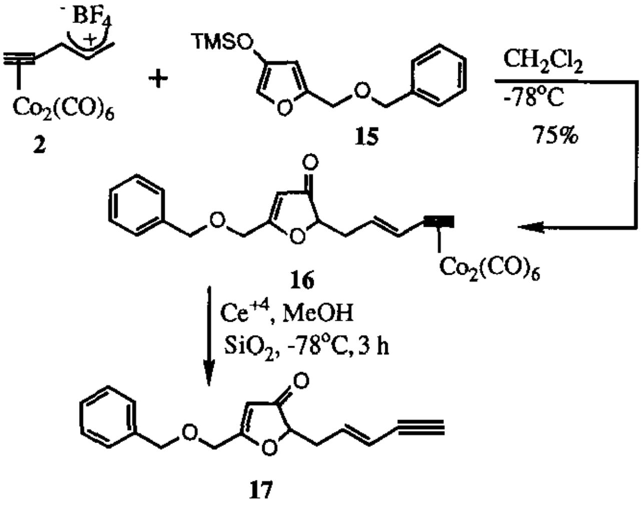
Isoxazole (**13**) was subjected to hydrogenolysis using Raney nickel in acetic acid under hydrogen. The dihydrofuranone (**14**) was obtained as a very viscous light red liquid in moderate to good yield of 75%. A key resonance in the nmr spectrum was observed at 5.70 (H-4) indicating that the isoxazole had been hydrogenolyzed. The mass spectrum was again supportive. The dihydrofuranone (**14**) was treated at -78°C with lithium diisopropylamide in THF followed by quenching with trimethylsilyl chloride. The trimethylsiloxy-substituted furan (**15**) was obtained in 88% yield as a light orange oil. The structure was confirmed by nmr (two singlets at 7.10 and 6.10 ppm corresponding to H-2 and H-4) and nominal and high resolution mass spectrometry.

The key alkylation reaction was carried out by adding furan (**15**) dropwise to the prepared cation (**2**) dissolved in methylene chloride at -78°C. The reaction (Scheme 4) was complete in less than 5 min. The isolated alkylated product (**16**) was obtained in 75% yield. ^1H nmr established the E-stereochemistry of the product from the coupling constant of

14.5 Hz between the two vinyl protons on the en-yne unit side chain. The reaction between the cation and the heterocycle thus occurs at the terminus of the α-vinyl cation (**2**). Interestingly, if the alkylation is performed above -45° C we noticed a significant amount of the internal attack product, suggesting that the latter may actually be thermodynamically favored.

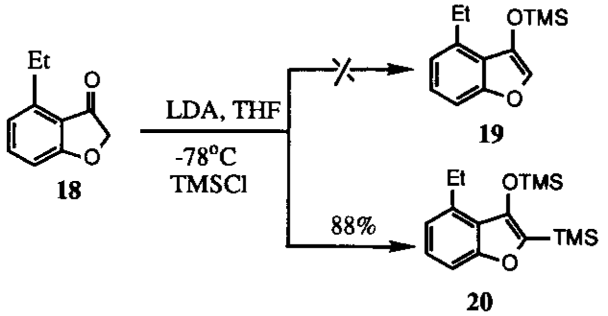
We suspect that selective formation of the E-isomer reflects a transoid structure of the cation (**2**) which minimizes steric interactions between the bulky (alkyne)$Co_2(CO)_6$ substituent and the internal hydrogens of the allyl unit. Since the cobalt complex functions as a powerful electron donating group,[1] we suggest that regioselective formation of the product from nucleophilic attack at C-1 on **2** is due to maximum overlap of the HOMO of the nucleophile with the LUMO of the electrophile, which has a larger coefficient on C-1. Furanone (**17**) is an attractive intermediate for the synthesis of the marine natural product kumausyne.[7] Initial efforts at selectively reducing the α,β-unsaturated moiety to the saturated alcohol derivative have not been successful thus far but we are currently seeking alternatives to achieve this goal.

Scheme 4



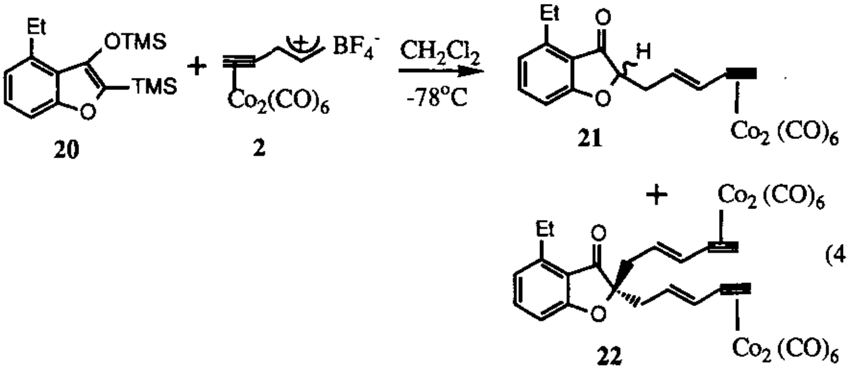
Panacene is one of many halogenated marine natural products isolated from *Aplysia brasiliana*, a large slug-like gastropod mollusk indigenous to the gulf coast of Florida.[16] A total synthesis of panacene has been accomplished by Feldman and coworkers.[17] We anticipated that alkylation of a suitable silyl enol ether by **2** would enable us to synthesize the benzo[*b*]furanone derivative (**21**), an attractive panacene precursor, in a regio- and stereoselective manner.

Our approach to panacene began with 4-ethylbenzo[*b*]-3(2*H*)-furanone (**18**) prepared according to Feldman and Hauser.[17,18] As shown in eq. 3, when **18** was added dropwise to a solution of lithium diisopropylamide in dry THF at -78° C followed by quenching with trimethylsilyl chloride, 2-trimethylsilyl-3-trimethylsiloxy-4-ethylbenzo[*b*]furan (**20**) was obtained in 88% yield. The nmr spectrum of **20** exhibited equal intensity resonances at 0.37(s) and 0.28(s) ppm indicating the presence of two trimethylsilyl groups and no olefinic resonance was present. The mass spectrum showed an appropriate molecular ion M^{+}=306.1 (100). A plausible explanation for this unexpected outcome could be the presence of excess lithium diisopropylamide which was able to remove the α-proton; the resulting dilithio derivative could then be disilylated to give **20** . No efforts have been made to correct this problem.



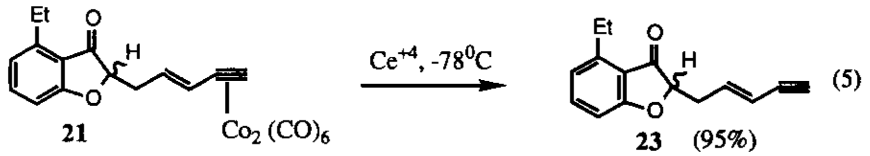
(3)

Nonetheless, disilyl derivative (**20**) was alkylated with the enyne cation (**2**) (eq. 4) in the usual fashion and the reaction was over within 5 min. Upon work-up and chromatography two products, (**21**) and (**22**), were isolated in a 1:2 ratio and a combined yield of 80%. Compound (**21**) was shown to be a monoalkylated product by ms (M^{+}-CO = 484) and ^{1}H nmr integration. Key ^{1}H nmr resonances for **21** appeared at 6.07 ppm (complexed acetylenic proton) and at 6.64 and 6.01 ppm (J=17.9 Hz, trans vinylic protons). Compound (**22**) proved to be dialkylated by ms and nmr integration. Trans vinylic proton resonances were observed at 6.54 and 5.87 ppm (J=14 Hz) and the complexed acetylenic resonance appeared at 6.04 (s). Both **21** and **22** showed the expected furanone carbonyl ir absorptions [**21** at 1715 cm^{-1}, **22** at 1710 cm^{-1}). How are complexes (**21**) and (**22**) formed in the reaction of **2** with **20** ? Although no mechanistic studies have been conducted, we suspect that **21** is the result of attack by **2** at C-2 of **20** followed by desilylation (by the Me_3SiBF_4 produced). Alternatively, Me_3Si migration from C-2 to O- of the initial alkylation product followed by a second alkylation by **2** at C-2 could produce **22** .

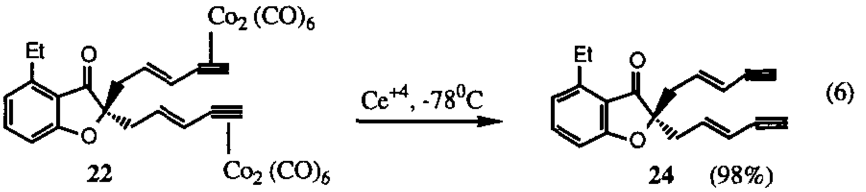


(4)

Further proof of the structures of **21** and **22** was secured by their individual demetallation with ceric ammonium nitrate/silica gel in methanol or acetone at -78°C (eq. 5,6). The reactions were over after 2 h. After evaporation and chromatography, the resulting colorless acetylenic compounds (**23**) and (**24**) were isolated and characterized spectroscopically. For **23** key resonances (*inter alia*) were observed at 5.65 (d, J=15.9 Hz, 1H, vinylic), 4.54 (m,1 H, H-2), and 2.83 (d, J=2.1 Hz, 1H, acetylenic H). The mass spectrum of **23** exhibited a peak for the molecular ion at m/z=226.0 (8.3) and a satisfactory hrms was obtained. For **24** the nmr spectrum contained resonances (*inter alia*) at 6.08 (m, 2 H), 5.56 (d, J=15.9 Hz, 2 H, trans H's), 2.79 (m, 2 H, acetylenic protons), and 2.58 (m, 4 H, two sets of methylenes for the 1,3-pentenyne). The mass spectrum showed a peak for the molecular ion at m/z = 290.2 (2.3) and correct hrms. Both the mono and dialkylated products thus exhibit the same regio- and stereochemistry as had been observed in the prior work on the furan series. En-yne (**23**), although obtained as the result of two unexpected reactions, nonetheless can be converted to the halogenated allene panacene (or its epimer) according to the method of Feldman and coworkers,[17] thus constituting a formal total synthesis.



21 **23** (95%)



22 **24** (98%)

These initial efforts have demonstrated the efficacy of introducing various alkyl, propargyl (and potentially allyl) side chains as well as the (E)-2,4-pentenyne unit via coupling of electrophilic complexes (**1**) and (**2**) with substituted furans.

EXPERIMENTAL

All reactions and manipulations were conducted under a nitrogen atmosphere utilizing standard Schlenk line techniques. Penten-4-yn-3-ol was prepared according to reference 19, the dicobalt hexacarbonyl propargyl alcohol complexes were synthesized according to reference 20. Compound (**11**)[21] was synthesized by a modified procedure. Precusor compounds to **18** were synthesized according to references 17, 18. Solvents and common reagents were obtained commercially and used as received or purified as follows: tetrahydrofuran and diethyl ether were distilled under nitrogen from sodium/benzophenone; methylene chloride and pentane were distilled under nitrogen from calcium hydride. Thin layer chromatography was carried out on 0.2 mm silica gel coated plastic sheets with F-254 indicator (EM). Column chromatography was carried out using flash silica gel (230-400 mesh). Gas chromatography was carried out on a Hewlett Packard 5790 instrument using a 1/8" x 6' column packed with OV101. Ir spectra were recorded as thin films on salt discs on a Perkin Elmer model 1420 spectrophotometer. ^1H- and ^{13}C-nmr spectra were recorded on a Varian XL-300 spectrometer equipped with a VXR-4000 data station. $CDCl_3$ was used as solvent unless otherwise specified. Low and medium resolution mass spectra were obtained on a Hewlet Packard 5985 or a Kratos MS 25 RF instrument at 12 or

70 ev. High accuracy mass spectra were obtained on a VG Instruments Zab E spectrometer. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana.

Hexacarbonyl-μ-(η ^{2}-[1-penten-4-yne-3-ol])-dicobalt (*Co-Co*) (2A)

A 250 ml round-bottom flask fitted with a gas inlet and a magnetic stirring bar was charged with 2.6 g (0.03 mol) of 1,4-pentenyne-3-ol in 50 ml of dry pentane under a flow of nitrogen. Then 13 g (0.03 mol) of dicobalt octacarbonyl was added and the mixture was allowed to stir at room temperature until no evolution of CO was observed (3 h). The solvent was evaporated and the residue was filtered through a column of neutral alumina with pentane followed by ether. After the ether was evaporated, a dark red oil (7.3 g) was obtained in 55% yield. Ir: 3400, 2250, 2100, 2000 1650 cm^{-1};^{1}H nmr: 6.10(s, 1 H), 5.9(m, 1 H), 5.50(d, J=17.4 Hz, 1 H), 5.30(m, 1 H), 5.10(d, J=10.2 Hz, 1 H); ms: M$^+$= 368 (2.7), 340 (63), 312 (100), 284 (94), 256 (98), 228 (78), 200 (68).

Hexacarbonyl-μ-(η ^{2}-[(1-penten-4-(1,3-ynylium)])-tetrafluoroborate]-dicobalt (*Co-Co*) (2)

To 6.01 g (0.02 mol) of (1-penten-4-yn-3-ol)$Co_2(CO)_6$ dissolved in 20 ml of dry ether and 10 ml of propionic anhydride at -45°C was added 10.0 ml of tetrafluoroboric acid diethyl ether complex. The salt, a dark red solid, was obtained after thoroughly washing the precipitate with ether. This salt was then used immediately to alkylate the oxygen heterocycles.

Hexacarbonyl-μ-(η ^{2}-[5-(2-propynyl)-5H-furan-2-one])-dicobalt (*Co-Co*) (6a)

[Propargyl alcohol]dicobalt hexacarbonyl (1.2 g, 3.5 mmol) was dissolved in 10 ml of propionic anhydride and the mixture was cooled to -45 °C followed by the addition of 10 ml of tetrafluoroboric acid diethyl etherate. The mixture was stirred at this temperature for 10 min. The resulting solid was washed with ether and dried under vacuum. To the resulting cationic salt dissolved in 10 ml of methylene chloride was added dropwise 0.50 g (3.2 mmol) of 2-trimethylsiloxyfuran dissolved in 20 ml of methylene chloride. After 10 min the reaction was over as determined by tlc. The mixture was treated with saturated sodium bicarbonate. After separation, the organic layer was treated with saturated brine. The organic phase was separated, dried and evaporated. After chromatography [(pentane/ether 2:1)/silica gel)] the isolated yield of 6a (red oil) was 1.2 g (72%). Physical and spectroscopic data are provided in Table 1.

Hexacarbonyl-μ-(η ^{2}-[5-(2-butynyl)-5H-furan-2-one])-dicobalt (*Co-Co*) (6b)

[Butynylium]$Co_2(CO)_6BF_4$ (1.94 g, 0.005 mol) derived from [2-butyn-1-ol]dicobalt hexacarbonyl and tetrafluoroboric acid[20] was dissolved in 25 ml of dry methylene chloride. The reaction mixture was cooled to -45°C then 0.90 ml (0.005 mol) of 2-trimethylsiloxyfuran dissolved in 20 ml of methylene chloride was added dropwise and the mixture was stirred for 5 min. After treatment with aqueous sodium bicarbonate and brine, separation of the layers, and drying over magnesium sulfate, the solvent was evaporated and the residue was chromatographed over silica (pentane/hexane 2:1) to furnish a brick red solid (1.5 g) in 78% yield. Physical and spectroscopic data are provided in Table 1.

Anal. Calcd for $C_{14}H_8O_8Co_2$: C, 39.84; H, 1.91. Found: C, 39.91; H, 1.84.

Hexacarbonyl-μ-(η ^{2}-[5-(2-pentynyl)-5H-furan-2-one])-dicobalt (Co-Co) (6c)

To 2.0 g (0.005 mol) of [2-pentyn-1-ol]$Co_2(CO)_6$ dissolved in 15 ml propionic anhydride at -45°C was added 15 ml of tetrafluoroboric acid diethyl etherate and the mixture was stirred at this temperature for 10 min. The solid that formed was washed several times with ether and dried under vacuum. The isolated red solid was dissolved in 25 ml dry methylene chloride, the solution cooled to -45°C, and 0.54 g (0.0034 mol) of 2-trimethylsiloxyfuran dissolved in 10 ml of methylene chloride was added dropwise. The mixture was stirred for 10 min at this temperature. After washing with aqueous sodium bicarbonate and brine, drying with magnesium sulfate, the solvent was evaporated and 0.91 g of a brick red solid (70%), **6c**, was obtained after chromatography over silica gel (pentane/ether 2:1). Physical and spectroscopic data are provided in Table 1. *Anal.* Calcd. for $C_{15}H_{10}O_8Co_2$: C, 41.32; H, 2.31. Found: C, 40.85; H, 2.41.

Hexacarbonyl-μ-(η ^{2}-[5-(2-octynyl)-5H-furan-2-one])-dicobalt (*Co-Co*) (6d)

In a round-bottomed flask *equipped with a side arm was added 2.9 g (0.007 mol) of [2-octyn-1-ol]*$Co_2(CO)_6$ *dissolved in* 10 ml dry ether and 5 ml of propionic anhydride. The mixture was cooled to -45°C and 5 ml of tetrafluoroboric acid diethyl etherate was added. The mixture was stirred for 15 min. The resulting oily red layer was washed several times with ether and after decantation the ether was completely removed under vacuum. To the oily residue was added 20 ml dry methylene chloride and the temperature was maintained at -45°C. Then 1.18 ml (0.007 mol) of 2-trimethylsiloxyfuran dissolved in 20 ml of methylene chloride was added dropwise and the mixture was allowed to stir for 5 min whereupon the reaction was complete. After treating the reaction mixture with aqueous sodium bicarbonate and brine, the organic layer was dried with magnesium sulfate. The solvent was evaporated and the residue chromatographed over silica gel using pentane/ether (2:1) as the eluents. The isolated yield of the dark red oil (**11**) was 3.0 g (65%). Physical and spectroscopic data are provided in Table 1.

(±)-Tetrahydrofuran-5-octyl-2-one (8). Oxidative demetallation of hexacarbonyl-μ-(η ^{2}-[5-(2-octynyl)-5H-furan-2-one])-dicobalt (*Co-Co*) (6d) and reduction of 7.

In a 100 ml round-bottomed flask equipped with a side arm was added 0.22 g (0.46 mmol) of **6d** dissolved in 20 ml acetone. This mixture was added dropwise to a mixture of silica gel (10 g) and ceric ammonium nitrate (20 g) in acetone at -78 °C. After 3 h the solid support was filtered and the solvent evaporated. The residue was treated with water and ether. The ether layer was dried with magnesium sulfate and was evaporated to give 0.075 g (0.39 mmol, 85%) of 7 . The crude product was treated with 10% Pd/C and hydrogen (1 atm) in ethanol overnight. The catalyst was removed by filtration through Celite. Afer the solvent Cevaporated, the residue was chromatographed on silica gel using pentane/ether as the eluent. The isolated yield of the light yellow liquid (**8**) was (98%). Ir: 1780, 1100, 1040 cm-1; *nmr: δ 4.50 (m, 1 H); 2.55 (m, 1 H);* 2.35 (m, 1 H); 1.75 (m, 8 H); 1.35 (m, 8 H); 0.89 (br t, J=7.5 Hz, 3 H); ms: M^+= 198 (0.1), 162.0 (1.0), 128.1 (10.1), 85.0 (100); hrms: Calcd for $C_{12}H_{22}O_2$: 198.162; Found: 198.162.

Hexacarbonyl-μ-(η ^{2}-[5-(E-2-penten-4-ynyl)-5H-furan-2-one])-dicobalt (*Co-Co*) (9) and hexacarbonyl-μ-(η ^{2}-[3-(1-penten-4-ynyl)]-5H-furan-2-one])-dicobalt (*Co-Co*) (10)

A 250 ml round-bottomed flask equipped with a side arm was charged with 0.5 g (0.001 mol) of [1-penten-4-yn-3-ol]$Co_2(CO)_6$ in 10 ml of dry ether and 5 ml of proprionic anhydride. The mixture was cooled to -45°C and 15 ml of tetrafluoroboric acid diethyl etherate was added and the red mixture was stirred for 10 min. The precipitate was thoroughly washed with ether and dissolved in 25 ml dry methylene chloride. Then 0.24 g (0.001 mol) of 2-trimethylsiloxyfuran dissolved in 15 ml of methylene chloride was added dropwise at -45°C and allowed to stir for 5 min.

Aqueous sodium bicarbonate was added to the mixture and the organic layer was treated with brine. After drying with magnesium sulfate, the solvent was evaporated. The isolated yields of the dark red oils (**9**) and (**10**) after chromatography [(pentane/ether 2:1)/silica, where compound (**10**) eluted first] were 56% (0.24 g) and 19% (0.082 g). Physical and spectroscopic data are provided in Table 1.

2-Benzyloxyacetaldehyde diethylacetal (11)

Benzyl alcohol (51.7 ml, 0.50 mol) was slowly added to a suspension of 50% NaH (24 g, 0.55 mol) in THF (500 ml) and then 2-bromoacetaldehyde diethylacetal (76 ml, 0.50 mol) and a catalytic amount of tetrabutylammonium iodide (1.8 g, 0.01 mol) were added. The reaction mixture was refluxed for 8 h. The precipitate of NaBr was filtered off, the solvent was evaporated, and the product was distilled; bp= 95-100°C/0.2 mm, Lit.,[21] b_{12} 143°C; the yield was 65% (73 g). Ir: 2990, 2800, 2000-1800, 1600, 1450, 1370, 1300, 1100, 750 cm^{-1}; nmr: 7.15 (s, 5 H); 4.67 (t, J=5.2 Hz, 2 H); 4.58 (s, 2 H); 3.65 (m, 4H); 3.52 (d, J=5.3 Hz, 2 H); 1.22 (dt, J=7.3, 7.3 Hz, 6 H); ms: 133.9 (14.0), 103.0 (100), 91.1 (48.3).

2-Benzyloxyacetaldoxime (12)

Hydroxylamine hydrochloride (17.0 g, 0.25 mol) dissolved in 20 ml of water was added to a solution (40 ml of 95% ethanol and 30 ml of water) of 2-benzyloxyacetaldehyde diethylacetal (18.32 g, 0.082 mol). The mixture was stirred at room temperature until the reaction was complete (about two to three days). Water (100 ml) was added and the organic phase was exhaustively extracted with about 200 ml of methylene chloride. The organic phase was dried over and evaporated and the residue was purified via chromatography on silica gel using pentane/ether (2:1). The yield of the colorless viscous liquid was 12.8 g (95%). Ir: 3300, 2830, 2000-1800, 1600, 1450, 1100 cm^{-1}; nmr: 7.52 (t, J=5.7 Hz, 1 H, syn); 7.35 (s, 5 H); 6.93 (t, J=3.5.Hz, 1 H, anti); 4.55 (s, 2H); 4.53 (s, 2 H); 4.38 (d, J=3.7 Hz, 2 H, anti); 4.12 (d, J=5.7 Hz, 2H, syn); ms: M^+= 165 (0.3), 164.1 (0.1), 106.9 (100) 108.1 (13.3), 92.1 (14.3).

3-Benzyloxymethyl-5-hydroxymethyl-isoxazole (13)

A mixture of benzyloxy acetaldoxime (38.0 g, 0.231 mol) and NBS (2 equiv.) in dry DMF was allowed to react at -20°C for 2 h and then at 0°C for 1 h. The mixture was diluted with ether such that *N*-bromosuccinimide precipitated and then, a solution of propargyl alcohol (60 ml) and triethylamine (34 ml, 0.23 mol) in dry ether was added. The reaction mixture was stirred at room temperature until complete as judged by tlc. After hydrolytic work-up, extraction with methylene chloride (200 ml) and purification via chromatography [flash silica gel, pentane/ether (2:1)], the isoxazole (**13**) was isolated as (39.5 g) a viscous liquid (80%). Ir: 3400, 3070, 3040, 2890, 1615, 1460, 1100, 750 cm^{-1}; nmr: 7.33 (s, 5 H); 6.33 (s, 1 H); 4.75 (s, 2 H); 4.60 (s, 2 H); 4.55 (s, 2 H); ms: M^+= 219.0 (1.6), 220.0 (1.8), 113.0 (26.3), 107.0 (23.9), 91.1 (100).

5-Benzyloxymethyl-2H-furan-3-one (14)

About 0.3 g of Raney Nickel suspended in a pH 9.0 solution was neutralized with acetic acid and poured into a 500 ml round-bottomed flask which was charged with 4.71 g (0.022 mol) of the isoxazole dissolved in 50 ml of acetic acid. The mixture was flushed with nitrogen followed by hydrogen and finally a balloon, filled with hydrogen, was attached to the flask via an adapter. The hydrogen absorption was continued until the reaction was judged complete via nmr. After the catalyst was filtered on a bed of Celite, the acid was neutralized with solid sodium bicarbonate and the organic compound was extracted with ether. The organic phase was dried over sodium sulfate and evaporated followed by chromatography over silica gel using pentane/ether (2:1) to give 2.55 g of **14** as a thick liquid 70%. Ir: 3400, 3060, 3040, 2920, 2890, 2000-1800, 1705, 1600, 1110 cm^{-1}; nmr: 7.35 (s, 5 H); 5.75 (s, 1 H); 4.63 (s, 2 H); 4.52 (s, 2 H) 4.33 (s, 2 H); ms: M^{+}= 204 (0.1), 113.1 (0.3), 107.1 (5.3), 98 (100), 91.1 (3.1).

4-Trimethysiloxy-2-benzyloxymethyl-furan (15)

To 0.50 ml (0.004 mol) of diisopropylamine dissolved in 10 ml dry THF was added 2.15 ml (0.0035 mol) of 1.6 M butyllithium at 0°C. The mixture was stirred under nitrogen for 30 min and was cooled to -78°C (dry ice/acetone). The furanone (14) (0.5 g, 0.003 mol) dissolved in 20 ml of dry THF was added dropwise. The mixture was stirred for 30 min followed by the addition of 0.35 ml (0.003 mol) of trimethylsilyl chloride. The mixture was allowed to warm to room temperature and dry pentane was added to separate the product from the lithium salt. After several filtrations and addition of pentane and the solvent was evaporated; the resulting liquid product (0.73 g) was obtained in 88% yield. Ir: 2980, 2000-1800, 1620, 1545, 1255, 1150, 850, 750 cm^{-1}; nmr: 7.35 (s, 5 H); 7.10 (s, 1 H); 6.10 (s, 1 H); 4.54 (s, 2 H); 4.38 (s, 2 H); 0.24 (s, 9 H); ms: M^{+}= 276.0 (48.3); 277.1 (11.3), 169.0 (85.9), 170.0 (44.8), 91.1 (100), 73.0 (85); hrms: Calcd for $C_{15}H_{20}O_3Si$: 276.1182; Found: 276.1176.

Hexacarbonyl-μ-(η^2-[2-((E)-2-penten-4-ynyl)-5-benzyloxymethyl-2H-furan-3-one])-dicobalt (*Co-Co*) (16)

To 0.5 g (0.0013 mol) of [1-penten-4-yn-3-ol]$Co_2(CO)_6$ dissolved in 10 ml of dry ether was added 0.21 g of tetrafluoroboric acid diethyl etherate at -45°C and the mixture was allowed to stir for 10 min. The resulting brick red solid was thoroughly washed with ether and was dissolved in 30 ml of dry methylene chloride followed by the dropwise addition of 0.37 g (0.0014 mol) of **15** dissolved in 20 ml of methylene chloride. Tlc analysis indicated the reaction was over within 5 min. The reaction mixture was poured into a solution of aqueous sodium bicarbonate and the organic phase was removed and further treated with brine. The organic phase was dried with magnesium sulfate and evaporated. After chromatography (pentane/hexane 2:1) on flash silica gel, the isolated yield of **16**, a dark red viscous liquid, was 0.54 g (75%). Ir: 2940, 2870 2100, 2060, 2030, 1710, 1615, 1260, 1110, 950, 750 cm^{-1}; nmr: 7.35 (s, 5 H); 6.62 (d, J=15 Hz, 1 H); 6.12 (s, 1 H); 5.97 (dt, J=7.3, 15 Hz,1 H); 5.71 (s, 1 H); 4.62 (s, 2 H); 4.55 (dd, J=4.9, 7.3 Hz, 1 H); 4.30 (s, 2 H); 2.80 (dq, J=7.3, 15 Hz,1 H); 2.61 (dt, J=7.3, 14.9 Hz, 1 H); ms: m/z: 498 (2.8), 499 (2.8), 470.0 (26.6), 442.0 (17.2), 386 (100); *Anal.* Calcd for $C_{23}H_{16}O_9Co_2$: C, 49.79; H, 2.88. Found: C, 49.84; H, 2.94.

2-(E-2-penten-4-ynyl)-5-benzyloxymethyl-2H-furan-3-one (17)

A mixture of 10 g of flash silica and 12 g of ceric ammonium nitrate was placed in a 250 ml round-bottomed flask with a side arm and a solution of 0.222 g (0.40 mmol) of **16** dissolved in 45 ml of acetone was added in 50 ml of acetone at -78°C. The liberated carbon monoxide was allowed to escape to the hood. After 3 h the mixture was filtered and the solvent was evaporated. The residue was washed with brine and dried with magnesium sulfate and the solvent was evaporated. The residue was passed through a short column of silica using pentane/ether (2:1). The amount isolated was 0.110 g (90%) of **17** as a light yellow viscous liquid. Ir: 2945, 2880, 2100, 2000, 1800, 1705, 1605, 1110 cm^{-1}; nmr: 7.35 (s, 5H); 6.15 (m, 1 H); 5.75 (s, 1 H); 5.50 (d, J=14.5 Hz, 1 H); 4.60 (s, 2 H); 4.45 (dd, J=6.3, 5.4 Hz, 1 H); 4.20 (s, 2 H); 2.65 (m, 1 H); 2.55 (d, J=2.0 Hz, 1 H); 2.45 (m, 1 H).

4-Ethyl-2-trimethysilyl-3-trimethylsilyloxybenzo[*b*]furan (20)

To 6.40 ml (0.05 mol) of diisopropylamine in 50 ml of dry THF was added 28.52 ml of 1.6 M butyllithium (0.05 mol) at 0°C and the mixture was stirred for 30 min and then cooled to -78°C. To the cooled solution was added dropwise 7.39 g (0.0046 mol) of **18** in 25 ml THF and the mixture was stirred at this temperature for 1 h. The mixture was then quenched with 8.0 ml of trimethylsilyl chloride and allowed to stir for another hour. Dry pentane was then added in order to extract the product from the lithium salts. The extraction process was repeated until there were no more salts in the organic phase. After evaporation, the product (**20**), an orange liquid, was obtained in 88% yield (1.24 g) and used without further purification. Ir: 2940, 1610, 1590, 1540, 1350, 1250, 1085, 850 cm^{-1}; nmr: 7.18 (m, 2 H); 6.96 (d, J=6.7 Hz, 1 H); 3.00 (q, J=7.5 Hz, 2 H); 1.25 (t, J=7.5 Hz, 3 H); 0.37 (s, 9 H); 0.28 (s, 9 H); ms: M$^+$= 306.1 (100), 307.1 (26.3), 232.0 (16.0), 73.1 (11.7).

Hexacarbonyl-μ-(η^2-[2-(E-2-penten-4-ynyl)-4-ethyl-2H-benzo[*b*]furan-3-one])-dicobalt (*Co-Co*) (21) and dodecacarbonyl-μ-(η^2-[2-(bis-E-2-penten-4-ynyl)-4-ethyl-2H-benzo[*b*]furan-3-one])-tetracobalt (*Co-Co*) (22)

A 250 ml round-bottomed flask equipped with a side arm was charged with 1.104 g (0.003 mol) of the alcohol complex (**2A**) and 15 ml of propionic anhydride was added. The mixture was cooled to -45°C (3-pentanone/dry ice). About 5 ml of tetrafluoroboric acid diethyl etherate was added via a syringe and the mixture was allowed to stir for 10 min at the same temperature. The brick red solid that formed was thoroughly washed with ether and dried under vacuum. The solid was dissolved in 50 ml of dry methylene chloride followed by the addition of 0.92 g (0.003 mol) of **20** dissolved in 10 ml of methylene chloride. After 10 min the reaction was over as indicated by tlc. Dilute sodium bicarbonate was added followed by treatment with brine. The organic phase was dried with magnesium sulfate and evaporated. The total yield after chromatography with pentane/ether (95:5)/flash silica gel was 80% and the dark red liquids were isolated in yields of 26.6% (0.41 g) (**21**) and 53.4% (**22**). In order of elution, **22** was the first to be isolated followed by **21** . Ir (**21**): 2990, 2940, 2100, 2060, 2020, 1715, 1600, 1500, 1240 cm^{-1}; ^{1}H nmr: 7.45 (t, J=7.4 Hz, 1 H); 6.89 (d, J=8.3 Hz, 1 H); 6.82 (d, J=7.4 Hz, 1 H); 6.64 (d, J=17.9 Hz, 1H); 6.07 (s, 1 H); 6.01 (m, 1 H); 4.57 (m, 1 H); 3.00 (q, J=7.5 Hz, 2 H); 2.87 (m, 2 H); 1.22 (t, J=7.5 Hz, 3 H); ^{13}C-nmr: 210.8; 199.8 (m); 173.7; 146.6; 138.2; 138.0; 130.7; 130.6; 121.8; 110.9 ; 84.0; 76.8; 74.0; 34.9; 25.0; 14.8; ms: 484 (M$^+$-28, 0.1), 455.8 (3.8), 427.9 (13.4), 399.8 (9.0), 371.9 (3.3), 343.9 (2.8), 162.0 (100). Ir(**22**): 2955, 2940, 2100, 2020, 1710, 1600, 1500, 1130, 750 cm^{-1}; nmr: (**22**) 7.41 (t, J=7.4 Hz, 1 H); 6.86 (d, J=8.3 Hz, 1 H); 6.76 (d, J=7.4 Hz, 1 H); 6.54 (d, J=14 Hz, 2 H); 6.04 (s, 2 H); 5.87 (m, 2 H); 2.90 (q, J=7.5 Hz, 2 H); 2.65 (d,J=7.4 Hz, 4 H); 1.25 (t, J=7.5 Hz, 3 H); ms: 455.8 (8.0), 294.2 (9.6), 267.2 (10.4), 238.2 (11.2), 210.1 (13.6), 182.0 (24.0).

2-(E-2-penten-4-ynyl)-4-ethyl-2H-benzo[*b*]furan-3-one (23) and bis-2-(E-2-penten-4-ynyl)-4-ethyl-2H-benzo[*b*]furan-3-one] (24)

Each compound (1.0 mmol) was individually dissolved in acetone (50 ml) and was added to a cold mixture of silica gel and ceric ammonium nitrate (about 10 g total) in acetone (100 ml) at -78°C and the mixture was allowed to stir at this temperature until the color of the reaction mixture turned yellow (3 h). The solid support was filtered and the solvent was evaporated. Water was added to the residue and ether was added to extract the organic product. The solvent was evaporated and the crude product was purified via chromatography: (pentane/ether 2:1)/flash silica gel. The yields were

95% and 98%. Compounds (**23**) (0.21 g, 95%) and (**24**) (0.28 g, 98%) were obtained as low melting solids. Nmr (**23**): 7.49 (t, J=7.4 Hz,1 H); 6.93 (d, J=8.3 Hz, 1 H); 6.87 (d, J=7.5 Hz, 1 H); 6.24 (m, 1 H); 5.65 (d, J=15.9 Hz, 1 H); 4.54 (m, 1 H); 2.99 (q, J=7.5 Hz, 2 H); 2.83 (d, J=2.1 Hz, 1 H); 2.84 (m, 1 H); 2.56 (m, 1 H); 1.23 (t , J=7.5 Hz, 3H); ms: M^+= 226.0 (8.3), 225.0 (7.6), 211.0 (19.0), 197.0 (100), 161.0 (69.9); hrms : Calcd for $C_{15}H_{14}O_2$: 226.0994; Found: 226.0994. Nmr (**24**): 7.51 (t, J=7.4 Hz, 1 H); 6.91 (d, J=8.19 Hz, 1 H); 6.86 (d, J=7.4 Hz, 1 H); 6.08 (m, 2 H); 5.56 (d, J=15.9 Hz, 2 H); 2.98 (q, J=7.5 Hz, 2 H); 2.79 (m, 2 H); 2.58 (m, 4 H); 1.25 (t, J=7.5 Hz, 3H); ms: M^+= 290.2 (2.3), 289.0 (3.8), 260.9 (7.7), 225.0 (32.0), 196.9 (100), 175.0 (37.3); hrms: Calcd for $C_{20}H_{18}O_2$: 290.1307; Found: 289.1340 $[M\text{-}H]^+$.

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REFERENCES

1 K. M. Nicholas, *Acc. Chem. Res.*, 1987, **20**, 207 .

2 Review: J. Wotiz, "Chemistry of Acetylenes," ed. by H. G. Viehe; Marcel Dekker: New York, 1969, p. 365.

3 K. M. Nicholas, M. Saha, and B. Bagby, *Tetrahedron Lett.*, 1986, **27**, 915.

4 K. M. Nicholas, A. Montana,and M. A. Khan, *J. Org. Chem.*, 1988, **53**, 5193.

5 K. M. Nicholas and S. Padmanabhan, *Tetrahedron Lett.*, 1982, **23**, 2556.

6 H. J. Jaffer and P.L. Pauson, *J. Chem. Res.*(S), 1983, 2201.

7 E. Kurosawa, T. Suzuki, and K. Koizuma, *Chemistry Lett.*, 1983, 1643.

8 F. J. Schmitz and D. J. Vanderah, *J. Org. Chem.*, 1976, **41**, 3480.

9 M. Itoh, *Agric. Biol., Chem.*, 1974, **38**, 485.

10 R. ter Heide in "Analysis of Foods and Beverages", ed. by . G. Charalambous, Academic Press, New York, 1978, p. 275.

11 G.T. Muys, B. van der Ven, and A.P. de Jonge, *Nature*, 1962, **194**, 995; J. M. Wheeler, G.M. Happ, J. Araujo, and J.M. Pasteels, *Tetrahedron Lett.*, 1972, 4635.

12 Review: D.M.X. Donnelly and M.J. Meegan, "Furans and Their Benzo Derivatives: Synthesis and Applications", in "Comprehensive Heterocyclic Chemistry", ed. by C.W. Bird and G.W.H. Cheeseman, Pergamon Press, London, 1984, p. 671.

13 C. W. Jefford, A. W. Sledeski, and J. Boukouvalas., *J. Chem. Soc. Chem. Commun.*, 1988, 364.

14 G. Casiraghi, *J. Org. Chem.*, 1990, **55**, 2565.

15 J. Boukouvalas, C. W. Jefford, D. Jaggi, and G. Bernardinelli., *Tetrahedron Lett.*, 1987, **28**, 4041; J. Boukouvalas, C. W. Jefford, and D. Jaggi, *Tetrahedron Lett.*, 1989, **30**, 1237.

16 R. B. Kinnel, A. J. Duggan, T. Eisner, and J. Meinwald, *Tetrahedron Lett.*, 1977, 3913.

17 K. S. Feldman, C. C. Mechem, and L. Nader, *J. Am. Chem. Soc.*, 1982, **104**, 4011.

18 F. M. Hauser and S. A. Pogany, *Synthesis*, 1980, 814.

19 L. Brandsma and H. D. Verkruijsse, "Synthesis of Acetylenes, Allenes and Cumulenes", Elsevier, New York, 1981, p. 78.

20 K. M. Nicholas, M. Saha, and V. Varghese, *Org. Synth.*, 1989, **76**, 141.

21 M. Rotbart, *Compt. Rend.*, 1933, **197**, 1225.

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