Novel Syntheses of Cyclopentenones and Alkenylsilanes from the Corresponding Alkyne−Dicobalt Hexacarbonyl Complexes

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Summary: Alkyne−$Co_2(CO)_6$ complexes, readily available through reduction of $CoBr_2$ with Zn in THF in the presence of alkynes while bubbling carbon monoxide at atmospheric pressure and room temperature, on reaction with CF_3COOH give the corresponding cyclopentenones. In the case of alkynylsilane complexes, the corresponding alkenylsilanes are formed.

Introduction

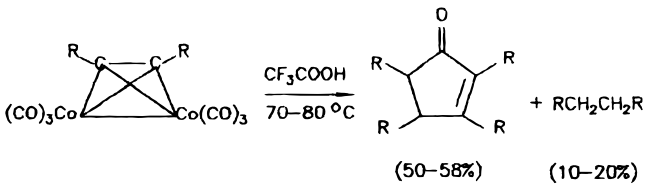
Carbonylation of alkynes using transition metal complexes is one of the most important transformations in synthetic organic chemistry.[1] Considerable attention has been focused on the construction of five-membered rings due to their occurrence in a diverse range of natural products.[2] Alkyne−dicobalt hexacarbonyl complexes have been widely employed for the synthesis of cyclopentenones (Pauson−Khand reaction[3]) and also in protecting alkyne moieties.[4] The Pauson−Khand reaction and related transformations involving the synthesis of cyclopentenones are still under active investigation.[5]

Herein, we report our results on the CF_3COOH-mediated intermolecular cyclization of alkynes with concomitant CO insertion to produce cyclopentenones.

Results and Discussion

In recent years, several convenient methods for *in situ* preparation of metal carbonyls and their derivatives have been developed in this laboratory.[6−10] One among these methods is the preparation of alkyne−dicobalt complexes in THF by the reduction of $CoBr_2$ with Zn in the presence of CO.[8] These complexes, prepared *in situ* in THF readily react with olefins to give the corresponding Pauson−Khand cyclopentenones. It was of interest to examine further utilization of these alkyne−dicobalt complexes in the development of new organic synthetic methods. In the course of these efforts, it was observed that alkyne−$Co_2(CO)_6$ complexes, prepared by the reduction of $CoBr_2$ with Zn, on reaction with CF_3COOH at 70−80 °C, give the corresponding cyclopentenones in moderate yields with interesting regioselectivities (Scheme 1, Table 1).

Scheme 1



It was found that this transformation is a general one and several other alkynes are also converted into the corresponding cyclopentenones. The results are summarized in Table 1. In all the cases, 10−20% of the corresponding alkanes are also formed. However, the carbonyl products can be readily separated from these side products.

It is of interest to note that minor amounts of 3-substituted cyclopentenones (**1b**, **2b**, and **3b**, Table 1) which are not generally formed under standard Pauson−Khand reaction conditions are also obtained here.[3a,11] There is a possibility that the presence of Zn or $ZnBr_2$ in the reaction mixture may have an effect. However, it should be pointed out that these 3-substituted cyclopentenones are not formed in the Pauson−Khand reaction using the alkyne−$Co_2(CO)_6$ complexes prepared using $CoBr_2$ and Zn with olefins in the absence of CF_3COOH.[8]

Wa have carried out several experiments in order to understand the mechanism and intermediates involved in this transformation. When the reaction was carried out with $(PhC{\equiv}CH)Co_2(CO)_6$ complex (1 equiv) in the presence of free PhC≡CH (1 equiv), there was no change in the yield of the products, indicating that the reaction involves only the complexed alkyne. The formation of the alkane side product is somewhat surprising since the alkyne−$Co_2(CO)_6$ complexes have been reported to give alkenes upon aqueous acid treatment.[11] However, this pattern of reactivity of the $(RC{\equiv}CR)Co_2(CO)_6$ complexes is not entirely unexpected since the $(RC{\equiv}CR)(Cp_2Zr)_2$ complex has been reported to give

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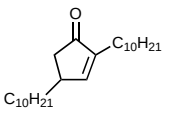
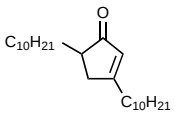
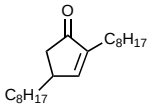
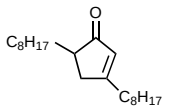
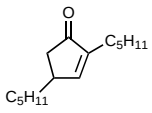
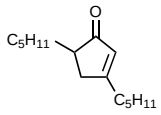
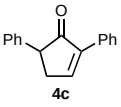
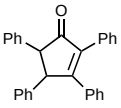
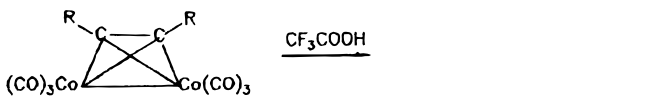
Table 1. Reaction of $(RC{\equiv}CR')Co_2(CO)_6$ Complexes with CF_3COOH

no.	alkyne	cyclopentenones[a,b]	yields (%)[c]
1	n-$C_{10}H_{21}C{\equiv}CH$	 **1a**	40
		 **1b**	15
2	n-$C_8H_{17}C{\equiv}CH$	 **2a**	40
		 **2b**	14
3	n-$C_5H_{11}C{\equiv}CH$	 **3a**	38
		 **3b**	12
4	PhC≡CH	 **4c**	35[d]
5	PhC≡CPh	 **5**	58

[a] All reactions were carried out using alkyne (10 mmol) complex. [b] All products were identified by spectral data (IR, ^{1}H NMR, and ^{13}C NMR-DEPT experiments). Mass spectral data are in accordance with the assigned structures. [c] Yields reported here are for products separated by column chromatography on silica gel using hexane/ethyl acetate (50:1) as an eluent and calculated on the basis of amount of alkyne used. [d] This product was separated by crystallization of the chromatographed mixture containing the 2,4-diphenylcyclopentenone (**4d**, 15%). Attempts to obtain a pure sample of the minor product **4d** were not successful. Spectral data for the mixture of **4c** and **4d** are given in the Experimental Section.

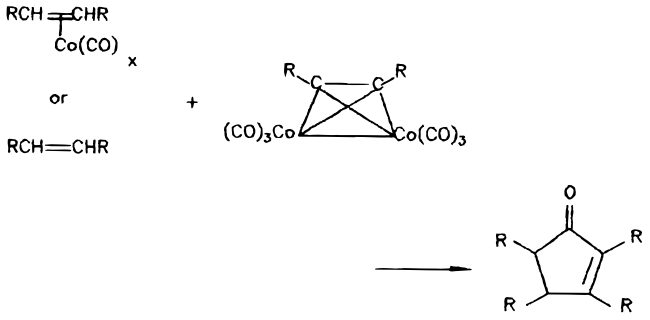
Scheme 2



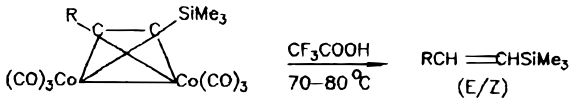
RCH_2CH_2R on treatment wiht H_2O.[12] Presumably, in the present case the CF_3COOH cleaves the $(RC{\equiv}CR)Co_2(CO)_6$ complex in a similar manner to give the corresponding alkane as a side product (Scheme 2).

The cyclopentenones may result from the reaction of the complexed or decomposed olefinic intermediates with the $(RC{\equiv}CR)Co_2(CO)_6$ complexes (Scheme 3).

Scheme 3



Scheme 4



6: R = n-C_8H_{17}	68 %	E/Z 1:2
7: R = n-C_6H_{13}	66 %	E/Z 1:2
8: R = n-C_5H_{11}	65 %	E/Z 1:2
9: R = C_6H_5	60 %	E/Z 2:1

Alternatively, the cyclopentenones may also result through the reduction of the initially formed cyclopentadienone intermediates by the $HCo(CO)_x$ species produced *in situ* in the medium. However, it should be noted that the cyclopentadienone formation has been previously observed only under elevated pressure of CO.[13]

In order to further understand this interesting transformation, we have examined the reactivities of alkynes containing the trimethylsilyl substituent. Such trimethylsilyl-substituted alkynes have been used previously to change the regioselectivity in the Pauson–Khand reaction.[14] We have found that in the case of the $(PhC{\equiv}CSiMe_3)Co_2(CO)_6$ complex, prepared *in situ* in THF, the reaction with CF_3COOH takes a long time (72 h) for completion (i.e. disappearance of the alkyne complex) and the corresponding alkenylsilane formed (Scheme 4) as a major product along with small amount of unidentified carbonyl compounds. This trend was also observed when the R group is alkyl, and the results are summarized in Scheme 4.

The *E*/*Z* ratios were determined by ^{1}H NMR analysis. Obviously, in these cases protonolysis of the C–Co bonds of the alkyne is the preferred pathway. The difference in the reactivity pattern of the phenyl and alkyl derivatives is also interesting. However, the isomeric alkenylsilanes may also result from the isomerization of the alkenylsilanes by the $H{-}Co(CO)_x$ species[15] present in the medium and hence it is not certain whether these products are formed directly from the alkyne complexes.

We have also carried out individual experiments using two different alkyne–$Co_2(CO)_6$ complexes (prepared separately or together). In these cases, a complex mixture of cyclopentenones was obtained. This may be

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attributed to the formation of a mixture of alkyne−dicobalt hexacarbonyl complexes through well-known exchange reactions.[16]

The reaction in the absence of CF_3COOH, in the case of the $(PhC{\equiv}CH)Co_2(CO)_6$ complex, resulted in the formation of the corresponding 1,2,4- and 1,3,5-triphenylbenzenes, a reaction reported with the alkyne−cobalt complexes.[19] Also, it was found that acetic acid is not effective for this transformation.

Although, the mechanistic picture is only tentative at this stage, the new methods of preparation of cyclopentenones and alkenylsilanes from (alkyne)cobalt complexes mediated by CF_3COOH described here should be of interest for further mechanistic studies and synthetic utilizations.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of predried nitrogen. All transfers and manipulations of compounds were carried out under a nitrogen atmosphere. Tetrahydrofuran was freshly distilled over benzophenone ketyl. All 1-alkynes and diphenylacetylenes and their silyl derivatives were prepared by following the reported procedures.[17] ^1H NMR and ^{13}C NMR spectra were recorded on JEOL-FX-100 and Brucker-AC-200 spectrometers with chloroform-*d* as solvent and TMS as reference ($\delta = 0$ ppm). All IR spectra were recorded on Perkin-Elmer Model 1310 and JASCO FT-5300 instruments with polystyrene as reference. Column chromatography was carried out using Acme silica gel (100−200 mesh). Anhydrous $CoBr_2$ was prepared from the hydrated complex by keeping it in the air oven at 150 °C for 5−6 h and further dried at 150 °C for 4 h under vacuum. It was kept under nitrogen in a desiccator. Activated zinc dust was prepared by treating commercial zinc dust with 1% H_2SO_4, washing with H_2O and acetone, and drying at 150 °C for 4 h under vacuum. Carbon monoxide was generated by dropwise addition of formic acid (98%) to concentrated H_2SO_4 (96%) at 90 °C using an apparatus recommended for utilization in the carbonylation of organoboranes.[18]

General Procedure for Reaction of CF_3COOH with $(RC{\equiv}CR')Co_2(CO)_6$ Complexes. Alkyne−dicobalt complex was prepared by following the reported procedure by reducing $CoBr_2$ (4.36 g, 20 mmol) with Zn (1.43 g, 22 mmol), and RC≡CR′ (10 mmol) in THF (60 mL) was stirred for 3 h while bubbling CO at 25 °C. Trifluoroacetic acid (10 mL) was added, and the contents were stirred at 70−80 °C for 24 h. The cobalt carbonyl species completely decomposed during this time. The contents were brought to room temperature, ether (30 mL) was added, and the mixture was washed successively with water (20 mL), 10% $NaHCO_3$ solution, and brine solution and dried over $MgSO_4$. The solvent was removed, and the residue was subjected to column chromatography on silica gel using hexane/ethyl acetate as eluent. The cyclopentenones isolated were identified. The structural assignments were based on the IR, ^1H and ^{13}C NMR-DEPT experiments, and mass spectral analysis. Spectral data obtained for all the cyclopentenones are summarized below.

1a: 40% (0.72 g); IR (neat) ν 2924, 2854, 1709, 1633, 1464, 1408, 1261, 798, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8−2.6 (m, 45H), 7.2 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1 ($-CH_3$), 22.7, 24.6, 27.6, 27.8, 29.3, 29.4, 29.6, 31.9 and 35.2 ($-CH_2$), 38.8 (−CH), 41.7 ($-CH_2$), 145.7 (quaternary) 161.2 (−CH), 209.5 (CO); MS (*m*/*z*) 362 (M^+, 40%), 237 (100%), 221 (90%), 135 (45%), 95 (50%), 55 (40%), 43 (60%).

1b: 15% (0.27 g); IR (neat) ν 2924, 2854, 1705, 1616, 1466, 1377, 1176, 1074, 798, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8−2.8 (m, 45H), 5.9 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0 ($-CH_3$), 16.8, 22.6, 27.0, 27.2, 29.3, 29.5, 31.4, 31.8 and 33.4 ($-CH_2$), 38.3 ($-CH_2$), 46.2 (−CH), 128.7 (−CH), 181.6 (quaternary), 212.3 (CO); MS (*m*/*z*) 362 (M^+, 10%), 235 (30%), 222 (60%), 109 (70%), 96 (95%), 55 (75%).

2a: 40% (0.61 g); IR (neat) ν 2926, 2854, 1709, 1464, 1377, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8−2.5 (m, 37H), 7.1 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0 ($-CH_3$), 22.6, 24.6, 27.6, 27.8, 29.2, 29.5, 29.6, 31.8 and 35.2 ($-CH_2$), 38.8 (−CH), 41.7 ($-CH_2$), 145.7 (quaternary), 161.0 (−CH), 209.2 (CO); MS (*m*/*z*) 306 (M^+, 30%), 209 (100%), 193 (70%), 95 (85%), 43 (65%).

2b: 14% (0.21 g); IR (neat) ν 2926, 1705, 1616, 1466, 1377, 1074, 798, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8−2.6 (m, 37H), 5.9 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0 ($-CH_3$), 22.6, 23.0, 25.2, 29.4, 29.6, 29.7, 31.4, 31.8 and 32.5 ($-CH_2$), 38.2 ($-CH_2$), 46.2 (−CH), 128.8 (−CH), 181.8 (quaternary), 212.4 (CO); MS (*m*/*z*) 306 (M^+, 10%), 194 (60%), 109 (50%), 96 (95%), 55 (100%).

3a: 38% (0.42 g), IR (neat) ν 2928, 2858, 1707, 1631, 1464, 1379, 1107, 729 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8−2.6 (m, 25H), 7.1 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9 ($-CH_3$), 22.5, 24.6, 27.2, 27.4, 31.5, 31.8 and 35.1 ($-CH_2$), 38.8 (−CH), 41.6 ($-CH_2$), 145.7 (quaternary), 161.3 (−CH), 209.5 (CO); MS (*m*/*z*) 222 (M^+, 20%), 151 (50%), 95 (100%), 67 (80%), 55 (95%).

3b: 12% (0.14 g); IR (near) ν 2928, 2860, 1701, 1618, 1464, 1174, 868, 727 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8−2.8 (m, 25H), 5.9 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 13.8 ($-CH_3$), 22.2, 22.3, 26.6, 26.8, 31.3, 31.7 and 33.3 ($-CH_2$), 38.2 ($-CH_2$), 46.1 (−CH), 128.6 (−CH), 181.3 (quaternary), 211.8 (CO); MS (*m*/*z*) 222 (M^+, 10%), 109 (40%), 96 (100%), 55 (65%).

4c: 35% (0.58 g); IR (KBr) ν 3061, 3026, 1693, 1599, 1494, 1452, 1300, 1118, 758, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.8−2.9 (m, 1H), 3.2−3.4 (m, 1H), 3.8 (m, 1H), 7.2−8.0 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 36.1 ($-CH_2$), 52.5 (−CH), 127.0, 127.1, 127.7, 128.5 and 128.8 (−CH), 131.6, 139.6, and 142.4 (quaternary), 157.6 (−CH), 206.4 (CO); MS (*m*/*z*) 234 (M^+, 90%), 206 (80%), 128 (60%), 102 (65%), 91 (95%), 77 (100%), 51 (98%).

4c + 4d: 50% (0.83 g); IR (neat) ν 3061, 3026, 1693, 1599, 1494, 1452, 1300, 1118, 758, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.5−3.0 (m, 2H), 3.1−3.4 (m, 2H), 3.8−4.2 (m, 2H), 7.1−7.5 (m, 16H), 7.6−8.0 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 36.0 ($-CH_2$), 43.7 (−CH), 45.6 ($-CH_2$), 52.5 (−CH), 126.9, 127.1, 127.2, 127.6, 128.4, 128.6, 128.8 and 129.0 (−CH), 131.5, 139.6 and 142.3 (quaternary), 157.5 (−CH), 160.4 (−CH), 206.3 and 206.9 (CO).

5: 58% (1.11 g); IR (KBr) ν 3061, 3024, 1952, 1876, 1693, 1628, 1601, 1493, 1444, 1149, 754, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.8 (bs, 1H), 4.6 (bs, 1H), 7.1−7.5 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 57.7 (−CH), 63.1 (−CH), 127.1, 127.2, 127.6, 127.8, 128.1, 128.3, 128.4, 129.0, 129.5, and 129.8 (−CH), 131.8, 134.7, 139.4, 140.1, 141.5 and 168.9 (quaternary) 205.8 (CO); MS (*m*/*z*) 386 (M^+, 100%), 309 (40%), 267 (50%), 176 (90%).

Reaction of $(RC{\equiv}CSiMe_3)Co_2(CO)_6$ Complexes with CF_3COOH. The procedure followed was same as described in the above experiment except the stirring of the mixture was continued for 3 days at 70−80 °C until the complex was disappeared. After usual workup, the corresponding alkenylsilanes were isolated. These products were identified by IR and ^1H and ^{13}C NMR spectral analysis and also by comparison with data reported for the pure *E* and *Z* isomers.[21] The spectral data for the mixture of *E* and *Z* (Scheme 4) alkenylsilanes are summarized below.

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6: 68% (1.44 g); IR (neat) ν 837, 987, 1248, 1464, 1608, 2854, 2926, 2957 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 1 × 9H), 0.12 (s, 2 × 9H), 0.7−2.2 (m, 3 × 34H), 5.53 (d, J = 12.0 Hz, 2 × 1H), 5.62 (d, J = 19.0 Hz, 1H), 5.95 (dt, J = 19.0, 6.1 Hz, 1H), 6.2 (dt, J = 14.0, 7.0 Hz, 2 × 1H); ^{13}C NMR ($CDCl_3$) δ −1.17, 0.21, 14.0, 22.7, 28.7, 29.3, 29.4, 29.6, 29.8, 31.9, 33.5, 36.7, 128.6, 129.4, 147.3, 149.2.

7: 66% (1.25 g); IR (neat) ν 837, 987, 1248, 1464, 1608, 2854, 2926, 2957 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 1 × 9H), 0.15 (s, 2 × 9H), 0.7−2.2 (m, 3 × 26H), 5.45 (d, J = 12.0 Hz, 2 × 1H), 5.65 (d, J = 19.0 Hz, 1H), 6.07 (dt, J = 19.0, 6.1 Hz, 1H), 6.28 (dt, J = 14.0, 7.0 Hz, 2 × 1H); ^{13}C NMR ($CDCl_3$) δ −1.17, 0.20, 14.0, 22.6, 28.7, 29.0, 29.3, 29.7, 31.8, 33.5, 36.7, 128.7, 129.4, 147.3, 149.2.

8: 65% (1.10 g); IR (neat) ν 837, 987, 1248, 1464, 1608, 2854, 2926, 2957 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 1 × 9H), 0.15 (s, 2 × 9H), 0.7−2.2 (m, 3 × 22H), 5.45 (d, J = 12.0 Hz, 2 × 1H), 5.65 (d, J = 19.0 Hz, 1H), 6.07 (dt, J = 19.0, 6.1 Hz, 1H), 6.28 (dt, J = 14.0, 7.0 Hz, 2 × 1H); ^{13}C NMR ($CDCl_3$) δ −1.20, 0.17, 13.9, 22.5, 28.4, 29.4, 31.4, 31.5, 33.4, 36.6, 128.7, 129.4, 147.3, 149.2.

9: 60% (1.05 g); IR (neat) ν 756, 841, 864, 987, 1248, 1446, 1493, 1574, 1604, 2957, 3024, 3061 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 1 × 9H), 0.25 (s, 2 × 9H), 5.94 (d, J = 15.2 Hz, 1H), 6.55 (d, J = 19.0 Hz, 2 × 1H), 6.99 (d, J = 19.4 Hz, 2 × 1H), 7.3−7.5 (m, 3 × 5H (aromatic) + 1H (olefinic)); ^{13}C NMR ($CDCl_3$) δ −1.0, −0.7, 126.5, 127.4, 127.9, 128.0, 128.2, 128.4, 128.6, 129.5, 132.9, 138.5, 143.8, 146.8.

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