# Rearrangement of 1-(1-Alkynyl)cyclopropanols to 2-Cyclopentenones via Their Hexacarbonyldicobalt Complexes. A New Use of Alkyne−$Co_2(CO)_6$ Complexes in Organic Synthesis

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**Abstract:** A novel rearrangement of 1-(1-alkynyl)cyclopropanols to 2-cyclopenten-1-ones proceeded on complexation of their alkynyl part with octacarbonyldicobalt ($Co_2(CO_8)$). 1-(1-Alkynyl)cyclopropanols with a wide range of substituents on their alkyne terminus rearranged to the corresponding 3-substituted 2-cyclopenten-1-ones in good yield. In case of the reactions of 1-alkynylcyclopropanols with an alkyl substituent on the cyclopropane ring, either 4-substituted or 5-substituted 2-cyclopenten-1-ones could be selectively obtained by appropriate choice of stereochemistry and protective group of the substrates. This rearrangement was successfully applied to cyclopentenone annulation reactions onto cycloalkenes. An efficient synthesis of alkynyl-substituted bicyclo[*n*.1.0]alkanol derivatives from the corresponding cycloalkenes according to Danheiser's protocol was developed, and bicyclic cyclopentenones were obtained in moderate to good yield by applying to these the cobalt-mediated rearrangement. Furthermore, the rearrangement was found to proceed catalytically on addition of triaryl phosphite as a ligand. In particular, when tri(*o*-isopropylphenyl) phosphite was used as ligand, 5−10 mol % of $Co_2(CO)_8$ and 10−20 mol % of the phosphite sufficed for the efficient conversion of 1-alkynylcyclopropanols to 2-cyclopentenones. Mechanistic studies revealed that the rate-determining step was the thermal or oxidative dissociation of a carbonyl ligand from the alkyne−$Co_2(CO)_6$ complex and that the coordinately unsaturated cobalt moiety so-formed inserted into the neighboring carbon−carbon bond of the cyclopropane to give a metallacyclic intermediate. This further rearranged to a metallacyclohexanone intermediate, which gave the cyclopentenone with liberation of a coordinatively unsaturated cobalt species.

Unlike the well-known chemistry of the vinylcyclopropane-cyclopentene rearrangement,[1] there has been no precedent for the corresponding alkynylcyclopropane rearrangement to cyclopentene derivatives with the exception of one specific example, that is, the pyrolysis of 2-methyl-1-ethynylcyclopropane to methylcyclopentene and other compounds.[2] This difficulty in achieving the rearrangement of alkynylcyclopropanes to cyclopentene derivatives presumably lies in the longer distance between the alkyne terminus and the cyclopropane ring compared to that between the latter and an alkene terminus.

Various transition metal catalysts are known to promote the vinylcyclopropane−cyclopentene rearrangement by forming a complex with the olefinic part of the molecule, and the reactions generally proceed under milder conditions than those of equivalent thermal reaction.[3] It is expected that by appropriate complexation with transition metal compounds, alkynylcyclopropanes could also be made to rearrange to cyclopentene derivatives, provided that the complexed transition metal moiety can activate the neighboring cyclopropane ring effectively.

Alkyne−hexacarbonyldicobalt ($Co_2(CO)_6$) complexes can be easily synthesized from alkynes and octacarbonyldicobalt ($Co_2(CO)_8$) simply by mixing, and these complexes are usually chromatographically isolable, stable compounds.[4] These alkyne−$Co_2(CO)_6$ complexes have been employed in organic synthesis mostly for three types of reaction, that is (1) as a protective group for alkynyl functionality;[5] (2) as a means to stabilize propargylic cations for nucleophilic attack (Nicholas type reaction);[6] and (3) as a component in the Pauson-Khand reaction to give 2-cyclopenten-1-ones by reaction with olefins.[7] Al-

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(1) (a) Hudlicky, T.; Reed, J. W. In *Comprehensive Organic Synthesis, Vol 5: Rearrangements of Vinylcyclopropane and Related Systems*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; p 899. (b) Goldschmidt, Z.; Crammer, B. *Chem. Soc. Rev.* **1988**, *17*, 229. (c) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247.

(2) Dalacker, V.; Hopf, H. *Tetrahedron Lett.* **1974**, 15.

(3) See ref 1. For a recent example, see: Ryu, I.; Ikura, H.; Tamura, Y.; Maenaka, J.; Ogawa, A.; Sonoda, N. *Synlett* **1994**, 941. References are cited therein.

(4) (a) Sternberg, H. W.; Greenfield, H.; Friedel, R. A.; Wotiz, J.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1954**, *76*, 1457. (b) Greenfield, H.; Sternberg, H. W.; Friedel, R. A.; Wotiz, J. H.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1956**, *78*, 120. (c) Hübel, W. In *Organic Syntheses via Metal Carbonyls; 1*, Wender, I., Pino, P., Eds.; Interscience: New York, 1968; Vol. 1. (d) Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson G., Ed.; Pergamon Press: Oxford, 1982; Vol. 5, p1.

(5) For examples, see: (a)Seyferth, D.; Wehman, A. T. *J. Am. Chem. Soc.* **1970**, *92*, 5520. (b) Nicholas, K. M.; Pettit, R. *Tetrahedron Lett.* **1971**, 3475. (c) Melikyan, G. G.; Vostrowsky, O.; Bauer, W.; Bestmann, H. J.; Khan, M.; Nicholas, K. M. *J. Org. Chem.* **1994**, *59*, 222. (d) Milgrom, L. R.; Rees, R. D.; Yahioglu, G. *Tetrahedron Lett.* **1997**, *38*, 4905.

(6) (a) Varghese, V.; Saha, M.; Nicholas, K. M. *Org. Synth.* **1988**, *67*, 141. (b) Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207. (c) Caffyn, A. J. M.; Nicholas, K. M. In *Comprehensive Organometallic Chemistry II, Vol 12: Transition Metal Alkyne Complexes: Transition Metal-stabilized Propargyl System*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; p 685. For some recent examples, see: (d) Schreiber, S. L.; Klimas, M. T.; Sammakia, T. *J. Am. Chem. Soc.* **1987**, *109*, 5749. (e) Tanaka, S.; Isobe, M. *Synthesis* **1995**, 859. (f) Nakamura, T.; Matsui, T.; Tanino, K.; Kuwajima, I. *J. Org. Chem.* **1997**, *62*, 3032. (g) Caddick, S.; Delisser, V. M. *Tetrahedron Lett.* **1997**, *38*, 2355.

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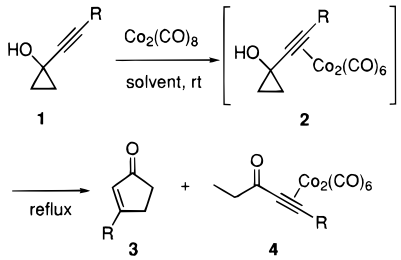
**Scheme 1**




though the unique properties of alkyne−$Co_2(CO)_6$ complexes are obvious from these reactions, it is expected that other useful reactions using alkyne−$Co_2(CO)_6$ complexes still remain to be explored. In this paper is described another use of alkyne−$Co_2(CO)_6$ complexes in organic synthesis, a novel rearrangement of 1-(1-alkynyl)cyclopropanols to 2-cyclopenten-1-ones via their $Co_2(CO)_6$ complexes.[8]

**Stoichiometric Reactions.** 1-Alkynylcyclopropanols with no substituents at the 2- and 3-positions of the cyclopropane ring were easily prepared in good yields by the reaction of alkynyl Grignard reagents with cyclopropanone hemiacetal.[9]

When 1-(1-octynyl)cyclopropanol **1a** (R = *n*-$C_6H_{13}$) was treated with 1.1 molar amounts of $Co_2(CO)_8$ in THF at room temperature under an argon atmosphere, complete formation of the $Co_2(CO)_6$ complex **2a** was observed within 30 min by thin-layer chromatography. This complex was stable at room temperature, but when the solution was heated to reflux for 8 h under argon, it disappeared completely, and 3-hexyl-2-cyclopenten-1-one **3a** was produced in 62% yield (Scheme 1). The intermediate alkyne−$Co_2(CO)_6$ complex **2a** was easily isolated by silica gel column chromatography under argon. Heating this isolated complex in refluxing THF gave the same rearranged product **3a** in a comparable yield. In general, 1-(1-alkynyl)-cyclopropanols themselves are thermally more stable than 1-alkyl or 1-alkenyl cyclopropanols, and in practice **1a** was recovered unchanged when it was heated in refluxing benzene for 2.5 h. Thus, complexation of $Co_2(CO)_6$ to the alkynyl part of **1a** is essential for the rearrangement.

As a novel 1-alkynylcyclopropanol−cyclopentenone rearrangement had been observed, we decided to investigate this reaction in detail. Examination of the effect of the solvent on this reaction using 1-(1-octynyl)cyclopropanol **1a** as a substrate revealed that use of ethereal solvents generally favored the formation of the cyclopentenone **3a**, and by carrying out the reaction in refluxing dimethoxyethane (DME) for 1.5 h, **3a** was obtained in 71% yield. On the other hand, use of hydrocarbon solvents favored another reaction pathway, that is, rearrangement of the 1-octynylcyclopropanol-$Co_2(CO)_6$ complex **2a** to an ethyl 1-octynyl ketone−$Co_2(CO)_6$ complex **4a**. For example, by carrying out the reaction in refluxing hexane, the complex **4a** could be obtained in about 70% yield, along with the cyclopentenone **3a** in 13% yield. Other solvents such as benzene, *t*-BuOH, EtOAc, and $CCl_4$ gave lower yields of the products (benzene, **3a**, 40%, **4a**, 40%; *t*-BuOH, **3a**, 27%, **4a**, 30%; EtOAc, **3a**, 35%, **4a**, 10%) or a complex mixture of unidentified products ($CCl_4$).

**Table 1.** Reactions of Various 1-Alkynylcyclopropanols **1** Using a Stoichiometric Amount of $Co_2(CO)_8$

| R | solvent | reaction time[a]/h | yield of **3**/% |
|---|---|---|---|
| *n*-$C_6H_{13}$(**1a**) | DME | 1.5 | 71 |
| Ph(**1b**) | DME | 1 | 91 |
| *t*-Bu(**1c**) | DME | 1.25 | 73 |
| $SiMe_3$(**1d**) | DME | 1.5 | 77 |
| $SiPh_3$(**1e**) | DME | 0.5 | 73 |
| $SiPh_3$(**1e**) | THF | 3 | 85 |
| Si*i*-$Pr_3$(**1f**) | DME | 0.16 | 62 |
| Si*i*-$Pr_3$(**1f**) | THF | 1.5 | 67 |
| $CH_2$OTBS(**1g**) | DME | 1.5 | 61 |
| $CH_2$S*t*-Bu(**1h**) | DME | 1.5 | 68 |
| $CH_2CH_2$OTBS(**1i**) | DME | 6 | 81 |
| $CH_2CH_2$OH(**1j**) | THF | 2 | 68 |
| S*n*-Bu(**1k**) | DME | 1.25 | 45 |
| COOEt(**1l**) | DME | 1.25 | 33 |

[a] Reaction time indicates the approximate time required for the cobalt complex **2** to disappear as judged by TLC.

Various other transition metal compounds known to form complexes with alkynes were also examined in this reaction but failed to give satisfactory results.[10] We also examined whether the presence of the unprotected hydroxyl group on the cyclopropane was essential for the success of this reaction. The reactions of various cyclopropanol derivatives such as the benzyl ether, acetate, and various silyl ethers were carried out under similar conditions, and it was found that while the reactions of the benzyl ether or acetate of **1a** were sluggish and the rearranged product **3a** was obtained in low yield, the reaction of the corresponding TBS ether gave the cyclopentenone **3a** in good yield.[11]

The results of the reactions of 1-alkynylcyclopropanols with various substituents on the alkyne using a stoichiometric amount of $Co_2(CO)_8$ are summarized in Table 1. Not only alkyl-substituted alkyne derivatives but also aryl- or silyl-substituted alkyne derivatives gave the corresponding 3-substituted 2-cyclopenten-1-ones in good to high yields. In particular, the efficient preparation of 3-silyl-substituted cyclopentenones is noteworthy as hitherto no good method has been reported for the synthesis of such compounds.[12] Interestingly, bulkiness of the substituent on the alkyne has a large effect on the reaction rate. In case of the reaction of the TMS derivative **1d**, it took about 1.5 h for the completion of the reaction in refluxing DME. On the other hand, the reaction of the triphenylsilyl derivative **1e** needed only 0.5 h, and furthermore, the reaction went to completion within 10 min when the triisopropylsilyl(TIPS) derivative **1f** was employed as substrate. Thus, the bulkier the substituent on the alkyne becomes, the faster the reaction proceeds. Various alkynyl substituents containing a functional group can also be employed in this reaction. A *tert*-butyldimethylsilyl ether, alkylthio group, and even an unprotected hydroxyl group are tolerated, and the corresponding function-

(7) (a) Schore, N. E. *Org. React.* **1991**, *40*, 1. (b) Schore, N. E. In *Comprehensive Organic Synthesis, Vol. 5: The Pauson-Khand Reaction*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; p 1037. (c) Pauson, P. L. In *Organometallics in Organic Synthesis. Aspects of a Modern Interdicsciplinary Field*; Meijere, A. de., Dieck, H. T., Eds.; Springer: Berlin, 1988; p 233. (d) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855. (e) Schore, N. E. In *Comprehensive Organometallic Chemistry II, Vol 12: Transition Metal Alkyne Complexes: Pauson-Khand Reaction*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; p 703.

(8) Preliminary communications: (a) Iwasawa, N. *Chem. Lett.* **1992**, 473. (b) Iwasawa, N.; Matsuo, T. *Chem. Lett.* **1993**, 997. (c) Iwasawa, N.; Iwamoto, M. *Chem. Lett.* **1993**, 1257.

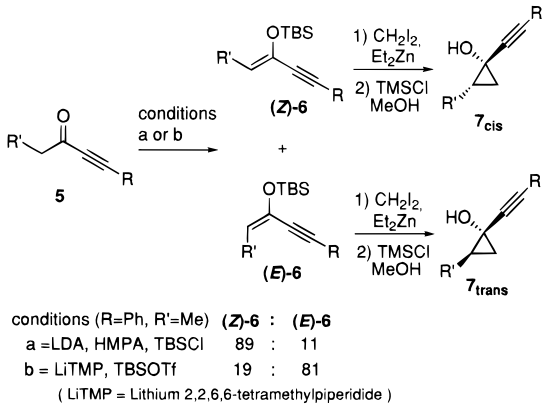
(9) Salaün, J.; Bennani, F.; Compain, J.-C.; Fadel, A.; Ollivier, J. *J. Org. Chem.* **1980**, *45*, 4129.

(10) Followings are the complexes examined. In some cases rearranged products were obtained in low yield, but reactions were generally sluggish and no satisfactory results were obtained: $Ni(COD)_2$, $Ni(PPh_3)_4$, $Fe_2(CO)_9$, $W(CO)_5$·THF, $Pd(PPh_3)_4$, $Pd(dba)_2$, $Cp_2W_2(CO)_4$, $Cp_2Mo_2(CO)_4$.

(11) At present, we suppose that the hydrogen at the 2-position of the cyclopentenone comes from the small amount of water present in the reaction medium, because rigorous elimination of water from the reaction mixture by carrying out the reaction in the presence of MS 4A made the reaction sluggish and the yield of the product decreased considerably.

(12) See for an example: Kim, S. H.; Jin, Z.; Fuchs, P. L. *Tetrahedron Lett.* **1995**, *36*, 4537.

**Scheme 2**




alized cyclopentenones were obtained in moderate to good yield. Furthermore, when a 1-(1-alkynyl)cyclopropanol having an electron-donating *n*-butylthio group, or an electron-withdrawing ethoxycarbonyl group, directly bonded to the alkyne was employed, the corresponding 3-*n*-butylthio- or 3-ethoxycarbonyl-2-cyclopentenone was obtained in moderate yields.

In the case of transformation of alkynylcyclopropanols with a substituent on the 2-position of the cyclopropane ring, two regioisomers, that is, the 4-substituted and/or 5-substituted 2-cyclopentenones, could be formed depending on which bond of the cyclopropane is cleaved. The required substrates could not be prepared according to the same procedure used for the preparation of compounds **1** due to the instability of the corresponding substituted cyclopropanone hemiacetals. Accordingly, we employed the following procedure: Alkynyl ketones **5** were converted to the corresponding silyl enol ethers **6**, and then cyclopropanation was carried out according to the modified Simmons-Smith reaction using diethylzinc and diiodomethane.[13] Finally, the silyl group was removed using a catalytic amount of TMSCl in MeOH to give the desired substituted cyclopropanols **7** in good yield. Since either *E* or *Z* silyl enol ethers can be prepared with good to high selectivities depending on the enolization conditions,[14] by this procedure selective preparation of either cis or trans substituted cyclopropanols (**7**$_{cis}$ or **7**$_{trans}$) is possible as shown in Scheme 2.

First the reaction of (1*R**,2*S**)-2-methyl-1-phenylethynylcyclopropanol **7a**$_{cis}$ (R = Ph, $R^1$ = Me, $R^2$ = $R^3$ = H) according to the standard procedure was examined. Heating the $Co_2(CO)_6$ complex of **7a**$_{cis}$ for 1.5 h in DME under an argon atmosphere gave almost equal amounts of 4-methyl-3-phenyl-2-cyclopenten-1-one **8a** and 5-methyl-3-phenyl-2-cyclopenten-1-one **9a** in a combined yield of 75%. As this rearrangement was nonregioselective, the reaction of various silyl ethers of **7a**$_{cis}$ was next examined. As shown in Table 2, part 2-1, the bulkiness of the silyl group greatly influences the regioselectivity of the rearrangement. Using the TMS ether, the ratio of **8a** and **9a** was 70:30 but by using the bulkier *tert*-butyldimethylsilyl or triisopropylsilyl ether and by carrying out the reaction in refluxing THF, the regioselectivity could be improved to 94:6 without lowering the yield of the products. On the other hand, in the reaction of (1*R**,2*R**)-2-methyl-1-phenylethynylcyclopropanol **7a**$_{trans}$ (R = Ph, $R^1$ = $R^3$ = H, $R^2$ = Me) 5-substituted isomer **9a** was obtained as the sole isomer detectable by $^1$H NMR, while when silyl ethers of **7a**$_{trans}$ were employed as substrates, the same 5-substituted isomer **9a** was obtained also in high regioselectivity, which however fell slightly as the bulkiness of the silyl group increased (Table 2, part 2-2).

**Table 2.** Examination of the Regioselectivity of the Rearrangement of 2-Methyl-1-phenylethynylcyclopropanol **7a** and 2,2-Dimethyl-1-phenylethynylcyclopropanol **10a** and Their Silyl Ethers

| $R^3$ | solvent | reaction time[a]/h | yield/% | **8a:9a** (**11a:12a**) |
|---|---|---|---|---|
| 2-1. R = Ph, $R^1$ = Me, $R^2$ = H (**7a**$_{cis}$) | | | | |
| H | DME | 1.5 | 75 | 50:50 |
| $SiMe_3$ | DME | 1.5 | 73 | 70:30 |
| Si*t*-$BuMe_2$ | DME | 1.25 | 83 | 91:9 |
| Si*t*-$BuMe_2$ | THF | 5 | 77 | 94:6 |
| Si*i*-$Pr_3$ | THF | 3 | 70 | 94:6 |
| 2-2. R = Ph, $R^1$ = H, $R^2$ = Me (**7a**$_{trans}$) | | | | |
| H | DME | 1.5 | 86 | <1:>99 |
| Si*t*-$BuMe_2$ | DME | 1.25 | 88 | 1:99 |
| Si*i*-$Pr_3$ | DME | 5 | 47 | 2:98 |
| 2-3. R = Ph, $R^1$ = $R^2$ = Me (**10a**) | | | | |
| H | DME | 1 | 80 | <1:>99 |
| Si*t*-$BuMe_2$ | DME | 1.5 | 88 | 3:97 |

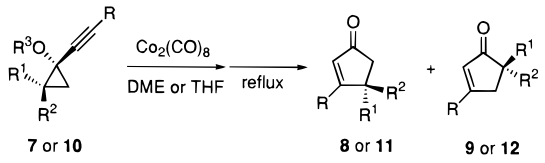
[a] Reaction time indicates the approximate time required for the cobalt complex **2** to disappear as judged by TLC.

**Table 3.** Reactions of Various 2-Substituted 1-(1-Alkynyl)-Cyclopropanols

| compd | R | $R^1$ | $R^2$ | $R^3$ | solvent | reaction time[a]/h | yield/ % | **8:9** (or **11:12**) |
|---|---|---|---|---|---|---|---|---|
| **7b**$_{trans}$ | Ph | H | *i*-Pr | H | DME | 2.5 | 86 | <1:>99 |
| **7b**$_{cis}$ | Ph | *i*-Pr | H | TBS | THF | 7 | 75 | 96:4 |
| **7c**$_{trans}$ | *n*-Hex | H | Me | H | DME | 2.5 | 83 | <1:>99 |
| **7c**$_{cis}$ | *n*-Hex | Me | H | TBS | THF | 14 | 71 | 77:23 |
| **7d**$_{trans}$ | *n*-Hex | H | *i*-Pr | H | DME | 2 | 88 | <1:>99 |
| **7d**$_{cis}$ | *n*-Hex | *i*-Pr | H | TBS | THF | 32 | 85 | 85:15 |
| **10b** | Ph | $-(CH_2)_5-$ | | H | DME | 1 | 83 | <1:>99 |
| **10c** | *n*-Hex | Me | Me | H | DME | 1.5 | 81 | <1:>99 |

[a] Reaction time indicates the approximate time required for the cobalt complex **2** to disappear as judged by TLC.

**Scheme 3**



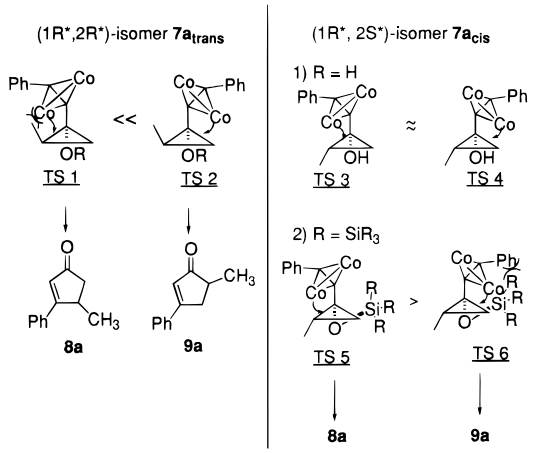

To make clear whether a methyl group cis to the alkyne or trans to the alkyne would play a dominating role in determining the regioselectivity, the reactions of 2,2-dimethyl-1-phenylethynylcyclopropanol **10a** (R = Ph, $R^1$ = $R^2$ = Me, $R^3$ = H) and its TBS ether were also examined. When **10a** itself was employed as substrate, 5,5-dimethyl-3-phenyl-2-cyclopenten-1-one **12a** was obtained as the sole product. The reaction of the corresponding TBS ether gave the same regioisomer as the major product with a small amount of the other regioisomer **11a** (Table 2, part 2-3). These results indicate that the substituent cis to the alkynyl group plays a dominant role in determining the regioselectivity of the reaction.

As will be discussed later, it is assumed that the reaction proceeds by the oxidative addition of the carbon−carbon bond of the cyclopropane to cobalt species to make a metallacyclic intermediate. The regioselectivity of this reaction is controlled by the relative ease of insertion of the cobalt species into the C1−C2 and the C1−C3 bonds of the cyclopropane. On the basis of these assumptions the regioselectivity of the reaction can be explained by considering the conformations available

(13) (a) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Heiness, C. M. *Org. React.* **1973**, *20*, 1. (b) Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron Lett.* **1968**, 3495. (c) Furukawa, J.; Kawabata, N. *Adv. Organomet. Chem.* **1974**, *12*, 83.

(14) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.

**Scheme 4**

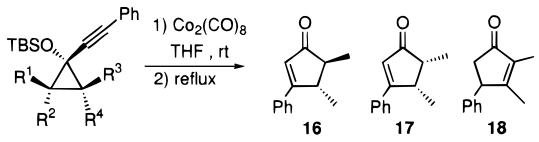



to the various 1-alkynylcyclopropanol−$Co_2(CO)_6$ complexes (Scheme 4). In the case of reaction of (1*R**,2*R**)-isomer **7a**$_{trans}$, 5-methyl-3-phenyl-2-cyclopenten-1-one **9a** is produced via TS2 without any serious steric repulsion, while the 4-methyl isomer **8a** must be produced via TS1 in which severe steric repulsion between the methyl group and the cobalt moiety exists. In the case of reaction of (1*R**, 2*S**)-isomer **7a**$_{cis}$, the unprotected derivative **7a**$_{cis}$ gave equal amounts of **8a** and **9a** because the reaction can proceed via either TS3 or TS4 with equal efficiency. When the silyl derivatives of **7a**$_{cis}$ are employed, the silyl groups would take a position to minimize the repulsion with the methyl group as shown in TS5 and TS6. Of these two conformations, TS5 is thought to be favored as in this case there is no steric repulsion between the phenyl group on the alkyne and the silyl group. Thus, the bulkier the silyl group becomes, the higher the selectivity becomes in favor of the formation of **8a**. As can obviously be seen from Scheme 4, the methyl group cis to the alkynyl group plays a dominant role in determining the regioselectivity.

The generality of these observations is supported by the data in Table 3. In the case of the reactions of monosubstituted 1-(1-alkynyl)cyclopropanols **7**, 5-substituted cyclopentenones were obtained with complete selectivity when **7**$_{trans}$ were used as substrates. On the other hand, 4-substituted cyclopentenones were obtained in good to high regioselectivity by employing *tert*-butyldimethylsilyl ethers of **7**$_{cis}$ as substrates. Furthermore, 5,5-disubstituted cyclopentenones including a spirocyclic derivative were obtained selectively starting from 2,2-disubstituted 1-(1-alkynyl)cyclopropanols **10**. As either diastereomer of the monosubstituted 1-(1-alkynyl)cyclopropanols can be prepared selectively depending on the reaction conditions used in preparation of the silyl enol ethers, either 4- or 5-substituted cyclopentenones can be synthesized selectively by appropriate choice of reaction procedure.

We next examined the reaction of 2,3-disubstituted 1-alkynylcyclopropanol derivatives to clarify the stereochemistry at the migrating carbon. As substrates, three diastereomers of 2,3-dimethyl-1-(phenylethynyl)cyclopropanol, that is, (2*S**,3*S**)-**13**, (1*S**,2*R**,3*S**)-**14**, and (1*R**,2*R**,3*S**)-**15**, were prepared by the same procedure used in the preparation of monosubstituted 1-alkynylcyclopropanols **7**, except that 1,1-diiodoethane was employed instead of 1,1-diiodomethane. The relative stereochemistries of these isomers were determined as follows. (*E*)- and (*Z*)-Silyl enol ethers, (*E*)-**6** and (*Z*)-**6** (R = Ph, R′ = Me), were separated by silica gel column chromatography (silica deactivated with 10% $H_2O$) and both isomers were subjected separately to the Simmons-Smith cyclopropanation using diiodoethane and diethylzinc. In both cases, two isomeric cyclopropanol TBS ethers were obtained, one of which was a common product of both reactions. This isomer could be definitely assigned as the 2,3-trans isomer **13**. The remaining two compounds were therefore the 2,3-cis isomers **14** and **15**, respectively, as fixed by the geometry of the silyl enol ethers employed.

**Scheme 5**




**13**(R$^1$=R$^4$=H, R$^2$=R$^3$=Me) 90 min, 82% yield, **16** only
**14**(R$^1$=R$^3$=H, R$^2$=R$^4$=Me) 15 min, 35% yield, **16** : **17** = 7 : 93
90 min, 79% yield, **16** : **17** : **18** = 15 : 33: 52
**15**(R$^1$=R$^3$=Me, R$^2$=R$^4$=H) 135 min, 8% yield, **16** : **17** =30 : 70

Due to the instability of the corresponding desilylated cyclopropanols reactions were directly carried out employing TBS ethers **13**−**15**. When each of these three diastereomers was treated with $Co_2(CO)_8$ and heated in refluxing THF, the reaction proceeded to give cyclopentenones, but the situation was not so simple as in previously discussed cases. In the case of the reaction of 2,3-trans isomer **13**, trans 4,5-dimethyl-3-phenylcyclopentenone **16** was obtained almost exclusively in good yield. When the reaction of 2,3-cis isomer **14** was carried out in refluxing THF for 15 min, 4,5-cis isomer **17** was obtained as the major product with a substantial amount of recovered **14**, while prolonged reaction time resulted in the formation of an inseparable mixture of 4,5-trans isomer **16**, cis isomer **17**, and 2,3-dimethyl-4-phenyl-2-cyclopenten-1-one **18** in 79% yield in a ratio of 33:15:52. The formation of **16** and **18** indicates that both partial epimerization and migration of the double bond of **17** occurred during the reaction. Rearrangement of the other 2,3-cis isomer **15** did not proceed smoothly, and decomplexation occurred as the major reaction pathway presumably due to severe steric hindrance imposed on the alkyne−$Co_2(CO)_6$ moiety by the two methyl groups on the same side of the cyclopropane ring (Scheme 5). These results strongly suggest that migration occurs chiefly with retention of configuration at the migrating carbon.

**Cyclopentenone Annulation Reaction.** To expand the synthetic utility of this reaction, we next examined the possibility of applying it to cyclopentenone annulation onto cycloalkenes. For this purpose, it is necessary to develop a new method for the preparation of alkynyl-substituted bicyclo[*n*.1.0]alkanol derivatives from the corresponding cycloalkenes. Danheiser and co-workers have reported that various substituted cyclopropanols can be synthesized by the reaction of *gem*-lithiobromocyclopropanes with alkylboranes such as trialkylboranes or catecholborane utilizing 1,2-migration of an alkyl group or hydrogen from boron to carbon.[15] We employed this protocol using alkynylboranes as the boron component.

Optimization of this reaction employing 7,7-dibromobicyclo[4.1.0]heptane **19** (*n* = 1) and several phenylethynylborane derivatives **21a** (R = Ph) revealed that while *B*-phenylethynyl 9-BBN did not give the desired product at all, probably due to facile migration of the $sp_3$-carbon of 9-BBN, use of the corresponding borates, in particular cyclic borates, gave the desired product **24a** (*n* = 1, R = Ph) in good yields. For example, treatment of 7,7-dibromobicyclo[4.1.0]heptane with

(15) Danheiser, R. L.; Savoca, A. C. *J. Org. Chem.* **1985**, *50*, 2401.

**Scheme 6**

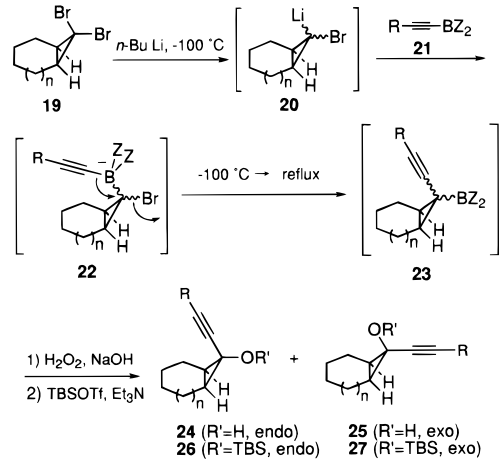


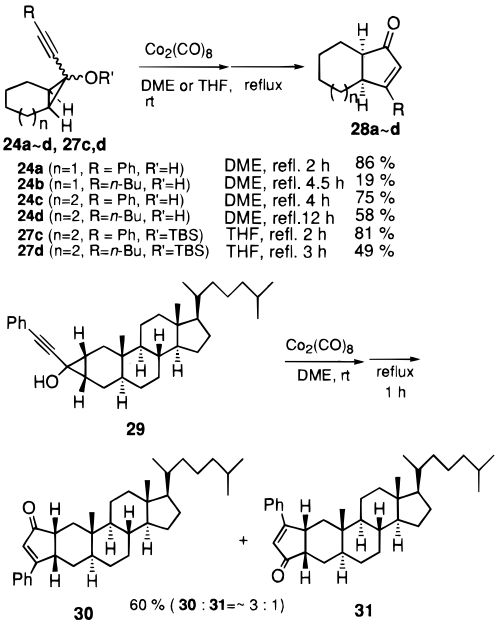

**Table 4.** Preparation of Various Bicyclic Cyclopropanols

| n | alkynylborane | yield / % | **24** : **25** or **26** : **27** |
|---|---|---|---|
| 1 | Ph—≡—B(O,O) | 65 | >99 : <1 (**24a**) |
| 1 | *n*-Bu—≡—B(O,O) | 65 | >99 : <1 (**24b**) |
| 2 | Ph—≡—B(O,O) | 50 | 40 : 60 (**26c**:**27c**) |
| 2 | *n*-Bu—≡—B(O,O) | 77 | 93 : 7 (**26d**:**27d**) |
| 2 | *n*-Bu—≡—B(O,O) | 56 | 68 : 32 (**26d**:**27d**) |
| 2 | *n*-Bu—≡—B(O,O) | 57 | 12 : 88 (**26d**:**27d**) |

*n*-BuLi at −100 °C generated the corresponding *gem*-lithiobromocyclopropane **20** ($n = 1$), which was reacted with a phenylethynylborate derivative to give an ate complex **22a** ($n = 1$, R = Ph). On slowly warming to room temperature and then heating to reflux migration of the phenylethynyl group occurred to give a cyclopropylborane derivative **23a**, which was oxidized with $H_2O_2$ to give the desired product **24a** in 65% yield (Scheme 6). In this reaction only one diastereomer was obtained, whose stereochemistry was assigned as the *endo*-alkynyl isomer as shown in **24a** by analogy with the results of Danheiser.[15]

Several other bicyclic alkynylcyclopropanols were prepared from the corresponding dibromocyclopropanes and alkynylborates as summarized in Table 4. Some features of this preparative method should be pointed out here. The reaction of *gem*-lithiobromobicyclo[4.1.0]heptane with 1-hexynylborate also gave only one diastereomer **24b** ($n = 1$, R = *n*-Bu) in good yield. In the case of the reaction of 8,8-dibromobicyclo[5.1.0]octane **19** ($n = 2$) with phenylethynylborate and 1-hexynylborate, the products, in particular the *exo* isomers **25c** ($n = 2$, R = Ph) and **25d** ($n = 2$, R = *n*-Bu), were insufficiently stable to be purified, and the crude products were directly treated with TBSOTf and $Et_3N$ to give the corresponding silylated mixture of *endo* isomers **26c,d** and *exo* isomers **27c,d**. These isomers were easily separable, and, interestingly, their ratio could be controlled by choice of the alkynylborate. By using a bulky borate such as 4,4,5,5-tetramethyl-1,3-dioxa-2-borolane, the *exo* isomer **27d** was obtained preferentially (**26d**:**27d** = 12:88), while using a less sterically demanding 1,3-dioxa-2-borinane derivative, the *endo* isomer **26d** was obtained as the major product (**26d**:**27d** = 93:7). Assignment of the stereochemistry of these compounds was based on the rate of silylation of the hydroxyl group. Silylation of the *endo* isomers **24c,d** was much faster than that of the *exo* isomers **25c,d** due to the steric congestion imposed on the hydroxyl group by the cycloheptane ring. Also the reactivity of each isomer in the alkynylcyclopropanol−cyclopentenone rearrangement supported this assignment as is described below.

**Scheme 7**




With several bicyclic alkynylcyclopropanols in hand, the alkynylcyclopropanol−cyclopentenone rearrangement of these compounds was examined. The reaction of 7-phenylethynylbicyclo[4.1.0]heptan-7-ol **24a** ($n = 1$, R = Ph) gave the desired bicyclo[4.3.0]non-8-en-7-one derivative **28a** in 86% yield on carrying out the reaction in refluxing DME for 2 h according to the standard procedure. However, the reaction of the corresponding hexynyl derivative **24b** ($n = 1$, R = *n*-Bu) was sluggish, and the desired product **28b** was obtained in only 19% yield under similar reaction conditions (Scheme 7). This can probably be ascribed to the fact that the reactions of phenylethynyl derivatives generally proceed quickly compared to the reactions of alkyl-substituted ethynyl derivatives, while decomplexation and decomposition of the substrate competed under these conditions due to the severe steric repulsion between the alkyne−$Co_2(CO)_6$ moiety and the cyclohexane ring.

We next examined the reaction of the *endo* bicyclo[5.1.0]-octanol derivatives **24c,d** and the *exo* TBS ethers **27c,d**. In contrast to the case of the bicyclo[4.1.0]heptan-7-ol derivatives **24a,b**, both of the *endo* isomers **24c** and **24d** gave the corresponding bicyclo[5.3.0]dec-9-en-8-one derivatives **28c,d** in good yield on carrying out the reaction in refluxing DME. This higher yield of the hexynyl derivative **24d** compared to that of **24b** is probably due to their being less congestion over the cycloheptane than the cyclohexane ring. Interestingly, the reactions of the silyl ethers of the *exo* isomers **27c** and **27d** proceeded much faster than those of the corresponding *endo* isomers **24c,d**, and the reaction went to completion within

several hours in refluxing THF.[16] This clear difference in reactivity of the *endo* and *exo* isomers is probably due to easy access of the cobalt moiety of the complexed *exo* isomers **27c,d** to the carbon−carbon bonds of the cyclopropane. The cobalt moiety is severely hindered from approaching these in the *endo* isomers **24c,d**.

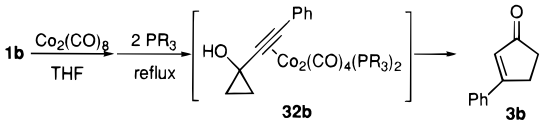
Finally this annulation reaction was applied to the steroidal skeleton. According to the above procedure, alkynylcyclopropanol **29** was prepared from cholest-2-ene in good overall yield. The rearrangement was carried out by the standard procedure to give two isomeric cyclopentenones in a ratio of about 3:1 in 60% yield. Careful NMR analysis suggested that the major product has the structure shown in **30**.[17]

As dibromocyclopropanation can be easily carried out by reacting a cycloalkene and bromoform in the presence of a base,[18] this method affords an alternative procedure for cyclopentenone annulation onto cyclic olefins. It should be noted that in the Pauson-Khand reaction, which is probably the most direct cyclopentenone annulation reaction, the reaction using cyclohexene gives the product only in very low yield.[7,19] Also the position of the original alkynyl substituent on the product double-bond is opposite to that in the present reaction.[7] Thus the two reactions are complementary.

**Catalytic Reactions.** All the reactions described so far were carried out using a stoichiometric amount of $Co_2(CO)_8$. However, it was thought that a coordinatively unsaturated $Co_2(CO)_6$ species is liberated when the rearrangement proceeds and that if this cobalt species could form an alkyne−$Co_2(CO)_6$ complex with another molecule of 1-(1-alkynyl)cyclopropanol, the reaction should proceed with only a catalytic amount of $Co_2(CO)_8$.[20] In practice, when 1-phenylethynylcyclopropanol **1b** was treated with a 10 or 20 mol % amount of $Co_2(CO)_8$, the rearranged product **3b** was obtained in 43 and 59% yield, respectively. Thus, the reaction did in fact proceed with a catalytic amount of $Co_2(CO)_8$; however, the efficiency was low, and a complex mixture of byproducts was also obtained. As we thought this low efficiency could be ascribed to instability of the liberated cobalt species, it was expected that the catalytic reaction could be made more efficient by the addition of an additive stabilizing this. As additives we chose to investigate phosphines and phosphites since it was known that carbonyl ligands of alkyne−$Co_2(CO)_6$ complexes are easily replaced by one or two molecules of phosphines or phosphites[21] and the electronic and steric character of the cobalt complexes should be changed by such ligand substitution.

First in order to make clear their influence on this reaction, the reaction with a stoichiometric amount of $Co_2(CO)_8$ was examined in the presence of various additives using 1-(phenylethynyl)cyclopropanol **1b** as a substrate. Although no change was observed at room temperature on addition of a phosphine or a phosphite to **1b**-$Co_2(CO)_6$ complex **2b**, complete formation of a new complex was observed within a few minutes at reflux temperature, and the reaction was observed to proceed from this new complex to give the cyclopentenone **3b**. The new complex was isolated in the case of triphenyl phosphite and was shown on the basis of integration of its NMR spectrum to be the ligand-exchanged complex **32b** (R═OPh) where two carbonyl ligands of the complex **2b** had been exchanged for two molecules of triphenyl phosphite. These results indicate that the reaction also proceeds from the ligand-exchanged complexes **32b** with comparable yields to the reaction of the hexacarbonyldicobalt complex **2b** (Scheme 8). The reactions in the presence of several representative phosphines or phosphites were carried out in THF to compare on the basis of reaction time the reactivity of the ligand-exchanged complexes.

**Scheme 8**




It was found that the reactivity of the ligand-exchanged complex **32b** was mainly controlled by the steric characteristics of the ligand. There was no big difference in reaction time between the reactions in the presence of tributylphosphine and triphenyl phosphite, which are electronically different but whose cone angles[22] are nearly the same (5 h, 71% yield for tributylphosphine; 6 h, 86% yield for triphenyl phosphite; 6 h, 90% yield without additive). On the other hand, the bulkiness of the ligand had a considerable effect on reactivity, and the bulkier the ligand became, (that is, the larger the cone angle of the ligand became), the faster the reaction proceeded. The reaction went to completion in 1 h in refluxing THF when triphenylphosphine was used as additive (84% yield), while the reaction in the presence of trimethyl phosphite was not complete even after 17 h in refluxing THF (43% yield). The amount of additive also had a large effect on reaction time, and use of 4 molar amounts of triphenyl phosphite retarded the reaction considerably (6 h, 4% yield) although further ligand exchange of the complex **32b** was not observed. Furthermore, when an equimolar amount of a bidentate phosphine ligand dppm was added, the reaction became much slower, and even after heating for 3 h in refluxing DME **3b** was obtained only in 20% yield, 42% of the dppm substituted complex **32b** ($(PR_3)_2$ = dppm) being recovered.

As it had been confirmed that the stoichiometric reaction in the presence of 2 molar amounts of phosphines or phosphites proceeded in the same manner as the reaction without additives, we next examined reactions using a 10 mol % amount of $Co_2(CO)_8$ and 20 mol % amount of these additives. As shown in Table 5, the addition of either phosphines or phosphites improved the yield of the rearranged product considerably in all cases. Significantly, the electronic parameter of the ligand became more influential in these catalytic reactions, and phosphites, which are less electron-donating than phosphines, gave better results than the latter. When triphenyl phosphite was employed as additive, **3b** was obtained in 91% yield, which is equal to the yield of the stoichiometric reaction. This can be explained by assuming that catalyst deactivation occurs by dimerization or oligomerization of the coordinatively unsaturated

(16) The reaction of the parent cyclopropanols **25c,d** was not examined due to thier instability. The reaction of **26c,d** took nearly the same reaction time as that of **24c,d** and gave the corresponding products in comparable yield.

(17) See the Experimental Section for the details of the determination of the regio and stereochemistries of **30** and **31**.

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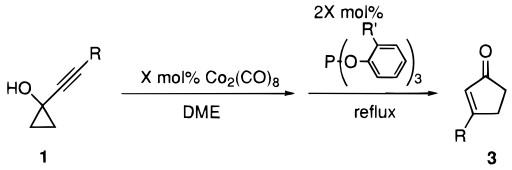
**Table 5.** Effect of Additives on the Catalytic Reactions[a]

| additives | $PR_3$/mol % | reaction time[b]/min | yield/% |
|---|---|---|---|
| none | | 60 | 43 |
| P(*n*-Bu)$_3$ | 20 | 30 | 59 |
| $PPh_3$ | 20 | 20 | 79 |
| P(O*i*-Pr)$_3$ | 20 | 30 | 74 |
| P(OPh)$_3$ | 20 | 60 | 91 |
| P(OPh)$_3$ | 40 | 240 | 91 |

[a] Reactions were run using 10 mol % amount of $Co_2(CO)_8$ in refluxing DME using **1b** as substrate. [b] Reaction time indicates the approximate time at which that the ligand-exchanged cobalt complex disappeared as judged by TLC.

**Table 6.** Effect of the ortho Substituent of Triphenylphosphite on the Catalytic Reactions




| R | R′ | cone angle | X/mol % | reaction time[a]/min | yield/% |
|---|---|---|---|---|---|
| Ph | H | 128 | 5 | 420 | 76[b] |
| Ph | Me | 141 | 5 | 120 | 84 |
| Ph | *i*-Pr | 148 | 5 | 15 | 95 |
| *n*-$C_6H_{13}$ | *i*-Pr | | 10 | 30 | 82 |
| $CH_2OSi$*t*-$BuMe_2$ | *i*-Pr | | 10 | 60 | 62 |
| $CH_2CH_2OSi$*t*-$BuMe_2$ | *i*-Pr | | 5 | 30 | 85 |
| $SiMe_3$ | *i*-Pr | | 10 | 30 | 63 |

[a] Reaction time indicates the approximate time at which the starting material **1** disappeared as judged by TLC. [b] **1** was recovered in 7% yield.

cobalt species to give cluster complexes.[23] This process is expected to be retarded when the electron density on cobalt is lowered by the less electron-donating phosphite ligand. In these reactions, the presence of ligand-exchanged complex **32b** was observed during the reaction, and $Co_2(CO)_4(P(OPh)_3)_2$ is thought to act as the real catalyst.

When the amount of the catalyst was reduced to 5 mol % of $Co_2(CO)_8$ and 10 mol % of $P(OPh)_3$ in the above reaction, the reaction did not go to completion even after prolonged reaction times, and **3b** was obtained in 76% yield with recovery of 7% of **1b**. As it was expected from the results obtained so far that a bulkier triaryl phosphite might accelerate the catalytic reaction more efficiently, we examined the reaction using various *ortho*-substituted triphenyl phosphites as additive with the results summarized in Table 6.

As expected, use of tri(*o*-tolyl) phosphite as additive promoted the reaction more effectively, and the reaction went to completion within 2 h even with only a 5 mol % amount of $Co_2(CO)_8$ and 10 mol % amount of phosphite giving the product in 84% yield. Furthermore, when a 10 mol % amount of tri(*o*-isopropylphenyl) phosphite was employed as additive, the reaction was dramatically accelerated, and the reaction was complete after 15 min, the cyclopentenone **3b** being obtained in 95% yield. However, tri(2,6-xylyl) phosphite was too bulky to replace carbonyl ligand of alkyne−cobalt complex **2b** and formation of a new complex was not observed during the reaction, nearly the same result being obtained as in the reaction with no additive.

The reactions of various 1-(1-alkynyl)cyclopropanols were examined using 5−10 mol % of $Co_2(CO)_8$ and 10−20 mol % of tri(*o*-isopropylphenyl)phosphite. Not only the 1-phenylethynylcyclopropanol **1b** but also alkyl- or silyl-substituted derivatives gave the corresponding 3-substituted 2-cyclopentenones in good to high yields (Table 6). This catalytic reaction is also applicable to the reaction of 2-methyl-1-(phenylethynyl)cyclopropanol, **7a**$_{trans}$ (10 mol % $Co_2(CO)_8$, 20 mol % $P(OPh)_3$, DME reflux, 1.6 h, 80% yield of **9a**), but the reaction of the silylated cyclopropanol derivative **7a**$_{cis}$ was not promoted effectively. This is presumably because the alkynyl part of the molecule was so crowded that the recomplexation step was retarded, resulting in interruption of the catalytic cycle.

**Mechanism of the Reaction.** Several reports have appeared on the effect of additives on the Pauson-Khand reaction. For example, addition of phosphine oxide improves the yield of cyclopentenones,[24] while addition of dimethyl sulfoxide accelerates the reaction considerably.[25] Furthermore, it has been reported that the Pauson-Khand reaction proceeds even at room temperature when a tertiary amine *N*-oxide such as trimethylamine *N*-oxide or *N*-methylmorpholine *N*-oxide is added to the alkyne-$Co_2(CO)_6$ complex in the presence of olefins.[26] With this knowledge in mind, we examined further the effect of various other additives on the reaction to obtain information on the mechanism of this rearrangement.

The reaction using **1a** as a substrate was examined employing several oxides as additive, and the reaction time necessary for consumption of the complex **2a** was compared. It revealed that addition of tributylphosphine oxide, hexamethylphosphoric triamide, and dimethyl sulfoxide all accelerated the reaction considerably. For example, the original reaction using a stoichiometric amount of $Co_2(CO)_8$ without an additive took about 90 min in refluxing DME for completion, while the reaction went to completion within 10 min on addition of 10 molar amounts of tributylphosphine oxide. It has been reported that phosphine oxide facilitates CO-$^{13}$CO exchange of $Co_4(CO)_{12}$,[27] and the acceleration of the rearrangement is thought to be related to the dissociation of the carbonyl ligand.

It is known that tertiary amine *N*-oxides attack the carbonyl ligands of transition metal carbonyl complexes generating coordinatively unsaturated species along with carbon dioxide and an amine.[28] When about 10 molar amounts of *N*-methylmorpholine *N*-oxide (NMO) was added to the alkyne−cobalt complex **2b** in THF, the reaction proceeded even at room temperature, and cyclopentenone **3b** was obtained in 37% yield accompanied by another rearranged product, methylene cyclobutanone **33**, obtained in 23% yield as a mixture of geometrical isomers. Further examination of effect of solvent revealed that when the reaction was carried out in ethanol, **3b** was obtained in 47% yield along with 9% of a cyclopentenone **34** having an ethoxycarbonyl group in the 2-position (Scheme 9). These facts indicate that dissociation of the carbonyl ligand of the alkyne−cobalt complex **2** is the rate determining step in this rearrangement. This is also supported by the fact that

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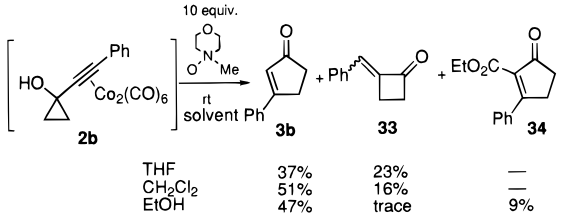
**Scheme 9**




carrying out the reaction in refluxing THF but under a CO atmosphere led to its complete suppression.

We also carried out a deuterium-labeling experiment to clarify the source of the hydrogen at the 2-position of the cyclopentenone. When the stoichiometric reaction was performed in $C_2H_5OD$, more than 90% of the hydrogen at the 2-position of cyclopentenone was deuterated. Therefore, the hydrogen at the 2-position of cyclopentenone was introduced as a proton.

These results suggest that this rearrangement of 1-(1-alkynyl)-cyclopropanols to 2-cyclopentenones is closely related to the Pauson-Khand reaction in its reaction mechanism. Although none of the intermediate complexes has been isolated or detected, we currently suppose the following mechanism for this reaction (Scheme 10). The first step of the reaction is the dissociation of a carbonyl ligand from the alkyne-$Co_2(CO)_6$ complex **2** to generate a coordinatively unsaturated alkyne-$Co_2(CO)_5$ complex **A**, which is formed thermally or by the addition of tertiary amine *N*-oxide. The coordinatively unsaturated cobalt species thus generated inserts into the carbon−carbon bond of the cyclopropanol to give a four-membered metallacyclic intermediate **B**, which rearranges into a metallacyclohexanone intermediate **C** by C−Co bond cleavage with proton transfer as indicated by path a. Reductive elimination between C1 and C2 gives a cyclopentenone−cobalt carbonyl complex **D**, which in turn gives the free cyclopentenone **3** with liberation of $Co_2(CO)_5L$ (L = CO or a solvent). The fact that the reaction using tertiary amine *N*-oxide at room temperature gives rise to the formation of the methylenecyclobutanone **33** indicates that the reaction can also proceed via path b to give **C′** and that in this case reductive elimination between C1 and C3 occurs at room temperature to give a methylenecyclobutanone−cobalt carbonyl complex **D′**. Also the formation of ethoxycarbonylated product **34** under the oxidative conditions implies that alkenyl cobalt species **E** might be formed in part in this case. The fact that both bulky substituents on the alkyne and bulky ligands accelerate the reaction can be ascribed to facilitation of ligand dissociation due to steric congestion.

Oxidative addition of the carbon−carbon bond of cyclopropanes to zerovalent cobalt species is not in general a facile process.[29] It is assumed that in this reaction the alkynyl part of the molecule is working as an anchor for the cobalt carbonyl, which enables an efficient insertion of the cobalt moiety into the proximal carbon−carbon bond of the cyclopropane to proceed. We have already found that direct substitution of the alkynyl part onto the cyclopropanol is not essential for this type of reaction,[30] and thus appropriate design of substrates should expand the scope of these synthetic reactions.

## Conclusion

A new use of alkyne−$Co_2(CO)_6$ complexes in organic synthesis has been disclosed. A hitherto unknown type of rearrangement of 1-(1-alkynyl)cyclopropanols to 2-cyclopentenones is achieved via their $Co_2(CO)_6$ complexes. This reaction has been applied to the synthesis of variously substituted 2-cyclopentenones, and furthermore found to be promoted by a catalytic amount of $Co_2(CO)_8$ in the presence of triaryl phosphite. Mechanistic studies have revealed that this reaction has a close relation with the Pauson-Khand reaction.

## Experimental Section

**General Techniques.** All reactions were carried out under an argon atmosphere under anhydrous conditions, unless otherwise noted. Solvents were distilled and stored over MS 4A. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium-benzophenone. Dimethoxyethane (DME) was distilled from $CaH_2$ and dried over MS 4A. Solvents employed for the reaction using $Co_2(CO)_8$ were degassed with sonication before use.

Column chromatography was conducted on silica gel (E. Merck, 7734, 70−230 mesh), unless otherwise noted. Preparative thin-layer chromatography (TLC) was carried out on silica gel (Wakogel-B5F).

$^1$H NMR spectra were recorded on Bruker AM500 (500 MHz) spectrometer using $CDCl_3$ as a solvent. IR spectra were recorded on a Horiba FT-300S spectrometer. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-D300 mass spectrometer operating at 70 eV.

**(1) Syntheses of 1-(1-Alkynyl)cyclopropanols 1 and 2-Substituted 1-(1-Alkynyl)cyclopropanols 7 and 10.** 1-(Phenylethynyl)cyclopropanols (**1b**) was prepared according to the literature.[9] Other 1-(1-alkynyl)cyclopropanols (**1a**, **1c**−**k**) were prepared according to the same procedure. 1-(Ethoxycarbonylethynyl)cyclopropanol (**1l**) (R = COOEt) was prepared from the literally known 1-ethynylcyclopropanol[31] by the following procedure. Hydroxyl group of 1-ethynylcyclopropanol was silylated with TBSOTf and $Et_3N$. The obtained 1-ethynyl-1-*tert*-butyldimethylsiloxycyclopropane was deprotonated with *n*-BuLi followed by reaction with ClCOOEt to give 1-*tert*-butyldimethylsiloxy-1-(ethoxycarbonylethynyl)cyclopropane. Acidic deprotection of the silyl group yielded **1l**. 2-Substituted 1-(1-alkynyl)cyclopropanols **7a**−**d** and **10a**−**c** were prepared as follows. Alkynones **5**[32] were converted to the corresponding TBS enol ethers by treatment with TBSOTf and $Et_3N$. The obtained silyl enol ethers were subjected to cyclopropanation by treatment with $Et_2Zn$ and $CH_2I_2$. Cis and trans isomers were separated at this stage. Acidic desilylation of the TBS ether of the alkynylcyclopropanols gave **7a**−**d** and **10a**−**c**. See the Supporting Information for the details of the preparation of these 1-alkynylcyclopropanols.

**(2) General Procedure for the Stoichiometric Reaction of 1-(1-Alkynyl)cyclopropanols with $Co_2(CO)_8$.** To a THF or DME solution (6 mL) of $Co_2(CO)_8$ (1.1 mmol) was added the same solution (10 mL) of 1-(1-alkynyl)cyclopropanol **1** (1 mmol) at room temperature, and after the complete formation of hexacarbonyldicobalt complex **2** was observed by thin-layer chromatography (in most cases within 30 min), the mixture was refluxed for an appropriate time under an atmospheric pressure of argon. (Usually the reaction was monitored by TLC. The end of the reaction was judged by the disappearance of the alkyne-$Co_2(CO)_6$ complex **2**.) Precipitated inorganic materials were removed by filtration through a small pad of silica gel, and after purification of crude product by silica gel TLC, 3-substituted-2-cyclopentenone **3** was obtained.

**3a**,[33] **3b**,[34] **3c**,[35] **3d**,[36] and **3l**[37] are known in the literatures. Full data of these compounds are described in the Supporting Information.

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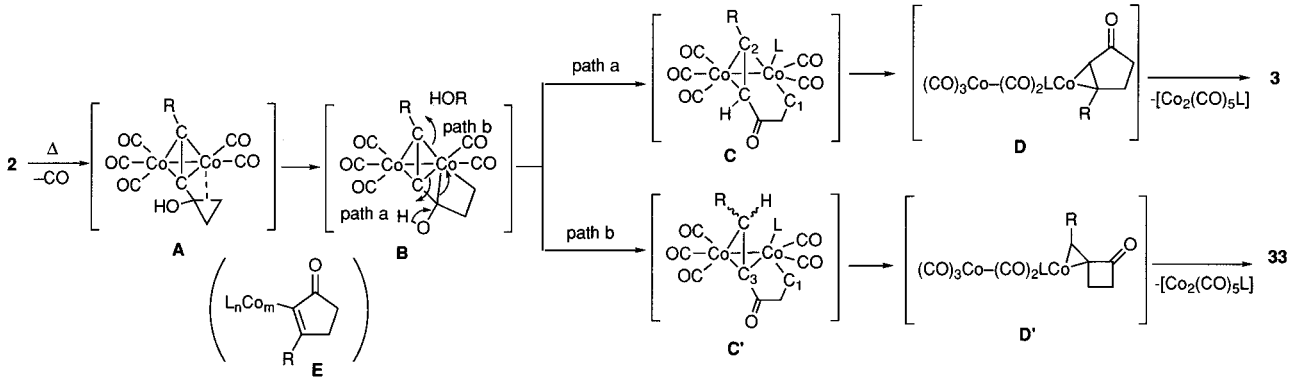
**Scheme 10**



**3-Triphenylsilyl-2-cyclopentenone (3e) (R = $SiPh_3$).** IR (KBr) 2924, 1711, 1109 $cm^{-1}$; $^1H$ NMR $\delta$ = 2.38−2.40 (2H, m), 2.83−2.85 (2H, m), 6.53 (1H, t, $J$ = 2.1 Hz), 7.38−7.41 (6H, m), 7.44−7.48 (3H, m), 7.50−7.52 (6H, m); $^{13}C$ NMR $\delta$ = 33.0, 35.2, 128.2, 130.3, 131.7, 136.0, 145.9, 178.5, 210.8. Anal. Calcd for $C_{23}H_{20}OSi$: C, 81.13; H, 5.92. Found: C, 80.99; H, 6.02.

**3-Triisopropylsilyl-2-cyclopentenone (3f) (R = TIPS).** IR (KBr) 2950, 2864, 1711, 1462, 1018 $cm^{-1}$; $^1H$ NMR $\delta$ = 1.07 (18H, d, $J$ = 7.4 Hz), 1.20−1.27 (1H, m), 2.30−2.32 (2H, m), 2.74−2.77 (2H, m), 6.41 (1H, t, $J$ = 2.0 Hz); $^{13}C$ NMR $\delta$ = 10.9, 18.5, 34.1, 34.7, 143.7, 181.5, 211.3. Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.43; H, 11.02.

**3-(*tert*-Butyldimethylsiloxymethyl)-2-cyclopentenone (3 g) (R = $CH_2OTBS$).** Mp 64.5−66.0 °C; IR (KBr) 2929, 2858, 1699, 1432, 1142, 1078, 843 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.65 (6H, s), 0.88 (9H, s), 2.39−2.41 (2H, m), 2.51−2.52 (2H, m) 4.42 (2H, d, $J$ = 0.6 Hz), 6.12−6.13 (1H, m); $^{13}C$ NMR $\delta$ = −5.6, 18.2, 25.7, 27.8, 34.9, 63.2, 128.3, 181.4, 209.1. Anal. Calcd for $C_{12}H_{22}O_2Si$: C, 63.67; H, 9.79. Found: C, 63.66; H, 9.52.

**3-(*tert*-Butylthiomethyl)-2-cyclopentenone (3h) (R = $CH_2S$*t*-Bu).** IR (neat) 2927, 1709, 1676, 1616, 1178 $cm^{-1}$; $^1H$ NMR $\delta$ = 1.29 (9H, s), 2.39−2.41 (2H, m), 2.67−2.69 (2H, m), 3.47 (2H, s), 6.07 (1H, t, $J$ = 1.1 Hz); $^{13}C$ NMR $\delta$ = 30.5, 30.65, 30.74, 35.5, 43.3, 131.1, 178.6, 209.5; HRMS calcd for $C_{10}H_{16}OS$: 184.0923. Found: 184.0939.

**3-(2-*tert*-Butyldimethylsiloxyethyl)-2-cyclopentenone (3i) (R = $CH_2CH_2OTBS$).** IR (neat) 2931, 1712, 1618, 1255, 1097 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.01 (6H, s), 0.82 (9H, s), 2.32−2.34 (2H, m), 2.56−2.58 (4H, m), 3.79 (2H, t, $J$ = 6.3 Hz), 5.94 (1H, t, $J$ = 1.2 Hz); $^{13}C$ NMR $\delta$ = −5.5, 18.1, 25.7, 31.9, 35.1, 36.6, 60.6, 130.5, 180.0, 209.9; HRMS calcd for $C_{13}H_{24}O_2Si$: 240.1546. Found: 240.1528.

**3-(2-Hydroxyethyl)-2-cyclopentenone (3j) (R = $CH_2CH_2OH$).** IR (neat) 3398, 2925, 1705, 1672, 1612, 1053 $cm^{-1}$; $^1H$ NMR $\delta$ = 2.27−2.29 (2H, m), 2.54−2.58 (4H, m), 3.55 (1H, br), 3.76 (2H, t, $J$ = 5.6 Hz), 5.90 (1H, t, $J$ = 1.2 Hz); $^{13}C$ NMR $\delta$ = 31.6, 35.0, 36.3, 59.4, 130.2, 180.9, 210.8; HRMS calcd for $C_7H_{10}O_2$: 126.0681. Found: 126.0698.

**3-Butylthio-2-cyclopentenone (3k) (R = S*n*-Bu).** IR (neat) 2929, 1701, 1682, 1547, 1265, 1178 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.91 (3H, t, $J$ = 7.4 Hz), 1.41 (2H, sextet, $J$ = 7.4 Hz), 1.65 (2H, quint, $J$ = 7.4 Hz), 2.42−2.44 (2H, m), 2.70−2.73 (2H, m), 2.86 (2H, t, $J$ = 7.4 Hz), 5.87 (1H, t, $J$ = 1.3 Hz); $^{13}C$ NMR $\delta$ = 13.5, 21.9, 30.2, 31.7, 32.4, 35.1, 123.7, 180.2, 205.3; HRMS calcd for $C_9H_{14}O_2S$: 170.0766. Found: 170.0774.

**(3) General Procedure for the Reaction of 2-Substituted 1-(1-Alkynyl)cyclopropanols with $Co_2(CO)_8$.** The reactions of 2-substituted 1-(1-alkynyl)cyclopropanols were carried out by the same procedure as described for the stoichiometric reaction of unsubsituted 1-alkynylcyclopropanols **1**. **8a**[38] and **9a**[39] are known in the literatures. Full data of these compounds are described in the Supporting Information.

**4-Isopropyl-3-phenyl-2-cyclopentenone (8b, R = Ph, $R^1$ = H, $R^2$ = *i*-Pr).** IR (neat) 2952, 2925, 1684, 1602, 1572, 1493, 1267 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.53 (3H, d, $J$ = 6.8 Hz), 1.01 (3H, d, $J$ = 6.8 Hz), 2.08−2.15 (1H, m), 2.34 (1H, d, $J$ = 18.7 Hz), 2.48 (1H, dd, $J$ = 6.6, 18.7 Hz), 3.51−3.53 (1H, m), 6.39 (1H, s), 7.41−7.46 (3H, m), 7.50−7.54 (2H, m); $^{13}C$ NMR $\delta$ = 14.5, 21.8, 28.4, 36.4, 46.2, 127.1, 128.6, 129.8, 130.6, 134.0, 178.2, 208.6; HRMS calcd for $C_{14}H_{16}O$: 200.1201. Found: 200.1177.

**5-Isopropyl-3-phenyl-2-cyclopentenone (9b, R = Ph, $R^1$ = H, $R^2$ = *i*-Pr).** IR (neat) 2954, 2925, 1689, 1603, 1572, 1495, 1448, 1178 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.80 (3H, d, $J$ = 6.8 Hz), 1.02 (3H, d, $J$ = 6.9 Hz), 2.27−2.33 (1H, m), 2.54−2.57 (1H, m), 2.74−2.79 (1H, m), 2.97−3.04 (1H, m), 6.52 (1H, t, $J$ = 1.5 Hz), 7.42−7.44 (3H, m), 7.64−7.66 (2H, m); $^{13}C$ NMR $\delta$ = 17.1, 20.8, 28.9, 30.9, 51.9, 126.8, 127.7, 128.9, 131.2, 134.1, 172.9, 211.2; HRMS calcd for $C_{14}H_{16}O$: 200.1201. Found: 200.1201.

**3-Hexyl-4-methyl-2-cyclopentenone (8c, R = *n*-Hex, $R^1$ = H, $R^2$ = Me).** IR (neat) 2931, 2925, 1709, 1614, 1458 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.87 (3H, t, $J$ = 6.9 Hz), 1.16 (3H, d, $J$ = 7.2 Hz), 1.25−1.48 (6H, m), 1.49−1.58 (2H, m), 1.97 (1H, dd, $J$ = 2.2, 18.6 Hz), 2.25 (1H, ddd, $J$ = 5.9, 9.0, 16.0 Hz), 2.41 (1H, dt, $J$ = 8.1, 16.0 Hz), 2.61 (1H, dd, $J$ = 6.6, 18.6 Hz), 2.80−2.86 (1H, m), 5.86 (1H, d, $J$ = 1.3 Hz); $^{13}C$ NMR $\delta$ = 14.0, 19.0, 22.5, 26.9, 29.1, 30.9, 31.5, 37.7, 44.0, 128.7, 187.0, 209.0. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.70; H, 11.14.

**3-Hexyl-5-methyl-2-cyclopentenone (9c, R = *n*-Hex, $R^1$ = H, $R^2$ = Me).** IR (neat) 2956, 2925, 1701, 1616, 1458 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.87 (3H, t, $J$ = 6.3 Hz), 1.14 (3H, d, $J$ = 7.6 Hz), 1.23−1.36 (6H, m), 1.49−1.58 (2H, m), 2.14 (1H, d, $J$ = 18.3 Hz), 2.35−2.41 (3H, m), 2.79 (1H, dd, $J$ = 7.0, 18.3 Hz), 5.87 (1H, t, $J$ = 1.7 Hz); HRMS calcd for $C_{12}H_{20}O$: 180.1515. Found: 180.1488.

**3-Hexyl-4-isopropyl-2-cyclopentenone (8d, R = *n*-Hex, $R^1$ = H, $R^2$ = *i*-Pr).** IR (neat) 2927, 1714, 1687, 1614, 1464 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.59 (3H, d, $J$ = 6.8 Hz), 0.85 (3H, t, $J$ = 6.9 Hz), 0.95 (3H, d, $J$ = 6.9 Hz), 1.21−1.34 (6H, m), 1.46−1.60 (2H, m), 2.09−2.15 (1H, m), 2.12 (1H, dd, $J$ = 2.2, 18.5 Hz), 2.18−2.24 (1H, m), 2.25 (1H, dd, $J$ = 6.8, 18.5 Hz), 2.33−2.40 (1H, m), 2.81−2.84 (1H, m), 5.91 (1H, q, $J$ = 1.4 Hz); $^{13}C$ NMR $\delta$ = 14.0, 14.6, 21.7, 22.5, 26.9, 27.6, 29.1, 31.2, 31.5, 35.8, 48.7, 129.9, 185.3, 209.3. HRMS calcd for $C_{14}H_{24}O$: 208.1828. Found: 208.1820.

**3-Hexyl-5-isopropyl-2-cycloopentenone (9d, R = *n*-Hex, $R^1$ = H, $R^2$ = *i*-Pr).** IR (neat) 2924, 1697, 1618, 1464 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.71 (3H, d, $J$ = 6.8 Hz), 0.85 (3H, t, $J$ = 6.9 Hz), 0.93 (3H, d, $J$ = 7.0 Hz), 1.21−1.33 (6H, m), 1.54 (2H, quint, $J$ = 7.5 Hz), 2.16−2.23 (1H, m), 2.28−2.38 (3H, m), 2.52 (1H, ddd, $J$ = 1.3, 7.0, 18.4 Hz), 5.87 (1H, quint, 1.3 Hz); $^{13}C$ NMR $\delta$ = 14.0, 16.8, 20.7, 22.5, 27.0, 28.5, 28.9, 31.5, 33.48, 33.55, 51.8, 129.7, 182.3, 211.9. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.49; H, 11.75.

**5,5-Dimethyl-3-phenyl-2-cyclopentenone (12a, R = Ph, $R^1$ = $R^2$ = Me).** Mp 85.0−86.0 °C; IR (KBr) 2924, 1681, 1597, 1572, 1450, 1136 $cm^{-1}$; $^1H$ NMR $\delta$ = 1.17 (6H, s), 2.86 (2H, d, $J$ = 1.6 Hz), 6.45 (1H, t, $J$ = 1.6 Hz), 7.40−7.42 (3H, m), 7.59−7.61 (2H, m); $^{13}C$ NMR $\delta$ = 25.2, 44.1, 45.1, 124.6, 126.7, 128.8, 131.1, 133.9, 170.4, 213.7. Anal. Calcd for $C_{13}H_{14}O$: C, 83.84; H, 7.57. Found: C, 83.89; H, 7.60.

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**3-Phenylspiro[4.5]-2-decen-1-one (12b, R = Ph, $R^1$ = $R^2$ = $(CH_2)_5$).** IR (neat) 2929, 2852, 1687, 1603, 1573, 1448, 1194 $cm^{-1}$; $^1H$ NMR $\delta$ = 1.30−1.44 (5H, m), 1.62−1.79 (5H, m), 2.89 (2H, d, *J* = 1.6 Hz), 6.48 (1H, t, *J* = 1.6 Hz), 7.42−7.44 (3H, m), 7.65−7.66 (2H, m); $^{13}C$ NMR $\delta$ = 23.0, 25.2, 33.5, 41.5, 49.3, 125.2, 126.8, 128.8, 131.1, 134.1, 171.0, 213.8; HRMS calcd for $C_{16}H_{18}O$: 226.1358. Found: 226.1346.

**3-Hexyl-5,5-dimethyl-2-cyclopentenone (12c, R = *n*-Hex, $R^1$ = $R^2$ = Me).** IR (neat) 2956, 2927, 1705, 1618, 1468 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.86 (3H, t, *J* = 6.9 Hz), 1.07 (6H, s), 1.25−1.32 (6H, m), 1.54 (2H, quint, *J* = 7.3 Hz), 2.34 (2H, t, *J* = 7.6 Hz), 2.40 (2H, d, *J* = 1.0 Hz), 5.82 (1H, t, *J* = 1.0 Hz); $^{13}C$ NMR $\delta$ = 14.0, 22.5, 25.1, 26.9, 28.9, 31.5, 33.4, 44.0, 48.2, 126.7, 179.8, 214.5; HRMS calcd for $C_{13}H_{22}O$:194.1671. Found: 194.1662.

**(4) Preparation of 2,3-Dimethyl-1-(1-phenylethynyl)cyclopropanols.** (*E*)- and (*Z*)-TBS enol ethers of 1-phenyl-1-pentyn-3-one were prepared as described in the preparation of 2-substituted 1-(1-alkynyl)-cyclopropanols. The products were carefully separated using silica gel deactivated with 10% water. Then each isomer was treated with $Et_2$-Zn and $CH_3CHI_2$. From both isomers, diastereomeric pairs of TBS ethers of 2,3-dimethylcyclopropanols were obtained. The isomer which was obtained from both (*E*)- and (*Z*)-isomers was assigned as 2,3-trans isomer **14**. The remaining two isomers were assigned as 2,3-cis isomers **13** and **15** based on the geometry of the silyl enol ether employed.

**(*E*)- and (*Z*)-Silyl Enol Ethers 6. (*Z*)-3-*tert*-Butyldimethylsiloxy-1-phenyl-3-pentene-1-yne ((*Z*)-6:$R^1$ = Ph, $R^2$ = Me).** IR (neat) 2858, 1641, 1489, 1319 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.28 (6H, s), 1.00 (9H, s), 1.70 (3H, d, *J* = 7.0 Hz), 5.24 (1H, q, *J* = 7.0 Hz), 7.29−7.32 (3H, m), 7.41−7.43 (2H, m); $^{13}C$ NMR $\delta$ = −4.2, 11.1, 18.2, 25.7, 86.8, 87.6, 114.8, 122.9, 128.2, 128.3, 131.2, 133.0; HRMS calcd for $C_{17}H_{24}OSi$: 272.1597. Found: 272.1567.

**(*E*)-3-*tert*-Butyldimethylsiloxy-1-phenyl-3-pentene-1-yne ((*E*)-6: $R^1$ = Ph, $R^2$ = Me).** IR (neat) 2929, 1633, 1489, 1338, 1252, 1192 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.21 (6H, s), 0.94 (9H, s), 1.79 (3H, d, *J* = 7.2 Hz), 5.36 (1H, q, *J* = 7.2 Hz), 7.30−7.32 (3H, m), 7.42−7.45 (2H, m); $^{13}C$ NMR $\delta$ = −4.4, 13.3, 18.2, 25.7, 85.1, 92.6, 115.0, 122.9, 128.33, 128.35, 131.3, 133.9; HRMS calcd for $C_{17}H_{24}OSi$: 272.1597. Found: 272.1584.

**TBS Ethers of 2,3-Dimethylcyclopropanols 13−15. (2*S**,3*S**)-1-*tert*-Butyldimethylsiloxy-2,3-dimethyl-1-(phenylethynyl)cyclopropane (13).** IR (neat) 2927, 1596, 1490, 1251, 1221 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.20 (3H, s), 0.25 (3H, s), 0.70 (1H, quint, *J* = 6.4 Hz), 0.80 (1H, quint, *J* = 6.4 Hz), 0.89 (9H, s), 1.16 (3H, d, *J* = 6.4 Hz), 1.17 (3H, d, *J* = 6.4 Hz), 7.25−7.29 (3H, m), 7.36−7.39 (2H, m); $^{13}C$ NMR $\delta$ = −4.2, −3.8, 11.9, 14.9, 18.0, 25.8, 29.2, 29.3, 54.7, 84.2, 90.7, 123.5, 127.7, 128.2, 131.3; HRMS calcd for $C_{19}H_{28}OSi$: 300.1910. Found: 300.1930.

**(1*S**,2*R**,3*S**)-1-*tert*-Butyldimethylsiloxy-2,3-dimethyl-1-(phenylethynyl)cyclopropane (14).** IR (neat) 2929, 1599, 1248, 1043 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.25 (6H, s), 0.90 (9H, s), 0.98 (6H, d, *J* = 4.0 Hz), 1.21 (2H, q, *J* = 4.0 Hz), 7.25−7.27 (3H, m), 7.35−7.37 (2H, m); $^{13}C$ NMR $\delta$ = −3.7, 6.4, 18.5, 23.8, 26.0, 49.9, 81.4, 94.2, 123.5, 127.7, 128.2, 131.3. Anal. Calcd for $C_{19}H_{28}OSi$: C, 75.94; H, 9.39. Found: C, 75.72; H, 9.16.

**(1*R**,2*R**,3*S**)-1-*tert*-Butyldimethylsiloxy-2,3-dimethyl-1-(phenylethynyl)cyclopropane (15).** IR (neat) 2929, 1596, 1491, 1255, 1184, 1120 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.20 (6H, s), 0.87 (9H, s), 1.04 (6H, d, *J* = 4.0 Hz), 1.25 (2H, q, *J* = 4.0 Hz), 7.27−7.29 (3H, m), 7.39−7.40 (2H, m); $^{13}C$ NMR $\delta$ = −4.0, 8.8, 17.7, 25.7, 56.4, 87.3, 87.7, 123.5, 127.8, 128.2, 131.4. Anal. Calcd for $C_{19}H_{28}OSi$: C, 75.94; H, 9.39. Found: C, 75.72; H, 9.19.

**(5) Procedure for the Reaction of 2,3-Dimethyl-1-(phenylethynyl)cyclopropanols with $Co_2(CO)_8$.** The reactions of TBS ethers of 2,3-dimethyl-1-(phenylethynyl)cyclopropanols **13**−**15** were carried out by the same procedure as describe for the stoichiometric reaction of unsubsituted 1-alkynylcyclopropanols **1**. The products were usually obtained as an inseparable mixture of **16**−**18**, and the ratios were determined by integration of $^1H$ NMR. As **16** was obtained as a single isomer, satisfactory characterization was carried out, but only $^1H$ NMR data are shown for **17** and **18**.

The stereochemistries of the products were determined by the differential NOE spectra of these compounds. In the case of the 4,5-cis isomer **17**, 8.7% of NOE was observed between the methine protons of C-4 and C-5, while no NOE was observed between these protons in the case of 4,5-trans isomer **16**. Furthermore, the coupling constants between these protons (for **16**, *J* = 1.8 Hz and for **17**, *J* = 7.2 Hz) supported this assignment.

***trans*-4,5-Dimethyl-3-phenyl-2-cyclopentenone (16).** IR (neat) 2962, 1697, 1595, 1448, 1186 $cm^{-1}$; $^1H$ NMR $\delta$ = 1.23 (3H, d, *J* = 7.0 Hz), 1.26 (3H, d, *J* = 7.5 Hz), 2.14 (1H, dq, *J* = 1.8, 7.5 Hz), 3.02 (1H, dq, *J* = 1.8, 7.0 Hz), 6.34 (1H, s), 7.42−7.43 (3H, m), 7.52−7.54 (2H, m); $^{13}C$ NMR $\delta$ = 16.0, 19.5, 44.0, 50.1, 126.7, 127.4, 128.8, 130.6, 133.6, 177.6, 210.9; HRMS calcd for $C_{13}H_{14}O$: 186.1045. Found: 186.1040.

***cis*-4,5-Dimethyl-3-phenyl-2-cyclopentenone (17).** $^1H$ NMR $\delta$ = 1.10 (3H, d, *J* = 7.2 Hz), 1.18 (3H, d, *J* = 7.5 Hz), 2.73 (1H, quint, *J* = 7.5 Hz), 3.59 (1H, quint, *J* = 7.2 Hz), 6.42 (1H, s), 7.42−7.45 (3H, m), 7.54−7.60 (2H, m).

**2,3-Dimethyl-4-phenyl-2-cyclopentenone (18).** $^1H$ NMR $\delta$ = 1.77 (3H, s), 1.80 (3H, s), 2.34 (1H, dd, *J* = 2.1, 18.8 Hz), 2.88 (1H, dd, *J* = 7.0, 18.8 Hz), 3.78 (1H, dd, *J* = 2.1, 7.0 Hz), 7.05−7.07 (2H, m), 7.19−7.22 (1H, m), 7.28−7.31 (2H, m).

**(6) General Procedure for the Preparation of Bicyclic Alkynylcyclopropanols.** Alkynylborates were prepared according to the literature procedure.[40]

To a THF solution (2.5 mL) of a dibromocyclopropane (2.0 mmol) was added dropwise a 1.65 M hexane solution (1.2 mL, 2.0 mmol) of *n*-BuLi at −100 °C, and the mixture was stirred at this temperature for 10 min. Then a THF solution (1.8 mL) of alkynylborate (2.1 mmol) was added to this mixture at −100 °C, and the mixture was slowly warmed to room temperature overnight. Then the mixture was heated to reflux for 10 h. At 0 °C, 10% aqueous NaOH solution (3 mL) and 30% $H_2O_2$ solution (3 mL) were added successively, and the mixture was further stirred at room temperature overnight. Then the products were extracted with ether three times, and the combined extracts were dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by silica gel column chromatograpy to give the bicyclic alkynylcyclopropanol.

In the case of the reaction of 8,8-dibromobicyclo[5.1.0]octane, the crude product was directly treated with TBSOTf and $Et_3N$ in $CH_2Cl_2$, and the product was isolated as their TBS ether. Due to their instability, **25c**,**d** were employed as their TBS ether for the rearrangement reaction. **24c**,**d** were deprotected just before use by the procedure described for the preparation of 2-substituted 1-(1-alkynyl)cyclopropanols.

**(1*R**,6*S**,7*R**)-7-(Phenylethynyl)bicyclo[4.1.0]heptan-7-ol (24a).** IR (KBr) 3203, 2935, 1599, 1491, 1188, 1091 $cm^{-1}$; $^1H$ NMR $\delta$ = 1.15−1.22 (2H, m), 1.34−1.41 (2H, m), 1.43−1.48 (2H, m), 1.70−1.75 (2H, m), 1.88−1.92 (2H, m), 2.41 (1H, br), 7.28−7.30 (3H, m), 7.41−7.43 (2H, m); $^{13}C$ NMR $\delta$ = 19.6, 21.0, 25.1, 54.9, 87.4, 89.6, 123.1, 128.1, 128.3, 131.4. Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.79; H, 7.71.

**(1*R**,6*S**,7*R**)-7-(1-Hexynyl)bicyclo[4.1.0]heptan-7-ol (24b).** IR (neat) 3344, 2935, 1448, 1194, 1092 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.89 (3H, t, *J* = 7.2 Hz), 1.09−1.22 (2H, m), 1.25−1.32 (4H, m), 1.38−1.45 (2H, m), 1.47−1.52 (2H, m), 1.58−1.63 (2H, m), 1.79−1.84 (2H, m), 2.20 (1H, br), 2.28 (2H, t, *J* = 6.9 Hz); $^{13}C$ NMR $\delta$ = 13.6, 18.7, 19.5, 20.9, 21.9, 24.0, 30.9, 54.9, 77.7, 90.4; HRMS calcd for $C_{13}H_{20}O$: 192.1514. Found: 192.1538.

**(1*R**,7*S**,8*R**)-8-*tert*-Butyldimethylsiloxy-8-(phenylethynyl)bicyclo-[5.1.0]octane (24c).** IR (neat) 2920, 2854, 1490, 1253, 1130 $cm^{-1}$; $^1H$ NMR $\delta$ = 0.20 (6H, s), 0.87 (9H, s), 1.09−1.19 (1H, m), 1.22−1.36 (6H, m), 1.78−1.81 (2H, m), 1.88−1.90 (1H, m), 2.12−2.17 (2H, m), 7.27−7.30 (3H, m), 7.40−7.43 (2H, m); $^{13}C$ NMR $\delta$ = −4.1, 17.7, 25.7, 27.0, 29.3, 32.8, 32.9, 58.5, 87.3, 88.6, 123.5, 127.9, 128.2, 131.4. Anal. Calcd for $C_{22}H_{32}OSi$: C, 77.59; H, 9.47. Found: C, 77.53; H, 9.49.

**(1*R**,7*S**,8*S**)-8-*tert*-Butyldimethylsiloxy-8-(phenylethynyl)bicyclo-[5.1.0]octane (25c).** IR (neat) 2927, 1599, 1491, 1244, 1089 $cm^{-1}$;

(40) Brown, H. C.; Bhat, N. G.; Srebnik, M. *Tetrahedron Lett.* **1988**, *29*, 5289.

$^1$H NMR $\delta$ = 0.26 (6H, s), 0.94 (9H, s), 1.10−1.20 (1H, m), 1.33−1.37 (6H, m), 1.79−1.83 (2H, m), 1.89−1.91 (3H, m), 7.25−7.28 (3H, m), 7.35−7.39 (2H, m); $^{13}$C NMR $\delta$ = −3.8, 18.5, 23.5, 26.2, 29.0, 31.6, 32.9, 53.3, 81.6, 93.8, 123.5, 127.7, 128.2, 131.2. Anal. Calcd for $C_{22}H_{32}OSi$: C, 77.59; H, 9.47. Found: C, 77.88; H, 9.58.

**(1*R**,7*S**,8*R**)-8-*tert*-Butyldimethylsiloxy-8-(1-hexynyl)bicyclo-[5.1.0]octane (24d).** IR (neat) 2956, 1471, 1230, 1132, cm$^{-1}$; $^1$H NMR $\delta$ = 0.14 (6H, s), 0.83 (9H, s), 0.89 (3H, t, $J$ = 7.2 Hz), 1.04−1.19 (5H, m), 1.23−1.30 (2H, m), 1.39−1.43 (2H, m), 1.45−1.50 (2H, m), 1.75−1.76 (2H, m), 1.83−1.86 (1H, m), 2.04−2.06 (2H, m), 2.25 (2H, t, $J$ = 7.0 Hz). Anal. Calcd for $C_{20}H_{36}OSi$: C, 74.93; H, 11.32. Found: C, 74.85; H, 11.18.

**(1*R**,7*S**,8*S**)-8-*tert*-Butyldimethylsiloxy-8-(1-hexynyl)bicyclo-[5.1.0]octane (25d).** IR (neat) 2927, 1250, 1082, cm$^{-1}$; $^1$H NMR $\delta$ = 0.18 (6H, s), 0.87 (3H, t, $J$ = 7.3 Hz), 0.89 (9H, s), 1.10−1.14 (3H, m), 1.26−1.36 (4H, m), 1.37−1.47 (4H, m), 1.76−1.86 (5H, m), 2.15 (2H, t, $J$ = 7.1 Hz); $^{13}$C NMR $\delta$ = −3.9, 13.6, 18.4, 18.5, 22.0, 23.5, 26.2, 29.1, 30.8, 31.1, 32.9, 53.2, 81.8, 84.2; HRMS calcd for $C_{20}H_{36}$-OSi: 320.2536. Found: 320.2555.

**(1*R**,7*S**,8*R**)-8-(Phenylethynyl)bicyclo[5.1.0]octan-8-ol (24c).** IR (neat) 3298, 2922, 1600, 1490, 1321, 1097 cm$^{-1}$; $^1$H NMR $\delta$ = 1.07−1.15 (1H, m), 1.20−1.38 (4H, m), 1.43−1.49 (2H, m), 1.77−1.80 (2H, m), 1.87−1.90 (1H, m), 2.14−2.17 (2H, m), 2.44 (1H, br), 7.29−7.30 (3H, m), 7.43−7.45 (2H, m); $^{13}$C NMR $\delta$ = 26.9, 29.1, 32.6, 32.7, 57.6, 87.3, 87.7, 123.1, 128.1, 128.2, 131.6. Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.66; H, 7.99.

**(1*R**,7*S**,8*R**)-8-(1-Hexynyl)bicyclo[5.1.0]octan-8-ol (24d).** IR (KBr disk) 3259, 2921, 1459, 1107 cm$^{-1}$; $^1$H NMR $\delta$ = 0.90 (3H, t, $J$ = 7.3 Hz), 1.05−1.15 (4H, m), 1.26−1.31 (4H, m), 1.39−1.44 (2H, m), 1.47−1.52(2H, m), 1.74−1.80 (2H, m), 1.84−1.90 (1H, m), 2.05−2.08 (2H, m), 2.28 (2H, t, $J$ = 7.0 Hz); $^{13}$C NMR $\delta$ = 13.6, 18.6, 21.9, 26.9, 29.2, 31.0, 31.8, 32.8, 57.7, 78.0, 88.0; HRMS calcd for $C_{14}H_{22}O$: 206.1670. Found: 206.1658.

**Steroidal Cycloparopanol 29.** IR (neat) 3354, 2943, 1442, 1365, 1093, 754 cm$^{-1}$; $^1$H NMR $\delta$ = 0.63 (3H, s), 0.75 (3H, s), 0.84 (3H, d, $J$ = 2.2 Hz), 0.85 (3H, d, $J$ = 2.1 Hz), 0.88 (3H, d, $J$ = 6.4 Hz), 1.72−1.76 (1H, m), 2.05−2.10 (1H, m), 2.58 (1H, s), 7.30−7.31 (3H, m), 7.39−7.41 (2H, m); $^{13}$C NMR $\delta$ = 12.0, 12.1, 18.7, 20.9, 22.5, 22.8, 23.8, 24.19, 24.23, 24.5, 25.4, 28.0, 28.2, 29.6, 32.0, 33.5, 33.8, 35.8, 36.0, 36.2, 39.1, 39.5, 40.0, 42.3, 53.6, 55.0, 56.3, 56.4, 87.3, 89.5, 123.2, 128.0, 128.4, 131.2; HRMS Calcd for $C_{36}H_{52}O$: 500.4018. Found: 500.4029.

**(7) General Procedure for the Reaction of Bicyclic Alkynylcyclopropanols with $Co_2(CO)_8$.** The reactions of bicyclic alkynylcyclopropanols were carried out by the same procedure as described for the stoichiometric reaction of unsubsituted 1-alkynylcyclopropanols **1**.

**9-Phenylbicyclo[4.3.0]nona-8-en-7-one (28a).** IR (neat) 2935, 1684, 1589, 1568, 1446, 1174 cm$^{-1}$; $^1$H NMR $\delta$ = 0.98−1.06 (1H, m), 1.15−1.24 (1H, m), 1.27−1.36 (1H, m), 1.52−1.70 (3H, m), 2.12−2.22 (2H, m), 2.65 (1H, dt, $J$ = 3.5, 6.5 Hz), 3.45 (1H, dt, $J$ = 6.5, 10.1 Hz), 6.44 (1H, s), 7.41−7.45 (3H. m), 7.60−7.63 (2H, m); $^{13}$C NMR $\delta$ = 21.9, 22.35, 22.40, 30.7, 40.5, 47.6, 125.2, 127.1, 128.9, 130.8, 133.3, 177.5, 210.0. Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.67; H, 7.70.

**9-Butylbicyclo[4.3.0]nona-8-en-7-one (28b).** IR (neat) 2927, 1701, 1610, 1450 cm$^{-1}$; $^1$H NMR $\delta$ = 0.92 (3H, t, $J$ = 7.4 Hz), 1.05−1.12 (1H, m), 1.20−1.40 (5H, m), 1.47−1.67 (4H, m), 1.90−2.00 (2H, m), 2.24−2.31 (1H, m), 2.38−2.45 (2H, m), 2.77−2.82 (1H, m), 5.86 (1H, d, $J$ = 1.1 Hz); $^{13}$C NMR $\delta$ = 13.8, 21.4, 21.7, 22.53, 22.55, 28.1, 28.9, 31.0, 43.0, 46.6, 127.0, 185.6, 211.2; HRMS Calcd for $C_{13}H_{20}O$: 192.1514. Found: 192.1526

**10-Phenylbicyclo[5.3.0]deca-9-en-8-one (28c).** IR (neat) 2924, 1693, 1674, 1593, 1446 cm$^{-1}$; $^1$H NMR $\delta$ = 1.33−1.46 (4H, m), 1.62−1.65 (3H, m), 1.67−1.76 (1H, m), 1.87−1.91 (1H, m), 2.06−2.12 (1H, m), 2.73−2.78 (1H, m), 3.59−3.63 (1H, m), 6.40 (1H, d, $J$ = 1.3 Hz), 7.40−7.44 (3H, m), 7.50−7.53 (2H, m); $^{13}$C NMR $\delta$ = 27.3, 27.6, 28.2, 30.1, 31.0, 46.9, 52.0, 127.1, 128.2, 128.8, 130.4, 134.1, 177.9, 210.9; HRMS Calcd for $C_{16}H_{18}O$: 226.1358. Found: 226.1350

**10-Butylbicyclo[5.3.0]deca-9-en-8-one (28d).** IR (neat) 2918, 1699, 1614, 1456 cm$^{-1}$; $^1$H NMR $\delta$ = 0.91 (3H, t, $J$ = 7.4 Hz), 1.33−1.70 (12H, m), 1.89−1.96 (2H, m), 2.21−2.27 (1H, m), 2.37−2.44 (1H, m), 2.50−2.54 (1H, m), 2.91−2.97 (1H, m), 5.93 (1H, s); $^{13}$C NMR $\delta$ = 13.8, 22.5, 27.8, 28.2, 29.0, 29.1, 30.9, 31.1, 49.2, 51.6, 128.8, 185.3, 211.7; HRMS Calcd for $C_{14}H_{22}O$: 206.1670. Found: 206.1672.

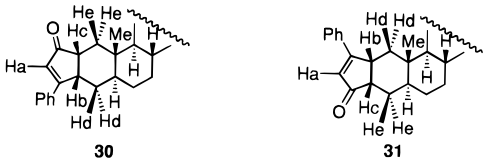


**Figure 1.**

**Steroidal Cyclopenetenone 30.** IR (neat) 2941, 2856, 1693, 1570, 1464, 1381 cm$^{-1}$; $^1$H NMR $\delta$ = 0.61 (3H, s), 0.82 (3H, s), 0.83 (3H, d, $J$ = 1.9 Hz), 0.84 (3H, d, $J$ = 1.8 Hz), 0.88 (3H, d, $J$ = 6.5 Hz), 1.91−1.96 (1H, m), 2.10 (1H, dd, $J$ = 7.7, 13.5 Hz), 2.73 (1H, dt, $J$ = 13.5, 6.3 Hz), 3.54−3.58 (1H, m), 6.18 (1H,. d, $J$ = 1.8 Hz), 7.42−7.43 (5H, m); $^{13}$C NMR $\delta$ = 11.3, 12.0, 18.6, 20.8, 22.5, 22.8, 23.8, 24.2, 28.0, 28.2, 28.6, 28.8, 31.5, 35.59, 35.63, 35.8, 36.1, 38.7, 39.5, 39.8, 39.9, 41.4, 42.4, 44.3, 53.7, 56.2, 56.4, 127.4, 127.8, 128.8, 130.0, 134.3, 177.5, 211.9; HRMS Calcd for $C_{36}H_{52}O$: 500.4018. Found: 500.4017.

**Steroidal Cyclopentenone 31.** IR (neat) 2931, 2868, 1684, 1597, 1446, 1190, 1092 cm$^{-1}$; $^1$H NMR $\delta$ = 0.65 (3H, s), 0.83 (3H, d, $J$ = 2.4 Hz), 0.85 (3H, d, $J$ = 2.3 Hz), 0.87 (3H, d, $J$ = 6.5 Hz), 0.93 (3H, s), 2.31 (1H, dd, $J$ = 6.4, 11.3 Hz), 2.40−2.44 (1H, m), 3.44−3.47 (1H, m), 6.35 (1H,. s), 7.41−7.42 (3H, m), 7.53−7.55 (2H, m); $^{13}$C NMR $\delta$ = 12.1, 16.6, 18.7, 21.6, 22.5, 22.8, 23.8, 24.1, 26.0, 26.4, 28.0, 28.2, 31.4, 35.6, 35.7, 35.8, 35.9, 36.2, 39.5, 40.0, 40.2, 42.6, 43.0, 50.0, 55.3, 56.3, 56.4, 127.1, 127.9, 128.8, 130.4, 133.8, 176.5, 211.0; HRMS Calcd for $C_{36}H_{52}O$: 500.4018. Found: 500.4027.

In this reaction **30** and **31** were obtained in about 3:1 ratio. Assignment of the regiochemistry of the products was carried out as follows. The major isomer **30** has the olefinic proton Ha at $\delta$ = 6.18 which is coupled ($J$ = 1.8 Hz) with the bridgehead proton Hb ($\delta$ = 3.54−3.58). Also moderate NOE is observed between Hb and the *ortho* proton of the phenyl group. The signal at $\delta$ = 2.73 is assigned as Hc because strong NOE is observed with Hb, and CH−COSY and DEPT spectra indicate that this signal is a methine proton. HH−COSY spectrum also indicates that Hb is coupled with Hc and one of Hd ($\delta$ = 1.6, dt, $J$ = 8.5, 13.4 Hz), while Hc is coupled with Hb and both of He ($\delta$ = 2.10, dd, $J$ = 7.5, 13.5 Hz and $\delta$ = 0.96, coupling uncertain due to overlapping). The fact that one of Hd appears as a double triplet suggests that this proton is further coupled with another proton with a coupling constant of 8.5 Hz. This is compatible with **30** but not with **31** due to the presence of the bridgehead methyl group as shown in Figure 1. The fact that one of He clearly appears as a double doublet also supports this assignment.

Facial selectivity of this annulation reaction was determined at the cyclopropanation step. Although we have not been successful in assigning the structure at this stage, we have observed moderate NOE between Hc and the bridgehead methyl group ($\delta$ = 0.82), which enabled the assignment as shown in **30**. This assignment is quite reasonable because attack from $\beta$-face is thought to be unfavorable due to the presence of the axial methyl group.

As the cyclopropanation gave one isomer selectively and the employed alkynylcyclopropanol was diastereomerically pure, the other isomer **31** obtained on the rearrangement was assigned as the regioisomer of the major isomer **30**.

**(8) Stoichiometric Reaction in the Presence of Additive.** To a DME solution (5 mL) of $Co_2(CO)_8$ (0.50 mmol) was added a DME solution (5 mL) of 1-alkynylcyclopropanol (0.45 mmol) at room temperature under an argon atmosphere. After the mixture was stirred for 30 min, a DME solution (5 mL) of an additive (usually 1.00 mmol) was added to the mixture. The mixture had been heated to reflux until the starting material disappeared. After filtration through a small pad of silica gel, the filtrate was concentrated, and the residue was subjected to silica gel TLC to give the corresponding 2-cyclopentenone derivative.

**(9) Catalytic Reaction in the Presence of Tri(*o*-isopropylphenyl)-phosphite.** To a DME solution (1 mL) of $Co_2(CO)_8$ (0.027 mmol) was added a DME solution (1 mL) of 1-alkynylcyclopropanol (0. 53 mmol) at room temperature under an argon atmosphere. After the

mixture was stirred for 30 min, a DME solution (7 mL) of tri(*o*-isopropylphenyl) phosphite (0.053 mmol) was added to the mixture. The mixture had been heated to reflux until the starting material disappeared. After filtration through a small pad of silica gel, the filtrate was concentrated, and the residue was subjected to silica gel TLC to give the corresponding 2-cyclopentenone derivative.

**(10) Oxidative Reaction Employing NMO.** To a $CH_2Cl_2$ solution (2 mL) of $Co_2(CO)_8$ (0.41 mmol) was added a $CH_2Cl_2$ solution (2 mL) of 1-phenylethynylcyclopropanol (0.32 mmol) at room temperature under an argon atmosphere. After the mixture was stirred for 30 min, 20 mL of $CH_2Cl_2$ was added, and then NMO (3.80 mmol) was added to the mixture in one portion. After the mixture was stirred at room temperature overnight, it was filtered through a small pad of silica gel, and the filtrate was concentrated. The residue was subjected to silica gel TLC to give the products.

**(*Z*)-2-Benzylidenecyclobutanone ((*Z*)-33).** IR (neat) 1732, 1630, 1088, 1070, 1024 $cm^{-1}$; $^1H$ NMR $\delta = 2.70$ (2H, dt, $J = 2.3$, 8.6 Hz), 2.90−2.94 (2H, m), 6.29 (1H, t, $J = 2.3$ Hz), 7.33−7.39 (3H, m), 7.94−7.96 (2H, m); $^{13}C$ NMR $\delta = 21.3$, 42.0, 128.5, 129.8, 129.9, 133.4, 134.7, 145.7, 196.9; HRMS Calcd for $C_{11}H_{10}O$: 158.0732. Found: 158.0717.

**(*E*)-2-Benzylidenecyclobutanone ((*E*)-33).** IR (neat) 2935, 1738, 1645, 1452, 1296, 1101 $cm^{-1}$; $^1H$ NMR $\delta = 2.96$ (2H, dt, $J = 2.7$, 7.8 Hz), 3.10−3.13 (2H, m), 7.01 (1H, t, $J = 2.7$ Hz), 7.36−7.39 (3H, m), 7.48−7.50 (2H, m); $^{13}C$ NMR $\delta = 23.5$, 45.7, 126.4, 128.9, 129.9, 130.0, 134.5, 146.1, 199.5; HRMS Calcd for $C_{11}H_{10}O$: 158.0732. Found: 158.0721.

**2-Ethoxycarbonyl-3-phenyl-2-cyclopentenone (34).** IR (neat) 2979, 1734, 1699, 1616, 1446, 1346, 1230, 1188, 1026 $cm^{-1}$; $^1H$ NMR $\delta = 1.23$ (3H, t, $J = 7.2$ Hz), 2.61−2.63 (2H, m), 3.03−3.05 (2H, m), 4.28 (2H, q, $J = 7.2$ Hz), 7.40−7.47 (3H, m), 7.50−7.52 (2H, m); $^{13}C$ NMR $\delta = 13.9$, 29.6, 34.8, 61.4, 127.5, 128.7, 131.2, 134.0, 134.1, 165.1, 172.3, 203.6; HRMS Calcd for $C_{14}H_{14}O_3$: 230.0943. Found: 230.0943.

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**Supporting Information Available:** Complete experimental details for the preparation of **1l** and general procedure for the preparation of 2-substituted 1-(1-alkynyl)cyclopropanols **7** and **10**. $^1H$ NMR, $^{13}C$ NMR, IR, and elemental analysis or HRMS data for 1-(1-alkynyl)cyclopropanols **1a**−**l**, 2-substituted 1-(1-alkynyl)cyclopropanols **7a**−**d**, **10a**−**c**, and their TBS ethers, cyclopentenones **3a**-**d**, **3l**, **8a**, and **9a**, and $^1H$ NMR data for alkynylborates (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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