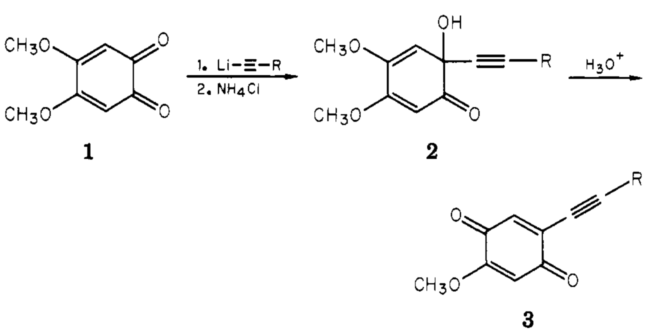
Scheme I



	R	% yield of 2	% yield of 3
a	C_6H_5	95	97
b	$CH_2OCH_2C_6H_5$	95	92
c	$(CH_2)_3CH_3$	94	94
d	$C(CH_3)$=CH_2	90	94[a]
e	$(CH_2)_4C{\equiv}CH$	71[b]	85
f	$CO_2C_2H_5$	92	94[c]
g	H	70	94
h	OC_2H_5	80	
i	$CH_2N(C_2H_5)_2$	90	

[a] Product slowly decomposes upon removal of solvent. [b] Five equivalents of the octadiyne was used to maximize the yield. [c] Crude yield.

(a latent quinone carbanion), the reactions of quinones or protected bromoquinols with π-allylnickel complexes,[10] the utilization of monoketals of quinones,[11] the use of (1,4-dimethoxynaphthyl)lithium reagents,[12] and the reactions of quinones with alkylboranes.[13]

Finally, it should be noted that the quinols, **2a–i**, possess multifunctionality that is amenable to both nucleophilic and electrophilic reagents as well as cycloaddition reactions.[14] In addition, alkynylquinones have not been reported prior to this work and our previous report on the synthesis of 2,5-dialkylated 1,4-quinones. As a result, their chemistry is nearly unexplored and thus warrants study.

Acknowledgment. We express our appreciation to the National Cancer Institute (CA-11890) for financial support of this work.

Registry No. 1, 21086-65-7; **2a**, 82511-09-9; **2b**, 82511-10-2; **2c**, 82521-45-7; **2d**, 82511-11-3; **2e**, 82511-12-4; **2f**, 82511-13-5; **2g**, 82511-14-6; **2h**, 82511-15-7; **2i**, 82511-16-8; **3a**, 82511-17-9; **3b**, 82511-18-0; **3c**, 82511-19-1; **3d**, 82511-20-4; **3e**, 82511-21-5; **3f**, 82511-22-6; **3g**, 82511-23-7; $LiC{\equiv}CC_6H_5$, 4440-01-1; $LiC{\equiv}CCH_2OCH_2C_6H_5$, 64080-63-3; $LiC{\equiv}C(CH_2)_3CH_3$, 17689-03-1; $LiC{\equiv}CC(CH_3){=}CH_2$, 38341-85-4; $LiC{\equiv}C(CH_2)_4C{\equiv}CH$, 82511-24-8; $LiC{\equiv}CCO_2C_2H_5$, 72036-30-7; $LiC{\equiv}CH$, 1111-64-4; $LiC{\equiv}COC_2H_5$, 31612-88-1; $LiC{\equiv}CCH_2N(C_2H_5)_2$, 82511-25-9.

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[14] For a review of cyclohexadienones, see Waring, A. J. *Alicyclic Chem.* **1966**, *1*, 129.

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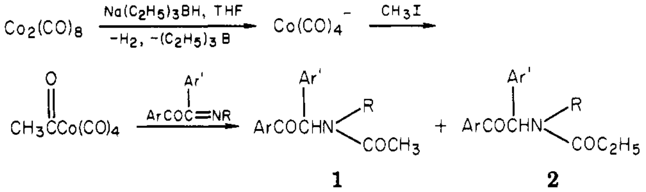
Received March 26, 1982

Metal Carbonyl Catalysis of Organoborane Reactions. Cobalt Carbonyl Catalyzed Reductive Carbonylation of Schiff Bases

Summary: Schiff bases react with trialkyl or triarylboranes and carbon monoxide, in the presence of catalytic amounts of cobalt carbonyl, to give amides.

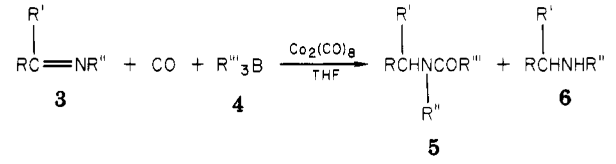
Sir: We recently reported that the stoichiometric reaction of α-keto imines with acetylcobalt tetracarbonyl affords the acetamide 1 as the principal product with the unexpected propionamide 2 being obtained as a byproduct in several cases.[1] The acetylcobalt carbonyl was generated in situ by first reacting dicobalt octacarbonyl with triethylborohydride to give the mononuclear anion[2] and then treating the latter with methyl iodide under a carbon monoxide atmosphere.


$$Co_2(CO)_8 \xrightarrow[-H_2,\ -(C_2H_5)_3B]{Na(C_2H_5)_3BH,\ THF} Co(CO)_4^- \xrightarrow{CH_3I}$$
$$CH_3C(O)Co(CO)_4 \xrightarrow{ArCOC(Ar'){=}NR} \underset{\mathbf{1}}{ArCOCH(Ar')N(R)COCH_3} + \underset{\mathbf{2}}{ArCOCH(Ar')N(R)COC_2H_5}$$

As previously noted, methyl iodide is not required for the formation of 2. Furthermore, while the reductive acylation reaction (giving 1) is sensitive to steric effects, we have subsequently found that this factor is of less significance for the preparation of 2. Specifically, 2 (Ar = Ar′ = Ph, R = 2,6-$(CH_3)_2C_6H_3$) was obtained in 61% yield by reaction of the appropriate α-keto imine, for 24 h, with the solution resulting from $Co_2(CO)_8$ and triethylborohydride. The same reaction, with added methyl iodide, effected over a 120-h reaction period (essentially no reaction occurred after 24 h), afforded 1 (Ar = Ar′ = Ph, R = 2,6-$(CH_3)_2C_6H_3$) in only 6% yield.[1]

It seemed conceivable that triethylborane, formed during the generation of the cobalt tetracarbonyl anion, participates in the reaction that gives 2. It this reasoning is correct, then the reaction of α-keto imines (or other Schiff bases) with organoboranes and carbon monoxide should afford a variety of β-keto amides. *No* reaction occurs under these conditions. However, it was gratifying to learn that the presence of catalytic amounts of cobalt carbonyl does indeed result in the reductive carbonylation and alkylation of Schiff bases by organoboranes and carbon monoxide. We now report on this new catalytic process.

Carbonylation of a Schiff base (3) with an equimolar amount of an organoborane (4) and a catalytic quantity of dicobalt octacarbonyl affords the amides 5 in good yields (Table I). This reaction can be effected, in tetrahydrofuran (THF) or hexane, under mild conditions [60 °C (1 atm of pressure)]. The reaction is faster in THF than in hexane, and the product yields are higher in THF. The saturated amine (6) was also formed in some instances.


$$\underset{\mathbf{3}}{RC(R'){=}NR''} + CO + \underset{\mathbf{4}}{R'''_3B} \xrightarrow[THF]{Co_2(CO)_8} \underset{\mathbf{5}}{RCH(R')N(R'')COR'''} + \underset{\mathbf{6}}{RCH(R')NHR''}$$

As the results in Table I indicate, the metal carbonyl catalyzed reaction is a versatile one since variations can be made on the nature of both the organoborane and the

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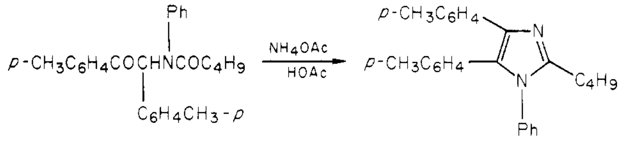
Table I. Products Obtained from the $Co_2(CO)_8$ Catalyzed Reaction of 3, 4, and CO in THF

3, R, R′, R″	4, R‴	product[a]	yield,[b] %	mp, °C
PhCO, Ph, Ph	C_2H_5	5	50	118-119
		6	48	
	n-C_4H_9	5	82	77-78
		6	18	
	n-C_7H_{15}	5	55	
		6	22	
	$PhCH_2CH_2$	5	50	114-116
		6	10	
	$PhCH(CH_3)CH_2$	5	80	133-135
	Ph	5	67[c]	144-145
p-$CH_3C_6H_4CO$, p-$CH_3C_6H_4$, Ph	n-C_4H_9	5	87	115-116
p-$CH_3OC_6H_4CO$, p-$CH_3OC_6H_4$, Ph	C_2H_5	5	74	84.0-84.5
PhCO, Ph, p-$CH_3OC_6H_4$	C_2H_5	5	33	
		6	65	
p-$CH_3OC_6H_4$, H, Ph	C_2H_5	5	62	

[a] The structures of the products were assigned on the basis of analytical (C, H, N) and spectral (IR, NMR (^1H, ^{13}C), MS) data. [b] Yields are of pure products. [c] Yield was 44%, using hexane as the solvent.

Schiff base. It is applicable to aliphatic and aromatic organoboranes and to simple as well as to α-keto imines. The organoboranes, when not commercially available, were generated from the appropriate olefin by hydroboration, and, therefore, one can convert olefins to amides in this manner. The reaction is regiospecific and, in the case of α-keto imines (3, R = carbonyl-containing group), gives β-keto amides. These compounds are of considerable use in the synthesis of 1,3-azoles.[3] For example, treatment of 5 (R = p-$CH_3C_6H_4CO$, R′ = p-$CH_3C_6H_4$, R″ = Ph, R‴ = n-C_4H_9) with ammonium acetate in acetic acid afforded 2-n-butyl-1-phenyl-4,5-di-p-tolylimidazole (7) in 80% yield.



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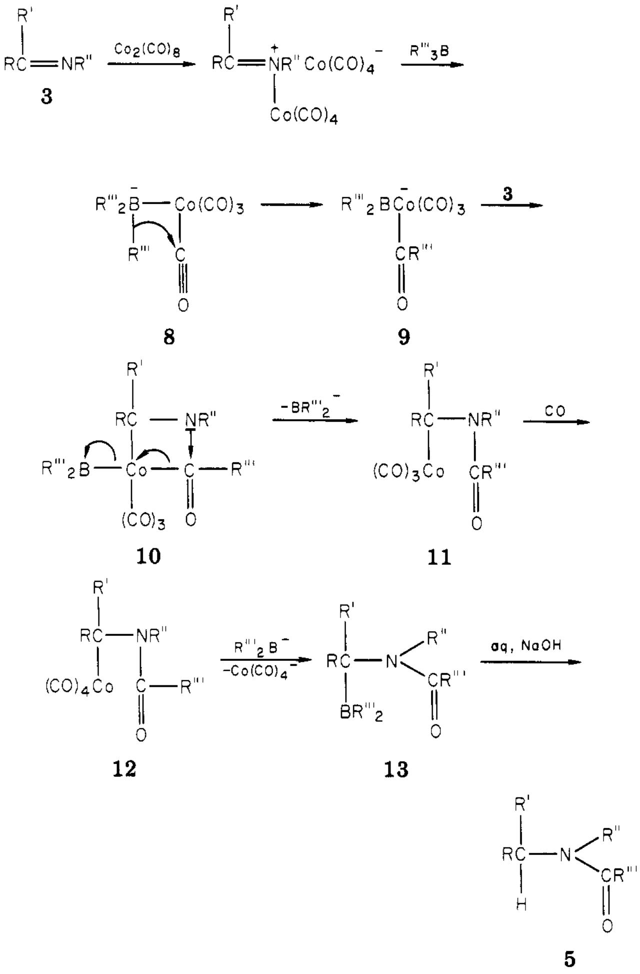
A possible pathway for the cobalt carbonyl catalyzed organoborane–Schiff base–carbon monoxide reaction is outlined in Scheme I. Reaction of 3 with the catalyst may give an ion pair, the anionic component being the cobalt tetracarbonyl anion. The latter may then interact with the organoborane (4) to give 8. A strong interaction between 4 and $Co(CO)_4^-$ is not required; in fact, there is evidence against such an interaction on exposure of triphenylborane to $Co(CO)_4^-$ in an argon atmosphere.[4] All that is necessary is a weak interaction of sufficient duration, under a carbon monoxide atmosphere, to enable migration of an alkyl or aryl group to occur from boron to a carbonyl carbon to give 9. Addition of 9 to the Schiff base (to give 10) and subsequent acyl transfer and elimination of dialkyl or diarylboron anion would afford 11. Carbonylation of 11 to 12 and then regeneration of $Co(CO)_4^-$ by displacement by R'''_2B^- would give 13. The amide (5) would then result on boron–carbon bond cleavage. It must be stressed that Scheme I simply provides a working hypothesis for rationalizing the catalytic process; the emphasis of this research has been in the synthetic aspects of the chemistry.

The following general procedure was used. A mixture of $Co_2(CO)_8$ (0.2 mmol) and organoborane (2.0 mmol; commercially available or prepared by hydroboration of suitable olefins with borane–THF) in anhydrous THF (50 mL) was stirred for 15 min and then the Schiff base (3; 2.0 mmol) was added. The reaction mixture was heated at 60 °C for 24–28 h (followed by thin-layer chromatography) and then hydrolyzed at room temperature with 5 N sodium hydroxide. The amide was extracted with ether and purified by silica gel column chromatography, using hexane–ether as eluant.

Scheme I



In conclusion, simple and β-keto amides can be formed in good yields by the cobalt carbonyl catalyzed reaction of Schiff bases with organoboranes and carbon monoxide under mild conditions. To our knowledge, this is the first example of metal carbonyl catalysis of an organoborane

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reaction. The use of cobalt and other metal carbonyls, as catalysts for other organoborane reactions, is under active investigation.

Acknowledgment. We are indebted to Professor J. M. Burlitch of Cornell University for providing unpublished data as well as for a useful discussion. Mrs. Amaratunga is a holder of a Commonwealth Scholarship. This research is supported by the Natural Sciences and Engineering Research Council of Canada.

Registry No. 3 (R = PhCO; R′ = R″ = Ph), 4198-95-2; **3** (R = *p*-$CH_3C_6H_4CO$; R′ = *p*-$CH_3C_6H_4$; R″ = Ph), 82537-51-7; **3** (R = *p*-$CH_3OC_6H_4CO$; R′ = *p*-$CH_3OC_6H_4$; R″ = Ph), 82537-52-8; **3** (R = PhCO; R′ = Ph; R″ = *p*-$CH_3OC_6H_4$), 4198-96-3; **3** (R = *p*-$CH_3OC_6H_4$; R′ = H; R″ = Ph), 836-41-9; **4** (R‴ = C_2H_5), 97-94-9; **4** (R‴ = *n*-C_4H_9), 122-56-5; **4** (R‴ = *n*-C_7H_{15}), 3244-73-3; **4** (R‴ = $PhCH_2CH_2$), 1883-35-8; **4** (R‴ = $PhCH(CH_3)CH_2$), 51136-87-9; **4** (R‴ = Ph), 960-71-4; **5** (R = PhCO; R′ = R″ = Ph; R‴ = C_2H_5), 80783-92-2; **5** (R = PhCO; R′ = R″ = Ph; R‴ = *n*-C_4H_9), 82537-53-9; **5** (R = PhCO; R′ = R″ = Ph; R‴ = *n*-C_7H_{15}), 82544-30-7; **5** (R = PhCO; R′ = R″ = Ph; R‴ = $PhCH_2CH_2$), 82537-54-0; **5** (R = PhCO; R′ = R″ = Ph; R‴ = $PhCH(CH_3)CH_2$), 82537-55-1; **5** (R = PhCO; R′ = R″ = R‴ = Ph), 81640-85-9; **5** (R = *p*-$CH_3C_6H_4CO$; R′ = *p*-$CH_3C_6H_4$; R″ = Ph; R‴ = *n*-C_4H_9), 82537-56-2; **5** (R = *p*-$CH_3OC_6H_4CO$; R′ = *p*-$CH_3OC_6H_4$; R″ = Ph; R‴ = C_2H_5), 82537-57-3; **5** (R = PhCO; R′ = Ph; R″ = *p*-$CH_3OC_6H_4$; R‴ = C_2H_5), 80783-96-6; **5** (R = *p*-$CH_3OC_6H_4$; R′ = H; R″ = Ph; R‴ = C_2H_5), 82537-58-4; **6** (R = PhCO; R′ = R″ = Ph), 5722-91-8; **6** (R = PhCO; R′ = Ph; R″ = *p*-$CH_3OC_6H_4$), 19339-72-1; **7**, 82537-59-5; dicobalt octacaronyl, 10210-68-1.

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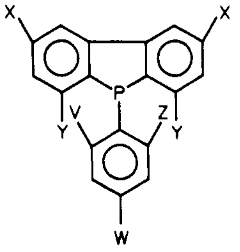
Received June 29, 1982

Preferred Geometry of the Through Space 2p-3d Overlap Effect

Summary: Six 5-aryldibenzophospholes have been prepared and the rates of their S_N2 reactions with benzyl chloride in chloroform solution measured.

Sir: In order to determine the preferred geometry of the 2p–3d overlap effect, [1-7] we have prepared the six dibenzophospholes listed in Table I. The essentially rigid geometrical relationship between the methoxy groups and phosphorus in compounds **1** and **2**, as against the variable geometrical relationships possible for **3**, **4**, and **5**, have enabled us to determine the geometrical requirement for the occurrence of maximum through space 2p–3d overlap effects. It is apparent from the relative rate data for the reactions of compounds **1–6** with benzyl chloride that the maximum acceleration results when the 5-aryl group containing an *o*-methoxy substituent can be orthogonal to the dibenzophosphole ring. Thus, the transition state that affords the maximum through space 2p–3d overlap is that shown in **7** or **7a**, in which an *o*-methoxy substituent of the orthogonal 5-aryl group occupies a quasi-apical position of an incipient trigonal-bipyramidal configuration.

Table I. Rate Data for the Reactions of Dibenzophospholes with Benzyl Chloride in Chloroform Solution at 31.0 °C



compd	rel rate	$\Delta H^\ddagger$, kcal/m	$\Delta S^\ddagger$, eu
1, X = OMe; V = W = Y = Z = H	3.92	12.8	−41
2, Y = OMe; X = W = V = Z = H	15.6	12.0	−43
3, Z = OMe; X = Y = V = W = H	13.3	14.9	−32
4, W = OMe; X = Y = V = Z = H	1.77	12.0	−46
5, V = Z = OMe; X = Y = W = H	77.7	16.3	−24
6, X = Y = Z = V = W = H	1.00[a]	13.8	−41

[a] $k = 1.78 \times 10^{-6}$ L mol^{-1} s^{-1} at 26.0 °C; $k = 2.50 \times 10^{-6}$ L mol^{-1} s^{-1} at 31.0 °C; $k = 3.56 \times 10^{-6}$ L mol^{-1} s^{-1} at 36.0 °C. Each value of *k* derived from three independent experiments; average deviation ±3%. Estimates of precision measures are ±1.2 kcal/mol for $\Delta H^\ddagger$ and ±5.0 eu for $\Delta S^\ddagger$.

It is of importance to point out that the crystal and molecular structure of 5-(*p*-bromophenyl)-5-phenyldibenzophospholium bromide has been determined by Allen et al.,[8] who have found that the endocyclic C–P–C bond angle is only 93.9°. (In fact, the transition state depicted in **7** or **7a** is modeled on Allen's crystal structure for the salt.) This indicates significant deformation of bond angles for the quaternary phosphonium moiety compared with an acyclic phosphonium salt and helps to explain why 5-aryldibenzophospholes undergo quaternization reactions much more slowly than the corresponding triarylphosphines.[1-8] Furthermore, Allen et al. point out that the bond angle strain (and accompanying ring strain) "would be relieved on formation of a quinquecovalent trigonal bipyramidal phosphorane, in which the endocyclic C–P–C bond angle would be 90°, assuming that the five-membered ring occupies apical–equatorial positions as is generally found". This does much to explain why dibenzophospholium salts undergo alkaline cleavage (*with ring opening*) very rapidly in comparison with the normal hydrolysis of their acyclic analogues.[8] This observation is pertinent to the present study because a possible through space 2p–3d interaction of the type shown in the transition-state **7a** (with the consequent quasi-trigonal-bipyramidal configuration about phosphorus) would help to alleviate the angle strain that otherwise grows as quaternization proceeds.

The reactions were carried out at three different temperatures, and the values of ΔH‡ and ΔS‡ were determined. It is apparent from the data that a large decrease in ΔS‡ arises only when an *o*-methoxy group is present on the 5-aryl group, as in the reactions of compounds **3** and **5**. At the same time, the interaction of the methoxy groups of **3** with the phosphorus compensates to a large degree for any possible loss of stabilization of the transition state by interaction with the solvent, and, therefore, the value

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