Dehalogenative Coupling of *gem*-Dihalides and Benzyl Halides by Means of Hexacarbonyltungsten(0) and Related Compounds

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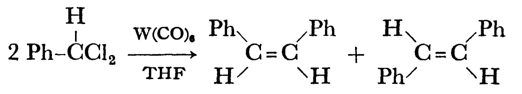
$W(CO)_6$ and WCl_6–$LiAlH_4$ systems have been found to cause coupling of *gem*-dihalides and benzyl halides giving olefins and bibenzyl derivatives, respectively. The tungsten reagents also cause coupling of some alcohols. The carbene intermediate was suggested from the formation of a cyclopropane derivative.

Dehalogenative coupling of organic halides by transition metal complexes is of importance for the formation of carbon-carbon bond.[1] Transition metal complexes such as iron, nickel, cobalt, and palladium complexes cause coupling of *gem*-dihalides to give olefins or cyclopropane derivatives.[2]

Coffey reported that metal carbonyls such as $Fe(CO)_5$ or $W(CO)_4(pyridine)_2$ cause coupling of *gem*-dihalides, but not $W(CO)_6$ probably because of the complete shielding of tungsten atom by carbon monoxide ligands.[3] However, in the course of studies on the reactions with tungsten compounds, we found that $W(CO)_6$ as well as WCl_6–$LiAlH_4$ is highly reactive for the reactions of *gem*-dihalides, benzyl halides, and also alcohols at room temperature. In this paper, we report on the coupling reactions of *gem*-dihalides, benzyl halides and some alcohols by lower valent tungsten compounds to give coupling products, the mechanism also being given.

Results and Discussion

Reaction of gem-*Dihalides.* The reaction of hexacarbonyltungsten(0), $W(CO)_6$, with benzylidene dichloride in THF at room temperature under nitrogen atmosphere gave (*E*)- and (*Z*)-stilbenes in 41 and 7% yields, respectively.[4]



$$2\,\mathrm{Ph{-}\overset{H}{C}Cl_2} \xrightarrow[\text{THF}]{\mathrm{W(CO)_6}} \begin{matrix}\mathrm{Ph} & & \mathrm{Ph}\\ & \mathrm{C{=}C} & \\ \mathrm{H} & & \mathrm{H}\end{matrix} + \begin{matrix}\mathrm{H} & & \mathrm{Ph}\\ & \mathrm{C{=}C} & \\ \mathrm{Ph} & & \mathrm{H}\end{matrix}$$

The coupling reactions of benzylidene dichloride by zerovalent tungsten carbonyl complexes, and also tungsten hexachloride, WCl_6, plus lithium aluminum hydride, $LiAlH_4$, are summarized in Table 1. In order to attain good yields, it was important to use a half equivalent amount of *gem*-dihalides to tungsten reagents.

TABLE 1. COUPLING OF BENZYLIDENE DICHLORIDE BY TUNGSTEN(0) CARBONYLS

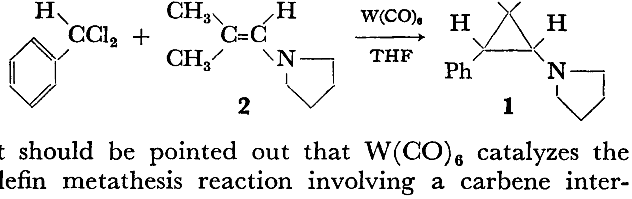
Tungsten carbonyl	Stilbene yield,% [a] *E*	*Z*
$W(CO)_6$	41	7
$W(CO)_6$–$AlCl_3$[b]	64	8
$W(CO)_5PPh_3$	56	7
$W(CO)_5NH_2C_6H_{11}$	40	5
WCl_6–$LiAlH_4$[b]	43	8

a) Based on benzylidene dichloride. b) An amount (0.4 mmol) equivalent to tungsten compounds was added.

Coffey reported that $W(CO)_6$ causes no coupling of *gem*-dihalides in refluxing benzene.[3] On the contrary, $W(CO)_6$ was found to cause readily coupling of the dihalides even at room temperature. Addition of an equivalent amount of $AlCl_3$ to the $W(CO)_6$ system increases the yield. This is probably because $AlCl_3$ eliminates CO ligand from $W(CO)_6$ furnishing the coordinatively unsaturated site. Triphenylphosphinepentacarbonyltungsten(0) is as reactive as $W(CO)_6$–$AlCl_3$. WCl_6 alone is not reactive for the reaction. However, addition of $LiAlH_4$ causes the reaction. This suggests that WCl_6 is reduced by $LiAlH_4$ to some lower valent tungsten species such as W(II) which is active for the reaction.

The coupling reactions of other *gem*-dihalides by $W(CO)_6$ and WCl_6–$LiAlH_4$ reagents are summarized in Table 2. We see that $W(CO)_6$ is as reactive as WCl_6–$LiAlH_4$ for the coupling reaction. Although the coupling occurs with alkyl dihalides, the yield is lower than that of aromatic halides. Since $W(CO)_6$ is relatively stable against air and easy to handle, this provides a convenient synthetic route for symmetric olefins.

Mechanism. Coffey[3] and Joshi[5] suggested a carbene mechanism for transition metal carbonyl-promoted coupling reaction. Furukawa and Kiji also suggested a carbenoid intermediate in the reaction of $Ni(COD)_2$, $Fe(CO)_5$ or $Co(CO)_8$ with *gem*-dihalides by obtaining cyclopropane derivatives.[2] On the other hand, the reaction with $Co_2(CO)_8$ proceeds step by step by a radical process.[6] In order to investigate the intermediate, we attempted to trap a carbene intermediate. From the reaction of benzylidene dichloride and $W(CO)_6$ in the presence of 1-(2-methyl-1-propenyl)-pyrrolidine (**2**), cyclopropane derivative (**1**) was obtained in 13% yield together with 9% yield of stilbene. This shows that a carbene intermediate is involved during the course of reaction. Similarly cyclopropane (**1**) was formed in 1% yield by the reaction with WCl_6–$LiAlH_4$ system.



It should be pointed out that $W(CO)_6$ catalyzes the olefin metathesis reaction involving a carbene intermediate.[7] Thus there is another route for the formation of **1**, *viz.*, $W(CO)_6$ and the stilbene formed by the

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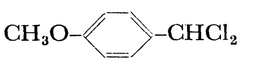
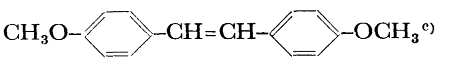
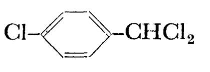
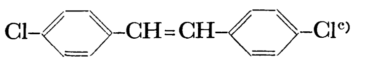
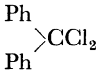
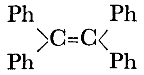
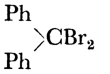
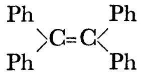
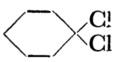
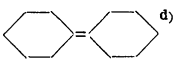
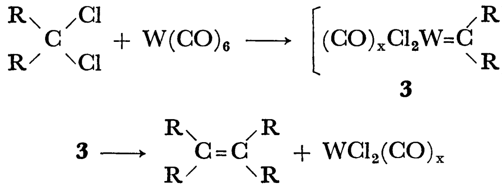
Table 2. Coupling of *gem*-dihalides by $W(CO)_6$ or WCl_6–$LiAlH_4$

gem-Dihalide	Product	Yield, %[a] *E*	Yield, %[a] *Z*	Reagent[b]
	 [c]	34 47	4 8	A B
	 [c]	60 62	4 11	A B
$PhCHBr_2$	$PhCH{=}CHPh$	61 60	3 5	A B
 Ph_2CCl_2	 $Ph_2C{=}CPh_2$	80 46		A B
 Ph_2CBr_2	 $Ph_2C{=}CPh_2$	63 37		A B
	 [d]	6 1		A B

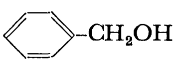
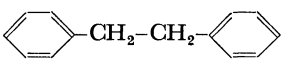
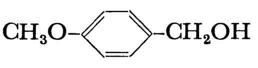
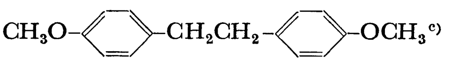
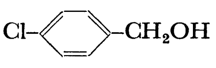
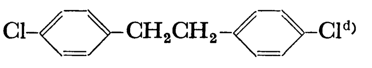
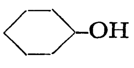
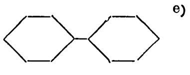
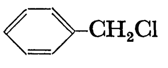
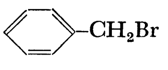
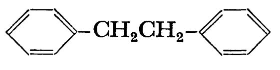
a) Based on *gem*-dihalides. b) A: WCl_6–$LiAlH_4$, B: $W(CO)_6$. c) D. F. Hoeg and D. I. Lusk, *J. Organomet. Chem.*, **5**, 1 (1966). d) W.D. Emmons, *Org. Synth.*, **47**, 34 (1967).

coupling of benzylidene dichloride, give rise to a carbene complex, $XW{=}C{<}^{Ph}_{H}$ which then would react with olefin **2** to give **1**. However, this possibility could be ruled out from the fact that only 0.5% yield of **1** was obtained when the reaction of stilbene and $W(CO)_6$ was performed under similar reaction conditions. Thus we suggest the following reaction path involving the formation of a carbene-W complex (**3**) from the reaction of *gem*-dihalides and $W(CO)_6$, and subsequent dimerization of the carbene derived from the carbene complex (**3**).

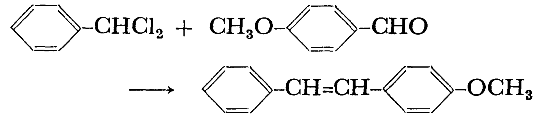


Cross Coupling of Benzylidene Dichloride with Benzaldehyde. Benzaldehyde has been found to react with $W(CO)_6$ or WCl_6–$LiAlH_4$ to give stilbene derivatives in a high yield. Carbene-W complex is thought to be an intermediate of this coupling reaction.[8] It is expected that cross coupling between *gem*-dihalides and benzaldehyde could take place on being treated with $W(CO)_6$ or WCl_6–$LiAlH_4$. We found that from the reaction of benzylidene dichloride and *p*-methoxybenzaldehyde in the presence of WCl_6–$LiAlH_4$, *p*-methoxystilbene (*E* and *Z*) was obtained in 8% yield together with stilbene (*E*, 5%, *Z*, 1%) and *p*,*p*-dimethoxystilbene (*E*, 44%, *Z*, 2%). $W(CO)_6$ similarly brings about the cross coupling.

Table 3. Tungsten-promoted coupling of alcohols and benzyl halides

Substrate	Product	Yield,[a] %	Reagent[b]
		76 60	A B
	 [c]	41 22	A B
	 [d]	69 13	A B
	 [e]	2 0.1	A B
		2 8	A B
		29 21	A B

a) Based on the starting alcohols or halides. b) A: WCl_6–$LiAlH_4$, B: $W(CO)_6$. c) J. S. Buck and S. S. Jenkins, *J. Am. Chem. Soc.*, **51**, 2163 (1929). d) R. L. Datta and F. V. Fernandes, *J. Am. Chem. Soc.*, **38**, 1812 (1916). e) W. Hückel and D. Neunhoeffer, *Justus Liebigs Ann. Chem.*, **477**, 106 (1930).



Reaction of Alcohols and Benzyl Halides. The transition metal-promoted dehydroxygenative coupling of alcohols to dimeric compounds is known.[9] In connection with coupling of *gem*-dihalides described above, we carried out reactions of alcohols, and found that $W(CO)_6$ and WCl_6–$LiAlH_4$ are also active for coupling reaction. In this case, reaction gives saturated hydrocarbons but no olefins. The results are summarized in Table 3. Coupling of benzyl alcohols proceeds smoothly to give bibenzyl derivatives. However, alkyl alcohols are far less reactive. Benzyl halides were also found to undergo coupling to give bibenzyl derivatives.

In conclusion it was made clear that zerovalent tungsten carbonyls such as $W(CO)_5L$ (L=CO, $P(Ph)_3$, and $C_6H_{11}NH_2$) and WCl_6–$LiAlH_4$ cause coupling of *gem*-dihalides, benzyl halides, and some alcohols to give olefins or dimeric hydrocarbons.

Experimental

Materials. Benzylidene dibromide,[10] diphenyldibromomethane,[11] *p*-methoxybenzylidene dichloride,[12] *p*-chlorobenzylidene dichloride,[13] and 1-(2-methyl-1-propenyl)pyrrolidine,[14] were prepared according to the reported methods. Other starting materials were of commercial grade. THF was refluxed and distilled from a dark purple solution of sodium benzophenone dianion under nitrogen. WCl_6 was purified by sublimation. $W(CO)_5PPh_3$ was prepared from $W(CO)_6$ and triphenylphosphine according to the literature.[15] Cyclohexylaminepentacarbonyltungsten(0) was prepared from $W(CO)_6$ and cyclohexylamine.[16]

General Procedure for Coupling of gem-*Dihalides by Tungsten Carbonyls.* In a flame-dried, 50-ml centrifuge tube containing a magnetic stirring bar, were placed 10 ml of THF and tungsten carbonyl (0.4 mmol), the tube then being sealed with a No-Air stopper. After the tube had been flushed with nitrogen, 0.2 mmol of *gem*-dihalides was added by means of a syringe. The mixture was stirred for 6 h at room temp under nitrogen atmosphere. The tube was then cooled to −78 °C, and the precipitated tungsten complexes were removed by filtration. The filtrate was poured into ether and the ether layer was washed with water and dried with Na_2SO_4. After evaporation of the solvent, the products were analyzed and isolated by gas chromatography. The products were identified by comparison of melting point, IR, NMR, and retention time with those of authentic samples. The results are summarized in Tables 1 and 2.

General Procedure for Coupling of gem-*Dihalides by* WCl_6–$LiAlH_4$. In a flame-dried, 50-ml centrifuge tube containing a magnetic stirring bar, was placed 10 ml of THF by means of a syringe, and the tube was sealed with a No-Air stopper. After the tube had been flushed with nitrogen, the solvent was cooled to −78 °C, and WCl_6 (0.4 mmol) and $LiAlH_4$ (0.4 mmol) were added under nitrogen atmosphere. The solution turned dark brown from green. Then 0.2 mmol of *gem*-dihalides was added with a syringe. The mixture was stirred for 6 h at room temp under nitrogen atmosphere. The reaction mixtures were quenched with 20% aq NaOH. The organic materials were extracted with ether. The ethereal solution was washed with water and concentrated. The products were analyzed by VPC. The results are summarized in Tables 1 and 2.

Trapping of Carbene Intermediate. In a flame-dried, 50-ml centrifuge tube containing a magnetic stirring bar, were placed 10 ml of THF and 0.4 mmol of $W(CO)_6$ and the tube was sealed with a No-Air stopper. After the tube had been flushed with nitrogen, 0.2 mmol of benzylidene dichloride and excess amounts (10 ml) of 1-(2-methyl-1-propenyl)pyrrolidine (**2**) were added. The mixture was stirred for 6 h at room temp under nitrogen atmosphere. After the same work-up as described above the products were analyzed by VPC to obtain 1-(2,2-dimethyl-3-phenylcyclopropyl)pyrrolidine (**1**) and stilbene in 13 and 9% yields, respectively. These products were identified by comparison with standard samples.

Cross Coupling of Benzyl Chloride with Benzaldehyde. Reaction was carried out using the same procedure as described above charging WCl_6, $LiAlH_4$ (0.8 mmol each), benzylidene dichloride (0.2 mmol), *p*-methoxybenzaldehyde (0.2 mmol), and THF (10 ml). Products analysis was carried out by VPC using authentic samples. The products were *p*-methoxystilbene (*E* and *Z*, 8%), stilbene (*E*, 5%, *Z*, 1%), and *p,p*-dimethoxystilbene (*E*, 44%, *Z*, 2%).

Coupling of Alcohols. Reactions were performed as in the coupling of *gem*-dihalides under the same reaction conditions. The results are given in Table 3. The products were identified by comparison with authentic samples.

Preparation of 1-(2,2-Dimethyl-3-phenylcyclopropyl)pyrrolidine (1). In a 300-ml, three-necked, round-bottomed flask equipped with a magnetic stirring bar, dropping funnel, nitrogen inlet, and a condenser with a bubble counter at the top was placed a solution of 3.5 g of CuCl, 45 ml of 1-(2-methyl-1-propenyl)pyrrolidine (**2**) and 200 ml of abs ether. Then 20 ml of phenyldiazomethane in 50 ml of ether was added dropwise over 2 h under nitrogen. The mixture was stirred for 20 h at room temp and then filtered, ether being evaporated. The residue was distilled to give the starting pyrrolidine (**2**) and colorless oil, bp 103—105 °C/1 Torr (*ca.* 1 g) which was purified by preparative VPC (column OV-17) and assigned to 1-(2,2-dimethyl-3-phenylcyclopropyl)pyrrolidine. IR (neat): 2992, 1445, 1456, 1183, 754, and 703 cm^{-1}. NMR (C_6D_6): δ 7.12(s, 5H), 2.80—2.12(m, 4H), 1.85(d, 1H, J= 6.6 Hz), 1.78—1.48 (m, 4H), 1.41 (s, 3H), 1.12 (d, 1H, J= 6.6 Hz), and 0.84 (s, 3H). MS: *m/e* 215 (M^+). Found: C, 83.92; H, 9.59%. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83%. Infrared spectra were recorded on a Japan Spectroscopic IR-E spectrometer. NMR spectra were obtained with a JEOL C-60HL spectrometer with TMS as an internal standard. Mass spectra were obtained with a Hitachi RMS-4 spectrometer.

References

1) M. F. Semmelhack, *Org. React.*, **19**, 119 (1972).

2) J. Furukawa, A. Matsumura, Y. Matsuoka, and J. Kiji, *Bull. Chem. Soc. Jpn.*, **49**, 829 (1976).

3) C. E. Coffey, *J. Am. Chem. Soc.*, **83**, 1623 (1961).

4) Yields are based on the starting halides or alcohols.

5) K. K. Joshi, *J. Chem. Soc., A*, **1966**, 594.

6) D. Seyferth and M. D. Miller, *J. Organomet. Chem.*, **38**, 373 (1972).

7) J. M. Basset, J. L. Bilhou, R. Mutin, and A. Theolier, *J. Am. Chem. Soc.*, **97**, 7376 (1977). for a review for olefin metathesis, see N. Calderon, E. A. Ofstead, and W. A. Judy, *Angew. Chem. Int. Ed. Engl.*, **15**, 404 (1976).

8) Presented at 35th National Meeting of the Chemical Society of Japan, Sapporo, August 1976.

9) (a) E. E. van Tamelen and M. A. Schwartz, *J. Am. Chem. Soc.*, **87**, 2277 (1965); (b) K. B. Sharpless, R. P. Haznlik, and E. E. van Tamelen, *ibid.*, **90**, 209 (1968), **91**, 1552 (1969); (c) J. E. McMurry, and M. Silvestri, *J. Org. Chem.*, **40**, 2687 (1975).

10) Th. Curtius and E. Quedenfeldt, *J. Prakt. Chem.*, **58**, 369 (1898).

11) S. Friedel, *Bull. Soc. Chim. Fr.*, **33**, 339 (1897).

12) H. Schmidt, *Ber.*, **41**, 2331 (1908).

13) F. Asinger and G. Lock, *Monatsh. Chem.*, **62**, 323 (1933).

14) A. Brossi, *Org. Synth.*, **53**, 48 (1973).

15) T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).

16) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).