tion reactions of complexes of types I and II is under investigation.

It was known that $RCCo_3(CO)_9$ compounds are degraded to $RCBr_3$ by bromine in carbon tetrachloride,[9] and thus it was not surprising that treatment of I and II (Ar = Ph) with electrophilic reagents which also are oxidizing agents (*e.g.*, nitric–sulfuric mixed acid, acetyl nitrate, nitronium tetrafluoroborate, 30% oleum, etc.) caused massive decomposition. However, treatment of $PhCCo_3(CO)_9$ with bromine in methanol followed by basic (10% aqueous NaOH) hydrolysis of the reaction product gave benzoic acid in 80% yield, and thus an alternate scheme for the degradation of such complexes is available.

Satisfactory carbon and hydrogen analyses ($\pm 0.3\%$) were obtained for all new compounds prepared in this study. Our investigations in this area are continuing.

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[9] U. Krüerke and W. Hübel, *Chem. Ind.* (*London*), 1264 (1959).

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A Method for the Introduction of Two Carbon Appendages at a Carbonyl Carbon. Application to Double Chain Branching and Spiro Annulation Operations

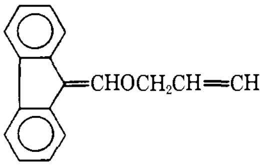
Sir.

This communication reports a general two-step sequence for the replacement of carbonyl oxygen by two functionalized carbon substituents which can be elaborated to form rings or more complex chains. The process leads to the formation of spiro ring systems in a novel and quite flexible way starting from a cyclic ketone and to the introduction of a pair of branches starting from an acyclic ketone. Two modifications of the method will be described, one being applicable to aryl conjugated ketones and the other to nonconjugated ketones.

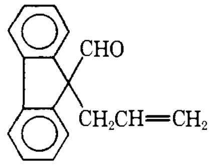
Treatment of allyloxymethyltriphenylphosphonium chloride (mp 136–138° dec)[1,2] at −45° in 2:1 tetrahydrofuran(THF)–hexamethylphosphorictriamide[3] with 1 equiv of *sec*-butyllithium in cyclohexane gave a red-brown solution containing the ylide **1**, the formation of which was verified by reaction with fluorenone (−45° for 30 min, then 0° for 16 hr) to give the enol ether **2**[2] in 62% yield. Thermolysis of **2** at 152° for 45 min afforded the doubly branched unsaturated aldehyde **3**[2] (74% yield). This aldehyde is a useful intermediate for the generation of a variety of spiro systems by standard synthetic operations such as are outlined below. In a similar way benzaldehyde was converted in a two-step branching sequence to 2-phenyl-4-pentenal[2] in 70% overall yield.

$(C_6H_5)_3P{=}CHOCH_2CH{=}CH_2$

1

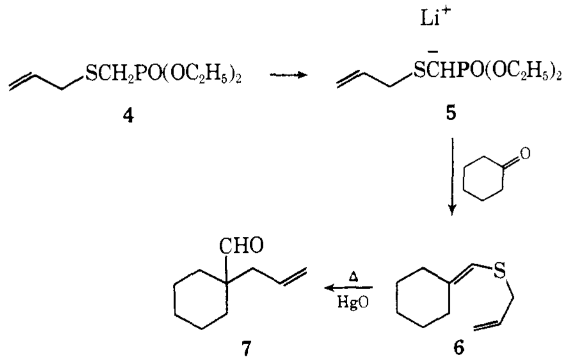


2



3

Although ylide **1** gave good yields of allyl enol ethers with aromatic aldehydes and ketones, no enol ethers could be obtained with alicyclic or enolizable ketones, *e.g.*, cyclohexanone, as substrates. Therefore, some modification was required to broaden the scope of the branching-annulation sequence. Toward this end, diethyl allylthiomethylphosphonate, **4**,[2] bp 77–78° (0.11 mm), was prepared in 67% yield by the Arbusov reaction of triethyl phosphite and allyl chloromethyl sulfide.[4] Slow addition[5] of *sec*-butyllithium in cyclohexane to a THF solution of **4** at −78° afforded the anion **5**, which upon reaction with cyclohexanone (30 min at −78°, warming to 25° over 15 min, then 15 hr at 50°) gave the allyl vinyl sulfide **6**.[2,6] Heating **6** at 160–180° afforded only starting material and intractable tars; this was not unexpected, since thioaldehydes polymerize quite readily.[7] However, when **6** was heated at 190° for 10 min in the presence of 3 equiv of red mercuric oxide, 1-allyl-1-cyclohexanecarboxaldehyde (**7**),[2,8] could be obtained in 82% yield by distillation from the black residue of HgS–HgO. This result supports the working hypothesis that mercuric oxide might promote the rapid conversion of an intermediate thioaldehyde to the corresponding aldehyde and thereby exclude complex side



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[1] Prepared from allyl chloromethyl ether [C. D. Hurd, L. G. Ginger, L. L. Gershbein, and W. A. Yarnall, *J. Amer. Chem. Soc.*, **74**, 5128 (1952)] and triphenylphosphine in acetonitrile.

[2] This compound was characterized satisfactorily by (a) analytical and (b) spectroscopic (infrared and nuclear magnetic resonance) data.

[3] All Wittig reactions, all reactions involving organometallic reagents, and all thermal rearrangements were conducted under an atmosphere of argon.

[4] L. A. Walter, L. H. Goodson, and R. J. Fosbinder, *J. Amer. Chem. Soc.*, **67**, 655 (1945).

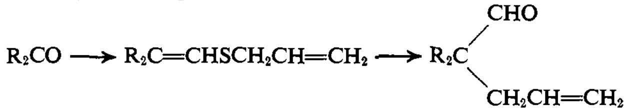
[5] Faster than dropwise addition caused localized heating and decomposition of the phosphonate anion.

[6] For a report on the application of lithium reagents from (1-methylthio)alkylphosphonate esters to the synthesis of vinyl sulfides and ketones, see E. J. Corey and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970).

[7] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, p 148.

[8] Mp of 2,4-DNP, 153–154° [lit. mp 156–157°; see K. C. Brannock, *J. Amer. Chem. Soc.*, **81**, 3379 (1959)].

Table I. Conversion of Carbonyl Compounds into Unsaturated Aldehydes by the Wittig Reaction–Thio-Claisen Rearrangement Sequence



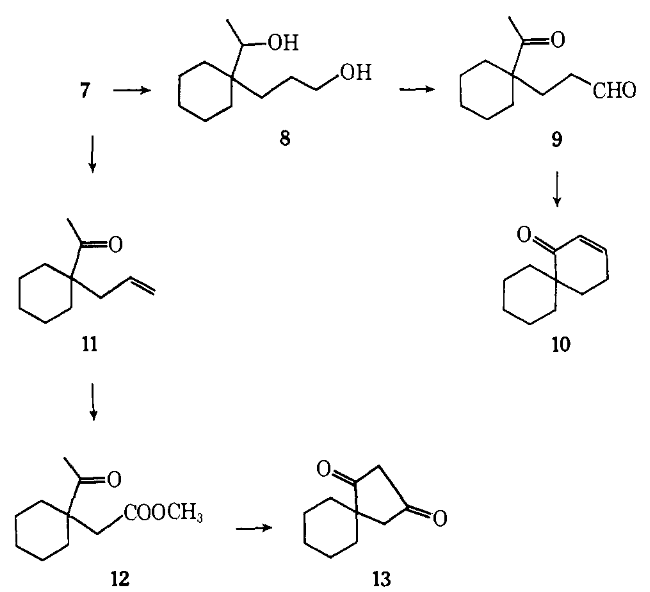
$$R_2CO \longrightarrow R_2C{=}CHSCH_2CH{=}CH_2 \longrightarrow R_2C\begin{smallmatrix}\diagup CHO \\ \diagdown CH_2CH{=}CH_2\end{smallmatrix}$$

Starting carbonyl compound	Yield of vinyl sulfide, %[a]	Yield of aldehyde, %[c]
Cyclohexanone	83	82[d]
Cyclooctanone	19[b]	72[e]
Cyclododecanone	54[b]	74[e]
Fluorenone	81	43[f,g]
Norbornanone	65	83[d,h]
Adamantanone	72	45[f]
Camphor	Trace	
Benzaldehyde	83	39[d]

[a] Purified by preparative tlc on silica gel; all vinyl sulfides gave satisfactory elemental analyses. [b] Reaction carried out in 10:1 tetrahydrofuran–hexamethylphosphorictriamide. [c] Purified by distillation; the 2,4-DNP derivatives all gave satisfactory elemental analyses. [d] Reaction time 10 min at 190°. [e] Reaction time 2 hr at 190°. [f] Reaction time 2 hr at 210°. [g] Purified by distillation followed by preparative tlc. [h] As a 3:2 mixture of epimers.

reactions. This technique should broaden the scope and utility of the thio-Claisen rearrangement.[9] Table I records the results of a number of mercuric oxide promoted thio-Claisen rearrangements as well as data on the preparation of the requisite allyl vinyl sulfides.

The following transformations illustrate the utility of α-allyl alicyclic aldehydes in the synthesis of spiro compounds using as an example the monocyclic intermediate **7**. The individual steps were performed following standard procedures with no attempt at optimization. The diol **8**[2b] was obtained (86%) from **7** by reaction with methyllithium and subsequent hydroboration with disiamylborane.[10] Oxidation of **8**[11] gave keto aldehyde **9**[2b] (45%) which yielded the spiro enone **10**[2] (44%) by treatment with potassium hydroxide in methanol at reflux. The unsaturated ketone **11**,[2] formed in 88% yield from **7** by reaction with methyllithium followed by oxidation,[11] was transformed into the ester **12**[2] in 40% yield by the sequence: (a) ethylene ketalization with ethylene glycol in the presence of methyl orthoformate-p-toluenesulfonic acid[12] and (b) oxidative cleavage of C=C to CHO[13] followed by ketal hydrolysis and conversion of the aldehyde to carboxylic acid[14] and methyl ester **12** (CH_2N_2). As previously demonstrated,[15] the ester **12** undergoes facile cyclization to the spiro diketone **13**.



The chain extension, spiro annulation, and mercuric oxide-promoted thio-Claisen rearrangement described above should be of considerable value in synthesis. There is flexibility relative to the ketonic substrate, the allylic grouping introduced (*e.g.*, methallyl instead of allyl), and the reactions used for chain elaboration and cyclization.[16]

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[9] Although the thio-Claisen rearrangement of simple allyl vinyl sulfides has not previously been reported, there is ample precedent for thio-Claisen rearrangements in other systems. See (a) H. Kwart and M. H. Cohen, *J. Org. Chem.*, 32, 3135 (1967); (b) H. Kwart and T. J. George, *Chem. Commun.*, 433 (1970); (c) Y. Makisumi and A. Murabayashi, *Tetrahedron Lett.*, 2449 (1969); (d) L. Brandsma and D. Schuijl-Laros, *Recl. Trav. Chim. Pays-Bas*, 89, 110 (1970); (e) P. J. W. Schuijl, H. J. T. Bos, and L. Brandsma, *ibid.*, 88, 597 (1969); (f) C. Y. Meyers, C. Rinaldi, and L. Bonoli, *J. Org. Chem.*, 28, 2440 (1963); (g) B. W. Bycroft and W. Landon, *Chem. Commun.*, 168 (1970).

[10] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 83, 1241 (1961).

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[15] B. D. Akehurst and J. R. Bartels-Keith, *ibid.*, 4798 (1957).

[16] This work was assisted financially by the National Institutes of Health and the National Science Foundation.

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Preparation and Structure of $[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$, an Unusual Iridocycle

Sir:

Considerable attention has been given recently to the oxidative addition reactions[1] of coordinatively unsaturated transition element compounds. In view of its reactivity the d^8 system, $IrCl(CO)(PR_3)_2$, has been of special interest.[2] Herein, we report the preparation and structural determination of *trans*-$[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$, I, a novel species formed when the addendum is the π-aromatic cation, $[C_3(C_6H_5)_3]^+$.

Addition of triphenylcyclopropenium tetrafluoroborate to a methanolic solution of *trans*-$IrCl(CO)(P(CH_3)_3)_2$ and recrystallization of the product from a CCl_4–CH_2Cl_2 mixture yielded intense purple crystals of the complex I. *Anal.* Calcd for $IrC_{29}H_{35}OBF_4Cl_3P_2$: C, 41.10; H, 4.17; Cl, 12.58; P, 7.32. Found: C, 40.25; H, 4.06; Cl, 13.20; P, 7.12. Infrared spectrum (KBr pellet): ν(C–O) = 2060 cm^{-1}.

trans-$[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$ crystallizes in the orthorhombic space group $P2_12_12_1$

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[1] J. P. Collman and W. R. Roper, *Advan. Organometal Chem.*, 7, 53 (1968), and references therein.

[2] See, for example, L. Vaska, *Accounts Chem. Res.*, 1, 335 (1968); A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1562 (1969); J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, 7, 1298 (1968).