H_2Se (prepared in a side-arm test tube by hydrolysis of Al_2Se_3 and condensed in dry N_2 atmosphere directly into the nmr tube) contained in a quartz nmr tube was cooled to −78° in a Dry Ice–acetone bath. To the nmr tube was added 1 ml of anhydrous hydrogen fluoride and the mixture was agitated to form a clear solution. The solution was then saturated with boron trifluoride. A TMS capillary was inserted and the pmr spectrum was obtained at −80°.

Protonation of Alkyl Tellurides in HF–BF_3.—Approximately 1 ml of anhydrous hydrogen fluoride was placed into a quartz nmr tube and cooled to −78° in a Dry Ice–acetone bath. To the nmr tube was added 100 mg of alkyl telluride and the mixture was agitated to form a clear solution. The solution was then saturated with boron trifluoride. A TMS capillary was inserted and the pmr spectrum was obtained at −80°.

Trimethylselenonium Fluorosulfate.—To a solution of 11.4 g (0.1 mol) of methyl fluorosulfate in 50 ml of anhydrous 1,1,2-trichlorotrifluoroethane was added a solution of 9.4 g (0.1 mol) of dimethyl selenide in 50 ml of anhydrous 1,1,2-trichlorotrifluoroethane at room temperature. The mixture was agitated for 10 min and the white precipitate was filtered off. The product was twice washed with 1,1,2-trichlorotrifluoroethane and dried in a stream of dry N_2, mp 83–85°.

Triethylselenonium Fluorosulfate.—The procedure was similar to that used for the preparation of trimethylselenonium fluorosulfate except that 12.8 g (0.1 mol) of ethyl fluorosulfate and 10.8 g (0.1 mol) of diethyl selenide were used. In order to isolate the product it was necessary to extend the reaction time at 0° to 1 hr, after which the white precipitated triethyl selenonium ion was isolated as before, mp 25–28°.

Trimethyltelluronium Fluorosulfate.—The procedure was similar to that used for the preparation of trimethylselenonium fluorosulfate except that 14.3 g (0.1 mol) of dimethyl telluride was used, mp 128–130°. All melting points were determined in sealed capillary tubes. They are dependent on rate of heating (2°/min in the melting range, after having determined it by 10°/min).

Trimethylsulfonium Fluorosulfate and Triethylsulfonium Fluorosulfate.—The preparations used were similar to those of the corresponding selenonium ions, using dimethyl and diethyl sulfide, respectively. $(CH_3)_3S^+SO_3F^-$ had mp 174–176° and $(C_2H_5)_3S^+SO_3F^-$ had mp 25°.

All isolated onium fluorosulfate salts gave correct elemental analyses.

Acknowledgment.—Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No.—Methyl fluorosulfate, 421-20-5; ethyl fluorosulfate, 371-69-7; dimethyl sulfide, 75-18-3; diethyl sulfide, 352-93-2.

Regiospecific Alkylation of Organocopper Enolates

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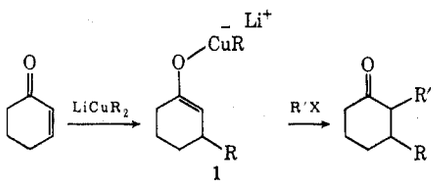
Regiospecific alkylation of lithium and magnesium enolates, generated from enol acetates[1] or the 1,4 addition of Grignard reagents,[2] has been known for some time. The latter process allows the introduction of two different alkyl groups in one synthetic operation. However, to varying degrees, these methods suffer from problems of polyalkylation resulting from proton transfer. A recent paper by Grieco and coworkers prompts us to report our studies in this area.[2d]

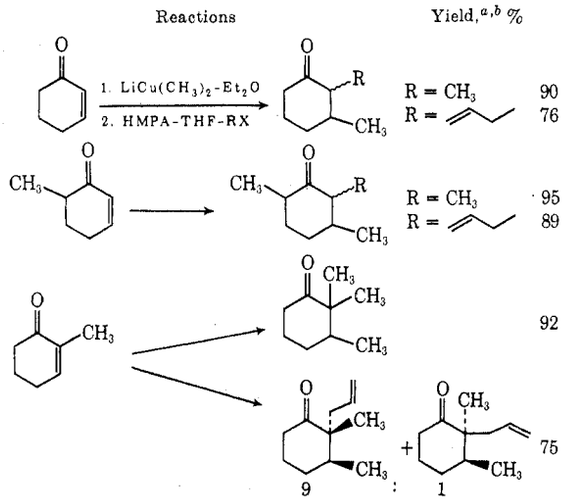
The organocopper enolates (**1**) generated by the addition of lithium dialkylcuprates to enones offer the possibility of eliminating the problems of polyalkylation since these are presumably highly covalent and, therefore, less likely to undergo proton transfer. One also can take advantage of the higher stereoselectivity and generally higher yields of 1,4-addition products produced with the organocopper reagents. We would like to report that these intermediate enolates may be alkylated regiospecifically in unhindered cases without significant amounts of polyalkylation occurring. There has been no direct evidence reported as to the structure of the intermediate (**1**), but in our experience, as



1

well as others,[2e] the unreactivity of **1** under the normal alkylation conditions (methyl iodide, ether, 25°) indicates that the structure is best interpreted as an organocopper enolate. A representative group of cyclohexenones (Table I) which was studied showed that

TABLE I



[a] Distilled yields. [b] Analysis by vpc compared with independently prepared samples.

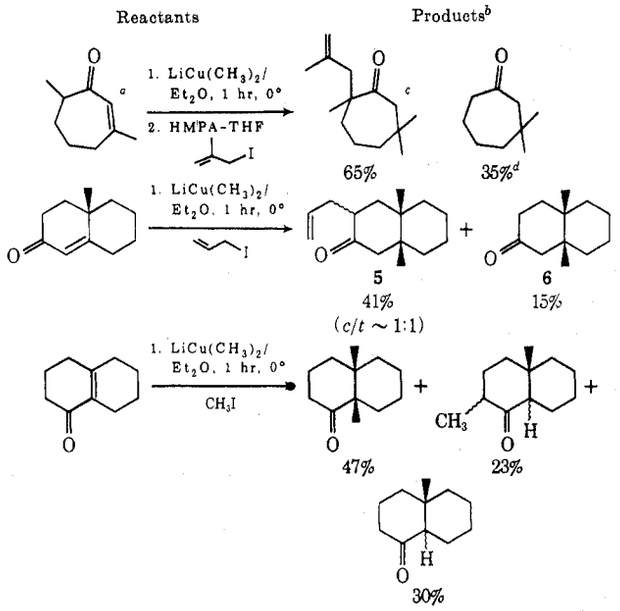
alkylation can be accomplished regiospecifically and in high yield under mild conditions. Significantly, no evidence of polyalkylation was found even in the presence of excess allyl halides.

One limitation of this method (and presumably that of the magnesium enolate also) was encountered. The preservation of enolate regiospecificity during alkylation requires that the rate of alkylation be significantly greater than proton transfer. In the case of β,β-disubstituted enones this criterion is not met. Treatment of β,β-disubstituted enones under the usual conditions for 1,4 addition followed by alkylation resulted in varying amounts of equilibration prior to alkylation. As can be seen (Table II), it appears that reduction

(1) H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 2502 (1968).

(2) (a) G. Stork, G. L. Nelson, F. Rouesac, and O. Gringore, *J. Amer. Chem. Soc.*, **93**, 3091 (1971); (b) G. Stork, *Pure Appl. Chem.*, **17**, 383 (1968); (c) P. Hudrlik, Ph.D. Dissertation, Columbia University, 1969; (d) P. A. Grieco and R. Finkelhor, *J. Org. Chem.*, **38**, 2100 (1973); (e) G. H. Posner and J. J. Sterling, *J. Amer. Chem. Soc.*, **95**, 3076 (1973).

TABLE II

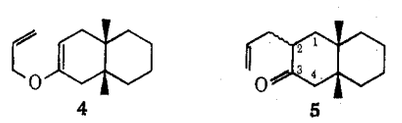


[a] Method of synthesis; see ref 6. [b] Analysis by vpc, compared with independently synthesized samples. [c] Structure assigned by nmr $(CH_3)_2CCH_2C(=O)C(CH_3)CH_2C(=CH_2)CH_3$ protons α to carbonyl, δ 2.61 (1, d, J = 12 Hz), 2.17 (1, d, J = 12 Hz). [d] Isolated yields.

in the size of the alkyl halide increases the ratio of alkylation to equilibration. This suggests that the problem lies in steric hindrance retarding the alkylation rate rather than the covalent nature of the organocopper enolate. To investigate this hypothesis the lithium enolate **2** was generated from enol acetate **3**[3]

2 3

(methyllithium, dimethoxyethane, 0°).[1] This enolate was unreactive when treated with excess allyl iodide even in the presence of small amounts of hexamethylphosphoric triamide (HMPA) (~20%). If the medium is made sufficiently polar (~50% HMPA) exclusive O-alkylation results producing enol ether **4** (80%). The structure of **4** was determined by subjecting the enol ether to Claisen rearrangement (at reflux in pyridine) to produce the epimeric **5** (1:1 α/β), identical



4 5

with the product of the trapping experiment, whose structure was verified by independent synthesis.[4] This suggests that, when β substitution is present, enolate equilibration, resulting in loss of regiospecificity, will be a major, if not the exclusive, process. This result is not altogether surprising considering the steric conjestion in **2** which hinders approach of reagents to C-4.[5]

(3) J. A. Marshall and A. Hochstetler, *J. Amer. Chem. Soc.*, **91**, 648 (1969).

(4) Prepared by carbomethoxylation of ketone **6**, alkylation ($NaH/CH_2=CHCH_2I$), decarbomethoxylation ($LiI \cdot 3H_2O$/collidine); see Experimental Section.

(5) One must also recognize that other steric factors in the fused-ring *cis*-decalin system undoubtedly contribute to the inability to alkylate enolate **2**.

Further studies will be reported elsewhere concerning the reactivity of copper enolates with vinyl ketones.

Experimental Section

All boiling points are uncorrected. Ir spectra were recorded on a Perkin-Elmer IR-257 and are reported in cm^{-1}; nmr spectra were recorded on a Varian T-60 spectrometer and are reported on ppm (δ) downfield from TMS. Tetrahydrofuran (THF), *p*-dioxane, and 1,2-dimethoxyethane (DME) were dried by distillation from lithium aluminum hydride, hexamethylphosphoric triamide by distillation under reduced pressure from calcium hydride, and pyridine from barium oxide.

Representative Alkylation Procedure. Preparation of 2,2,3-Trimethylcyclohexanone.—A solution of lithium dimethylcuprate in anhydrous ether (20 ml) was prepared from purified cuprous iodide (Alfa) (760 mg, 4.0 mmol) and 2.3 *M* methyllithium (Ventron) in ether (3.5 ml, 8.0 mmol). After 15 min at 0°, 2-methyl-2-cyclohexen-1-one[7] (220 mg, 2.0 mmol) in 2 ml of dry Et_2O was added. The mixture was maintained at 0° with stirring for 1 hr. A solution of 5 ml of anhydrous THF and 5 ml of anhydrous HMPA was added, followed by rapid addition of excess methyl iodide (1 ml). The mixture was allowed to warm to room temperature and stirred for 3 hr. The reaction mixture was poured into a 10% aqueous ammonium hydroxide solution, and the organic layer was separated, washed successively with 10% ammonium hydroxide, water, and saturated brine, and dried over magnesium sulfate. Evaporation of the solvent and distillation (Kugelrohr oven 80°) at 24 mm afforded 250 mg (92%) of colorless 2,2,3-trimethylcyclohexanone (lit.[8] bp 90–100° at 100 mm): ir 1705; nmr 1.06 (s, 3), 1.03 (s, 3), 1.02 (broad doublet, 3); vpc[9] analysis indicated ≥97% purity (single peak, retention time 23 min).

Preparation of *cis*- and *trans*-3-Allyl-*cis*-9,10-dimethyl-2-decalone (5).—*cis*-9,10-Dimethyl-2-decalone[3] (180 mg, 1.0 mmol) in 20 ml of anhydrous *p*-dioxane was treated with sodium hydride (washed) (96 mg, 4.0 mmol) and 2.0 ml (23.0 mmol) of dimethyl carbonate. The mixture was heated at 85° for 18 hr under nitrogen, during which time the solution became deep red. The cooled reaction mixture was acidified with aqueous acetic acid and poured into water. After extraction with ether (three times), the combined organic layers were washed with water, dried over magnesium sulfate, and evaporated to an orange oily β-keto ester (204 mg) which exhibited a positive ferric chloride test: ir 1745, 1715, 1655, 1615.

A sample of the crude β-keto ester (473 mg, 1.9 mmol) in anhydrous *p*-dioxane (5 ml) was added to a suspension of sodium hydride (48 mg, 2.0 mmol) in 8 ml of dry dioxane. After gas evolution ceased (35 min), the deep red solution was treated with excess allyl iodide (504 mg, 3.0 mmol), and the mixture was heated at 85° for 3 hr under nitrogen. The products were isolated by ether extraction and dried over magnesium sulfate. Evaporation of the solvent gave 492 mg of crude β-keto ester: ir 1740, 1710, 1640; nmr 6.20–4.80 (m, 3), 3.73 (s, 3), 1.0 (s, 6).

The crude alkylated β-keto ester (492 mg) was added dropwise to a hot (~120°) solution of lithium iodide trihydrate (564 mg, 3.0 mmol) in 30 ml of collidine, and the mixture was heated at reflux under nitrogen for 5 hr. The organic products were isolated by ether extraction as usual to afford a dark oil. A short path distillation (Kugelrohr) at 100° (0.5 mm) gave 318 mg of colorless **5**: ir 1710, 1640, 915; nmr 6.20–4.80 (m, 3), 1.13, 1.00, 0.97, 0.78 (C-9, 10 methyl); mass spectrum P^+ calcd 230.3620, found 230.3615. The spectral data and vpc behavior[10] were identical with the product of the enolate trapping experiment.

***cis*-9,10-Dimethyl-$\Delta^{1,2}$-octal-2-ol Acetate (3).**—A solution of lithium dimethylcuprate, from 11.4 g (60 mmol) of cuprous iodide and 72 ml (120 mmol) of 1.67 *M* methyllithium in 150 ml of anhydrous ether at 0° under nitrogen, was treated with 10-methyl-$\Delta^{1,9}$-octal-2-one (4.92 g, 30 mmol) in 20 ml of anhydrous ether and stirred for 1 hr at 0°. Acetyl chloride (10 ml, excess)

(6) G. Stork, M. Nussim, and B. August, *Tetrahedron Suppl.*, **8**, Part I, 105 (1966).

(7) W. S. Johnson, D. G. Martin, and E. W. Warnhoff, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 161.

(8) E. C. Horning, M. G. Horning, and E. J. Platt, *J. Amer. Chem. Soc.*, **71**, 1771 (1949).

(9) 20% SE-30, 6 ft, 100°.

(10) 20% SE-30, 6 ft, 170°.

was rapidly added at 0° *via* syringe (foaming) and the mixture was warmed to room temperature and stirred (3 hr).

The crude mixture was filtered free of salts and evaporated. Benzene was added and evaporated to remove the last traces of acetyl chloride. Distillation of the residue under reduced pressure [Kugelrohr oven temperature 100° (0.5 mm)][3] afforded 6.2 g (93%) of colorless **3**: ir 1750, 1685; nmr 5.10 (t, J = 2 Hz, 1), 2.20 (s, 3), 1.10 (s, 6).

***cis*-9,10-Dimethyl-$\Delta^{2,3}$-octal-2-ol Allyl Ether (4).**—A solution of methyllithium (1.2 ml of 1.67 M solution, 2.0 mmol) was evaporated under nitrogen stream and 5 ml of anhydrous DME added along with a small amount of triphenylmethane as indicator. A solution of 444 mg (2.0 ml) of **3** in 2 ml of DME was added dropwise at 0° (pale pink color remains). Anhydrous HMPA (5 ml) was added followed by 1 ml (excess) of allyl iodide at room temperature.

The usual ether–water work-up afforded after chromatography on silica gel (10 g) and elution with hexane–benzene (9:1) 325 mg of enol ether **4** (80%): ir 1665, 1645; nmr 6.20–4.80 (m, 4), 1.12 (s, 6); mass spectrum P^+ calcd 230.3620, found 230.3627.

Rearrangement of Enol Ether (4).—Enol ether **4** (30 mg) was heated at reflux in 1 ml of anhydrous pyridine for 20 hr under nitrogen. The pyridine was evaporated *in vacuo* and residue taken up in ether, filtered, and evaporated to afford a yellow oil (25 mg). Analysis of the material by vpc[10] and tlc (silica gel; benzene) established the identity of the major product with allyl ketone (**5**).

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—**3**, 22738-17-6; **4**, 42449-61-6; *cis*-**5**, 42449-62-7; *trans*-**5**, 42449-63-8; 2,2,3-trimethylcyclohexanone, 39257-08-4; 2-methyl-2-cyclohexen-1-one, 1121-18-2; methyl iodide, 74-88-4; *cis*-9,10-dimethyl-2-decalone, 5523-99-9; allyl iodide, 556-56-9; 10-methyl-$\Delta^{1,9}$-octal-2-one, 826-56-2; acetyl chloride, 75-36-5.

Palladium(II)–π-Allyl Complexes. An Improved Synthesis of Di-μ-chlorobis(1,3,4,5,6-pentamethylbicyclo[2.2.0]hexa-2,5-diene)palladium(II)

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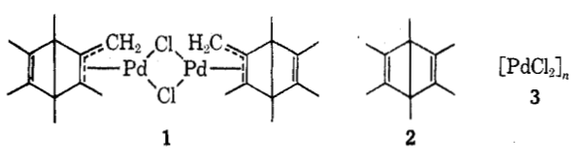
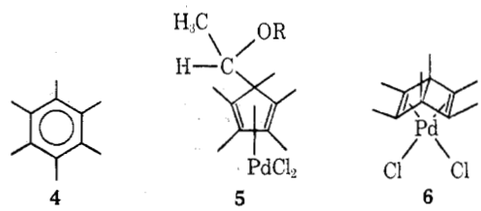
The title compound **1**,[1] derived from hexamethylbicyclo[2.2.0]hexa-2,5-diene (**2**), is unique among π-allyl complexes insofar as it contains two cyclobutene rings.[2] Even so, a convenient synthesis of **1** has not yet been developed. The general procedure of Hüttel and Christ for preparing π-allyl–palladium(II) complexes is not applicable to the synthesis of **1**, since the starting alkene must be heated with palladium(II) chloride (**3**) in 50% aqueous acetic acid containing hydrochloric acid.[3] When **2** is allowed to react with palladium(II) salts and complexes under homogeneous conditions in the presence of hydroxylic solvents, it is either isomerized to hexamethylbenzene (**4**) (neutral media)[4] or converted to cyclopentadiene complexes of general structure **5** (acid media).[5] Shaw and Shaw studied the action of methanolic sodium methoxide on hexamethylbicyclo[2.2.0]hexa-2,5-dienepalladium(II) chloride (**6**) and isolated **1** in low yield (0.41 g of **6** → 0.05 g of **1**).[1] However, this approach to **1** is not only inefficient but hinges on the manipulation of a highly unstable precursor.[6]



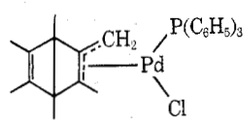
1 **2** **3**

We have found that π-allyl complex **1** can be isolated in gram quantities by adherence to a simple procedure: a solution of **2** (commercially available and thermally stable[7]) in dichloromethane is allowed to stir heterogeneously with anhydrous **3** at room temperature, the critical reaction variable being time. In one experiment, 10.0 g of **2** and 2.0 g of **3** gave, after *504* hr and column chromatography on alumina, 2.3 g of **1**, a 62% yield of that complex based on starting palladous chloride.

The structure of **1** was confirmed by its elemental composition (C, H, Cl), by comparison of its spectral parameters (ir, nmr) with those published for the authentic compound,[1] and by its known conversion to triphenylphosphine complex **7**.[1]



4 **5** **6**



7

The formation of **1** proceeds simultaneously with some aromatization of **2** and with reduction of some Pd(II) to Pd(0). Material balances and descriptions of chromatography fractions for two runs are given in Table I. Run 1 was monitored by nmr spectroscopy, and the relative quantities (based on 100 mol %) of **1**, **2**, and **4** as a function of time were determined; the results are displayed in Figure 1. After about 300 hr both the aromatization of **2** and the formation of **1** were nearly complete, presumably because all starting palladous chloride had been consumed.

It seems plausible that π-allyl complex **1** arises *via* loss of hydrogen chloride from intermediate complex **8**[8] while aromatization of **2** is promoted by "monomeric" palladium(II) chloride.

(1) B. L. Shaw and G. Shaw, *J. Chem. Soc. A*, 602 (1969).

(2) The structure, synthesis, and chemistry of palladium(II)–π-allyl complexes have been reviewed in detail; see P. M. Maitlis, "The Organic Chemistry of Palladium," Academic Press, New York, N. Y., 1971, pp 175–252.

(3) See ref 2, pp 176–177.

(4) C. J. Attridge and S. J. Maddock, *J. Organometal. Chem.*, **26**, C65 (1971).

(5) P. V. Balakrishnan and P. M. Maitlis, *J. Chem. Soc. A*, 1721 (1971).

(6) H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967).

(7) W. Schäfer and H. Hellman, *Angew. Chem., Int. Ed. Engl.*, **6**, 518 (1967).

(8) See ref 2, p 112, for a discussion of Pd(II) complexes of this structural type.