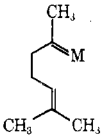
(8) (a) G. Dall'Asta, *J. Polym. Sci., Part A-1*, **6**, 2397 (1968), and references cited therein. (b) Dall'Asta reported the polymerization of 1-methylcyclobutene, but the polymer was largely saturated: G. Dall'Asta and R. Manetti, *Atti Acad. Naz. Lincei Rend. Cl. Sci. Fis. Mat. Nat.*, **41**, 351 (1966) [*Chem. Abstr.*, **67** 33003q (1967).

(9) The metathesis reaction has been capricious in our hands; sometimes the reaction is inexplicably slow.

(10) An astonishing variety of catalyst recipes have been reported.[6] We have chosen the mixture $WCl_6/Sn(CH_3)_4$ because of its reported compatability with esters.[17b]

(11) T. J. Katz, J. McGinnis, and C. Altus, *J. Am. Chem. Soc.*, **98**, 606 (1976).

(12) The reactive (chain carrying) metallocarbene derived from 1-methylcyclobutene is **8**.



8

(13) All new compounds possessed spectral and analytical data in accord with the assigned structures.

(14) A cyclobutene/hexene/catalyst ratio of 8/44/1 was used.

(15) Only two isomers could be resolved (mol wt, 152.1558 and 152.1563) by VPC. Materials from the two pathways possessed identical spectral data and retention times on a 200-ft. DB-TCP capillary column. We have not established the configuration about the double bonds.

(16) (a) T. Katz, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, INOR81; (b) C. P. Pinazzi, I. Guilmet, and D. Reyx, *Tetrahedron Lett.*, 989 (1976); (c) R. Rossi, P. Diversi, A. Lucherini, and L. Porri, *ibid.*, 879 (1974); (d) British Patent 1125529 [*Chem. Abstr.*, **69**, 105851f (1968)].

(17) There are scattered reports of the metathesis of functionalized olefins. (a) Nitrile: G. Foster, *Chem. Abstr.*, **75**, 63172b (1971). (b) Ester: P. B. van Dam, M. C. Mittelmeijer, and C. Boelhouwer, *Chem. Commun.*, 1221 (1972); P. B. van Dam, M. C. Mittelmeijer, and C. Boelhouwer, *J. Am. Oil Chem. Soc.*, **51**, 389 (1974); W. Ast, G. Rheinwald, and R. Kerber, *Makromol. Chem.*, **177**, 39 (1976). (c) Acids: K. Hummel and Y. Imanoglu, *Colloid Polym. Sci.*, **253**, 225 (1975); *Chem. Abstr.*, **83**, 96094w (1975).

(18) Geraniol acetate is relatively stable in the presence of active metathesis catalyst $WCl_6/Sn(CH_3)_4$. Catalyst activity was checked by injecting aliquots of 2-pentene. Within minutes at room temperature 2-butene and 3-hexene are produced.

(19) J. McGinnis, T. J. Katz, and S. Hurwitz, *J. Am. Chem. Soc.*, **98**, 605 (1976).

(20) (a) P. Krausz, F. Garnier, and J. E. Dubois, *J. Am. Chem. Soc.*, **97**, 437 (1975); (b) S. Warwel and W. Laarz, *Chem. Ztg.*, **99**, 502 (1975); (c) A. Agapiou and E. McNelis, *Chem. Commun.*, 187 (1975).

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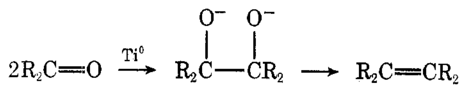
Received June 10, 1976

Synthesis of Unsymmetrical Olefins by Titanium(0) Induced Mixed Carbonyl Coupling. Some Comments on the Mechanism of the Pinacol Reaction

Summary: Unsymmetrical olefins can be synthesized in useful yields by titanium induced ketone coupling if one component is used in excess. Mixed coupling is particularly efficient for diaryl ketones, and a mechanism is proposed to account for this.

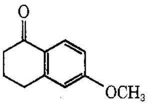
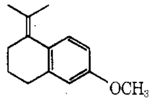
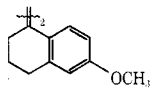
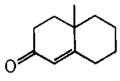
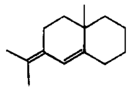
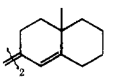
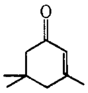
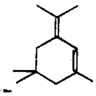
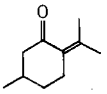
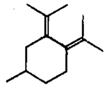
Sir: We recently reported an improved carbonyl coupling procedure employing active titanium(0). Olefins were isolated in high yields.[1] Since the reaction occurs by a two-step pathway involving initial reductive dimerization of the carbonyl to a pinacol, followed by deoxygenation to olefin, one might expect the intermolecular version of this reaction to be limited to the synthesis of symmetrical olefins.



$$2R_2C{=}O \xrightarrow{Ti^0} R_2\overset{O^-}{\overset{|}{C}}{-}\overset{O^-}{\overset{|}{C}}R_2 \longrightarrow R_2C{=}CR_2$$

Pinacol formation is generally presumed to occur by dimerization of anion radicals,[2] and the synthesis of unsymmetrical olefins by our method therefore requires that we be able to carry out mixed pinacol couplings. There is little information in the literature concerning mixed pinacol reactions,[3-6] but the few scattered reports that do exist indicate that one generally obtains a mixture of the three possible pinacols in a nearly statistical ratio. Recently, while this work was in progress, another report appeared describing several mixed pinacol reactions. Again, the mixed products appear to be found in approximately statistical amounts, although complete product analyses were not reported.[7]

Table I. Titanium Induced Mixed Coupling Reactions between Acetone and Other Ketones (Acetone/Ketone, 4:1)

Entry	Ketone	Products	Isolated yield, %[a]
1	Adamantanone	Isopropylideneadamantane	63
		Biadamantylidene	12
2	4-*tert*-Butylcyclohexanone	4-*tert*-Butylisopropylidenecyclohexane	55
		Bi-4-*tert*-butylcyclohexylidene	22
3	3-Cholestanone	3-Isopropylidenecholestane	54
		Bi-3-cholesterylidene	29
4	Cycloheptanone	Isopropylidenecycloheptane	50
		Bicycloheptylidene	26
5	1-Indanone	1-Isopropylideneindan	71
		Bi-1-indanylidene	24
6	Acetophenone	2-Methyl-3-phenyl-2-butene	65
		2,3-Diphenyl-2-butene	16
7	Benzophenone	1,1-Diphenyl-2-methylpropene	94
		Tetraphenylethylene	tr
8	Fluorenone	Isoptropylidenefluorene	84
		Bifluorenylidene	0
9			85
		+ 	9
10			67
		+ 	26
11			63
12			55

[a] The crude product mixtures were purified by column chromatography on silica gel and the products identified by spectral methods (NMR, MS).

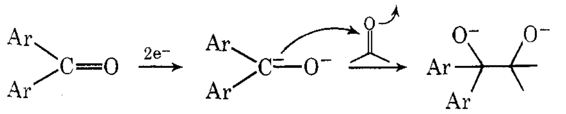
We felt, therefore, that our olefin-forming reaction would probably only be synthetically useful in cases where an excess of one inexpensive carbonyl component could be used and where the major olefinic by-product could be easily removed. Acetone is the obvious choice as one component of the reaction since it may be used in excess and its self-coupling product, tetramethylethylene, is volatile. We therefore examined unsymmetrical olefin formation by reaction of acetone with other ketones. Our results are given in Table I.

In all cases, the isopropylidene products can be isolated in synthetically useful yields. The isopropylidene group is a common structural unit of many sesquiterpenes, and, since the Wittig reaction is not applicable to the synthesis of these tetrasubstituted olefins, this one-step mixed coupling may prove of value. Further, the synthesis and spectroscopic study of *vic*-diisopropylidene compounds such as that derived from pulegone (reaction 12) has been an active field recently,[8] and the present synthesis is quite efficient.

In examining these results, we were struck by the fact that, while mixed coupling of acetone with most other ketones gave the mixed product in a nearly statistical amount, reaction with the diaryl ketones, benzophenone and fluorenone, gave essentially *only* mixed product. Indeed, even when acetone and benzophenone were reacted in equimolar amounts, mixed coupling was still highly favored.

This is most surprising when one considers that the reduction potentials (E_{redn}) of benzophenone and fluorenone are both 1.0–1.5 V less negative than that of acetone.[9] One would expect the corresponding anion radicals to form more rapidly than that of acetone, leading to a preponderance of symmetrical coupling. Since this is not the case, we consider it unlikely that the mixed pinacol reaction of acetone with diaryl ketones is in fact a radical coupling process.

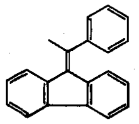
An alternate mechanistic hypothesis can be devised. Stabilized radical anions, such as those derived from diaryl ketones, are known to reduce further to dianions, and the E_{redn} for this second reduction is less negative than E_{redn} for acetone.[9] We suggest that these dianions are formed and that mixed coupling results by nucleophilic addition to acetone.



While we have no evidence to suggest that normal pinacol reactions between similar species are other than radical couplings, the nucleophilic addition of a stabilized dianion to a free ketone may well be general for mixed reactions in which one component is much more easily reduced than the other. This then suggests that our olefin synthesis need not be limited to cases where one inexpensive component is used in excess. Rather, we ought to be able to obtain good yields of mixed coupling of any two ketones as long as one component reduces to a dianion before the other reduces to an anion radical. We have carried out several such reactions successfully and the results are given in Table II.

In a representative procedure, anhydrous $TiCl_3$ (2.87 g, 18.6 mmol) was slurried in 30 ml of dry dimethoxyethane under argon, and lithium[10] pieces (0.45 g, 65 mg-atoms) were added. After 1-h reflux, the black mixture was cooled, and a solution of benzophenone (0.42 g, 2.3 mmol) and cyclohexanone (0.226 g, 2.3 mmol) in 2.0 ml of dimethoxyethane was added. The mixture was stirred for 2 h at room temperature and then refluxed for 20 h. After the mixture cooled to room temperature, 50 ml of petroleum ether was added over 15 min. The organic layer was decanted from the black residue, filtered through a 1-cm pad of Florisil, and concentrated. Chromatography on 15 g of silica gel gave bicyclohexylidene (11 mg, 6%, hexane elution), cyclohexylidenediphenylmethane (445 mg, 78%, hexane/benzene elution), and tetraphenylethylene (74 mg, 19%, benzene elution).

Table II. Titanium Induced Mixed Carbonyl Couplings of Diaryl Ketones with Other Partners (Ratio of Ketones, 1:1).

Entry	Ketones	Products	Isolated yield, %
1	Benzophenone + acetone	1,1-Diphenyl-2-methylpropene	81
		Tetraphenylethylene	14
2	Benzophenone + cyclohexanone	Cyclohexylidenediphenylmethane	78
		Tetraphenylethylene	19
		Bicyclohexylidene	6
3	Benzophenone + 3-cholestanone	3-Cholesterylidenediphenylmethane	82
		Tetraphenylethylene	14
		Bi-3-cholesterylidene	5
4	Benzophenone + hexanal	1,1-Diphenyl-1-heptene	84
		Tetraphenylethylene	9
		6-Dodecene	8
5	Benzophenone + di-*tert*-butyl ketone	Tetraphenylethylene	90
6	Fluorenone + acetone	Isopropylidenefluorene	74
		Bifluorenylidene	8
7	Fluorenone + cycloheptane	Cycloheptylidenefluorene	77
		Bifluorenylidene	7
		Bicycloheptylidene	17
8	Fluorenone + acetophenone		70
		2,3-Diphenyl-2-butene	15
		Bifluorenylidene	8

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

References and Notes

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(2) See H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, New York, N.Y., 1972, pp 167–169.
(3) J. Wiemann, *C. R. Hebd. Seances Acad. Sci.*, **212**, 764 (1941).
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(10) In our original publication[1] we used potassium metal to effect this reduction. We have subsequently found lithium to be nearly as effective and far safer to use.

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Received April 13, 1976