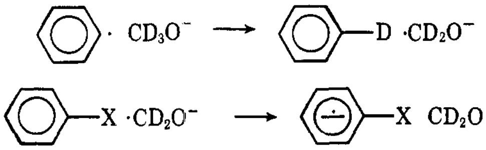
Table I. Reactions of Trimethylsilyl Anions with Aryl Halides

Reagent	ArX	ArTMS	ArH	Total[a] yield, %	ArTMS/ ArH
Me_3SiK[b]	Cl	86	5	91	17
	Br	92	7	99	13
	I	68	26	94	2.6
Me_3SiNa[c]	Cl	87	5	92	17
	Br	91	8	99	11
	I	70	27	97	2.6
Me_3SiLi[d]	Cl	69	4	73	17
	Br	84	7	91	12
	I	63	26	89	2.4

[a] Percent yield based on aryl halide determined by VPC analysis after workup (20 ft × ⅛ in. 10% SE-30; internal standard, decane). [b] Generated by the reaction of hexamethyldisilane and potassium methoxide in HMPT at 25 °C. [c] Generated by the reaction of hexamethyldisilane and sodium methoxide in HMPT at 25 °C. [d] Generated by the reaction of hexamethyldisilane and methyllithium in HMPT/Et_2O at 0 °C, then allowed to warm to 25 °C.[2j]

part of the reaction may be proceeding via a phenylpotassium intermediate.[2a] Whether this phenyl anion comes from nucleophilic attack of silyl anion on halogen or from the reduction of phenyl radical by silyl anion cannot be distinguished at this time.

The relative rates with regard to halogen substitution and the observation of reduction product are reminiscent of other aromatic nucleophilic substitution reactions proposed to proceed by radical-chain mechanisms.[8] Sakurai has shown that trimethylsilyl anion is a convenient one-electron donor.[2e] Replacement of CH_3OK with CD_3OK[10] in the reaction of iodobenzene and hexamethyldisilane affords reduction product with 64% d_1 incorporation,[9] consistent with the chain-carrying properties ascribed to methoxide found in the growing list of aromatic free radical-chain mechanisms.[8,11] The observation



that some but not all of the hydrogen-atom source in the reduction product is methoxide is compatible with the finding that, for the cases using TMSLi, which contains no methoxide owing to the method of generation, reduction product is still observed. Further investigations will be necessary before these reactions are fully understood.[12] However, it appears from the present deuterium incorporation data that the iodobenzene reaction with TMSK may involve *at least* two aromatic intermediates, phenyl radical and phenyl anion.

A typical procedure is as follows. To 1.91 g (0.027 mol) of potassium methoxide[13] in 50 mL of anhydrous HMPT[14] under argon at 25 °C was added 3.12 g (0.018 mol) of *p*-bromotoluene followed by 4.38 g (0.029 mol) of hexamethyldisilane.[15] The yellow reaction mixture was allowed to stir for 6 h. Aqueous NH_4Cl (5%) was added to the reaction mixture and this was extracted twice with pentane. The pentane layers were combined and dried (Na_2SO_4). Distillation under reduced pressure afforded 2.46 g (82% isolated yield) of *p*-tolyltrimethylsilane, 99.6% pure by vapor phase chromatography (VPC).[17]

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(5) For example, the reaction of *o*-, *m*-, and *p*-bromotoluene with TMSK afforded substitution/reduction ratios of 3, 10, and 13, respectively.
(6) As the temperature is raised above 25 °C the yields and ratio of substitution/reduction decreases. If the reaction is run at 0 °C in HMPT/Et_2O (10:1 ratio), the substitution/reduction ratio apparently increases although the mass balance (yield) of the substitution product does not increase significantly.
(7) Benzene, 1-bromo-4-trimethylsilylbenzene, and bromobenzene were not observed in the reaction mixture (<1%) under analytical conditions (VPC) independently shown to separate authentic mixtures. Trimethylsilylbenzene and 1,4-bis(trimethylsilyl)benzene were observed in 1 and 2% yields, respectively.
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(10) Made from CD_3OD (Aldrich) and potassium hydride.
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(13) Obtained from Alfa.
(14) Distilled from lithium wire under reduced pressure and redistilled from CaH_2. HMPT was handled with the precautions appropriate to a potential carcinogen.
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(18) National Science Foundation Predoctoral Fellow, 1973–1976.
(19) Alfred P. Sloan Research Fellow, 1977–1979.

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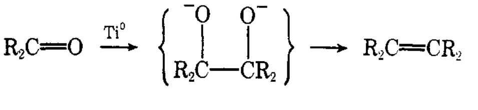
Synthesis of Cycloalkenes by Intramolecular Titanium-Induced Dicarbonyl Coupling

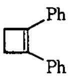
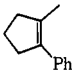
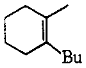
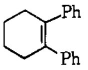
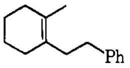
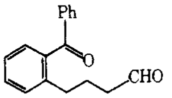
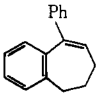
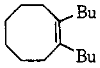
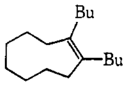
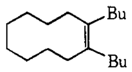
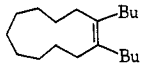
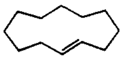
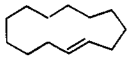
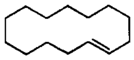
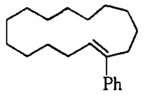
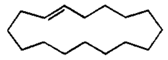
Summary: Cycloalkenes of ring size 4–16 are prepared in good yield by treatment of dicarbonyl compounds with a reagent prepared from $TiCl_3$/Zn–Cu.

Sir: We have reported recently that ketones and aldehydes can be reductively coupled to olefins by treatment with low valent titanium.[1–3] The intermolecular version of this reaction works best when identical carbonyl species are coupled to give symmetrical olefins,[2] but we have also demonstrated that, in



$$R_2C{=}O \xrightarrow{Ti^0} \left\{ \begin{array}{cc} {}^-O & O^- \\ | & | \\ R_2C & \!\!-\!\!-CR_2 \end{array} \right\} \longrightarrow R_2C{=}CR_2$$

Table I. Cycloalkene Formation by Dicarbonyl Coupling

Dicarbonyl substrate	Cycloalkene	Yield, %[a]
$PhCO(CH_2)_2COPh$		87
$CH_3CO(CH_2)_3COPh$		70
$CH_3CO(CH_2)_4COBu$		79
$PhCO(CH_2)_4COPh$		95
$CH_3CO(CH_2)_4COCH_2CH_2Ph$		50
		80
$BuCO(CH_2)_6COBu$		67
$BuCO(CH_2)_7COBu$		68
$BuCO(CH_2)_8COBu$		75
$BuCO(CH_2)_9COBu$		76
$CHO(CH_2)_{10}CHO$		76
$CHO(CH_2)_{11}CHO$		52
$CHO(CH_2)_{12}CHO$		71
$CHO(CH_2)_{13}COPh$		80
$CHO(CH_2)_{14}CHO$		85

[a] The figures given represent isolated yields.

certain cases, unsymmetrical olefins can be prepared in good yield.[3] Mechanistically, we have shown that the coupling reaction proceeds by an initial pinacol dimerization, followed by titanium-induced deoxygenation.

The pinacol coupling of ketones and aldehydes is, of course, mechanistically similar to the acyloin coupling of esters[4] in that one-electron donation to the carbonyl group produces an intermediate ketyl which then dimerizes. Since the acyloin reaction of diesters is of great value in synthesis owing to its effectiveness in the construction of medium and large rings, we began a study of the titanium-induced *intra*molecular coupling of dicarbonyl compounds with a view toward developing a general synthesis of medium- and large-ring olefins. We now wish to report that we have successfully coupled dicarbonyl compounds to construct cycloalkenes of ring size 4–16, and that good yields were obtained in all cases. Our results are presented in Table I.

Several points should be emphasized. The first is that the cyclization reaction appears general for both aldehydes and ketones. The examples we report are structurally simple, however, and clearly one would not expect other, readily reducible functional groups (ester, nitro, nitrile, sulfoxide, etc.) to be compatible with the reaction conditions. The second point is that the yields of medium-ring olefins (ring size 7–11) are remarkably high compared with those of other known methods of ring synthesis.[5] The Thorpe–Ziegler[6] dinitrile cyclization, for example, fails utterly to produce ring sizes 9–13. The acyloin cyclization, a much better method,[4] also shows a dip in yields for ring sizes 9–11. The titanium-induced dicarbonyl coupling, by contrast, appears equally effective for all ring sizes. A final point involves the titanium reagent itself. For our *inter*molecular coupling experiments, we employed active titanium powder prepared from $TiCl_3$ by reduction with either metallic potassium[2] or lithium.[3] Although both of these reagents systems effect intramolecular coupling as well, we have found[7] that a safer and even more effective coupling reagent can be prepared by reducing anhydrous $TiCl_3$ with Zn–Cu couple under inert atmosphere in dimethoxyethane (DME) solution.

In a representative procedure, $TiCl_3$ (1.031 g, 6.68 mmol) and Zn–Cu couple[8] (1.011 g, 15.4 mmol) were placed in a flask via a Schlenk tube under argon. Anhydrous dimethoxyethane (20 ml) was added and the mixture was refluxed for 1 h. Nonadecane-5,15-dione (182 mg, 0.61 mmol) in 40 ml of DME was added to the refluxing slurry via a motor-driven syringe pump over a 30-h period. After an additional 14-h reflux period, the reaction mixture was cooled to room temperature, passed through a small Florisil pad, and concentrated at the rotary evaporator. After a short chromatography on alumina, 1,2-di-*n*-butylcycloundecene (122 mg, 0.46 mmol, 76%) was isolated: mp 80.5–82.5 °C (acetone); NMR (CCl_4) 1.8–2.3 (m, 8 H), 1.4–1.25 (br, 22 H), 0.93 (t, 6 H); *m/e* 264 (M^+). The other examples reported in Table I were carried out in a similar manner.

In conclusion, the titanium-induced intramolecular coupling of dicarbonyl compounds to form cycloalkenes appears to be a most promising procedure. Because of its generality with respect to ring size, and the high product yields obtained, we feel that this method may well prove to be a significant advance in medium- and large-ring carbocyclic synthesis.

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(5) For a comparison of the effectiveness of various large-ring syntheses, see J. Sicher in "Progress in Stereochemistry", Vol. 3, Butterworths, New York, N.Y., 1962, pp 202-263.
(6) For a review of the Thorpe–Ziegler reaction, see J. P. Schaefer and J. J. Bloomfield, *Org. React.*, **51**, 1 (1976).
(7) This discovery was made in our laboratory by Dr. Larry Krepski.
(8) The Zn–Cu couple is prepared by adding zinc dust (9.8 g, 150 mmol) to 40 ml of deoxygenated water, purging the slurry with nitrogen gas for 15 min, and then adding $CuSO_4$ (0.75 g, 4.7 mmol). The black slurry was filtered under nitrogen, washed with deoxygenated water, acetone, and ether, and then dried in vacuo. The couple can be stored indefinitely under nitrogen. This procedure is due to Dr. Larry Krepski, Ph.D. Thesis, University of Colorado, 1975.

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