mixture was submitted to the previous hydrolytic and extractive workup. Removal of the solvent and distillation of the residue, followed by flash chromatography[18] (80:20 light petroleum ether/ethyl acetate) on a portion of the crude product, afforded (−)-isopropylphenylcarbinol: 0.53 g; $[\alpha]^{25}{}_{D}$ −18.5° (*c*, 3.4 in ether); pure by GLC. The ee% of the recovered isopropylphenylcarbinol was also evaluated by HPLC on csp.[5] The optical rotations of the carbinols are summarized as follows: 2,2-dimethyl-4-nonyn-3-ol, $[\alpha]^{25}{}_{D}$ +2.63° (*c*, 6.2 in hexane) (run 25); 2,2-dimethyl-4-nonyn-3-ol, $[\alpha]^{25}{}_{D}$ +1.98° (*c*, 3.4 in hexane) (run 29); 2-methyl-4-nonyn-3-ol, $\alpha^{25}{}_{D}$ +3.85° ($l = 1$) (run 38); ethylphenylcarbinol, $[\alpha]^{25}{}_{D}$ −3.0° (run 39); 4-nonyn-3-ol, $\alpha^{25}{}_{D}$ −2.1° ($l = 1$) (run 41); 2-methyl-4-nonyn-3-ol, $\alpha^{25}{}_{D}$ −2.2° ($l = 1$) (run 42).

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Titanium(IV) Chloride Catalyzed Cyclopropanations of Alkenes Using Zinc Dust, Copper(I) Chloride, and Dihalomethanes

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The addition of catalytic amounts of titanium(IV) chloride greatly facilitates the cyclopropanation reactions of alkenes with dibromomethane using zinc dust and copper(I) chloride in ether. The rates of reaction and yields of cyclopropane products obtained from alkenes not bearing Lewis acid sensitive functional groups are as good or better than those found by using dibromomethane with ultrasound promotion. They are also comparable to those obtained by using diiodomethane under various conditions.

Several years ago, we reported[1] that Simmons–Smith type cyclopropanations[2] of alkenes using the inexpensive, convenient to handle dibromomethane can be accomplished rapidly and with yields similar to those obtained with diiodomethane if the reactions are carried out under sonocation in an ultrasonic cleaning bath. In this ultrasound procedure, the method of Rawson and Harrison[3] employing zinc dust and copper(I) chloride for in situ generation of the necessary zinc–copper couple is used.

In the course of attempting to measure the rates of alkene cyclopropanation under both ultrasonic and nonultrasonic conditions, we were plagued with problems of poor reproducibility.[4] Thus, we undertook a search for possible reaction catalysts or inhibitors, which led to the discovery that the addition of catalytic amounts of titanium(IV) chloride strongly facilitates the reactions of alkenes with dibromomethane, zinc dust, and copper(I) chloride in ether. The rates of reaction and yields of cyclopropanation products are similar to those observed earlier by us under the less convenient sonocation conditions[1] and in several instances are somewhat better (see Table I). Only in the case of the Lewis acid sensitive vinyl ether 3,4-dihydro-2*H*-pyran and with crotyl alcohol is the yield significantly decreased by using titanium(IV) chloride instead of ultrasonic conditions. With 3,4-dihydro-2*H*-pyran and titanium(IV) chloride, large amounts of a high-boiling polymer are formed. Efforts to significantly increase the yields of the latter cyclopropanations by varying reaction conditions were unsuccessful.

Table I. Cyclopropanations of Various Alkenes Using Dibromomethane and Zinc Dust–Copper(I) Chloride in Ether

starting alkene	yield,[a] % $TiCl_4$ promoted[b]	 ultrasound promoted[c]
cyclohexene	58	60
cyclooctene	73	72
1-hexene	49	30
1-octene	50	28
α-pinene	55	40
β-pinene	77	50
crotyl alcohol	36	57
3,4-dihydro-2*H*-pyran	17	41

[a] Yield based on reacted alkene of distilled cyclopropanated product. [b] The $TiCl_4$-promoted reactions are generally carried out at 45–50 °C over a period of about 2 h with 0.2 mol of alkene, 0.6 mol of CH_2Br_2, 0.8 mol of zinc dust, 0.08 mol of CuCl, and 0.012 mol of $TiCl_4$ in 100 mL of ether. [c] The ultrasound promoted reactions[1] were generally carried out over a period of 2–4 h with 0.2:0.4:0.8:0.08 mol of the reactants in 100 mL of ether in a 150-W Bransonic cleaning bath at 45–50 °C.

In the early stages of this work, some investigations of the effects of varying the amount of titanium(IV) chloride on the rates and yields of cyclopropanation products were carried out. It was found that use of greater than 1–2 mol % of titanium(IV) chloride based on the dibromomethane employed resulted in reactions that went out of control. This was due both to the exothermicity of the rapid reactions and to rapid release of ethylene in a side reaction,[4] which made condensation of the refluxing ether difficult.

For the titanium(IV) chloride promoted cyclopropanations reported in Table I, the alkene to dibromomethane to zinc dust mole ratios used were all close to 1 to 3 to 4. However, in the ultrasound-promoted reactions the mole ratios were all close to 1 to 2 to 4. The higher dibromomethane to alkene mole ratios were employed in the present titanium(IV) chloride promoted cyclopropanations to overcome the side reaction of dibromomethane giving ethylene.[4] Even with the present 1 to 3 to 4 mole ratio, some unreacted alkene was still observed in several of the runs with slowly reacting alkenes such as 1-octene and α-pinene.

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Table II. Cyclopropanations of Various Alkenes Using Diiodomethane and a Zinc–Copper Couple in Ether

	$TiCl_4$ promoted[a]		not promoted[b]		
starting alkene	yield,[c] %	time, h	yield,[c] %	time, h	ref
cyclohexene	69	2	72	16	5
cyclooctene	90	2	60	96	6
1-octene	56	3	48[d]	31	7
α-pinene	61	2	12	unk	8
β-pinene	65	2	28	48	9
crotyl alcohol	42	2	52	48	10
3,4-dihydro-2*H*-pyran	<2	4	65	16	11

[a] The $TiCl_4$-promoted reactions were generally carried out at 45–50 °C on 0.1–0.2 mol alkene scale in 100–150 mL of ether with use of 1 to 2 to 3 mol ratios of alkene to CH_2I_2 to zinc dust with copper(I) chloride being 10 mol % of the zinc dust used and titanium(IV) chloride being 2 mol % of the CH_2I_i used. [b] The nonpromoted reactions were carried out under a variety of conditions. For further information, see the original references cited. [c] Yield based on reacted alkene of distilled product except where noted. [d] Alkene used in excess. Yield based on starting CH_2I_2.

Table II gives the results of some titanium(IV) chloride promoted cyclopropanations of various alkenes with diiodomethane and zinc dust–copper(I) chloride. Here the alkene to diiodomethane to zinc dust mole ratios used were generally 1 to 2 to 3. The lower diiodomethane to alkene mole ratios were employed because in initial experiments with cyclohexene it was found that competing ethylene formation from diiodomethane is less serious than with dibromomethane. However, with several of the slower reacting alkenes, competing ethylene formation was still a problem resulting in incomplete alkene conversions. It is seen that the titanium(IV) chloride promoted cyclopropanations with diiodomethane gave yields that were similar to, but in most cases not significantly greater than, those obtained with dibromomethane. Thus, for cyclopropanations of alkenes not bearing Lewis acid sensitive functional groups the titanium(IV) chloride promoted procedure using the less expensive dibromomethane is the method of choice.

Studies are currently in progress in our laboratory to learn the function of the titanium(IV) chloride in facilitating the present alkene cyclopropanations. Also, we are investigating how or if the rate- and yield-enhancing effects of titanium(IV) chloride can be extended to efficient cyclopropanations of Lewis acid sensitive functional group containing alkenes.

Experimental Section

Methods. Boiling points are uncorrected. ^1H and ^{13}C NMR spectra were measured at 300 MHz with a GE QE-300 instrument. Unless otherwise specified, analyses of distilled reaction products were performed by GLC methods with an SE-30 or a Carbowax 20M column. Zinc dust (Fisher Scientific), copper(I) chloride (Mallinckrodt), dibromomethane and diiodomethane (Aldrich), anhydrous ether (Fisher Scientific), and titanium(IV) chloride (Apache Chemicals) were used without further purification. The various alkenes were obtained commercially and, when necessary, redistilled before use.

General Procedure for Cyclopropanations Using Dibromomethane or Diiodomethane. A 500-mL, three-neck, round-bottom flask is fitted with a double condenser system (Allihn on bottom, Friedrich on top), a mechanical stirrer, and a pressure-equalizing dropping funnel containing ether for use in maintaining solvent volume during the course of reaction. A gas collection apparatus or gas bubbler is attached to the Friedrich condenser to measure the amount of ethylene evolved and/or to monitor the course of the reaction. The zinc dust, copper(I) chloride, ether, dihalomethane, and alkene are added in the order listed. After stirring is commenced, the titanium(IV) chloride is added by syringe (*Caution*! Use of greater than 2 mol % of titanium(IV) chloride based on starting dihaloalkane has resulted in unmanageable reactions), and the reaction mixture is heated at 45–50 °C with an oil bath. The oil bath is lowered if the reaction becomes too vigorous, and the ether volume is replenished through the addition funnel when necessary. Upon completion of the reaction, as indicated by a slowing or stopping of gas evolution, the contents of the reaction flask are transferred to another vessel, cooled in ice, and treated while stirring with saturated aqueous ammonium chloride (ca. 25 mL per 0.1 mol of starting zinc dust). Initial addition must be done carefully to avoid foaming of the contents out of the vessel. The solids are removed by vacuum filtration (*Caution*! Potential fire hazard if air is drawn through the zinc residue. The residue should be thoroughly wet with water before disposal.) and washed twice with *n*-pentane. The aqueous layer of the filtrate is separated and washed twice with *n*-pentane, and the combined organic layers are washed three times with 10% sodium hydroxide and once with saturated aqueous sodium chloride solution and dried over anhydrous sodium sulfate. The solvents are removed on a steam bath through a Vigreux column or a rotary vacuum evaporator, and the remaining oil is distilled.

Cyclopropanation with CH_2Br_2 of (a) Cyclohexene. The reaction of 16.4 g (0.20 mol) of cyclohexene, 104 g (0.60 mol) of dibromomethane, 52 g (0.80 mol) of zinc dust, 7.9 g (0.080 mol) of copper(I) chloride, and 2.28 g (0.012 mol) of titanium(IV) chloride in 100 mL of ether for 0.5 h gave after workup and distillation 11.8 g of material, bp 60–117 °C (atm) [lit.[1] bp 114–117 °C (atm)], which was 95% by weight bicyclo[4.1.0]heptane (58% yield) and 5% by weight of unreacted dibromomethane. The distillation pot residue weighed 2.5 g. For the bicyclo[4.1.0]heptane product: ^1H NMR ($CDCl_3$) δ 0.0 (m, 1 H), 0.5 (m, 1 H), 0.8 (m, 2 H), 1.2 (m, 4 H), 1.6 (m, 2 H), and 1.9 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.4 (2 C), 10.2 (1 C), 21.4 (2 C), and 23.9 (2 C).

(b) Cyclooctene. The reaction of 22.0 g (0.20 mol) of cyclooctene, 104 g (0.60 mol) of dibromomethane, 52.3 g (0.80 mol) of zinc dust, 7.9 g (0.080 mol) of copper(I) chloride, and 2.28 g (0.012 mol) of titanium(IV) chloride in 100 mL of ether for 2 h gave after workup and distillation 17.9 g (73% yield) of greater than 98% pure bicyclo[6.1.0]nonane, bp 67–72 °C (31 Torr), $n^{19}{}_D$ 1.4711 [lit.[1] bp 69–71 °C (30 Torr), $n^{25}{}_D$ 1.4673]. The distillation pot residue weighed 1.3 g. For the bicyclo[6.1.0]nonane product: ^1H NMR ($CDCl_3$) δ −0.3 (m, 1 H), 0.6 (m, 3 H), 0.9 (m, 2 H), 1.3–1.8 (m, 8 H), and 2.0 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.8 (1 C), 15.5 (2 C), 26.7 (2 C), 27.2 (2 C), and 29.9 (2 C).

(c) 1-Hexene. The reaction of 16.8 g (0.20 mol) of 1-hexene, 122 g (0.70 mol) of CH_2Br_2, 58.8 g (0.90 mol) of zinc dust, 8.90 g (0.090 mol) of copper(I) chloride, and 2.66 g (0.014 mol) of titanium(IV) chloride in 100 mL of ether for 2.2 h evolved 5.3 L of gas and after workup and distillation gave 9.63 g of material, bp 84–104 °C (atm), $n^{27}{}_D$ 1.4002 [lit.[1] bp 94–96 °C (atm), $n^{31}{}_D$ 1.4010], which is greater than 98% pure *n*-butylcyclopropane (49% yield). The distillation pot residue weighed 3.8 g. For the *n*-butylcyclopropane product: ^1H NMR ($CDCl_3$) δ 0.0 (m, 2 H), 0.4 (m, 2 H), 0.6 (m, 1 H), 0.9 (m, 3 H), 1.2 (m, 2 H), and 1.3–1.5 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 4.3 (2 C), 10.9, 14.1, 22.5, 31.9, and 34.5.

(d) 1-Octene. The reaction of 22.4 g (0.20 mol) of 1-octene, 104 g (0.60 mol) of dibromomethane, 52.3 g (0.80 mol) of zinc dust, 7.9 g (0.080 mol) of copper(I) chloride, and 2.28 g (0.012 mol) of titanium(IV) chloride in 100 mL ether for 2 h gave on workup and distillation at bp 62–65 °C (40 Torr), $n^{19}{}_D$ 1.4200 [lit.[1] bp 90–100 °C (47 Torr), $n^{22}{}_D$ 1.4176], 12.9 g of a 94:6 by weight mixture of *n*-hexylcyclopropane (50% yield based on reacted alkene) and 1-octene. The distillation pot residue weighed 5.5 g. For the *n*-hexylcyclopropane product: ^1H NMR ($CDCl_3$) δ 0.0 (m, 2 H), 0.4 (m, 2 H), 0.6 (m, 1 H), 0.9 (m, 3 H), 1.2 (b q, 2 H), and 1.2–1.4 (b m, 8 H); ^{13}C NMR ($CDCl_3$) δ 4.4 (2 C), 10.9, 14.1, 22.7, 29.3, 29.7, 32.0, and 34.9.

(e) α-Pinene. The reaction of 27.2 g (0.20 mol) of α-pinene, 122 g (0.70 mol) of CH_2Br_2, 58.8 g (0.90 mol) of zinc dust, 8.90 g (0.090 mol) of copper(I) chloride, and 2.66 g (0.014 mol) of titanium(IV) chloride in 150 mL of ether for 1.7 h evolved 7000 mL of gas and gave on workup and distillation 17.1 g of material, bp 81–91 °C (40 Torr) [lit.[1] bp 82–84 °C (35 Torr)], which contained 92% by weight of 2,7,7-trimethyltricyclo[4.1.1.0^{2,4}]octane (55% yield based on reacted alkene) and 8% by weight of unreacted α-pinene. The distillation pot residue weighed 5.5 g. For the 2,7,7-trimethyltricyclo[4.1.1.0^{2,4}]octane product: ^{1}H NMR ($CDCl_3$) δ 0.4 (m, 1 H), 0.9 (m, 2 H), 1.1 (d, J = 10.5 Hz, 1 H), 1.2 (s, 3 H), 1.25 (s, 3 H), 1.4 (s, 3 H), 1.8 (m, 2 H), 2.0 (b t, 1 H), and 2.2 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.9, 19.0, 20.3, 21.0, 25.5, 26.9, 27.0, 27.4, 41.0, 41.6, and 45.4.

(f) β-Pinene. The reaction of 27.2 g (0.20 mol) of β-pinene, 104 g (0.60 mol) of dibromomethane, 52.3 g (0.80 mol) of zinc dust, 7.92 g (0.080 mol) of copper(I) chloride, and 2.28 g (0.012 mol) of titanium(IV) chloride in 125 mL of ether for 1.9 h gave on workup and distillation 23.0 g (77% yield) of 97% pure 6,6-dimethylspiro[bicyclo[3.1.1]heptane-2,1′-cyclopropane], bp 78–92 °C (25 Torr), $n^{23}{}_D$ = 1.4765 [lit.[1] bp 71–73 °C (18 Torr), $n^{25}{}_D$ 1.4765]. The distillation pot residue weighed 7.2 g. For the 6,6-dimethylspiro[bicyclo[3.1.1]heptane-2,1′-cyclopropane]: ^{1}H NMR ($CDCl_3$) δ 0.15 (m, 2 H), 0.35 (m, H), 0.45 (m, 1 H), 1.0 (s, 3 H), 1.1 (m, 1 H), 1.2 (s, 3 H)) 1.25 (m, 1 H), 1.6 (d, J = 9.7 Hz, 1 H), 1.7–2.1 (m, 4 H), and 2.2 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 16.3, 19.6, 21.8, 24.2, 26.6, 26.7, 27.2, 40.7, 40.9, and 51.2.

(g) Crotyl Alcohol. The reaction of 14.4 g (0.20 mol) of *trans*-crotyl alcohol, 69.5 g (0.40 mol) of dibromomethane, 32.7 g (0.50 mol) of zinc dust, 4.95 g (0.050 mol) of copper(I) chloride, and 0.76 g (0.0040 mol) of titanium(IV) chloride in 300 mL of ether for 0.5 h gave after workup and distillation at bp 49–52 °C (21 Torr) 8.5 g of a 52:48 by weight mixture of *trans*-2-methylcyclopropanemethanol (36% based on reacted alcohol) and unreacted crotyl alcohol. The distillation pot residue weighed 1.8 g. For a pure sample of the *trans*-2-methylcyclopropanemethanol product: ^{1}H NMR ($CDCl_3$) δ 0.2 (m, 1 H), 0.3 (m, 1 H), 0.6 (m, 1 H), 0.7 (m, 1 H), 1.0 (d, J = 6.0 Hz, 3 H), 2.5 (s, 1 H), and 3.4 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 11.0, 18.3, 22.0, and 66.7.

(h) 3,4-Dihydro-2*H*-pyran. The reaction of 8.41 g (0.10 mol) of freshly redistilled 3,4-dihydro-2*H*-pyran, 52.2 g (0.30 mol) of dibromomethane, 26.2 g (0.40 mol) of zinc dust, 3.96 g (0.040 mol) of copper(I) chloride, and 1.42 g (0.0075 mol) of titanium(IV) chloride in 75 mL of ether for 2 h evolved 700 mL of gas and gave after workup and distillation 27.6 g of a mixture, bp 83–114 °C (atm), which was estimated by ^{1}H NMR analysis to be 92% by weight of CH_2Br_2. It also contained about 6% by weight of the desired 2-oxabicyclo[4.1.0]heptane (17% yield). The distillation pot residue weighed 4.5 g. For a pure sample of the 2-oxabicyclo[4.1.0]heptane product: ^{1}H NMR ($CDCl_3$) δ 0.4 (m, 1 H), 0.5 (m, 1 H), 0.8 (m, 1 H), 1.4 (m, 2 H), 1.8 (m, 2 H), 3.2 (m, 1 H), and 3.4–3.5 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.9, 11.1, 19.6, 22.0, 51.1, and 64.2.

Cyclopropanation with CH_2I_2 of (a) Cyclohexene. The reaction of 16.4 g (0.20 mol) of cyclohexene, 107 g (0.40 mol) of diiodomethane, 39.2 g (0.60 mol) of zinc dust, 5.90 g (0.060 mol) of copper(I) chloride, and 1.52 g (0.0080 mol) of titanium(IV) chloride in 100 mL of ether for 1.6 h evolved 2000 mL of gas and gave on workup and distillation 13.7 g of material, bp 50–122 °C, $n^{23}{}_D$ 1.4569 [lit.[1] bp 114–117 °C, $n^{25}{}_D$ 1.4550], which was 96% by weight bicyclo[4.1.0]heptane (69% yield). The distillation pot residue weighed 3.1 g. The ^{1}H NMR spectrum of the bicyclo[4.1.0]heptane product was identical with that of a sample prepared by using dibromomethane.

(b) Cyclooctene. The reaction of 11.0 g (0.10 mol) of cyclooctene, 53.6 g (0.20 mol) of diiodomethane, 19.6 g (0.30 mol) of zinc dust, 2.97 g (0.030 mol) of copper(I) chloride, and 0.95 g (0.0050 mol) of titanium(IV) chloride in 50 mL of ether for 1.9 h evolved 600 mL of gas and gave after workup and distillation 16.2 g of a mixture with bp 78–85 °C (55 torr). NMR examination showed that it consisted of 69% by weight bicyclo[6.1.0]nonane (90% yield) and 31% by weight of unreacted diiodomethane. The distillation pot residue weighed 0.70 g. The ^{1}H NMR spectrum of the bicyclo[6.1.0]nonane product was identical with that of a sample prepared by using dibromomethane.

(c) 1-Octene. The reaction of 16.8 g (0.15 mol) of 1-octene, 80.4 g (0.30 mol) of diiodomethane, 29.4 g (0.45 mol) of zinc dust, 4.5 g (0.045 mol) of copper(I) chloride, and 1.14 g (0.0060 mol) of titanium(IV) chloride in 125 mL of ether for 2.8 h gave after workup and distillation 13.4 g of a 42:58 by weight mixture of *n*-hexylcyclopropane (56% yield based on reacted alkene) and unreacted 1-octene, bp 61–87 °C (85 Torr). The distillation pot residue weighed 1.4 g. The ^{1}H NMR spectrum of the *n*-hexylcyclopropane product was identical with that of the sample prepared by using dibromomethane.

(d) α-Pinene. The reaction of 27.2 g (0.20 mol) of α-pinene, 107 g (0.40 mol) of diiodomethane, 39.2 g (0.60 mol) of zinc dust, 5.94 g (0.60 mol) of copper(I) chloride, and 1.52 g (0.0080 mol) of titanium(IV) chloride in 100 mL of ether for 2 h evolved 2300 mL of gas and gave after workup and distillation, bp 69–87 °C (40 Torr), 21.4 g of a 57:43 by weight mixture of 2,7,7-trimethyltricyclo[4.1.1.0^{2,4}]octane (61% yield based on reacted alkene) and unreacted α-pinene. The distillation pot residue weighed 3.0 g. The ^{1}H NMR spectrum of the cyclopropane product was identical with that of the sample prepared by using dibromomethane.

(e) β-Pinene. The reaction of 21.8 g (0.16 mol) of β-pinene, 64.3 g (0.24 mol) of diiodomethane, 20.9 g (0.32 mol) of zinc dust, 3.20 g (0.032 mol) of copper(I) chloride, and 0.91 g (0.0048 mol) of titanium(IV) chloride in 80 mL of ether for 1.8 h evolved 880 mL of gas and gave after workup and distillation 15.7 g (65% yield) of greater than 98% pure 6,6-dimethylspiro[bicyclo[3.1.1]heptane-2,1′-cyclopropane], bp 78–82 °C (26 Torr), $n^{23}{}_D$ 1.4753 [lit.[1] bp 71–73 °C (18 Torr), $n^{25}{}_D$ 1.4765]. The distillation pot residue weighed 6.4 g. The ^{1}H NMR spectrum of the cyclopropane product was identical with that of the sample prepared by using dibromomethane.

(f) Crotyl Alcohol. The reaction of 9.37 g (0.13 mol) of *trans*-crotyl alcohol, 53.6 g (0.20 mol) of diiodomethane, 17.0 g (0.26 mol) of zinc dust, 2.60 g (0.026 mol) of copper(I) chloride, and 0.38 g (0.002 mol) of titanium(IV) chloride in 200 mL of ether for 2 h evolved 730 mL of gas and gave after workup and distillation, bp 65–75 °C (54 Torr), 6.3 g of a mixture containing 63% by weight of *trans*-2-methylcyclopropanemethanol (42% yield based on reacted alkene) and 26% unreacted crotyl alcohol. The distillation pot residue weighed 1.1 g. The ^{1}H NMR spectrum of the *trans*-2-methylcyclopropanemethanol product was identical with that of the sample prepared by using dibromomethane.

(g) 3,4-Dihydro-2*H*-pyran. The reaction of 8.41 g (0.10 mol) of freshly distilled 3,4-dihydro-2*H*-pyran, 53.6 g (0.20 mol) of diiodomethane, 19.6 g (0.30 mol) of zinc dust, 2.97 g (0.030 mol) of copper(I) chloride, and 0.76 g (0.0040 mol) of titanium(IV) chloride in 100 mL of ether for 3.7 h gave after workup and distillation 35.8 g of material, bp 110 °C (85 Torr), estimated by NMR to be mainly (97%) unreacted diiodomethane. Less than 1% each of unreacted starting material or 2-oxabicyclo[4.1.0]heptane was observed. The distillation pot residue weighed 8.9 g.

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Registry No. $TiCl_4$, 7550-45-0; dibromomethane, 74-95-3; diiodomethane, 75-11-6; cyclohexene, 110-83-8; bicyclo[4.1.0]heptane, 286-08-8; cyclooctene, 931-88-4; bicyclo[6.1.0]nonane, 286-60-2; 1-hexene, 592-41-6; butylcyclopropane, 930-57-4; 1-octene, 111-66-0; hexylcyclopropane, 4468-61-5; α-pinene, 80-56-8; 2,7,7-trimethyltricyclo[4.1.1.0^{2,4}]octane, 32549-17-0; β-pinene, 127-91-3; 6,6-dimethylspiro[bicyclo[3.1.1]heptane-2,1′-cyclopropane], 119680-92-1; crotyl alcohol, 6117-91-5; *trans*-2-methylcyclopropanemethanol, 21003-36-1; 3,4-dihydro-2*H*-pyran, 110-87-2; 2-oxabicyclo[4.1.0]heptane, 286-16-8.