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Carbon-Halogen Bond Activation by Nickel Catalyst : Synthesis of Alkenes, from 1,2-Dihalides

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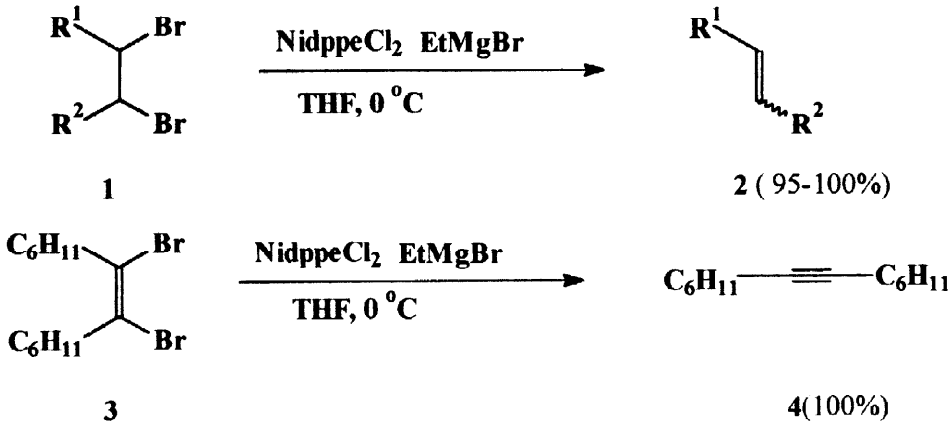
Abstract: Unsaturated hydrocarbons can easily be prepared in a few seconds starting from 1,2 dibromides in the presence of a catalytic amount of Nickel diphenylphosphinoethane dichloride ($NidppeCl_2$) and tri.n.butyl tin hydride, (TBTH) at room temperature. The dependencie of the nature of starting dihalides is investigated.

The 1,2-dihalide alkene functional group interconversion (F.G.I.) is of interest in the organic chemistry of protecting groups[1]. Many reagents have beeen described in the literature that are able to give this reaction.

They employ stoichiometric amounts of low valent metals or a metal catalyst that must be regenerated *in situ* by a reducing agent[2]. Many of these reaction conditions are incompatible with the presence of other functional groups or they use expensive or exotic catalysts. In a previous paper we found a new method to gain carbon-carbon double bond starting from *vic*-dibromides, which employs a catalytic amount of $NidppeCl_2$ and commercially available EtMgBr as the source of Ni(0) (Scheme 1)[3].

Scheme 1



1 **2** (95-100%)

3 **4**(100%)

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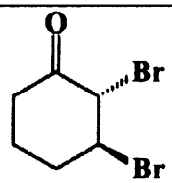
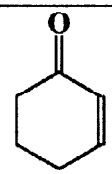
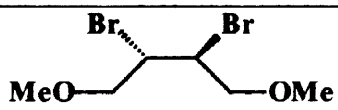
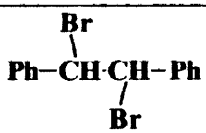
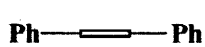
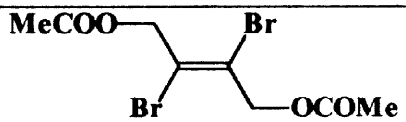
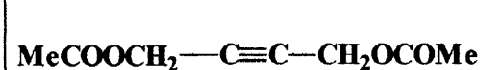
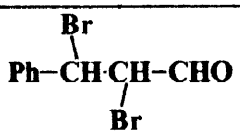
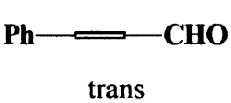
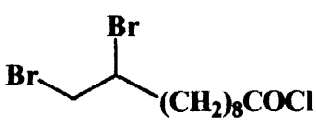
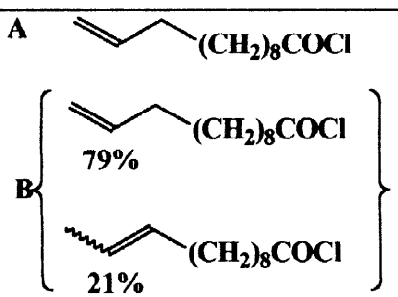
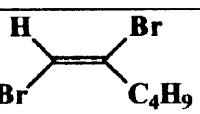
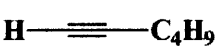
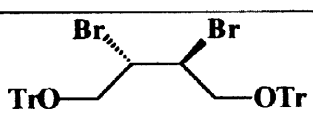
Table: Reaction of 1,2 Dibromides with TBTH in the presence of a catalytic amount of $NidppeCl_2$[a].

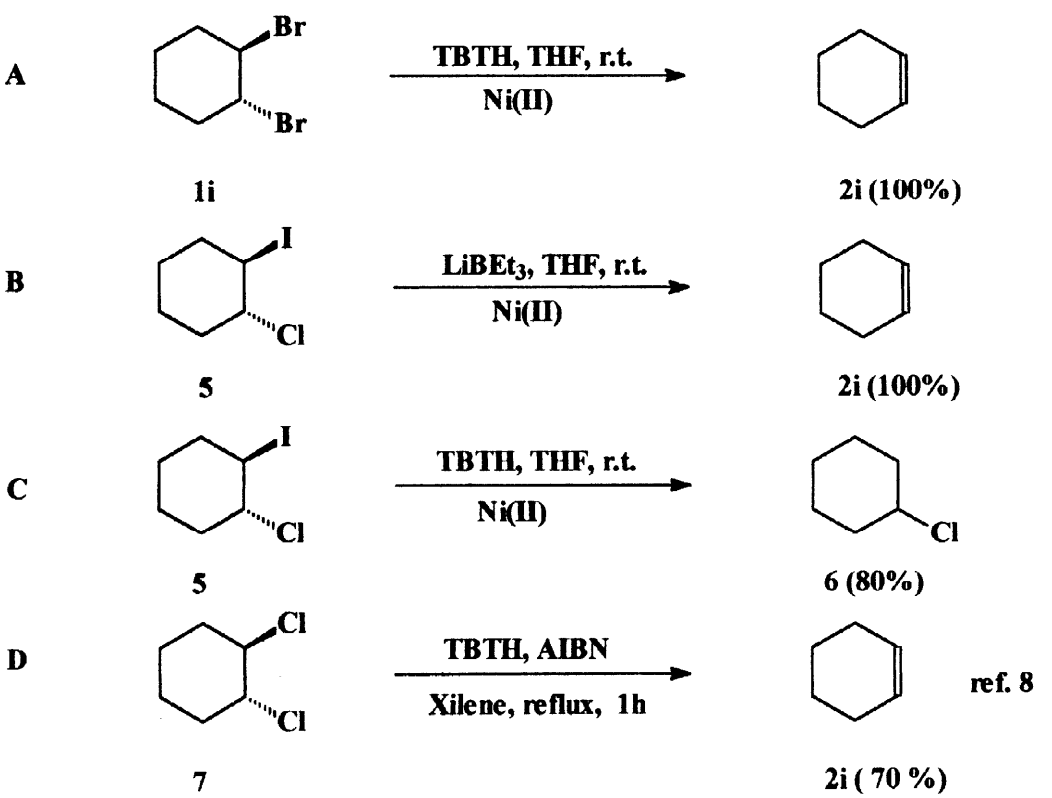
Run	Compound 1	Product 2	Rndt(%)	Notes
1(a)			52[4]	b
2(b)			100	c
3(c)			100	c
4(d)			100	-
5(e)		 trans	100	-
6(f)			A 26 B 63	d,e
7(g)			100	-
8(h)			5	d

Notes: [a]The conversions are calculated on the recovered materials and refer to a run time of 30 min.; the reactions were performed at room temperature under argon atmosphere in THF as solvent with $1.90\cdot10^{-4}$ mol of $NidppeCl_2$ and $1\cdot10^{-2}$ mol of reagent. [b]No increase in the yield was obtained by employing one molar excess of TBTH. [c]Diastereomeric cis- trans mixture. [d]Yield calculated on the basis of ^1H NMR spectroscopy. [e]$3\cdot10^{-2}$ equivalents of TBTH are employed.

The reaction requires two molar equivalents of Grignard reagent per mole of dihalide employed, and doesn't give good results in the preparation of α–β unsaturated aldehydes.

On the other hand, the preparation of terminal alkynes, starting from a suitable 1,2-alk-1-enyl halide, requires three molar equivalents of Grignard reagent per mole of dihalide. The Table reports the results obtained by employing in this F.G.I. the commercially available tri *n*.butyl tin hydride (TBTH) or $LiBEt_3H$ (Superhydride©), rather than ethyl magnesium bromide. The Table highlights that the reaction conditions are compatible with the presence of many functional groups such as ethers, esters, unsaturated carbonyl compounds, acyl dichlorides and terminal alkynes. Note that in more drastic reaction conditions some of these functional groups are affected by TBTH[5], with our procedure and due to the short reaction times employed, TBTH is only able able to react with the catalyst present in the solution. As far as the mechanistic aspects of the reaction are concerned the nature of the dihalide employed is responsible for the course of the reaction (Scheme 2) and allows us to direct the reaction to the formation of different kinds of products (**2i** versus **6**) (Scheme 2, steps **A** and **C**).

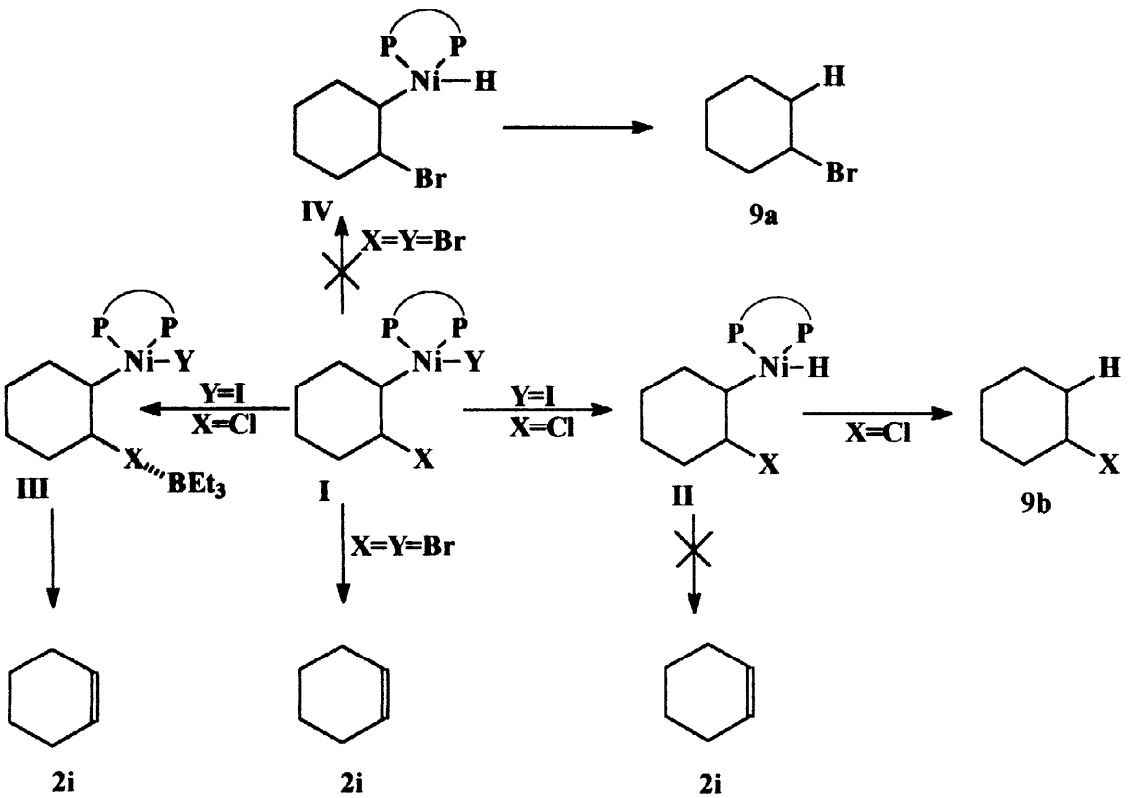
Scheme 2



Likewise, by using the Superhydride© instead of TBTH as our source of hydrides it seems to be possible to obtain alkenes or chlorides (Scheme 2, steps **B** and **C**).

On the basis of the data collected in Scheme 2 and in the Table we can draw some conclusions about the reaction (Scheme 3).

Scheme 3



When in the intermediate **I** of Scheme 3, Y is iodine, TBTH interconverts the Ni-iodine bond into a Ni-hydride bond. On the contrary, when Y is bromine NidppeYX is eliminated with the formation of the compound **2i**.

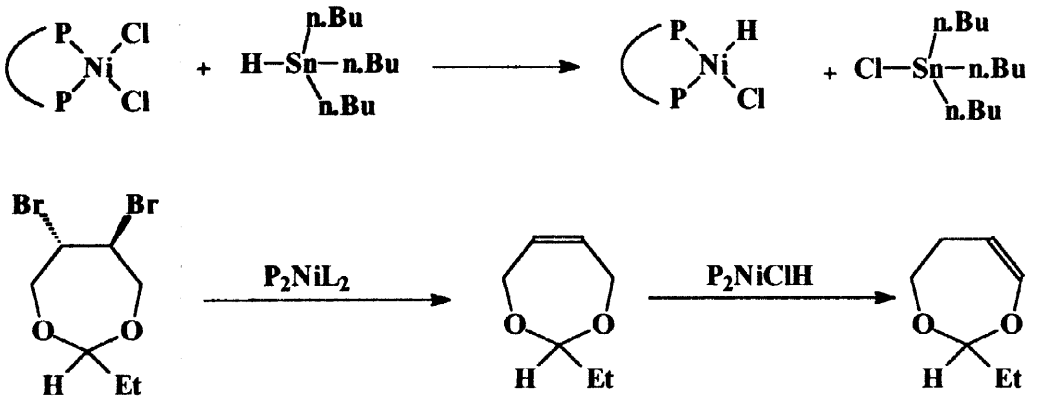
The intermediate **II** (X=Cl) gives cyclohexyl chloride through a reductive elimination reaction without the formation of **2i**.

On the other hand, the presence of BEt_3 obtained as a byproduct of the reaction of $NidppeCl_2$ with the Superhydride©, promotes the elimination of Nidppedihalide on the intermediate **III** (Y=I and X=Cl), with the formation of cyclohexene. (**2i**).

The lack of compound **9a** seems to demonstrate that the interconversion of **I** (X=Y=Br) in **2i** through the formation of the intermediate **IV**, does not take place.

The presence of catalytic amounts of NidppeClH in the reaction mixture was indirectly postulated when 2,3 dimethyl-1,3-diox-5-ene was reacted in the reaction conditions that we adopted (Scheme 4). In fact as previously

Scheme 4



10a **10b** **10c**

described[6], this species is more effective in the flash isomerization of the allyl structure **10b** into the vinyl compound **10c** that is actually recovered.

In conclusion, 1,2-dihalides can easily be interconverted into halides or into unsaturated hydrocarbons in relation to the nature of precursors and hydride donors used (TBTH or $LiBEt_3H$). The reaction is mediate by $NidppeCl_2$ which seems to be quite an effective catalyst of the reaction.

Experimental Section

Materials and instruments. Tetrahydrofurane was purified by distillation on $LiAlH_4$ before use. Glc analyses were performed on a Perkin Elmer 8600, on a DB1, 12mx0.22mm capillary column, using argon as the carrier gas, equipped with a flame ionization detector. ^1H and ^{13}C NMR (200 and 50 MHz, respectively) spectra were recorded on a Varian Gemini 200 spectrometer; all NMR data were obtained using $CDCl_3$ solutions. Chemical shifts (δ, ppm) refer to tetramethylsilane (TMS) (^1H NMR) or $CDCl_3$ (^{13}C NMR) as the internal standard. Ir spectra (ν, cm^{-1}) were recported on a Perkin Elmer FT-IR, 1760X spectrophotometer, using liquid films. Mass spectra (m/e, I%) were taken on a Perkin Elmer 8500 Gas Chromatograph equipped with a Q-Mass 910 detector. All isolated compounds gave satisfactory elemental analyses.

***Cis* 1,4-Dimethoxybut-2-ene (2b).** 35.00g of methyl iodide (0.25 mol) in 40 ml of anidrous benzene, were slowly added to a well stirred suspension of 8.81g of *cis* 1,4-but-2-enediol (0.10mol), 28.00g of NaOH (0.70 mol),16.00g of anidrous K_2CO_3 (0.12 mol) and 3.40g of tetrabutyl ammonium bisulfate in 100ml of anidrous benzene and warmed at 40 °C for 30 min. The reaction mixture was warmed at 60 °C for 4h, and cooled at room temperature. The solvent was eliminated by accurate distillation. The resulting mixture gave 9.10g of chemically pure *cis* 1,4-dimethoxybut-2-ene (78%) having: p.eb. 141°C a P.atm.; IR (ν, cm^{-1}): 3025, 2982, 2926, 2891, 2818, 1452, 1411, 1372, 1335, 1284, 1194, 1112, 956, 912, 683; MS (m/e, I%): M^+-1(115, 0.1);

(84, 24.8); (71, 13.9); (69, 10.1); (58, 6.1); (55, 22.0); (51, 4.54); (45, 66.5); (41, 100.0); (39, 75.1); (37, 2.6); ^{1}H-NMR: 3.34(s, 6H, $2CH_3$); 4.01(d, j:4.8, 4H, $2CH_2$); 5.72(t, j:4.8, 2H, 2CH=); ^{13}C-NMR: 57.89 (2C), 68.02 (2C), 129.23 (2C).

***Cis* 1,4-Dirityloxybut-2-ene (2h).** 28.11g of triphenylmethyl chloride (101 mmol) was slowly added to a solution of 4.40g of cis 1,4-but-2-enediol (50 mmol) in 100ml of anidrous pyridine at 0 °C. The mixture was stirred for 24h, hydrolized with water and than extracted with diethyl ether. After the evaporation of the solvent, at reduced pressure the residue gave chemically pure 25.70g (90%) of 1,4-cis dirityloxybut-2-ene having: IR (ν, cm^{-1}): 3085, 3058, 3031, 2921, 2862, 1596, 1490, 1448, 1410, 1318, 1219, 1182, 1153, 1087, 1057, 1031, 1002, 908, 765, 733, 704; ^{1}H-NMR:3.52(d, j:3.75, 4H, $2CH_2$); 5.74(t, j:3.75, 2H, 2CH=); 7.40÷7.10(m, 30H, Ar); ^{13}C-NMR: 60.58(2C), 86.38(2C), 126.80(6C), 127.69(12C), 128.56(12C), 128.69 (2C), 144.01(6C).

1,4-Diacetoxybut-2-yne (2d). 16.5g of acetyl chloride (0.21 mol) was slowly added to a solution containing 0.54g of triethyl benzyl ammonium bromide (2.0 mmol) in 50ml of $CHCl_3$, 10ml of an aqueous 10M solution of KOH at 0 °C and 8.60g of 2-butyne-1,4-diol (0.10 mol). After 2h at room temperature, the solution was extracted with $CHCl_3$ and after the solvent had been eliminated the crude product was distilled and gave 16.15g (95%) of 1,4-diacetoxybut-2-yne having: IR (ν, cm^{-1}): 2947, 2360, 1748, 1436, 1379, 1361, 1222, 1156, 1029, 966, 917, 851, 668, 604; ^{1}H-NMR: 2.10(s, 6H, $2CH_3$); 4.72(s, 4H, $2CH_2$); ^{13}C-NMR: 20.30(2C), 51.73(2C), 80.48(2C), 169.78(2C).

2-Ethyl-1,3-dioxep-5-ene (10b). In a Dean Stark apparatus 17.60g of 1,4-but-2-enediol (0.20 mol) and 11.61g of propanal (0.20 mol) with 0.2g of p.toluensulfonic acid in 200ml of benzene were reacted at the reflux of the solvent. After the water had been eliminated, the benzenic solution was cooled to room temperature, 10g of K_2CO_3 were added filtered off and distilled at reduced pressure to gave 20.49g (80%) of chemically pure 2-ethyl-1,3-dioxep-5-ene having: P.eb. 73°C a 220mmHg; IR (ν, cm^{-1}): 3032, 2968, 2938, 2879, 2732, 1557, 1466, 1448, 1388, 1364, 1280, 1266, 1202, 1168, 1135, 1102, 1079, 1035, 1019, 981, 948, 918, 792, 681, 638; MS (m/e, I%): M^+(128, 0.4); (114, 0.2); (108, 0.3); (99, 8.3); (95, 0.5); (70, 2.6); (57, 8.0); (42, 100.0); (39, 63.2); ^{1}H-NMR: 0.94(t. j:7.5, 3H); 1.67(dq, j:7.5, 5.8, 1H); 4.16(dd, j:14.4, 1.8, 2H); 4.40 (dd, j:14.4, 2.4, 2H); 4.69(t, j:5.8, 1H); 5.72(dd, j:1.8, 2.4, 2H); ^{13}C-NMR: 9.07, 26.64, 65.04 (2C), 105.62, 128.30 (2C).

Synthesis of *vic* dibromides: general procedure. A solution of Br_2 (20 mmol) in 20ml of CCl_4 was slowly added into the alkene or alkyne (20 mmol) solution in 100ml of the same solvent, at -25 °C. After 15 min. at room temperature, anidrous Na_2CO_3 (2.0g) was added. The mixture was stirred for 5 min. and then filtered off.

The solvent was eliminated at reduced pressure and the obtained chemically pure dihalide was reacted without further purifications.

2,3-Dibromocyclohexan-1-one (1a). IR (ν, cm^{-1}): 2955, 1721, 1594, 1499, 1470, 1454, 1434, 1419, 1332, 1316, 1258, 1221,1175, 1143, 1107, 1092, 1068, 963, 863; ^{1}H-NMR: 2.50÷2.00(m, 4H, CH_2CH_2); 2.90÷2.55(m,1H,CHHCO); 3.20÷2.90 (m,1H, CHHCO); 4.60÷4.40(m, 1H, CHBrCH_2); 4.85÷4.65(m, 1H, CHBrCO); ^{13}C-NMR:(main diastereomer) 21.38, 27.15, 35.04, 50.50, 53.03, 200.13.

2,3-Dibromo-1,4-dimethoxybutane (1b). IR (ν, cm^{-1}): 2987, 2928, 2899, 1729, 1454, 1380, 1304, 1190, 1156, 1114, 958, 913, 853, 788; ^{1}H-NMR(diastereomeric mixture) 3.34(s, 1.85H, $2OCH_3$); 3.40(s, 4.15H, $2OCH_3$); 3.79÷3.67(dd, j:7.69, 4.86, 2.77H, $2CH_2$); 4.03÷3.97(dd, j:3.54, 1.26, 1.23H, $2CH_2$); 4.50÷4.40(m, 2H, 2CHBr); ^{13}C-NMR: 51.08(2C), (57.85, 58.84) (2C), 74.37(2C).

1,2-Dibromo-1,2-diphenylethane (1c). IR (ν, cm^{-1}): 3060, 3025, 2978, 1490, 1449, 1296, 1237, 1202, 1161, 1137, 1073, 1032, 908, 808, 761, 691; ^{1}H-NMR: 5.45(s, 2H,2CH); 7.60÷7.30(m, 10H, Ar); ^{13}C-NMR: 56.05, 127.88, 128.64, 128.72, 128.95.

2,3-Dibromo-1,4-diacetoxybut-2-ene (1d). IR (ν, cm^{-1}): 2943, 2884, 1743, 1619, 1431, 1372, 1220, 1137, 1096, 1032, 979, 914, 832, 732, 603; ^{1}H-NMR: 2.12(s, 1.2H, $2CH_3$); 2.15(s, 4.8H, $2CH_3$); 5.02(2s, 4H, $2CH_2$); ^{13}C-NMR: 20.39(2C), [64.57(2C), 67.07(2C)]; [119.31(2C), 127.00(2C)]; [169.69(2C), 170.00(2C)].

10,11-Dibromoundecanoylchloride (1f). IR (ν, cm^{-1}): 2930, 2856, 1708, 1463, 1432, 1402, 1343, 1227, 1142, 953, 787, 763, 723, 679, 645; ^{1}H-NMR: 1.90÷1.20(m, 13H); 2.20÷2.00(m, 1H, C<u>H</u>HCH$_2$Br); 2.89(t, j:7.28, 2H, C<u>H</u>CO); 3.62(dd, j:10.09, 10.09, 1H, CH<u>H</u>Br); 3.85(dd, j:10.09, 4.42, 1H, C<u>H</u>HBr); 4.26÷4.08(m, 1H, =C<u>H</u>Br); ^{13}C-NMR: 24.99, 26.83, 28.31, 28.65, 28.88, 29.00, 35.94, 36.29, 47.04, 53.00, 177.94.

1,2-Dibromo-1-hexene (1g). IR (ν, cm^{-1}): 3087, 3058, 2959, 2930, 2871, 1608, 1464, 1428, 1379, 1260, 1234, 1211, 1114, 1014, 963, 934, 778, 747, 710, 696, 635; ^{1}H-NMR: 0.91(t, j:5.42, 0.97H, CH_3); 0.94(t, j:5.29, 2.03H, CH_3); 1.48÷1.22(m, 2H, C<u>H</u>$_2$CH$_3$); 1.66÷1.48(m, 2H, C<u>H</u>$_2$CH$_2$CH$_3$); 2.52(td, j:6.94, 1.09, 0.65H, CH_2C=Ccis); 2.60(t, j:7.04, 1.35H, CH_2C=Ctrans); 6.40(s, 0.67H, =CHtrans); 6.56(t, j:1.09, 0.33H, =CHcis); ^{13}C-NMR: (trans)13.69, 21.47, 30.17, 40.87, 105.39, 134.08, (cis) 13.83, 21.56, 29.17, 36.63, 102.06, 126.98.

2,3-Dibromo-1,4-dirityloxybutane (1h). IR (ν, cm^{-1}): 3087, 3061, 3033, 2936, 1589, 1491, 1448, 1383, 1325, 1220, 1184, 1154, 1063, 1032, 1014, 1002, 975, 912; ^{1}H-NMR: 4.60÷3.40(2m, 6H, $2CH_2O$ +2CHBr); 7.50÷7.20(m, 30H, Ar); ^{13}C-NMR: (treo) 52.75(2C), 65.81(2C), 87.34(2C), 127.21(12C), 128.62(6C), 143.43(6C); (eritro) 51.77(2C), 65.54(2C), 87.34(2C), 127.21(12C), 128.62(6C), 146.86(6C).

2,3-Dibromo-3-phenylpropanal (1e). (erytro/treo:90/10): *Eritro*: ^{1}H-NMR: 4.76(dd, j:7.00, 3.38, 1H, C<u>H</u>CHO); 5.37(d, j:7.00, 1H, PhC<u>H</u>); 7.60÷7.10(m, 5H, Ar); 9.33(d, j:3.38, 1H, CHO); ^{13}C-NMR: 51.20,59.02, 128.12 (2C),128.18(2C),129.145, 136.82, 187.57. *Treo*:^{1}H-NMR: 4.86(dd, j:11.55, 4.47, 1H, C<u>H</u>CHO); 5.24(d, j:11.55, 1H, PhC<u>H</u>); 7.60÷7.20(m, 5H, Ar); 9.39(d, j:4.47, 1H, CHO); ^{13}C-NMR: 47.75, 53.74, 128.07(2C), 128.86(2C), 129.51, 136.82, 187.57.

1,2-Dibromocyclohexane (1i). b.p.: 105 ^{0}C (20mmHg); IR (ν, cm^{-1}): 2940, 2857, 1447, 1426, 1353, 1337, 1296, 1249, 1196, 1176, 1155, 1118, 1029, 993, 967, 899, 857, 805, 685, 659; ^{1}H-NMR: 1.60÷1.40(m, 4H); 2.00÷1.70(m, 4H); 2.55÷2.35(m, 2H); 4.50(s, 2H); ^{13}C-NMR: 22.31(2C), 31.90(2C), 56.10(2C).

2-Ethyl-5,6-dibromo-1,3-dioxepane (10a). (diastereomeric mixture): IR (ν, cm^{-1}): 2967, 2936, 2879, 1465, 1453, 1390, 1372, 1346, 1303, 1279, 1249, 1235, 1194, 1148, 1124, 1097, 1074, 1038, 1023, 1004, 987, 967, 935, 899, 846, 787, 742, 714, 639, 554; ^{1}H-NMR: 0.95, 0.92(2t, j:7.5, 3H); 1.62(m, 2H); 4.30÷3.68(m, 6H); 4.74, 4.68(2t, j: 7.5, 1H); ^{13}C-NMR: (8.81, 9.07) (1C), (26.17, 26.67) (1C), 54.59, 54.72, (64.25, 65.04, 65.51) (2C); (103.55, 105.60) (1C).

1-Iodo-2-chlorocyclohexane (5). 13.30g of anidrous $CuCl_2$ (0.10 mol) and 12.70g of iodine (0.05 mol) were added to a solution of 8.20g of cyclohexene (0.10mol) in pentane. The mixture was stirred for 4h at room temperature, filtered and the solid phase washed with pentane. After the solvent had been eliminated at reduced pressure, 20.0g (82%) of 1-iodo-2-chlorocyclohexane were recovered as a red oil with a chemical purity of 95% having: IR (ν, cm^{-1}): 2938, 2859, 1444, 1433, 1350, 1340, 1271, 1224, 1214, 1199, 1163, 1116, 1078, 996, 973, 902, 860, 814, 738, 685, 657, 558; MS (m/e, I%): M^++2(246, 1.33); M^+(244, 3.96); (128, 1.55); (127, 5.62); (117, 12.73); (82, 7.68); (81, 100.0); (79, 16.7); (77, 5.5); (75, 4.8); (67, 3.56); (67, 3.56); ^{1}H-NMR: 2.10÷1.10(m, 6H, C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$CHI); 2.60÷2.10(m, 2H, C<u>H</u>$_2$CHCl); 4.55÷4.15(m, 2H, C<u>H</u>IC<u>H</u>Cl); ^{13}C-NMR: 22.40, 24.38, 32.41, 34.60, 35.42, 63.64.

Alkenes and alkynes from 1,2-dibromides with TBTH and $NidppeCl_2$: General Procedure.
A solution of TBTH (10 mmol) in THF (20ml) was added under argon atmosphere, into a solution containing 0.100g of $NidpeCl_2$, (0.19 mmol) in 100ml of freshly distilled THF and the dibromide (5 mmol), at room temperature. After 15 min. the reaction mixture was hydrolized with water and extracted with diethyl ether and dried on anidrous Na_2SO_4. After the elimination of the solvent, the usual workup, gave a residue oil which when distilled, gave chemically pure samples of the corresponding unsaturated hydrocarbons.

Cyclohexene (2i) from 1-iodo-2-chlorocyclohexane (5). 10 ml of a 1M solution of $LiBEt_3H$ at 0 °C were added into a solution of 0.100g of $NidppeCl_2$ (0.19 mmol) in 150 ml of THF containing 1.22g of 1-iodo-2-chlorocyclohexane (5 mmol) and stirred for 30 min.. After the solution had been hydrolized with water, the organic layer was extracted with diethyl ether, and the solvent was eliminated. The resulting cycloexene (100%) was recovered as the sole reaction product, which was confirmed by comparison with an authentic sample.

Chlorocycloexane (6) from 1-iodo-2-chlorocyclohexane (5). 2.69 ml of aTBTH in 20 ml of freshly distilled THF were added into a solution of 0.100g of $NidppeCl_2$ (0.19 mmol) in 150 ml of the same solvent, containing 1.22g of 1-iodo-2-chlorocyclohexane (5 mmol), at room temperature. After 15 min. the mixture was idrolized with water and extracted with diethyl ether. After the solvent had been eliminated, chlorocyclohexane (80%) was recovered by distillation as the sole reaction product.

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References and Notes

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4. The low yield obtained is probably due to the formation of the enolate of the ketone **2.** Analogously, in the same reaction conditions adopted to convert **2** into **1**, the phenyl chloromethyl ketone is converted to the corrsponding phenyl methyl ketone with a 50% overall yield.
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