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Inorganic Chemistry Article

Conversion of Methanol to 2,2,3-Trimethylbutane (Triptane) over Indium(III) Iodide

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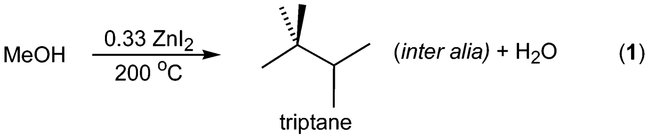
InI_3 is able to catalyze the conversion of methanol to a mixture of hydrocarbons at 200 °C with one highly branched alkane, 2,2,3-trimethylbutane (triptane), being obtained in high selectivity. The mechanism for InI_3-catalyzed reactions appears to be basically the same as that proposed for the previously studied ZnI_2-catalyzed system in which sequential methylation of olefins is followed by competing reactions of the resulting carbocation: proton loss to give the next olefin vs hydride transfer to give the corresponding alkane. Although the reaction conditions and typical triptane yields achievable with ZnI_2 and InI_3 are quite similar, the two systems behave rather differently in a number of important particulars, including significant differences between the detailed product distributions. Most of the differences in behavior can be ascribed to the stronger Lewis acidity of InI_3, including the ability to activate some alkanes, the higher activity for methylation of arenes, and the fact that methanol conversion can be observed at somewhat lower temperatures with InI_3 than with ZnI_2.

Introduction

Over the last 20 years, the growth in energy demands combined with the forecast depletion in oil reserves has resulted in a significant amount of research into alternative energies and petrochemical feedstocks.[1] It appears likely that in the future methanol will play an increasingly important role as it is cheap, readily synthesized, and relatively easy to transport and store.[2] A common approach involves the dehydrative conversion of methanol to hydrocarbons over acidic catalysts.[3] These reactions often proceed with low selectivity, and different classes of hydrocarbons can be obtained depending on the nature of the catalyst and the temperature (typically 200−450 °C). In exceptional cases such as the methanol-to-gasoline (MTG) and methanol-to-olefins (MTO) processes, which operate at temperatures above 300 °C to produce aromatic-rich and light olefin-rich products, respectively, selectivity is ascribed to the shape-selective zeolitic and aluminophosphate catalysts.[4−6]

In 1978, Kim et al. reported the reaction of methanol with zinc iodide at 200 °C.[7] In contrast to the usual behavior with non-shape-selective catalysts, the alkane-rich hydrocarbon mixture contained one highly branched alkane, 2,2,3-trimethylbutane (common name, triptane), in overall yields of up to 20% (based on moles of carbon), corresponding to as much as one-half of the gasoline-range fraction (eq 1). A cheap and efficient route to triptane would provide access to a valuable fuel component and gasoline additive (research octane number, 112).



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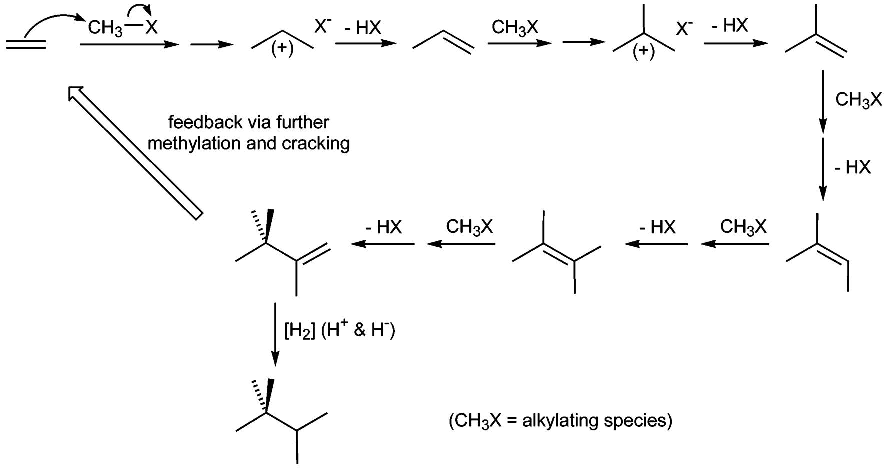
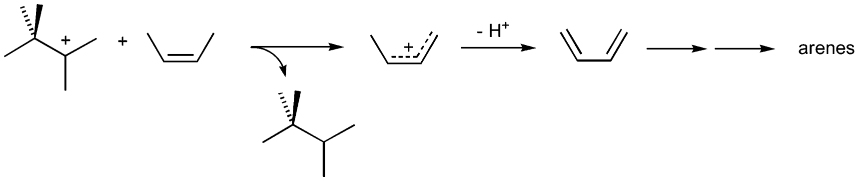
10.1021/ic7014447 CCC: $37.00

Scheme 1



Scheme 2



Our mechanistic studies on this complicated reaction[8] indicated that the reaction proceeds by two separate stages: an initiation stage, involving formation of one (or more) reactive C−C-bonded species, probably ethylene, and a growth stage involving elaboration of these species by successive methylation of olefins, leading ultimately to triptane and other hydrocarbons. The initiation stage is catalyzed heterogeneously; it does not take place if the ZnI_2 is fully dissolved in methanol prior to heating. Initiation can be completely bypassed by addition of a suitable promoter, either an unsaturated compound (olefin or arene) or a higher alcohol (the latter presumably functions as a facile precursor to an olefin). The growth stage is homogeneous, proceeding equally well whether or not any solid is present. It involves a carbocation-based route involving successive olefin methylation and deprotonation (Scheme 1), always favoring the most highly substituted carbocations and olefins, respectively. The exact nature of the methylating agent is not clear.

In the proposed mechanism the net transfer of H_2 from one olefinic hydrocarbon to another, resulting in an alkane and a multiply unsaturated species (the latter eventually ends up as an arene), takes place via hydride transfer from an unsaturated hydrocarbon to a carbocation, as illustrated in Scheme 2. Triptane yields are enhanced by addition of P−H-bonded species such as phosphorous or hypophosphorous acid, which serve as alternate hydride sources.[9]

We previously disclosed (in the patent literature[10]) that InI_3 also functions as a catalyst for this transformation. The reaction conditions and typical triptane yields achievable with ZnI_2 and InI_3 are quite similar, and hence, it might be expected that the basic mechanism for conversion of methanol to triptane would be much the same. However, the two systems behave rather differently in a number of important particulars, including significant differences between the detailed product distributions. We report here our studies on the InI_3-catalyzed conversion as well as some experiments using a combined ZnI_2/InI_3 catalyst system. We find that InI_3 (unlike ZnI_2) is able to activate (some) alkanes under the reaction conditions, a fact which can account for much of the difference in behavior, and also carries implications about the possibilities for further improvements in selectivity.

Results

Conversion of Methanol over InI_3. A number of iodide salts of the late transition and early p-block metals were screened using the standard conditions for ZnI_2-catalyzed dehydrative conversion of methanol into triptane:[8] heating a mixture of methanol and the metal salt in a 3:1 molar ratio along with a small amount of a promoter (10 mol % *tert*-butyl methyl ether was used for these experiments) for 3 h at 200 °C in a closed thick glass vessel. Salts tested included MnI_2, FeI_2, RuI_3, CoI_2, RhI_3, IrI_3, NiI_2, PdI_2, PtI_2, CuI, CdI_2, AlI_3, InI, InI_3, SnI_2, and SnI_4. In all cases partial dehydration of methanol to dimethyl ether (DME) and formation of small amounts of methyl iodide were observed, and a number of the reactions produced some hydrocarbon products; however, detectable levels of triptane were obtained only for three cases. Besides InI_3, RhI_3 and IrI_3 gave low yields of triptane

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[8] Bercaw, J. E.; Diaconescu, P. L.; Grubbs, R. H.; Kay, R. D.; Kitching, S.; Labinger, J. A.; Li, X.; Mehrkhodavandi, P.; Morris, G. E.; Sunley, G. J.; Vagner, P. *J. Org. Chem.* **2006**, *71*, 8907−8917.

[9] Bercaw, J. E.; Grubbs, R. H.; Hazari, N.; Labinger, J. A.; Li, X. *Chem. Commun.* **2007**, 2974−2976.

[10] Kay, R. D.; Morris, G. E.; Sunley, G. J. PCT WO 2005023733, 2005.

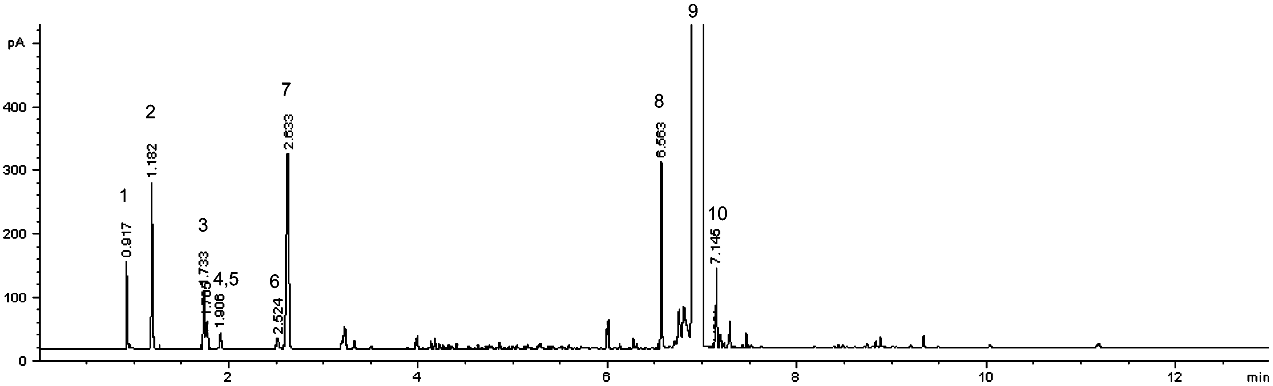

Figure 1. GC trace of a typical reaction catalyzed by InI_3. Labeled peaks: 1, *i*-butane; 2, 2-methylbutane; 3, 2,3-dimethylbutane; 4, 2-methylpentane; 5, 3-methylpentane; 6, 2,4-dimethylpentane; 7, triptane; 8, pentamethylbenzene; 9, tetradecane (added as solvent); 10, hexamethylbenzene.

Table 1. PIANO Analysis Results[a]

compound or class	wt %, InI_3[b]	wt %, ZnI_2[b]
n-paraffins	0.6	1.3
isoparaffins	58.7	45.0
arenes	23.3	10.7
naphthenes	4.6	5.2
olefins	0.4	14.2
i-butane	2.8	2.6
2-methylbutane	9.1	2.9
2-methylpentane	2.3	0.4
3-methylpentane	1.6	0.3
2,3-dimethylbutane	5.3	1.8
total C_6 isoparaffins	9.1	2.5
2,3-dimethylpentane	2.4	0.7
2,4-dimethylpentane	1.5	0.4
triptane	26.6	24.9
total C_7 isoparaffins	30.7	26.2
triptene		5.6
total C_8 isoparaffins	4.3	3.8
1,2,3,5-tetramethylbenzene	1.7	0.5
1,2,4,5-tetramethylbenzene	1.2	0.3
pentamethylbenzene	13.1	0.6
hexamethylbenzene	5.5	3.4

[a] The organic layers resulting from standard reactions (see Experimental Section) using InI_3 and ZnI_2 were analyzed. [b] Fraction of product in organic layer.

(5 ± 2% on the basis of moles carbon charged)[11] and have not been investigated further. In contrast, triptane yields of up to 15 ± 3% can be achieved using InI_3, comparable to the yield of triptyls (combined yield of triptane and triptene) obtained from reactions involving ZnI_2 (17 ± 3%),[8] warranting further study.

Mixtures of InI_3 and methanol, in molar ratios varying from 1:2 to 1:4, along with a promoter (typically 2.5 mol % *i*-propanol) were heated in a closed vessel at 200 °C. Approximately 2 h are required for complete conversion of methanol/DME to hydrocarbons and water. Increasing the relative amount of methanol inhibits reaction: at a molar ratio of 1:5 only traces of triptane form under the above conditions. However, more than 5 equiv of methanol per In can be converted as follows: 1−2 equiv of methanol per In are added, and the reaction is carried out as described, the reaction mixture is cooled, and all volatiles are removed in vacuo. A fresh charge of methanol is then added, and the cycle is repeated. Using this protocol, activity for converting methanol to triptane appears to be sustained indefinitely. Analysis of the dried residue after a reaction cycle by powder-pattern XRD shows that InI_3 is the major species present.

Reactions can be carried out at temperatures as low as 160 °C, although longer reaction times (about 8 h) are required to achieve complete conversion; no reaction is observed at 140 °C. If DME is used as a feedstock the reaction proceeds more rapidly and at still lower temperatures: complete conversion is seen after 4 h at 160 °C, and substantial formation of triptane is observed after 24 h at 120 °C; no reaction was found at 100 °C. For comparison, ZnI_2 is inactive below 180 °C with methanol and 140 °C with DME.[8]

After cooling to room temperature, the reaction mixture contained two liquid phases (an upper organic layer and a lower aqueous layer) and a significant amount of solid. The organic layer was analyzed using a variety of techniques including GC, GC/MS, and ^1H and ^{13}C NMR spectroscopy. A typical GC trace is shown in Figure 1. The largest peak in the GC trace is triptane; several other alkanes are present in significant quantities. The main arene peaks observed are pentamethylbenzene (PMB) and hexamethylbenzene (HMB). No methanol or dimethyl ether is observed in the organic layer.

Typical yields (determined by comparison of peak heights to that of an added internal standard, having previously calibrated response factors) are around 15% for triptane and 3% for HMB, based on total carbon in the feed (methanol plus promoter). As with ZnI_2,[8] several factors must be controlled in order to obtain reproducible results. These include ensuring that the entire reaction vessel is heated so that there is no temperature gradient, only comparing results from vessels with the same headspace, and using reagents of the same purity.

Selected samples were subjected to PIANO (paraffin, isoparaffin, arenes, naphthene, olefin) analysis, a standard refinery GC routine, which revealed that a large number of components were present. Selected results (including all major peaks) of the PIANO analysis are summarized in Table

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(11) Diaconescu, P. L.; Grubbs, R. H.; Labinger, J. A.; Mehrkhodavandi, P. PCT WO 2006023516, 2006.

Table 2. Effect of Halide on Triptane Yield[a]

molar % InI_3	molar % $InBr_3$	molar % $InCl_3$	triptane yield (%)
100	0	0	16.7
80	20	0	10.5
60	40	0	4.9
60	0	40	3.9
0	100	0	1.5
0	0	100	0

[a] All reactions were performed using the standard reactions conditions with *i*-propanol added as an initiator. The combined molar ratio of MeOH:InX_3 (X = I, Br, or Cl) was held fixed at 3:1.

1; results for an analogous reaction with ZnI_2 are included for purposes of comparison (see Discussion below). The two major classes of compounds present are isoparaffins and arenes, with a negligible amount of olefins.

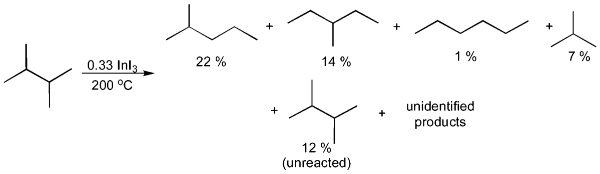
Other indium halides are much less effective, as shown in Table 2: use of $InBr_3$ or $InCl_3$ as sole catalyst gives small amounts of or no triptane, respectively, while even partially replacing InI_3 with either $InBr_3$ or $InCl_3$ reduces the yield of triptane.

In the absence of promoter, if the InI_3 is completely predissolved prior to heating or stirred during heating, the solution remains homogeneous after 2 h at 200 °C with no visible organic layer after cooling, and product analysis shows only the partial dehydration of methanol to DME. Promoter-free conversion can still be achieved so long as solid is present during the reaction. With additive, it makes no difference whether or not the mixture is predissolved and/or stirred.

A number of additives may serve as promoters in addition to those mentioned above, including higher alcohols such as *tert*-butanol and a wide variety of olefins ranging from terminal (1-hexene) to highly substituted (2,3-dimethyl-2-butene). Certain alkanes can promote conversion as well. Addition of 5 wt % of 2,3-dimethylbutane or 2,3-dimethylpentane gives results quite similar to those obtained with the promoters described above, except for significantly increased amounts of the alkane added. Apparent recoveries of the latter (relative to amount added) are close to quantitative: 103% for 2,3-dimethylbutane and 91% for 2,3-dimethylpentane. However, since these alkanes are also products of methanol conversion, the values need to be corrected for the amounts formed in normal reactions, yielding values corresponding to 90% and 86% recovery, respectively. Several other alkanes, including triptane, 2,2-dimethylbutane, hexane, and pentane, fail to promote reaction in predissolved solutions of InI_3 in methanol: no new hydrocarbons form, only the partial dehydration of methanol to DME is observed, and the added alkane is recovered quantitatively.

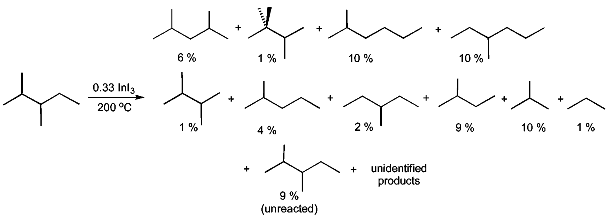
A similar experiment was carried out using 2,3-dimethylbutane as promoter and ^{13}C-labeled methanol both to verify that the alkane detected consists of both methanol-derived product and unreacted promoter and to demonstrate the partial conversion of promoter to triptane. Products were analyzed by GC/MS; Figures 2 and 3 show the MS patterns for the GC fractions of 2,3-dimethylbutane and triptane, respectively. For the former, the major set of peaks from 71 to 76 *m*/*z* correspond to the $(P-Me)^+$ fragment ions. Of these the largest is at 71 ($^{12}C_5H_{11}$) and the next-largest at 76 ($^{13}C_5H_{11}$) with weaker peaks at intermediate values resulting from mixed isotopologs. There is also a P^+ peak at 86 *m*/*z* for unlabeled 2,3-dimethylbutane, while the parent ions for other isotopologs are much weaker or not present. For triptane, the main signals again correspond to $(P-Me)^+$ ions; there is barely any detectable signal in the P^+ region. The largest signal at 91 *m*/*z* is due to fully labeled $^{13}C_6H_{13}$; the next largest, at 86 m/z, is due to singly labeled $^{12}C_5{}^{13}C_1H_{13}$; weaker peaks are observed at intermediate values. However, there is no peak at 85 *m*/*z*, which would arise from completely unlabeled triptane.

Reactions of Alkanes and Olefins with InI_3. Heating 2,3-dimethylbutane for 2 h at 200 °C in the presence of InI_3 (InI_3 is virtually insoluble in 2,3-dimethylbutane, so the reaction mixture is heterogeneous) effects a substantial degree of isomerization. Analysis by GC and GC/MS reveals the presence of 2-methylpentane, 3-methylpentane, and hexane along with unreacted starting material; smaller peaks corresponding to cracking products such as *i*-butane as well as several unidentified species were also observed, as shown in eq 2, where the indicated amounts refer to weight percent relative to the starting alkane. No isomerization is observed when a mixture of 2,3-dimethylbutane and ZnI_2 is heated for 2 h at 200 °C.



(2)

The C_7 alkanes 2,3-dimethylpentane and triptane are similarly isomerized (eqs 3 and 4); products include 2,4-dimethylpentane, 2-methylhexane, and 3-methylhexane along with cracking products such as *i*-butane, 2-methylbutane, 2,3-dimethylbutane, 2-methylpentane, and 3-methylpentane. Cracking products are more prevalent for C_7 compounds than for C_6 compounds. In contrast, no isomerization at all is observed when 2,2-dimethylbutane is subjected to the same conditions; *n*-hexane gives only trace amounts of isomerized and cracked products.



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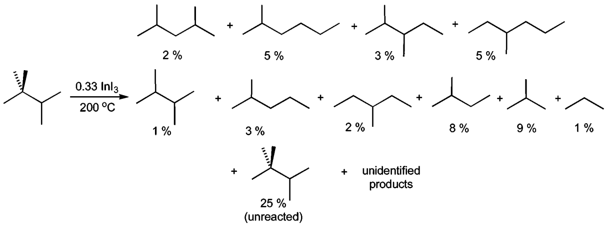


(4)

Heating 2,3-dimethylbutane with InI_3 in methanol also causes isomerization, but the degree of isomerization de-

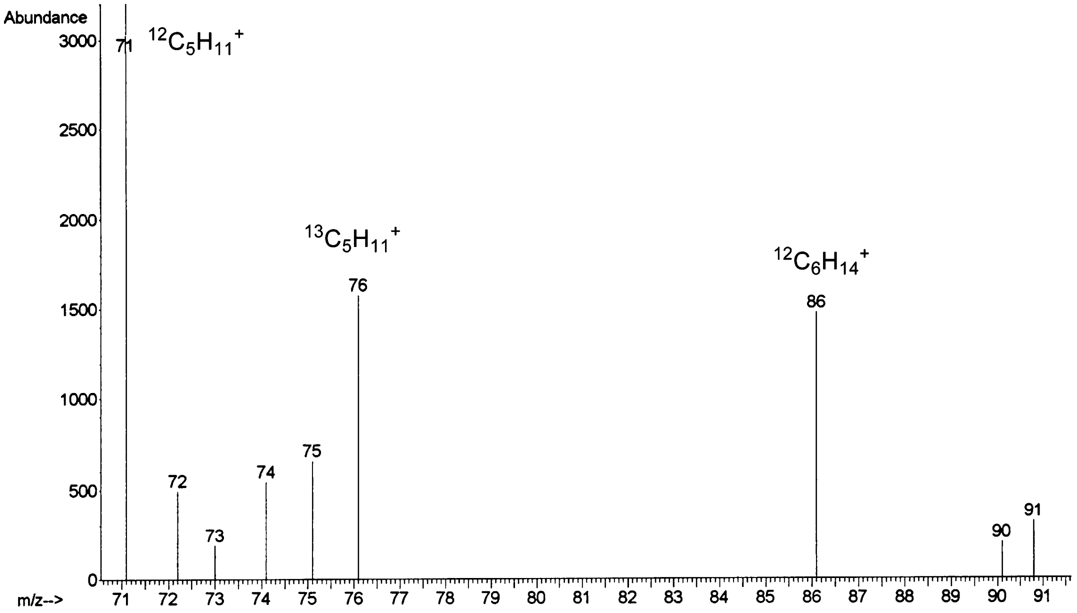


Figure 2. MS of the 2,3-dimethylbutane fraction from reaction between InI_3, ^{13}C-labeled methanol, and 2,3-dimethylbutane.

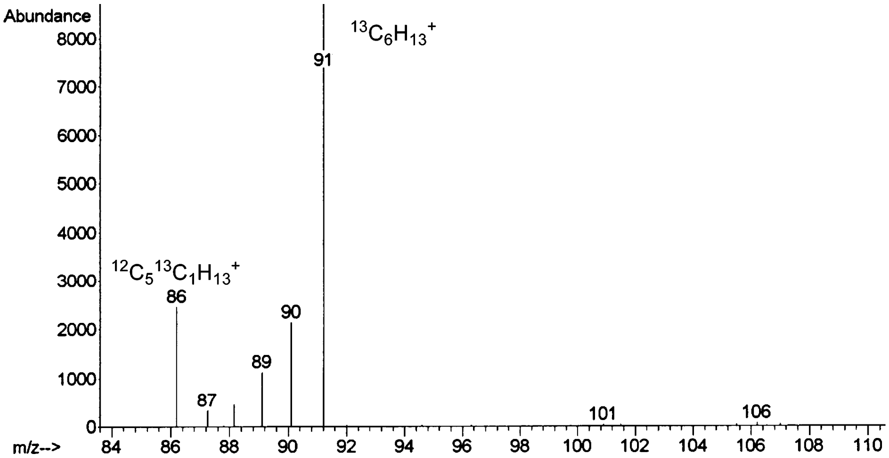


Figure 3. MS of triptane fraction from reaction between InI_3, ^{13}C-labeled methanol, and 2,3-dimethylbutane.

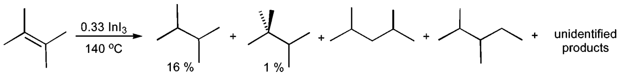
Table 3. Isomerization of 2,3-Dimethylbutane by InI_3 in Methanol

molar ratio of 2,3-dimethylbutane to MeOH	ratio 2,3-dimethylbutane:2-methylpentane[a]
no MeOH	0.54:1
1:1	2.4:1
1:2	12:1

[a] Determined by GC after heating for 2 h at 200 °C. See Experimental Section for details.

creases as the ratio of methanol to alkane is increased, as shown in Table 3.

Several experiments were also performed investigating reactions between InI_3 and olefins in the absence of methanol. (In general, mass balance was poor in these reactions, like those described above, and the identities of only a few of the products were determined; GC traces show a large number of very weak peaks that are not readily assignable.) The reactions of 2,3-dimethyl-2-butene and triptene with InI_3 at 140 °C for 3 h led mainly to formation of the corresponding saturated hydrocarbons along with much smaller amounts of compounds resulting from carbon−carbon bond breaking and forming (eqs 5 and 6). At still lower temperature reaction of 2,3-dimethyl-2-butene with InI_3 at 100 °C gave only 2,3-dimethylbutane along with a significant amount of unreacted olefin. Terminal olefins (1-hexene and 4-methyl-1-pentene) showed no reaction at all after being heated in the presence of InI_3 at 140 °C for 3 h.



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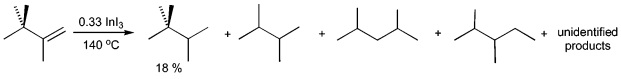

(6)

Effect of Phosphorus Reagents on InI_3-Catalyzed Reactions. As noted above, addition of H_3PO_3 or H_3PO_2 (6 mol % relative to methanol) substantially improves triptane yields in ZnI_2-catalyzed reactions.[9] In contrast, addition of 6 mol % H_3PO_2 to reaction mixtures containing InI_3, MeOH, and ^iPrOH results in a *decreased* yield of triptane, from ap-

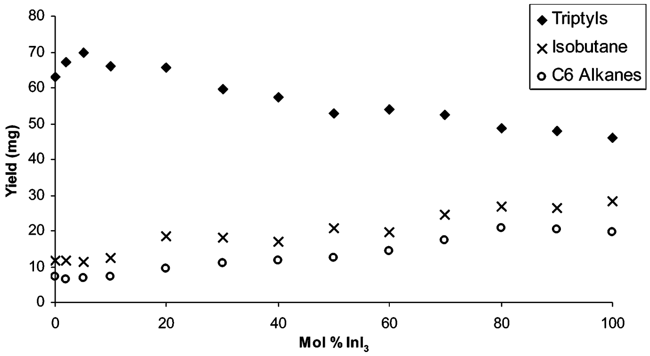

Figure 4. Effect of the relative ratio of ZnI_2 to InI_3 on yields of isobutane, C6 alkanes, and triptyls obtained from standard reactions (see Experimental Section for details).

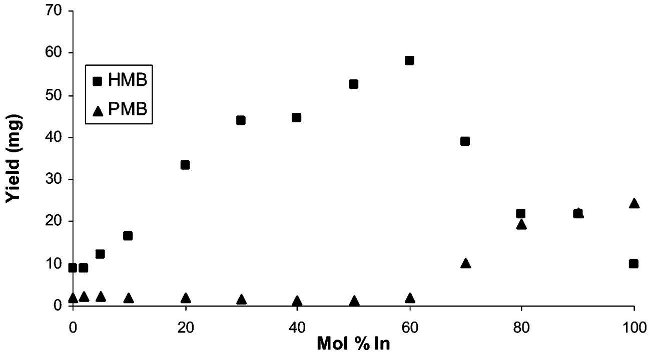

Figure 5. Effect of the relative ratio of ZnI_2 to InI_3 on yields of PMB and HMB obtained from standard reactions (see Experimental Section for details).

proximately 15% to 10%, along with a significant increase in the yields of *i*-butane and 2-methylbutane, a smaller increase in the yield of C_6 alkanes, and a significant decrease in the yields of PMB and HMB (Table 4). ^{31}P NMR spectroscopy shows that H_3PO_2 is oxidized to a mixture of H_3PO_3 and H_3PO_4 during the course of the reaction.

Conversion by Mixed ZnI_2−InI_3 Systems and Arene Methylation. A series of experiments containing different mixtures of ZnI_2 and InI_3 were performed using the standard reaction conditions with a small amount of *i*-propanol added as an initiator. In these reactions the combined molar amount of ZnI_2 and InI_3 was maintained at 1:3 with respect to moles of methanol. The yields of *i*-butane, combined C_6 alkanes, and triptyls as the ZnI_2 to InI_3 ratio was varied are shown graphically in Figure 4, while the corresponding yields for PMB and HMB are shown in Figure 5.

Figure 4 shows a small increase in the triptyls yield (combined yield of triptane and triptene) when low levels of InI_3 are used in the catalyst mixture, although it is only marginally above the variability within duplicate runs and may not be statistically significant. The yield of triptyls falls off substantially at higher InI_3 levels. The amount of triptene present decreases gradually as the mol % of InI_3 was increased (by NMR; precise quantification of the relative amounts of triptene and triptane is not obtainable from our routine GC analysis in which the peaks overlap significantly); no triptene was formed in reactions which contain 30 mol % or more of InI_3. In contrast, the yields of lower alkanes such as *i*-butane and the combined C_6 alkanes (2,3-dimethylbutane, 2-methylpentane, and 3-methylpentane) increase steadily with the fraction of InI_3. In Figure 5 the yield of HMB shows a pronounced maximum at roughly equivalent amounts of ZnI_2 and InI_3, while significant yields of PMB are found only at higher InI_3 concentrations.

Table 4. Effect of 6 mol % H_3PO_2 on Yield of Selected Species

compound	% yield with H_3PO_2[a]	% yield from normal reaction
i-butane	10.7	7.5
2-methylbutane	10.5	8.7
2,3-dimethylbutane	2.2	2.9
2-methylpentane	2.4	1.4
3-methylpentane	1.5	0.9
total C_6 isoparaffins	6.1	5.2
triptane	9.8	12.8
pentamethylbenzene	3.6	7.1
hexamethylbenzene	1.3	3.1

[a] In this reaction 6 mol % H_3PO_2 (relative to MeOH) was added to a standard reaction mixture.

Table 5. Relative Yields of Methylated Benzenes from *p*-xylene

compound	relative yield (%)[a]
p-xylene	51
trimethylbenzenes	14
tetramethylbenzenes	6
pentamethylbenzene	2
hexamethylbenzene	29

[a] Analyzed by GC after heating *p*-xylene with InI_3 in methanol at 150 °C for 2 h. Yields of isomers were combined for trimethylated and tetramethylated benzenes.

Reaction of *p*-xylene with a solution of InI_3 in methanol for 2 h at 150 °C produces a mixture of trimethylated, tetramethylated, pentamethylated, and hexamethylated benzenes; HMB is formed in greater yields than the less-methylated products, even though a significant amount of unreacted *p*-xylene remains, as shown in Table 5. A corresponding experiment with ZnI_2 instead of InI_3 results in no methylation at all under these conditions.

Discussion

Conversion of Methanol over InI_3. The InI_3-catalyzed conversion of methanol to hydrocarbons exhibits many features quite analogous to those for catalysis by ZnI_2.[8] In particular, reaction conditions are quite similar (although indium can be used at somewhat lower temperatures) and there are comparable yields of triptyls as well as hexamethylbenzene, a significant byproduct in both cases. Further parallels include (1) the fact that hydrocarbon formation in the absence of a promoter can only be achieved if solid is present during the reaction, suggesting that in both systems formation of the first C−C bond is catalyzed heterogeneously, and (2) strong dependence on the identity of the halide, with iodides significantly better than bromides and chlorides essentially inert. The reasons for this halide dependence are not fully clear at this time; possibilities include effects on the relative acidity of the metal halides and/or ability to generate reactive methylating agents from the corresponding methyl halides (formation of some methyl iodide is always observed with both InI_3 and ZnI_2). Additionally, in both systems conversion is significantly slowed or stopped altogether if the ratio of reactant (methanol or DME) to catalyst exceeds about 4:1, attributed to inhibition by water; when smaller amounts of reactant are converted over a single catalyst charge with removal of volatiles (including water) between runs, conversion can be continued indefinitely. These observations all suggest that the InI_3-catalyzed reaction proceeds via the same carbocation-based mechanism proposed for the ZnI_2 case.[8]

However, there are several major differences between the product distributions from the two catalyst systems, as shown in Table 1. Most notably, the yield of olefinic products from InI_3-catalyzed reactions is negligible, whereas around 14% of the products are olefins in the ZnI_2 system. In particular, only triptane is produced in the InI_3 systems, while both triptane and triptene are produced in ZnI_2 systems. In general, the amount of isoparaffins as well as arenes produced in indium reactions is considerably greater than in zinc reactions. Since the proposed mechanism for formation of alkanes (which by stoichiometry, from the dehydrative condensation of methanol, requires an additional equivalent of H_2) involves transfer of H_2 from one olefinic hydrocarbon to another, resulting in an alkane and a multiply unsaturated species that leads to arenes, these results clearly suggest that InI_3 is better than ZnI_2 at promoting H transfer via the mechanism of Scheme 2. The fact that substituted olefins such as 2,3-dimethyl-2-butene and triptene are substantially converted to the corresponding alkanes (as shown in eqs 5 and 6) by heating with InI_3 but not ZnI_2 further supports this conclusion.

Differences within product classes between InI_3- and ZnI_2-catalyzed reactions can also be seen in Table 1. The selectivity for the maximally branched alkane isomers is lower for InI_3 than for ZnI_2. In the ZnI_2 system the ratio of 2,3-dimethylbutane to other C_6 alkanes is around 3:1, while in the InI_3 system the ratio is approximately 5:4. A similar trend appears to be present for C_7 alkanes: the selectivity for triptane compared with other C_7 alkanes is not as high in InI_3-catalyzed reactions, although complete quantitative data could not be obtained for C_7 alkanes due to overlapping peaks in the GC trace. Another difference appears in the aromatic speciation: the ratio of hexamethylbenzene (HMB) to pentamethylbenzene (PMB) is much higher for zinc than indium. Possible explanations for both differences are discussed below.

Alkane Activation. As with the ZnI_2 system a variety of olefins and alcohols can initiate formation of triptane in the indium system; our mechanistic proposal[8] involved methylation of olefins (whether added directly or formed in situ by dehydration of alcohols), bypassing the more difficult first C−C bond formation step. In contrast, one of the major differences between the two systems is that (some) alkanes can initiate formation of hydrocarbons in the presence of InI_3 but not in the presence of ZnI_2. Indeed, several lines of evidence indicate that whereas alkanes are completely inert in the ZnI_2 system, those capable of forming relatively stable carbocations can be activated by InI_3.

In order to probe the reactivity of alkanes with InI_3, a number of C_6 and C_7 alkanes were heated at 200 °C in the presence of InI_3. In general, InI_3 is able to isomerize and crack alkanes which possess at least one tertiary carbon atom (eqs 2−4), but isomerization was slow or did not occur for alkanes with no tertiary carbon atoms. Although to the best of our knowledge this is the first report of the isomerization of alkanes by InI_3, it is not unexpected given that $AlCl_3$ can also catalyze alkane isomerization.[12] A carbocation-based mechanism is well established for isomerization using $AlCl_3$, and it seems likely that this is also the case for InI_3. The absence of any 2,2-dimethylbutane from isomerization of 2,3-dimethylbutane is consistent with this proposal. Previous studies have shown that isomerization of C_6 alkanes via a carbocation-based mechanism affords 2,2-dimethylbutane in concentrations well below equilibrium levels (if it is observed at all) because formation of 2,2-dimethylbutane (which possesses a quaternary carbon) requires strong acidity and/or long surface residence times to permit the stable *tert*-2,3-dimethyl-2-butyl cation to convert to the less stable *sec*-2,2-dimethyl-3-butyl cation.[13] Likewise, when 2,2-dimethylbutane was heated for 2 h at 200 °C in the presence of InI_3, no isomerization was observed; a similar experiment with *n*-hexane gave only trace amounts of isomerized and cracked products. These findings suggest that secondary carbocations are much less easily accessed than tertiary carbocations under these reaction conditions.

The observation that cracking products are more prevalent for C_7 compounds than C_6 compounds is also consistent with previous studies of carbocation-based alkane isomerization: as the size of the alkane chain increases, cracking becomes easier.[12] In addition, the degree of isomerization and cracking in the case of 2,3-dimethylpentane is significantly greater than for triptane, which suggests that either it is easier to form a carbocation from 2,3-dimethylpentane than triptane or the triptyl carbocation is less likely to undergo rearrangement than the carbocation formed from 2,3-dimethylpentane. An earlier study similarly found a higher rate of isomerization for 2,3-dimethylpentane than for triptane (although it utilized a nickel catalyst which may not be completely mechanistically similar).[14]

Generation of carbocationic intermediates is presumably also responsible for the ability of certain alkanes to promote triptane synthesis since under the reaction conditions carbocations are in equilibrium with olefins, which can in turn initiate formation of hydrocarbons as described above. The alkanes which do function as promoters possess tertiary carbon centers that can readily form stable carbocations and are generally identical to those that undergo isomerization. Triptane itself is isomerized on heating with InI_3 in the absence of methanol but does not initiate conversion of methanol to triptane. This may be explained by experiments showing that as the ratio of methanol to 2,3-dimethylbutane is increased, the amount of alkane isomerization decreases. Under methanol conversion conditions, where the initial ratio of methanol to alkane promoter is high, carbocation genera-

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(12) Ono, Y. *Catal. Today* **2003**, *81*, 3−16.

(13) Iglesia, E.; Soled, S. L.; Kramer, G. M. *J. Catal.* **1993**, *144*, 238−253.

(14) Ciapetta, F. G.; Hunter, J. B. *J. Ind. Eng. Chem.* **1953**, *45*, 155−159.

tion, which leads to alkane isomerization, must be slower still. Since in the absence of methanol both 2,3-dimethylbutane and 2,3-dimethylpentane undergo isomerization faster than triptane, it appears plausible that the first two could initiate formation of hydrocarbons from methanol while the corresponding activation of triptane is too slow to do so.

In the case of promotion by 2,3-dimethylbutane, some triptane would arise directly by methylation of the derived olefin, 2,3-dimethyl-2-butene, to give a C_7 carbocation which leads to triptane by hydride transfer (see Scheme 1). The experiment involving unlabeled 2,3-dimethylbutane as an initiator, and ^{13}C-labeled methanol supports this proposed mechanism. GC/MS shows that the predominant isotopologs of 2,3-dimethylbutane are the completely unlabeled and completely labeled ones, corresponding to unreacted additive and methanol-derived product, respectively. There are also smaller amounts of partially labeled species, which must arise from some exchange process. Previous experiments with the Zn system showed that methyl groups on olefins readily exchange under the methanol conversion reaction conditions,[8] so formation of small amounts of olefin by alkane activation would explain the partial labeling as well as initiation of hydrocarbon formation. Furthermore, the two major isotopologs for triptane correspond to singly labeled and fully labeled triptane; intermediate isotopologs were also observed, but no unlabeled triptane. Again, fully labeled triptane would arise via de novo synthesis from methanol, but a singly labeled triptane molecule must come from methylation of the C_6 olefin generated by activation of unlabeled 2,3-dimethylbutane.

In contrast to the evidence for alkane activation by InI_3, we never observed either alkane isomerization[15] or initiation of methanol conversion by alkanes when ZnI_2 is used as the catalyst. It seems likely that this difference represents greater Lewis acidity of InI_3 than ZnI_2, which facilitates carbocation generation to a greater extent. The observation that the selectivity for the most highly branched alkane isomer within a given C_n fraction is lower for InI_3 compared with ZnI_2 as catalyst most probably reflects this difference as well: the main growth mechanism would favor the most branched isomers in either case, but they would undergo some isomerization after formation with InI_3 but not with ZnI_2. Since the maximally branched isomers still remain the major species though, isomerization under methanol conversion conditions must be considerably slower that that observed for reactions of dry alkanes with InI_3, as confirmed by the experiments with varying alkane:methanol ratios.

Effect of Phosphorus Reagents on InI_3-Catalyzed Reactions. The effect of addition of phosphorus reagents such as H_3PO_2 and H_3PO_3 to ZnI_2-catalyzed reactions are explained by the P−H bond containing species serving as alternate hydride sources, thus reducing the fraction of hydrocarbon that must be diverted from the triptane-producing sequence into the arene pool (Scheme 2), resulting in an increase in the yield of triptane and a decrease in the yield of aromatic species.[9] In contrast, addition of 6 mol % H_3PO_2 to InI_3-catalyzed reactions results in a *decreased* yield of triptane, accompanied by large increases in the yields of *i*-butane and 2-methylbutane and a smaller increase in the yield of C_6 alkanes. This suggests that when these phosphorus additives are used with InI_3, the rate of hydride transfer to carbocations becomes faster relative to methylation of olefins compared to the Zn case (even though there is clear evidence that methylation is faster with In than Zn as well; see Table 5). Thus, conversion of lighter carbocations to alkanes competes more efficiently with carbon chain growth, reducing the selectivity for C_7 in favor of lighter alkanes. The observed decrease in the yields of PMB and HMB are consistent with hydrogen transfer from the phosphorus reagent as is the observation (by ^{31}P NMR spectroscopy) that H_3PO_2 is oxidized during the course of the reaction to a mixture of H_3PO_3 and H_3PO_4.

Conversion by Mixed ZnI_2−InI_3 Systems and Arene Methylation. The ZnI_2-catalyzed conversion of methanol affords some triptene; when triptene is heated with methanol and ZnI_2 some of it is hydrogenated to triptane, but there is also partial conversion to a variety of different products.[8] This instability to reaction conditions could be a factor that lowers overall triptyl selectivity, which in principle might be ameliorated by increasing the rate of hydride transfer as triptane is much more stable. Since InI_3 is better at facilitating hydrogen transfer, even though it gives somewhat poorer triptyl yields when used alone, it seemed possible that there could be an optimal catalyst combination of $InI_3 + ZnI_2$. Results from a series of experiments with different compositions of ZnI_2 and InI_3 (Figure 4) do show a slight increase in the triptyl yield at low concentrations of InI_3, but the magnitude is barely if at all statistically significant, and the yield decreases at higher InI_3 levels. There is a steady increase in yield of lighter alkanes as well as the overall amount of alkanes as the proportion of In increases. At the same time the yield of HMB increases dramatically to a maximum at around 60:40 In:Zn and then starts to decrease at higher InI_3 concentrations, while significant amounts of PMB begin to appear.

These observations are consistent with the postulate that InI_3 is more effective at promoting hydrogen transfer, most clearly evidenced by the much lower olefin yield with In than with Zn. That should accomplish the above goal of "protecting" a greater fraction of the C_7 product as stable triptane; however, it also means that a correspondingly greater fraction of the lighter intermediates is trapped as light alkanes rather than growing on to C_7. Subsequent activation of those alkanes does take place with In, but that process (in a methanol conversion reaction) appears to be too slow to permit more than a small amount to re-enter the growth sequence. These two trends offset one another, with the net

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(15) Our explanation for triptane selectivity in zinc-catalyzed reactions[8] included the suggestion that formation of alkanes might be somewhat reversible, but this is clearly not the case: no detectable isomerization or cracking of any alkanes can be detected in any reaction using ZnI_2. The basic framework of the mechanistic account for selectivity remains intact though; it is a consequence of relative rates of hydride transfer to carbocations vs methylation of olefins for intermediates of different carbon numbers. We will elaborate on this mechanistic discussion in a future publication.

result being a small decrease in overall triptyl selectivity for In compared to Zn.

The fact that more saturated alkanes are being produced with In also requires more hydrogen-deficient arenes to maintain the stoichiometry in H. (Hydrogen transfer has the net effect of disproportionating olefins to alkanes plus arenes, the thermodynamically favored state.) However, the increase in HMB yield with increasing In content is much steeper (Figure 5) than expected, suggesting a further postulate: that InI_3 is also more efficient at catalyzing the methylation of arenes than ZnI_2. Thus, as the mol % of In increases, not only does the total amount of arenes increase, but also HMB constitutes a larger fraction of the arene pool. This postulate was confirmed: experiments show that InI_3 catalyzes the methylation of *p*-xylene by methanol at 150 °C and that the rate of methylation increases as the benzene ring becomes more highly methylated (as would be expected for an electrophilic pathway[16]), so that HMB is the major product (Table 5). Under the same conditions no methylation is observed using ZnI_2.

At high InI_3 levels HMB starts to fall again, accompanied by growth of PMB. We believe this is simply a consequence of running out of methylating species: stoichiometry in hydrogen requires a high arene yield, and they cannot all be kept fully methylated; at high In content PMB becomes the major arene component. We previously suggested that the "paring" mechanisms proposed in the "carbon pool" mechanism for MTO[5,6] operate in the Zn-catalyzed conversion of methanol to continually regenerate light olefins as growth precursors;[8] such processes would effect the net demethylation of HMB to PMB (and perhaps less-substituted benzenes as well) as the methylating species run out late in the reaction. At the highest InI_3 levels the sum of PMB and HMB is considerably lower than at intermediate levels and not sufficient to balance the stoichiometry in H, so there must be additional H-deficient products, most probably polynuclear arenes (naphthalenes, etc.). GC traces for these cases do in fact exhibit more peaks at long retention times, where such compounds would be expected to show up, although we have not yet identified any specific products.

Conclusions

The mechanism for InI_3-catalyzed conversion of methanol to hydrocarbons appears to be basically the same as that proposed for the ZnI_2 system,[8] where sequential methylation of olefins is followed by competing reactions of the resulting carbocation: proton loss to give the next olefin vs hydride transfer to give the corresponding alkane. The exact nature of the methylating species is not known, but surely its generation is related to the acidity (Lewis and/or Brønsted) of the catalyst; and most of the differences in behavior can be ascribed to the stronger Lewis acidity of InI_3, including the ability to activate alkanes, the higher activity for methylation of arenes, and the fact that methanol conversion can be observed at somewhat lower temperatures with InI_3 than with ZnI_2. Presumably the greater activity for hydride transfer is also connected with this property, although the mechanistic reason for that is not immediately obvious; it might simply be a consequence of longer lifetimes of carbocation intermediates (the hydride-accepting species) under more Lewis acidic conditions.

Our qualitative explanation for the remarkable triptyl selectivity is based on two trends. First, methylation and deprotonation will always preferentially lead to the most highly substituted carbocations and olefins possible; second, the relative rate of hydride transfer compared to methylation changes as the molecule grows: it is greater for C_7 than at earlier growth stages, a consequence of the fact that triptene (unlike its most immediate precursors) is only a disubstituted olefin with some steric factors probably operating as well.[8] Despite the considerable difference in hydride transfer rate, implied by a number of observations, the two systems give rather similar overall triptyl yields as any advantage in protecting the C_7 species against further growth and/or other decomposition pathways that may result from triptene accumulation is offset (slightly more than offset in fact) by the interruption of the growth sequence caused by too-efficient trapping of lighter species as alkanes. Thus far we achieved significant yield improvements only by providing an alternate hydrogen source to reduce the requirement for formation of arenes; it seems possible that the observed ceilings on triptyl yield represent an *inherent* limit of triptane selectivity within the pool of aliphatic products.

It is not so clear why ZnI_2 and InI_3, out of the large number of metal iodide salts examined, are the only effective and highly selective catalysts for triptane formation. Having the right level of acidity is obviously important: too little will give no activity, and too much will tend to produce product distributions closer to thermodynamically governed values.[17] Solubility properties appear to be important as well; we suggested that the ability of hydride transfer steps to compete effectively with other processes is a key factor in the selective formation of triptane, and perhaps maintaining a homogeneous solution helps favor these bimolecular reactions. We hope to cast further light on these questions by ongoing modeling studies.

Experimental Section

General. Indium iodide (purchased from Alfa Aesar), zinc iodide (purchased from Sigma-Aldrich), methanol, dimethyl ether, and other organic compounds were reagent-grade commercial samples used without further purification. ^1H, ^{13}C, and ^{31}P NMR spectra were obtained on a Varian 300 MHz instrument. GC analyses were performed on an HP model 6890N chromatograph equipped with a 10 m × 0.10 mm × 0.40 μm DB-1 column. GC/MS analyses were performed on an HP model 6890N chromatograph equipped with a 30 m × 25 mm × 0.40 μm HP5-1 column and equipped with an HP 5973 mass-selective EI detector.

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(16) Theoretical studies confirm this reactivity order for zeolite-catalyzed methylation of methylated benzenes: Svelle, S.; Arstad, B.; Kolboe, S.; Swang, O. *J. Phys. Chem. B* **2003**, *107*, 9281−9289.

(17) For example, the distribution of alkanes obtained from reaction of methanol with polyphosphoric acid under similar conditions is much closer, though not identical, to that expected from thermodynamics; see: Pearson, D. E. *J. Chem. Soc., Chem. Commun.* **1974**, 397.

Standard Reaction Protocols. The following metal salts were screened as potential catalysts for the conversion of methanol into triptane: MnI_2, FeI_2, RuI_3, CoI_2, RhI_3, IrI_3, NiI_2, PdI_2, PtI_2, CuI, CdI_2, AlI_3, GaI_3, InI, InI_3, SnI_2, and SnI_4. In all cases they were tested using the standard protocol described below for InI_3 in both the presence and the absence of an initiator. Only the InI_3, RhI_3, and IrI_3 systems showed any activity for formation of triptane.

All reactions were performed in thick-walled pressure tubes equipped with Teflon stopcocks (Ace Glassware) rated up to 10 bar. The procedure for reactions involving InI_3 is based on the procedure reported earlier for ZnI_2.[8] In a typical standard experiment, the tube was equipped with a stir bar and charged with indium iodide (2.05 g, 4.1 mmol), methanol (0.5 mL, 12.4 mmol), and ^{i}PrOH (50 μL) as an initiator. (The indium iodide was generally weighed out in a glove box due to its hygroscopic nature; however, the reactions were carried out under an atmosphere of air). The pressure tube was placed in a preheated oil bath behind a blast shield and stirred at 200 °C for the desired period of time, usually 2−3 h. After heating, the tube was removed from the bath and allowed to cool to room temperature. The stopcock was removed, and chloroform (1.0 mL), containing a known amount of cyclohexane as an internal standard, was pipetted into the reaction mixture followed by water (0.5 mL). The stopcock was replaced, the mixture was shaken vigorously, and the organic layer was separated. A small aliquot was diluted with acetone or tetradecane for GC analysis. In cases of samples to be used for NMR analysis, deuterated chloroform was used for the extraction. Analogous procedures were used for reactions involving $InBr_3$ and $InCl_3$.

In reactions involving dimethyl ether, all ingredients except DME were loaded into the tube. The tube was then degassed using three consecutive freeze−pump−thaw cycles and frozen in liquid nitrogen. The desired amount of DME was condensed into the tube, which was allowed to warm to room temperature and then heated as usual.

Alkane Isomerization Experiments. The following procedure is a representative example. An Ace pressure tube equipped with a stir bar was charged with InI_3 (2.05 g, 4.13 mmol) and 2,3-dimethylbutane (0.53 g, 6.2 mmol). The reaction mixture was heated in a preheated, regulated oil bath behind a protective shield for 2 h at 200 °C and then worked up and analyzed using the standard protocol. In cases where methanol was added to the reaction mixture, the combined molar ratio of 2,3-dimethylbutane and methanol to InI_3 was fixed at 3:1.

Conversion by Mixed ZnI_2/InI_3 Experiments. All the reported reactions were carried out under homogeneous conditions (stirred and predissolved solutions). The following procedure is a representative example. An Ace pressure tube equipped with a stir bar was charged with methanol (1.0 mL, 24.8 mmol), ZnI_2 (0.96 g, 3.0 mmol), InI_3 (2.24 g, 4.5 mmol), and ^{i}PrOH (50 μL) as an initiator. (It should be noted that the combined molar amount of ZnI_2 and InI_3 was always 33% with respect to methanol; thus, as the molar amount of InI_3 present in the reaction was increased, the molar amount of ZnI_2 was decreased by the same amount). The reaction mixture was stirred to give a clear solution and then heated in a preheated regulated oil bath behind a protective shield for 2 h at 200 °C (in certain cases reactions were left for longer than 2 h to ensure complete conversion of methanol). The reaction was worked up and analyzed using the standard protocol.

Methylation of *p*-Xylene. A thick-walled pressure tube was equipped with a stir bar and charged with indium iodide (2.05 g, 4.1 mmol), methanol (0.5 mL, 12.4 mmol), and *p*-xylene (50 μL). The tube was heated in the normal fashion for 2 h at 150 °C and then worked up and analyzed using the standard protocol. The same procedure was used for a reaction using ZnI_2 instead of InI_3.

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