Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Enhanced Selectivity in the Conversion of Methanol to 2,2,3-Trimethylbutane (Triptane) over Zinc Iodide by Added Phosphorous or Hypophosphorous Acid

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Experimental protocol

Zinc iodide, methanol, isopropanol (used as initiator) and phosphorus compounds were reagent-grade commercial samples, used without further purification. GC analyses were performed on an HP model 6890N chromatograph equipped with a 10 m x 0.10 mm x 0.40 μm DB-1 column. ^{31}P and ^{13}C NMR spectra were obtained on a Varian 300 MHz instrument. Reactions were carried out in thick-walled pressure tubes equipped with Teflon stopcocks (Ace Glassware), as previously described.[i] In a typical experiment, zinc iodide (2.444 g, 7.65 mmol), methanol (1.0 ml, 791 mg, 24.7 mmol), isopropanol (50μL, 39.2 mg, 0.65 mmol), and $P(OCH_3)_3$ (200 μL, 210 mg, 1.69 mmol) were added to the pressure tube under argon. The mixture was stirred until dissolution was complete, and the tube placed into a preheated oil bath at 200 ^oC for 3 hours, after which time it was cooled to room temperature to give two layers. A solution of 83.4 mg cyclohexane (as reference standard) in 1 mL chloroform followed by 1 mL water was added; the organic layer was extracted, diluted with acetone, and analyzed by gas chromatography (GC). Reactions with different additives and quantities were carried out analogously. Since hypophosphorous acid is available commercially only as a 50% aqueous solution, and since water has an inhibitory effect,[1] a small modification was introduced for its reaction:

the tube was first charged with an amount of the solution corresponding to the desired molar quantity of H_3PO_2 and evacuated for 12-36 h to remove most of the water. The remaining components were then added and the reaction carried out as above. If water removal is omitted, substantially longer reaction times are required for complete conversion.

Selected results are shown in Table 1 of the main text, and a more complete listing is given in Table S1 below.

Table S1. Yields for reactions with varying additives

Additive, mol % (rel. to MeOH)	Reaction time, h	Temp., °C	Triptyl yield, mg	Triptyl yield, % based on MeOH	Triptyl yield, % based on total C
none	2	200	43	12	11
"	3	200	66	19	18
$P(OMe)_3$, 6.8 %	2	200	113	32	24
"	3	200	108	31	23
"	24	175	121	34	26
$P(OMe)_3$, 1.7%[b]	2	200	65	18	17
$P(OMe)_3$, 3.4%[b]	2	200	100	28	23
$P(OMe)_3$, 10.2%[b]	2	200	102	29	21
$P(OEt)_3$ 6.8 %	2	200	67	19	13
H_3PO_3, 6.8 %	2	200	86	24	22
"	3	200	89	25	23
H_3PO_2, 7.4 %	3	200	122	35	32
"	5	200	127	36	33
"	12[a]	200	130	37	34
"	24[a,b]	170	129	36	36
"	42[a,b]	170	132	37	37
H_3PO_2, 3.7 %	19.5[a]	180	92	26	26
H_3PO_2, 5.5 %	5[a]	200	110	31	29
"	30.5[a]	160	130	37	34
"	66[a]	150	138	39	36
H_3PO_2, 8.8 %	8[a]	200	130	37	34
H_3PO_2, 11.1 %	8[a]	200	133	38	35

[a] Water not removed before reaction. [b] No isopropanol (promoter) added

PIANO analyses

Analysis using a standard refinery "PIANO" method (for paraffins/isoparaffins/aromatics/naphthenes/olefins) was carried out at the BP Carson refinery by Eugene Zaluzec, on the organic products resulting from both a control reaction (no additive) and one containing H_3PO_2. The results for a selected group of individual compounds and for the aggregated classes of compounds are shown in Table

S2. It should be noted that the latter will not be completely accurate, as some of the peak assignments, especially minor peaks, may be open to question (we have verified the major peak assignments by comparison to our GC studies with authentic standards), but it should be a good approximation. It is clear that the addition of the phosphorus compound substantially increases (branched) alkanes relative to olefins, both individually and collectively, and decreases arenes as well.

Table S2. PIANO analytical results for organic liquid fractions

Compound or class	Wt. % in control	Wt. % with H_3PO_2
2-methylbutane	2.9	5.8
2-methylbut-2-ene	1.5	0.6
2,3-dimethylbutane	1.8	3.0
2,3-dimethylbut-2-ene	0.9	0.3
triptane	24.9	40.0
triptene	5.6	1.5
hexamethylbenzene	3.4	1.3
methyl iodide	1.4	13.7
n-alkanes	1.3	0.7
branched alkanes	45.0	63.0
olefins	14.2	4.9
arenes	10.7	4.9
naphthenes	5.2	2.0

Reactions of olefins with H_3PO_2

A solution of equimolar triptene and H_3PO_2 in methanol was heated at 160° for 12 h. ^{13}C NMR spectroscopy showed a number of new peaks, but no triptane. The ^{31}P spectrum (Figure S1) shows, *inter alia*, a signal centered at δ 37.8 consisting of a doublet ($^1J_{PH}$ = 537 Hz) of complex multiplets ($^2J_{PH} \approx 15$ Hz). This is consistent with the structure that would be obtained by adding the P-H bond to triptene, $HP(O)(OH)(CH_2CH(Me)Bu^t)$; the chiral center renders the methylene protons non-equivalent. Similar parameters have

been observed for a variety of HP(O)(OX)(CH_2R) derivatives.[ii] While addition of hypophosphite derivatives to olefins normally require a radical initiator (such as a peroxide, or Et_3B/O_2) and temperatures from 25-80°C, it seems reasonable that adventitious initiators could suffice for the small degree of reaction observed here at a much higher temperature.

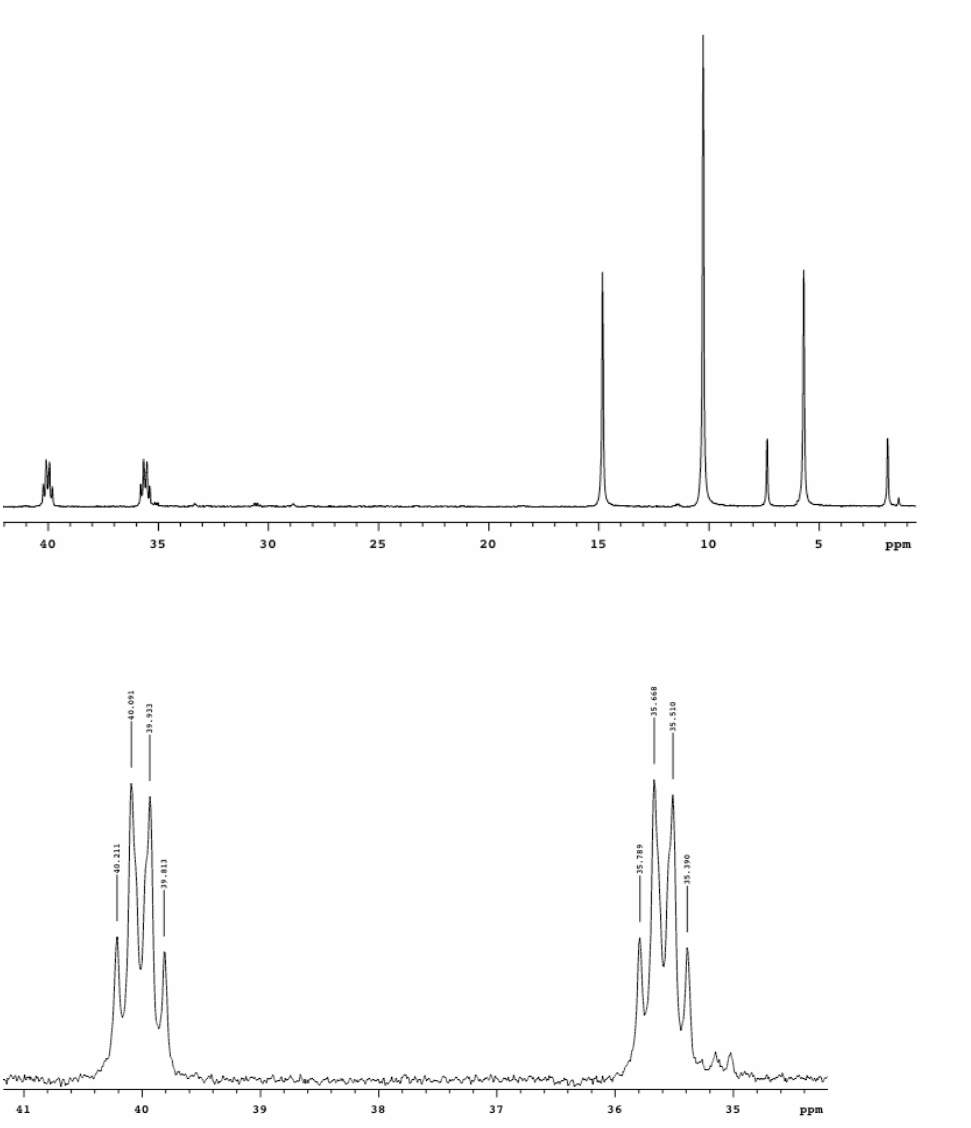

Figure S1. Top: ^{31}P spectrum of reaction mixture after heating triptene and hypophosphorous acid in methanol. Bottom: Expansion of downfield signal.

In contrast, when a solution of equimolar triptene and H_3PO_2 containing 0.5 equivalents of *p*-toluenesulfonic acid in tetraglyme was heated at 160° for 3 h, GC analysis showed significant hydrogenation of olefin — the ratio of triptane to triptene was about 1:4 (other species were also present) — and the ^{31}P spectrum showed the presence of H_3PO_3. 2,3-dimethylbut-2-ene behaved quite similarly, but hex-1-ene gave no hexane at all, only isomerization to hex-2-ene and hex-3-ene. We have not attempted to optimize these reactions in any way.

H_3PO_2 plus a catalytic amount of I_2 has been found to reduce diaryl alkenes such as stilbene in refluxing acetic acid; the proposed mechanism involves addition of HI (obtained by reduction of I_2 by H_3PO_2) to the double bond followed by C-I bond cleavage, so that H_3PO_2 serves only to continually regenerate HI.[iii] One might conceive of a related process operating in our system — some HI should be present in the acidic methanolic ZnI_2 solution. However, the reductions described immediately above involve H_3PO_2 but no HI, and substitution of HI for toluenesulfonic acid does not give any increase in hydrogenation rate, so it does not appear that HI does participate here. Conversely, the idea that the stilbene reduction might involve direct reaction of a carbocationic intermediate with a P-H bond, as in our proposed mechanism, appears to be excluded by the fact that HI (or I_2) is a required co-reagent.[3] Most likely the two reactions involve completely separate mechanisms; the radical path implicated for the earlier work would be expected to be much more favorable for the aryl alkenes studied there than for the aliphatic alkenes intermediate in triptane formation.

References

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iii. A. J. Fry, M. Allukian and A. D. Williams, *Tetrahedron*, 2002, **58**, 4411-4415.