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# Sequential Catalytic Condensation–Hydrogenation of Ketones

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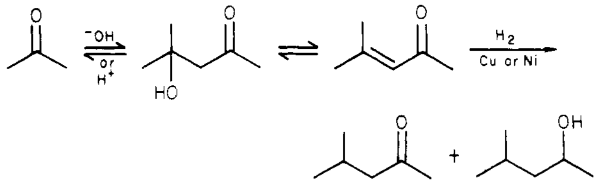
Aldol condensation and hydrogenation of the condensation product have been carried out simultaneously by using an immobilized acid catalyst (Nafion-H or Amberlite IR-120) and Pd/C under hydrogen. Acetone was converted to 4-methyl-2-pentanone in a one-pot multistep process at 60–140 °C and 20–300 psi of hydrogen. The yields of 4-methyl-2-pentanone were higher than the equilibrium-limited yields of mesityl oxide obtained in the absence of the hydrogenation catalyst, demonstrating that the equilibrium to mesityl oxide was shifted by mesityl oxide hydrogenation to 4-methyl-2-pentanone. 2-Propanol was the major byproduct because acetone hydrogenation was competitive with condensation. High-boiling products, found in aldol condensations, were not formed in the condensation–hydrogenation process. Use of $RhCl(PPh_3)_3$ or its polymer-bound analogue as the hydrogenation catalyst reduced the amount of acetone hydrogenation but slowed the condensation–hydrogenation reactions. The crossed aldol condensation–hydrogenation of benzaldehyde and acetone gave 4-phenyl-2-butanone with Nafion-H and Pd/C. The major side reaction was the competitive hydrogenation of benzaldehyde to toluene. The intramolecular condensation of 2,5-hexanedione gave mainly 2,5-dimethylfuran while the one-pot condensation–hydrogenation reaction gave 2,5-dimethyltetrahydrofuran.

The aldol condensation of ketones is the basis for several industrial processes such as the synthesis of 1-butanol from acetaldehyde via condensation, dehydration, and hydrogenation.[1] The synthesis of methyl isobutyl ketone and 4-methyl-2-pentanol from acetone is another example (eq 1). Aldol condensation of acetone, followed by dehydration, gives mesityl oxide. Then mesityl oxide is hydrogenated to methyl isobutyl ketone and further to 4-methyl-2-pentanol at 150–200 °C over Cu or Ni catalysts.[1] Recently, a single-step process has been developed which uses both zirconium phosphate to catalyze the condensation–dehydration and palladium to catalyze hydrogenation.[1] Both processes occur simultaneously with high selectivity in an exothermic reaction ($\Delta H = -28$ kcal/mol). Hydrogenation continuously removes mesityl oxide from the equilibrium with acetone, allowing a higher methyl isobutyl ketone yield per pass.



(1)

Our interest in polymer-bound catalysts[2–5] and multistep sequential catalytic synthesis[6–8] has, independently, led to the exploration of a similar, single-pot, multistep, catalytic synthesis of methyl isobutyl ketone. In this paper we present the results of aldol condensations catalyzed by polymer-bound acid catalysts (Amberlite IR-120[9] and Nafion-H[10]) carried out in the presence of hydrogen and a hydrogenation catalyst (Pd/C or $RhCl(PPh_3)_3$). Thus, simultaneous condensation–dehydration–hydrogenation was effected in one step in the conversions of (a) acetone to methyl isobutyl ketone, (b) benzaldehyde and acetone to 4-phenyl-2-butanone, and (c) 2,5-hexanedione to 2,5-dimethyltetrahydrofuran. Since the aldol condensation yields are limited by equilibrium considerations, the multistep sequential process is one way to raise yields by removing the condensation product from that equilibrium. The use of heterogenized catalysts would permit the development of continuous processes.

Table I. Effect of Quantity of Catalyst on the Condensation of Acetone[a]

| quantity of catalyst, % of acetone | yield of mesityl oxide, % | |
|---|---|---|
| | Nafion-H | Amberlite IR-120 |
| 0.1 | 4.8 | 3.2 |
| 0.2 | 7.4 | 5.4 |
| 0.5 | 10.6 | 9.3 |
| 2.0 | 19.7 | 19.8 |

[a] Acetone (27.0 mmol), 60 °C, 24 h.

Table II. Effect of Temperature and Time on the Condensation of Acetone[a]

| temp, °C | *t*, h | yield of mesityl oxide, % | |
|---|---|---|---|
| | | Nafion-H | Amberlite IR-120 |
| 60 | 1 | 10.5 | 4.6 |
| | 6 | 18.1 | 10.8 |
| | 12 | 19.0 | 16.4 |
| | 24 | 19.7 | 19.8 |
| 100 | 1 | 10.7 | 5.5 |
| | 6 | 18.4 | 14.0 |
| | 12 | 19.3 | 18.8 |
| | 24 | 19.8 | 19.8 |
| 140 | 1 | 10.9 | 9.7 |
| | 6 | 18.7 | 18.2 |
| | 12 | 18.7 | 18.3 |
| | 24 | 18.8 | 18.3 |

[a] Acetone (27.0 mmol), Ⓟ-$SO_3H$ (0.54 mmol).

## Results

Aldol condensations were catalyzed by both Nafion-H and Amberlite IR-120 solid-phase acid catalysts. Nafion-H is a perfluorinated aliphatic ether polymer with pendant sulfonic acid groups ($CF_2SO_3H$) of high thermal (to 205 °C) and hydrolytic stability. The $CF_2SO_3H$ groups are strongly acidic ("superacids"[12–14]). We employed granular

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(1) Weissermel, K.; Arpe, H. J. "Industrial Organic Chemistry"; Verlag Chemie: Weinheim and New York, 1978.

(2) Pittman, C. U., Jr.; Honnick, W. D.; Yang, J. J. *J. Org. Chem.* 1980, *45*, 684.

(3) Pittman, C. U., Jr.; Hanes, R. M. *J. Am. Chem. Soc.* 1976, *98*, 5402.

(4) Pittman, C. U., Jr.; Ng, Q.; Honnick, W.; Hanes, R. *Colloq. Int. CNRS* 1978, *No. 281*, 49–94.

(5) Pittman, C. U., Jr.; Hirao, A. *J. Org. Chem.* 1978, *43*, 640.

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(7) Pittman, C. U., Jr.; Smith, L. R. *J. Am. Chem. Soc.* 1975, *97*, 1749.

(8) Pittman, C. U., Jr.; Smith, L. R. In "Organotransition-Metal Chemistry"; Ishii, Y., Tsutsui, M., Eds.; Plenum: New York, 1975.

(9) Amberlite is a registered trademark of the Rohm and Haas Co.

(10) Nafion is a registered trademark of Du Pont de Nemours Co. Nafion-H is the free-acid form of the resin.

0022-3263/80/1945-5048$01.00/0

Table III. Aldol Condensation/Hydrogenation of Acetone Catalyzed by Ⓟ-SO$_3$H and Pd/C[a]

| | | | product yields, % | | | |
|---|---|---|---|---|---|---|
| | | | Nafion-H | | Amberlite IR-120 | |
| $P_{H_2}$, psi | temp, °C | $t$, h | 4-methyl-2-pentanone | 2-propanol | 4-methyl-2-pentanone | 2-propanol |
| 20 | 60 | 6 | 15 | 1 | 11 | 0.5 |
| | | 12 | 21 | 9 | 21 | 5 |
| | | 24 | 21 | 20 | 21 | 15 |
| 20 | 100 | 6 | 20 | 4 | 15 | 1 |
| | | 12 | 28 | 19 | 25 | 14 |
| | | 24 | 29 | 31 | 25 | 34 |
| 50 | 100 | 6 | 30 | 12 | 25 | 18 |
| | | 12 | 47 | 31 | 40 | 31 |
| | | 24 | 48 | 37 | 40 | 42 |
| 100 | 100 | 6 | 28 | 22 | 26 | 22 |
| | | 12 | 35 | 37 | 31 | 42 |
| | | 24 | 35 | 45 | 31 | 47 |
| 100 | 140 | 24 | 3 | 45 | 28 | 48 |

[a] Acetone (27.0 mmol), Ⓟ-SO$_3$H (0.54 mmol), Pd (0.054 mmol).

Table IV. Product Distribution as a Function of Time in the Aldol Condensation-Hydrogenation of Acetone[a]

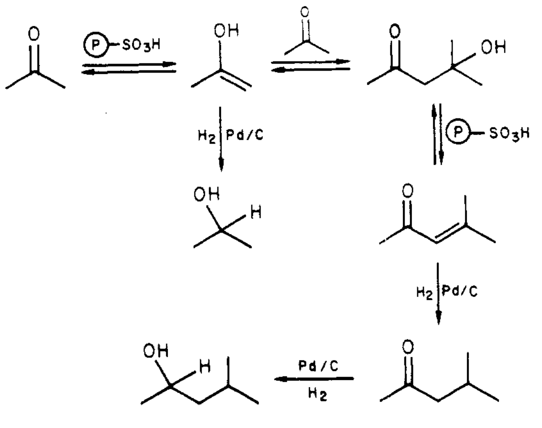
| | | % yield | | | | | | |
|---|---|---|---|---|---|---|---|---|
| catalyst | $t$, h | acetone | 2-propanol | mesityl oxide | 4-methyl-2-pentanone | 4-methyl-2-pentanol | others[b] | selectivity,[c] % |
| Nafion-H and Pd/C | 3 | 72 | 3 | 3 | 18 | 2 | 2 | 70 |
| | 6 | 49 | 12 | 4 | 30 | 3 | 2 | 69 |
| | 12 | 10 | 31 | 4 | 47 | 3 | 4 | 66 |
| | 24 | 4 | 37 | 3 | 48 | 3 | 4 | 64 |
| Amberlite IR-120 and Pd/C | 3 | 73 | 7 | 3 | 15 | 0.3 | 2 | 67 |
| | 6 | 51 | 18 | 3 | 25 | 0.5 | 2 | 65 |
| | 12 | 21 | 31 | 4 | 40 | 0.8 | 4 | 64 |
| | 24 | 10 | 42 | 3 | 40 | 1.2 | 5 | 60 |

[a] Acetone (27.0 mmol), Ⓟ-SO$_3$H (0.54 mmol), Pd (0.054 mmol), $H_2$ (50 psi), 100 °C. [b] These are products boiling lower than acetone and are presumed to be a mixture of propene and propane. No high-boiling products were observed. [c] Selectivity to 4-methyl-2-pentanone based on acetone consumed.

samples with titration-determined equivalent weights of 1100 and 1200 and 30–60-mesh sizes. It has been shown that Nafion-H is a good catalyst for alkylations,[11,12] methylations,[13] hydration,[14] acylation,[14] isomerizations,[15,16] disproportionations,[17] and other[18,19] reactions. Although Nafion-H has not previously been reported to be a catalyst for aldol condensations, Amberlite IR-120, a strongly acidic sulfonated polystyrene cation-exchange resin of medium porosity, has been used in this fashion.[20] Amberlite IR-120 granules of 20–50 mesh, having a 5.0-mequiv/g exchange capacity computed on an anhydrous basis, were employed in this study.

**Aldol Condensation–Hydrogenation of Acetone.** The conversion of neat acetone to mesityl oxide was catalyzed at 60 °C by either Nafion-H or Amberlite IR-120. As the quantity of catalyst was increased, the rate increased. The yield of mesityl oxide was equilibrium limited to ~20% (see Tables I and II) at 60, 100, and 140 °C. However, when Pd/C was used in addition to the resin acid and the reaction was pressurized to 20–100 psi with hydrogen, 4-methyl-2-pentanone was obtained, often in yields higher than 20%. For example, the yield of 4-methyl-2-pentanone, after 24 h at 50 psi of $H_2$ and 100 °C with Nafion-H and Pd/C, was 48% vs. the 20% mesityl oxide obtained under equivalent conditions without hydrogen. Thus, the dual catalyst system increased the yield of condensation product by shifting the acetone/mesityl oxide equilibrium via hydrogenation of mesityl oxide. Unfortunately, yields of 4-methyl-2-pentanone greater than 50% were not routinely achieved because the hydrogenation of acetone to 2-propanol was a major competing reaction. For example, at 50 psi of $H_2$ and 100 °C with Nafion-H and Pd/C (where 48% 4-methyl-2-pentanone was obtained), the yield of 2-propanol was 37%. Hydrogenation of acetone was a serious competitor with condensation–hydrogenation at all temperatures (from 60 to 140 °C) and pressures (from 20 to 100 psi) studied whether Nafion-H

Scheme I



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(13) Kaspi, J.; Olah, G. A. *J. Org. Chem.* **1978**, *43*, 3142, 3147.
(14) Olah, G. A.; Meider, D. *Synthesis* **1978**, 671, 672.
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(16) Olah, G. A.; Kaspi, J. *Nouv. J. Chim.* **1978**, *2*, 581.
(17) Olah, G. A.; Kaspi, J. *Nouv. J. Chim.* **1978**, *2*, 585.
(18) Olah, G. A.; Meider, D. *Synthesis* **1979**, 358.
(19) Olah, G. A.; Meider, D. *Nouv. J. Chim.* **1979**, *3*, 269, 275.
(20) Durr, G. *C. R. Hebd. Seances Acad. Sci.* **1953**, *236*, 1571.

Table V. Adol Condensation–Hydrogenation of Acetone Catalyzed by Nafion-H and $(PPh_3)_3RhCl$[a]

| | | % yield | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $P_{H_2}$, psi | *t*, h | acetone | 2-propanol | mesityl oxide | 4-methyl-2-pentanone | high boilers | 4-methyl-2-pentanol | selectivity,[b] % |
| 50 | 3 | 91 | | 7 | | 1 | | |
| | 6 | 77 | | 5 | 10 | 4 | | 43 |
| | 12 | 69 | 0.3 | 3 | 19 | 4 | 0.7 | 60 |
| | 24 | 52 | 3 | 1 | 36 | 4 | 1.5 | 74 |
| 100 | 3 | 93 | | 2 | 2 | 2 | | 36 |
| | 6 | 69 | 0.5 | 3 | 19 | 6 | | 61 |
| | 12 | 62 | 0.8 | 2 | 26 | 6 | 0.6 | 69 |
| | 24 | 33 | 3.0 | 1 | 47 | 12 | 1.4 | 70 |
| 300 | 3 | 75 | 0.5 | 2 | 10 | 10 | 0.7 | 42 |
| | 6 | 55 | 2 | 2 | 21 | 15 | 2.5 | 46 |
| | 12 | 40 | 4 | 2 | 31 | 17 | 3.0 | 52 |
| | 24 | 20 | 6 | 2 | 46 | 18 | 4.4 | 57 |
| 100[c] | 3 | 77 | 0.2 | 2.3 | 14 | 6 | 0.7 | 61 |
| | 6 | 61 | 0.7 | 1.9 | 25 | 9 | 2.0 | 65 |
| | 12 | 47 | 2.1 | 1.0 | 29 | 18 | 2.2 | 55 |
| | 24 | 27 | 4.2 | 0.7 | 49 | 27 | 2.6 | 67 |

[a] Acetone (27.0 mmol), Nafion-H (0.54 mmol), $(PPh_3)RhCl$ (0.054 mmol), 100 °C. [b] Molar selectivity (50 4-methyl-2-pentanone) vs. all other products. [c] Resin-bound catalyst $(Ⓟ\text{-}C_6H_4PPh_2)_3RhCl$ was employed (0.21 g of resin, 0.0054 mmol of Rh) as the hydrogenation catalyst.

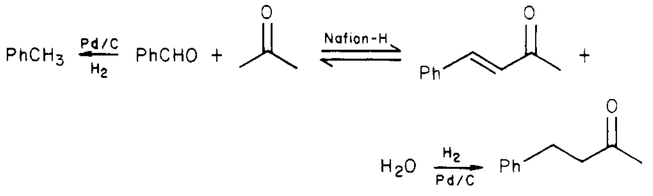
or Amberlite IR-120 was employed. Table III summarizes some representative results.

The hydrogenation of 4-methyl-2-pentanone to 4-methyl-2-pentanol was not a serious competitive pathway. As shown in Table IV, only small amounts of 4-methyl-2-pentanol (0–3%) were formed in reactions carried to high acetone conversions at 50 psi of $H_2$ and 100 °C. The overall path is summarized in Scheme I.

In contrast to acid-catalyzed aldol condensations of acetone, in which high-boiling products are produced ("acetone oil"), the simultaneous condensation–hydrogenations catalyzed by the resin acid–Pd/C systems gave no high-boiling products. This is important because high-boiling tarry byproducts from condensations can settle on catalyst surfaces and decrease catalyst activity. This major advantage of the dual catalyst reaction system results because mesityl oxide is removed from the product mixture before it can enter into further condensations.

To reduce the competitive hydrogenation of acetone, Wilkinson's catalyst, $RhCl(PPh_3)_3$, was used in place of Pd/C to catalyze hydrogenation. This homogeneous catalyst is known to be highly selective for reducing carbon–carbon double bonds.[21] Also it has previously been used as a selective hydrogenation catalyst after it was immobilized on resins.[6,7] The multistep reaction sequence proceeded slower with $RhCl(PPh_3)_3$ (homogeneously) as the hydrogenation catalyst than when Pd/C was used. For example, in the Nafion-H/$RhCl(PPh_3)_3$-catalyzed condensation–hydrogenation, 52% acetone remained unreacted after 24 h (at 50 psi, 100 °C) compared to only 4% when the Nafion-H/Pd/C system was used. The selectivity to 4-methyl-2-pentanone was noticeably better with $RhCl(PPh_3)_3$ because the competitive hydrogenation of acetone is suppressed relative to aldol condensation and mesityl oxide hydrogenation. Even at 300 psi and 100 °C, only 6.3% 2-propanol was observed after 24 h with the Nafion-H/$RhCl(PPh_3)_3$ system. The hydrogenation of 4-methyl-2-pentanone was not a serious side reaction. At 100 °C and 300 psi, the selectivity to 4-methyl-2-pentanone was 52% at 60% conversion and 57% at 80% conversion. At 100 °C and 100 psi the selectivities were 69% and 70% at 38% and 67% conversions, respectively. Representative results are shown in Table V.

Scheme II



The slower rate of the Nafion-H/$RhCl(PPh_3)_3$-catalyzed reactions might be the result of the lower hydrogenation activity of $RhCl(PPh_3)_3$ relative to Pd/C. Slower removal of mesityl oxide from the aldol condensation would result in slower acetone conversion since acetone and mesityl oxide are in equilibrium.

Polymer-bound Wilkinson's catalyst, $(Ⓟ\text{-}C_6H_4PPh_2)_3RhCl$, was prepared from a diphenylphosphinated polystyrene–1% divinylbenzene resin by ligand exchange as shown in eq 2. The polymer-bound

$$Ⓟ\text{—}C_6H_4PPh_2 + RhCl(PPh_3)_3 \xrightarrow[100\ °C,\ N_2]{\text{toluene}} \xrightarrow[\text{with benzene}]{\text{extract}} Ⓟ\text{—}C_6H_4(PPh_2)_3PhCl \quad (2)$$

catalyst had P/Rh ratio of 6, and 26% of the resin's phenyl rings were substituted with $PPh_2$ groups. The resin particle size was 200–400 mesh. Aldol condensation–hydrogenations were run in the rpesence of both Nafion-H and the polymer-bound Wilkinson's catalyst at 100 °C. As can be seen from the single example listed in Table V, the results were similar to those obtained by using $RhCl(PPh_3)_3$ homogeneously, except the use of the anchored rhodium resulted in a moderately faster consumption of acetone. The product distributions were similar. No appreciable leaching of rhodium from the polymer was observed in batch runs carried out at 100 °C.

High-boiling products were obtained in reactions catalyzed by Nafion-H/$RhCl(PPh_3)_3$. This is not surprising since hydrogenation was slower. Therefore, competitive condensations of mesityl oxide could occur.

**Crossed Aldol Condensation–Hydrogenation of Acetone and Benzaldehyde.** The crossed aldol condensation of acetone and benzaldehyde was catalyzed by both Nafion-H and Amberlite IR-120 at 60–150 °C (Scheme II). The rate of 4-phenyl-3-penten-2-one formation was faster with Nafion-H, but the yields were lim-

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[21] House, H. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: New York, 1972; pp 28–34.

Table VI. Effect of Temperature and Time on the Condensation of Acetone and Benzaldehyde Catalyzed by Nafion-H[a]

| temp, °C | *t*, h | yield of benzalacetone, % |
|---|---|---|
| 60 | 1 | 7 |
| | 3 | 13 |
| | 6 | 15 |
| | 12 | 18 |
| | 24 | 25 |
| | 36 | 27 |
| 100 | 1 | 21 |
| | 3 | 26 |
| | 6 | 28 |
| | 12 | 28 |
| | 24 | 28 |
| 150 | 1 | 23 |
| | 3 | 27 |
| | 6 | 27 |
| | 12 | 28 |
| | 24 | 28 |

[a] Acetone (13.5 mmol), benzaldehyde (13.5 mmol), Nafion-H (0.54 mmol).

Table VII. Aldol Condensation–Hydrogenation of Acetone and Benzaldehyde Catalyzed by Nafion-H and Pd/C[a]

| temp, °C | *t*, h | yield[b] | | | | |
|---|---|---|---|---|---|---|
| | | acetone | benzaldehyde | benzylacetone | toluene | others |
| 60 | 1 | 45 | 40 | 11 | 4 | 1 |
| | 3 | 38 | 18 | 23 | 19 | 1 |
| | 6 | 36 | 10 | 27 | 26 | 1 |
| | 12 | 36 | 9 | 27 | 27 | 1 |
| | 24 | 36 | 7 | 27 | 29 | 2 |
| | 36 | 35 | 6 | 27 | 30 | 2 |
| 100 | 1 | 38 | 35 | 24 | 2 | 1 |
| | 3 | 36 | 17 | 27 | 18 | 2 |
| | 6 | 35 | 9 | 29 | 25 | 2 |
| | 12 | 34 | 7 | 29 | 28 | 3 |
| | 24 | 34 | 4 | 29 | 31 | 3 |
| 150 | 1 | 43 | 36 | 14 | 6 | 2 |
| | 3 | 38 | 30 | 21 | 8 | 2 |
| | 6 | 31 | 18 | 36 | 12 | 3 |
| | 12 | 23 | 8 | 50 | 15 | 4 |
| | 24 | 21 | 2 | 51 | 21 | 5 |
| 150[c] | 24 | 32 | 23 | 32 | 11 | 3 |
| 150[d] | 24 | 16 | 0 | 53 | 19 | 7 |
| 150[e] | 24 | 8 | 0 | 41 | 29 | 10 |

[a] Acetone (13.5 mmol), benzaldehyde (13.5 mmol), Nafion-H (0.54 mmol), Pd (0.054 mmol), $H_2$ (50 psi). [b] Yield refers to mole percent of each compound vs. total moles of all the compounds present. [c] $H_2$ pressure was 25 psi. [d] $H_2$ pressure was 100 psi, and 5% 2-propanol was observed. [e] $H_2$ pressure was 300 psi, and 10% 2-propanol was observed.

ited to ~28% as shown in Table VI for reactions catalyzed by Nafion-H. Simultaneous sequential condensation–hydrogenation at 150 °C and 50 psi of $H_2$ with both Nafion-H and Pd/C gave a 51% yield of 4-phenyl-2-pentanone, demonstrating the equilibrium limitation has been removed by hydrogenation of the intermediate 4-phenyl-3-penten-2-one (see Table VII). However, a major side reaction was the hydrogenation of benzaldehyde to toluene. This reaction competes with the condensation–hydrogenation sequence and is especially serious at lower temperatures. At 150 °C reactions were run at 25, 50, 100, and 300 psi of $H_2$. In 24 h the yields of 4-phenyl-2-pentanone were 32, 51, 53, and 41%, respectively, and the yield of toluene increased from 11 to 29%. At 100 and 300 psi of $H_2$, 5 and 10% yields of 2-propanol were observed.

Scheme III

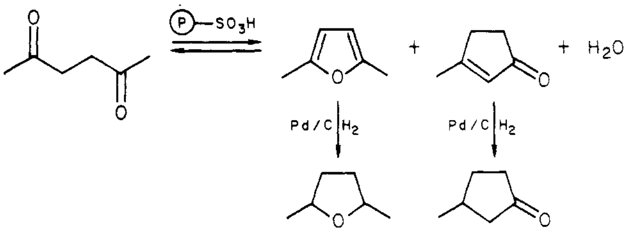

Table VIII. Intramolecular Condensation of 2,5-Hexanedione Catalyzed by Ⓟ-SO$_3$H[a]

| catalyst | temp, °C | yield, % | |
|---|---|---|---|
| | | 2,3-dimethylfuran | 3-methyl-1,2-cyclopentanedione |
| Nafion-H | 100 | 30 | 0 |
| | 150 | 29 | 2 |
| | 180 | 30 | 3 |
| Amberlite IR-120 | 100 | 24 | 0 |
| | 150 | 50 | 1 |
| | 180 | 89 | 0.2 |

[a] 2,5-Hexanedione (27.0 mmol), Ⓟ-SO$_3$H (0.54 mmol), 12 h.

Table IX. Intramolecular Condensation–Hydrogenation of 2,5-Hexanedione Catalyzed by Nafion-H and Pd/C[a]

| temp, °C | % conversion | yield, % | | |
|---|---|---|---|---|
| | | 2,5-dimethyltetrahydrofuran | 3-methylcyclopentanone | high boilers |
| 150 | 75 | 50 | 2 | 21 |
| 180 | 84 | 54 | 3 | 26 |

[a] 2,5-Hexanedione (27.0 mmol), Nafion-H (0.54 mmol), Pd (0.054 mmol), $H_2$ (50 psi), 12 h.

**Intramolecular Condensation–Hydrogenation of 2,5-Hexanedione.** The cyclization of 2,5-hexanedione to 2,5-dimethylfuran and 3-methyl-2-cyclopentenone was selected as a model intramolecular cyclization (Scheme III). The major product, with either Nafion-H or Amberlite IR-120, was 2,5-dimethylfuran. With Nafion-H the total cyclization yields appeared limited to about 30% while higher yields were achieved with Amberlite IR-120 (Table VIII). Cyclization–hydrogenation studies were carried out by using the dual Nafion-H and Pd/C catalyst system (Table IX). Both 2,5-dimethylfuran and 3-methyl-2-cyclopentenone were reduced, giving 2,5-dimethyltetrahydrofuran and 3-methylcyclopentanone, respectively. The saturated cyclic product yields increased to ~50% with the dual catalyst system at 50 psi of $H_2$ and 150–180 °C. The major limitation was the competitive formation of higher boiling products. These products were not identified and were presumed to be products resulting from acid-catalyzed reactions of the furan.

In any multistep process using two catalysts, one must demonstrate that one catalyst does not affect the progress of the reaction catalyzed by the other catalyst. Accordingly, we demonstrated independently that Pd/C did not catalyze the aldol condensation of acetone (110 °C) or the crossed aldol condensation of acetone and benzaldehyde (100 or 120 °C) in the absence of the acid catalyst.

Other approaches to multistep reactions using polymeric *reagents* have been developed by others. Leznoff has studied a large number of reactions where one function of a difunctional compound is first blocked by reaction onto a polymer support.[22] The unblocked function is then converted to a desired function followed by subsequent release (and regeneration) of the first group from the polymer in sequential steps. However, each step is conducted stoichiometrically and independently. Another ingeneous use of stoichiometric reactions conducted sequentially and using polymer supports is the "wolf and lamb" reaction concept of Patchornik et al.[23] In this approach, two different reagents are anchored to polymers, and a reagent acts as a soluble "messenger" between the solid phases. A reagent, such as acetophenone, can be converted to its enolate anion by polymeric tritytllithium, and this enolate may then react with a polymer-bound ester in a typical Claison condensation to generate the enolate of a $\beta$-diketone in a single pot. By cascading this product into a second pot containing polymer-bound hydrazine, for example, diazoles can be produced. However, these reactions are not catalytic. Therefore, the sequential approach described in this paper is fundamentally different.

### Experimental Section

**Aldol Condensation of Ketones.** In a typical preparation, acetone (2.0 mL, 27.1 mmol) and Nafion-H (0.6504 g, 0.542 mmol) were charged to a nitrogen-purged Fischer-Porter aerosol compatibility tube. The tube was sealed with a head containing a pressure gauge. The tube was warmed to the desired temperature and stirred for the specified reaction time. Upon completion, the tube was cooled to room temperature. Products were analyzed on a Hewlett-Pachard Model 5712A gas chromatograph using a $^1/_8$ in. × 6 ft copper column packed with 15% Carbowax 20M on Chromosorb W support [temperature program: from 60 °C (2 min) at 8 °C/min to 100 °C]. Each product was identified by addition of an authentic sample to the reaction solution, and the mixture was analyzed with three different temperature programs. The product was assigned only when the authentic samples gave a single peak with the experimental sample peak at the three different temperature programs used. Quantitative GLC data were obtained via electronic integration with a Hewlett-Packard Model 3380A reporting integrator. Area-normalization (with response-factor correction) calibration techniques were used to determine yields and product distributions. The temperature program for crossed condensation of benzaldehyde/acetone was from 150 °C (2 min) at 8 °C/min to 200 °C. Isothermal (150 °C) conditions were employed for the 2,5-hexanedione system.

**Aldol Condensation–Hydrogenation of Ketones.** In a typical preparation, acetone (5.0 mL, 67.8 mmol), Nafion-H (1.6260 g, 1.355 mmol), and 10% palladium on activated carbon (0.1442 g, 0.1355 mmol) were charged to a nitrogen-purged Fischer-Porter tube. The tube was sealed with a head containing a pressure gauge and a vent inlet valve. The tube was pressurized and vented three times with hydrogen followed by raising of the pressure to that desired with hydrogen. The tube was then placed in an oil bath, preequilibrated at the proper temperature, and stirred for the desired reaction time. The reaction was conducted at constant pressure by connecting the reaction tube to a gas reservoir via stainless-steel tubing and a pressure-control valve. Thus, the pressure to the reaction tube remained constant. The tube was then cooled and the gas was vented. The reaction solution was filtered and analyzed quantitatively by GLC according to the method described above.

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**Registry No.** Acetone, 67-64-1; mesityl oxide, 141-79-7; 4-methyl-2-pentanone, 108-10-1; 2-propanol, 67-63-0; Nafion-H, 63937-00-8; Amberlite IR-120, 9002-23-7; (PPh$_3$)RhCl, 14694-95-2; benzaldehyde, 100-52-7; benzylacetone, 2550-26-7; toluene, 108-88-3; 2,5-hexanedione, 110-13-4; 2,5-dimethylfuran, 625-86-5.

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# Novel Synthetic Reactions Using Bis(2,2,2-trifluoroethoxy)triphenylphosphorane

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Alkoxy- or (acyloxy)(2,2,2-trifluoroethoxy)triphenylphosphoranes which were prepared in situ by the ligand exchange of bis(2,2,2-trifluoroethoxy)triphenylphosphorane with alcohols or carboxylic acids were found to behave as potential alkylating or acylating reagents for the preparation of a variety of esters, amides, sulfides, and ketones.

The chemistry of phosphoranes has been developed mainly for the purpose of studying stereochemistry around the phosphorus atom.[1-4] However, with exception of phosphonium salts and phosphoranes with halogen ligands, no reports have appeared for the utilization of phosphoranes for synthetic reactions, except those for dehydration and/or alkylation leading to epoxides,[5] esters,[6] ethers,[6-9] and heterocycles.[9-14] In fact, reported synthetic routes for phosphoranes so far include only (i) the condensation of trivalent phosphorus compounds with quinones, $\alpha$-diketones or carboxylic acids,[15-17] (ii) the oxidative addition

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