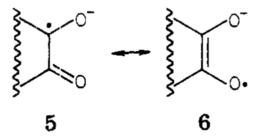
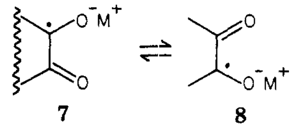
system. The out-of-plane structure would have magnetically nonequivalent α-hydrogen atoms if the cation migration is frozen. In the case of potassium cyclopentane-1,2-semidione we have been unable to detect such magnetic nonequivalence at −100 °C in THF (cooling a mixture of **1** and **2c** causes the percentage of **1** to increase; i.e., ΔH for ion-pair formation is positive).

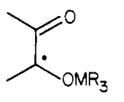
The fact that ion pairing causes a decrease in g and an increase in a^H must mean that the spin density at the carbonyl carbon in the semidione is increased by ion pairing ($g_{C\cdot} = 2.002$, $g_{O\cdot} = 2.015$). In valence-bond terms we conclude that the importance of structure **5** increases upon ion pairing. This suggests that the ion pairs may be better represented as fluctional structures, e.g., **7** and **8**, rather than as rigid chelate structures. In fact α-diones react with trisubstituted silicon, tin, germanium, and lead radicals to form covalent **9** in which the metal atom rapidly migrates between the oxygen atoms.[10]



5 **6**



7 **8**



9

Experimental Section

The bis(trimethylsiloxy)cycloalkene precursors to the C_4, C_5, C_6, C_7, and C_9 semidiones were prepared by standard procedures.[11] Potassium dimsylate in Me_2SO was prepared from KH, and standard solutions were stored frozen under nitrogen. The crown ethers (18-crown-6 and 15-crown-5) were obtained from Aldrich Chemical Co., and [2.2.1]- and [2.2.2]cryptands from PCR and E. Merck. The Me_2SO was dried by stirring over CaH_2 followed by fractional distillation at reduced pressure.

The semidiones were prepared by mixing deoxygenated solutions of the bis(trimethylsiloxy)alkene in Me_2SO with a deoxygenated solution of potassium dimsylate in Me_2SO in an inverted H-cell assembly.[12] Dilution experiments were performed by adding the required amount of iodide salt to the base side of the H-cell during degassing. After being mixed, the solutions were diluted by adding measured portions of deoxygenated Me_2SO through a septum.

ESR spectra were measured with a Varian V-4500 spectrometer using flat silica cells in a dual cavity. Splitting constants and g values were measured by using perylene radical cation (H_2SO_4) as a standard with $g = 2.002583 \pm 0.000006$.[13] Field intensities were determined with a modified Alpha Scientific proton NMR gaussmeter and a Hewlett-Packard frequency counter.

Registry No. Cyclobutane-1,2-semidione potassium [2.2.2]cryptand, 72659-21-3; cyclopentane-1,2-semidione potassium [2.2.2]-cryptand, 72659-22-4; cyclohexane-1,2-semidione potassium [2.2.2]-cryptand, 72659-23-5; cycloheptane-1,2-semidione potassium [2.2.2]cryptand, 72659-25-7; cyclononane-1,2-semidione potassium [2.2.2]cryptand, 72659-27-9; biacetyl semidione potassium [2.2.2]-cryptand, 72659-28-0; cesium cyclobutane-1,2-semidione, 72659-29-1; rubidium cyclobutane-1,2-semidione, 72659-30-4; potassium cyclobutane-1,2-semidione, 32587-19-2; cyclopentane-1,2-semidione potassium 18-crown-6, 72658-88-9; cesium cyclopentane-1,2-semidione, 72659-31-5; rubidium cyclopentane-1,2-semidione, 72659-32-6; potassium cyclopentane-1,2-semidione, 32587-21-6; sodium cyclopentane-1,2-semidione, 68058-48-0; lithium cyclopentane-1,2-semidione, 68058-49-1; cyclohexane-1,2-semidione potassium 18-crown-6, 72658-90-3; cesium cyclohexane-1,2-semidione, 72659-33-7; rubidium cyclohexane-1,2-semidione, 72659-34-8; potassium cyclohexane-1,2-semidione, 32587-23-8; potassium cycloheptane-1,2-semidione, 70136-03-7; potassium cyclononane-1,2-semidione, 70136-05-9; biacetyl semidione potassium 18-crown-6, 72658-91-4; potassium biacetyl semidione, 18851-56-4.

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[10] The trialkyltin, -silicon, -germanium, and -lead adducts of biacetyl and benzil have been reported (Cooper, J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1933. Schroeder, B.; Neumann, W. F.; Hillgaertner, H. *Chem. Ber.* **1974**, *107*, 3494). These are probably covalent adducts similar to **7** ⇌ **8** (Coppin, G. N.; Hudson, A.; Jackson, R. A.; Simmons, N. P. C. *J. Organomet. Chem.* **1977**, *131*, 371), although magnetic nonequivalence of the methyl groups in the biacetyl adduct has not been demonstrated. With silyl or germyl adducts the phenyl groups of benzil are nonequivalent.

[11] Rühlmann, K. *Synthesis* **1971**, 236.

[12] Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807.

[13] Segal, B. G.; Kaplan, M.; Fraenkel, G. K. *J. Chem. Phys.* **1965**, *43*, 4191.

Nickel-Catalyzed Michael Additions of β-Dicarbonyls

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Bis(2,4-pentanedionato)nickel(II) is found to be a mild, efficient, and simple to use catalyst for the Michael additions of β-dicarbonyls. Yields are higher than with traditional strongly basic catalysts, unwanted side reactions are reduced, and workup procedures are greatly simplified. The reactions appear to be quite general as β-diketones, β-keto esters, β-keto amides, and β-diesters are all found to react. A rational mechanism which suggests further research is presented.

The conjugate addition or Michael reaction[1] is one of the most important methods in organic synthesis for effecting carbon–carbon bond formation. Traditionally, these reactions are catalyzed by very strong bases such as alkali metal alkoxides. Several undesirable side reactions can be caused by these strongly basic catalysts,[1] including rearrangements, secondary condensations, isomerizations, polymerizations, bis additions, retrogressions, and transesterifications. Recently, phase-transfer catalysis has been utilized to circumvent some of these problems with α,β-unsaturated aldehydes.[2] Since there is considerable

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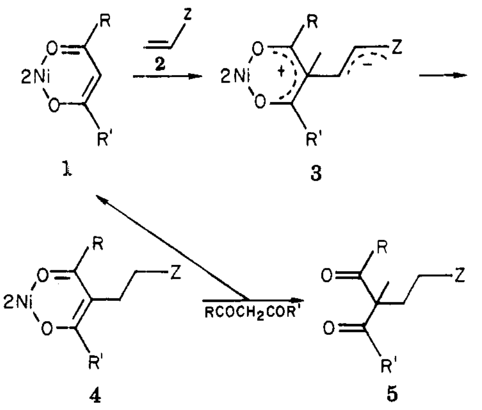
[1] For a comprehensive review of the Michael reaction see: Bergman, E. D.; Ginsberg, D.; Rappo, R. *Org. React.* **1959**, *10*, 179.

0022-3263/80/1945-1246$01.00/0

Scheme I[a]

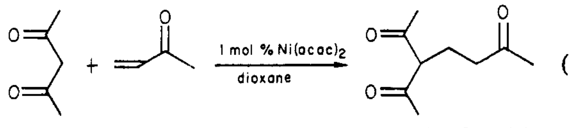


[a] R = alkyl, alkoxy, NR$_2$; R' = alkyl, alkoxy; Z = electron-withdrawing group.

current interest[3] in transition-metal-mediated organic synthesis, we present our findings that bis(2,4-pentanedionato)nickel(II), Ni(acac)$_2$, is a neutral, convenient catalyst for the Michael reaction of β-dicarbonyls.

Discussion

In the course of our studies[4] on the reactions of β-dicarbonyls with various electrophiles catalyzed by Ni(acac)$_2$, we were encouraged by results with the conjugate addition of 2,4-pentanedione to methyl vinyl ketone (eq 1) to explore the general applicability of Ni(acac)$_2$ as a catalyst for Michael additions to β-diketones.

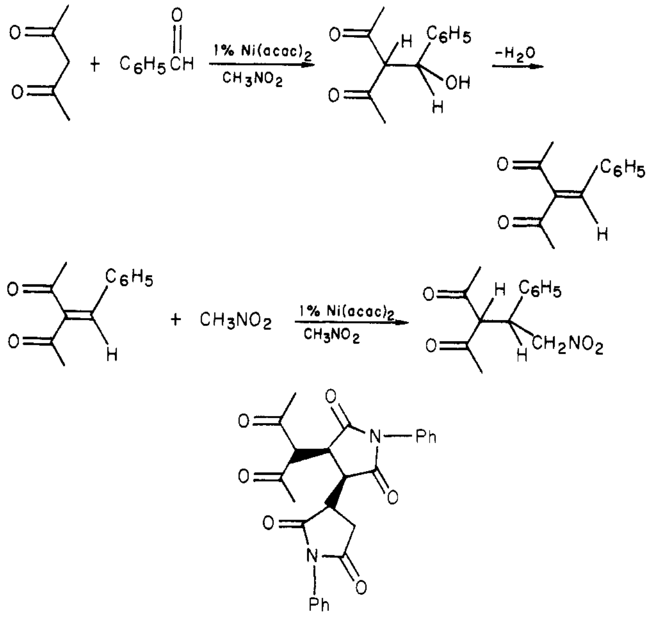


(1)

90% (lit.[5] 45%)

Further studies with 2,4-pentanedione, ethyl acetoacetate, and diethyl malonate as the Michael donors and methyl vinyl ketone, *trans*-dibenzoylethylene, *N*-phenylmaleimide, β-nitrostyrene, ethyl acrylate, 2-vinylpyridine, dimethyl acetylenedicarboxylate, and diethyl azodicarboxylate as representative Michael acceptors indicate that in each case high yields of Michael adducts were easily obtained (see Table I). Where comparisons can be made, the yields with Ni(acac)$_2$ as a catalyst are always as high or higher than those with the traditional strong base catalysts. Ni(acac)$_2$ apparently catalyzes these reactions under *essentially nonequilibrium* conditions, whereas the strongly basic catalysts often impart yield-lowering equilibrium[6] conditions. Ni(acac)$_2$ drives the reaction essentially to completion. As a comparison, sodium ethoxide catalysis[5] of the reactions between β-dicarbonyls and α,β-unsaturated ketones usually leads to substituted cyclohexenones by a secondary cyclization. These same reactions do, however, sometimes produce low yields of the Michael adduct if mild conditions are used.[5]

Scheme II



On a molecular level, we envision the catalysis as proceeding as shown in Scheme I.

Thus the electron-rich methine carbon of a coordinated β-dicarbonyl enolate, **1**, nucleophilically attacks the more positive carbon of a Michael acceptor, **2**. The resonance-stabilized zwitterion **3** thus formed undergoes proton transfer to give coordinated product **4**. Ligand exchange of **4** with excess β-dicarbonyl substrate regenerates the catalyst substrate complex[7] **1** and releases the Michael adduct **5**. We have previously presented convincing evidence for zwitterionic intermediates such as **3** in similar reactions.[4] Moreover, the nickel complexes of compounds **12** and **15** (Table I) have been obtained[4] from stoichiometric reactions of Ni(acac)$_2$ with dimethyl acetylenedicarboxylate and diethyl azodicarboxylate, respectively. These adducts rapidly undergo[4] ligand-exchange reactions with 2,4-pentanedione to produce Ni(acac)$_2$ and liberate compounds **12** and **15**. In addition, these two adducts are effective catalysts for the Michael additions of their respective precursors.

At this point we do not know whether the two minor side products from the reaction of 2,4-pentanedione with *N*-phenylmaleimide (entry 21, Table I) represent trapped zwitterion **3** or if they represent deprotonated initial product which undergoes a second Michael addition with *N*-phenylmaleimide. The former seems the more likely, as product (entry 8, Table I) is also formed in moderate yield (35%) by simply refluxing benzaldehyde, 2,4-pentanedione, and Ni(acac)$_2$ in nitromethane. This reaction most likely proceeds as in Scheme II. Further studies investigating the scope and limitations of this potentially useful synthetic procedure which could circumvent the

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(2) Krychtal, G. V.; Kulganek, V. V.; Kucherov, V. F.; Yanovskaya, L. A. *Synthesis* **1979**, 107.

(3) See, e.g.: Ugo, R., Ed. "Aspects of Homogeneous Catalysis"; D. Reidel Publishing Co.: Holland, 1974; Vol. 2. *Ibid.*, 1977, Vol. 3. Hegedus, L. S. *J. Organomet. Chem.* **1977**, *126*, 151. *Ibid.* **1975**, *103*, 421. Seyferth, D., Ed. "New Applications of Organometallic Reagents in Organic Synthesis"; Elsevier: New York, 1976.

(4) Eckberg, R. P.; Henry, R. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1977**, *16*, 2977. Kenney, J. W.; Nelson, J. H.; Henry, R. A. *J. Chem. Soc., Chem. Commun.* **1973**, 690. Howells, P. N.; Kenney, J. W.; Nelson, J. H.; Henry, R. A. *Inorg. Chem.*, **1976**, *15*, 124. Eckberg, R. P.; Nelson, J. H.; Kenney, J. W.; Howells, P. N.; Henry, R. A. *Ibid.* **1977**, *16*, 3128. Nelson, J. H.; Landen, G. L.; Stevens, B. N. *Synth. React. Inorg. Met.-Org. Chem.* **1979**, *5*, 435. Nelson, J. H.; Howells, P. N.; Landen, G. L.; DeLullo, G. C.; Henry, R. A. First International Symposium on Homogeneous Catalysis, Corpus Christi, TX, Nov 29–Dec 1, 1978. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum: New York, 1979; pp 921–39.

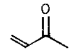
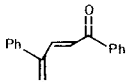
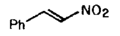
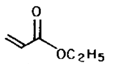
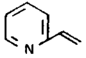
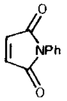
(5) Lacey, R. N. *J. Chem. Soc.* **1960**, 1625 and references therein.

(6) House, H. O. "Modern Synthetic Reactions", 2nd ed; W. A. Benjamin: Menlo Park, CA, 1972; pp 596–600.

(7) The actual catalyst is most likely bis(β-diketonato)nickel(II) formed from Ni(acac)$_2$ in situ by ligand exchange. This has been substantiated in the cases of the ethyl acetoacetate and *N*,*N*-diethylacetoacetamide reactions by electronic spectroscopy studies.[4]

Table I. Addition of Electrophiles to β-Dicarbonyls Catalyzed by 1 mol % of Ni(acac)$_2$

$$R^1COCH_2COR^2 + E \xrightarrow[\text{1 mol \% of Ni(acac)}_2]{\text{solvent}} R^1COCHECOR^2$$

entry[a]	R^1	R^2	E	solvent	t, h	T, °C	% yield	IR (Nujol) ν_{CO}, cm^{-1}	mp or bp (pres), °C
1	CH_3	CH_3		dioxane	19	85	90	1715, 1705	98 (0.2 mm)
2	CH_3	OC_2H_5		none	48	40	95	1740, 1718	127 (0.45 mm)
3	OC_2H_5	OC_2H_5		$CHCl_3$	48	40	90	1760, 1740	107 (0.2 mm)
4*	CH_3	CH_3		diglyme	20	82	96	1721, 1711, 1692, 1677	121-132
5*	CH_3	OC_2H_5		dioxane	48	90	98	1740, 1720, 1680	162-163
6*	OC_2H_5	OC_2H_5		dioxane	48	90	75	1760, 1740, 1680	64-64.5
7*	CH_3	$N(C_2H_5)_2$		CH_2Cl_2	70	25	85	1730, 1675, 1635	116-117
8	CH_3	CH_3		$CHCl_3$	48	35	78	1745, 1720	114.5-116
9	CH_3	OC_2H_5		dioxane	17	90	98	1740, 1720	76
10	OC_2H_5	OC_2H_5		dioxane	17	90	62	1730	64
11*	CH_3	$N(C_2H_5)_2$		$CHCl_3$	48	35	68	1730, 1620	162-163
12*	CH_3	CH_3	$CH_3CO_2C{\equiv}CCO_2CH_3$	CH_2Cl_2	12	20	50	1730, 1630	195-200 (10 mm)
13*	CH_3	OC_2H_5		C_6H_6	72	25	35	1730, 1650	143 (0.9 mm)
14*	OC_2H_5	OC_2H_5		C_6H_6	72	25	~4	1730, 1650	150 (0.85 mm)
15*	CH_3	CH_3	$C_2H_5CO_2N{=}NCO_2C_2H_5$	CH_2Cl_2	1	50	78	1760, 1695	114-116
16*	CH_3	OC_2H_5		CH_2Cl_2	2	25	87	1750, 1700, 1660, 1625	80-81
17*	OC_2H_5	OC_2H_5		CH_2Cl_2	2	25	71	1790, 1768, 1745	105-106
18*	CH_3	$N(C_2H_5)_2$		CH_2Cl_2	17	25	95	1750, 1705, 1650	80
19*	CH_3	CH_3		none	48	160	96	1740, 1718, 1615	150-151 (10 mm)
20	CH_3	CH_3		C_6H_6	12	65	≥45	1730, 1705	120-123 (0.15 mm)
21*	CH_3	CH_3		diglyme	60	140	64	1782, 1708, 1705	oil

[a] For entries with an asterisk, the product of the reaction has not been reported previously. The following entry numbers are followed by comments on that entry. (1) Lacey[5] obtained a 45% yield of 3-acetylheptane-2,6-dione using $NaOCH_3$ as the catalyst. (2) J. Decombe (*C. R. Hebd. Seances Acad. Sci.* **1937**, *205*, 680) obtained a 92% yield of the bis addition product $CH_3COC(CH_2CH_2COCH_3)_2CO_2C_2H_5$ using $NaOC_2H_5$ as the catalyst. (3) H. S. Rhinesmith (*J. Am. Chem. Soc.* **1936**, *58*, 596) obtained an 85% yield of the bis addition product $(CH_2CH_2COCH_3)_2C(CO_2C_2H_5)_2$ using $[C_6H_5CH_2N(CH_3)_3]OH$ as the catalyst. (4) Recrystallized from acetone/petroleum ether. Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 75.30; H, 6.20. (5) Recrystallized from C_2H_5OH. Anal. Calcd for $C_{22}H_{22}O_5$: C, 72.15; H, 6.01. Found: C, 72.30; H, 6.22. (6) Recrystallized from C_2H_5OH/H_2O. Anal. Calcd for $C_{23}H_{24}O_6$: C, 69.72; H, 6.06. Found: C, 70.01; H, 6.25. (7) Recrystallized from petroleum ether. Anal. Calcd for $C_{24}H_{27}NO_4$: C, 73.30; H, 6.87. Found: C, 73.10; H, 6.59. (8) V. V. Perekalin and A. S. Sopova (*Zh. Obshch. Khim.* **1954**, *24*, 513; *Chem. Abstr.* **1955**, *49*, 6180) report a 77% yield with $NaOC_2H_5$ as the catalyst. (9) Perekalin and Sopova (see comment for entry 8) report a 98% yield with $NaOC_2H_5$ as the catalyst. (10) Perekalin and Sopova (see comment for entry 8) report a 51.4% yield with $NaOC_2H_5$ as the catalyst. (11) Recrystallized from $CHCl_3$/hexane. Anal. Calcd for $C_{16}H_{22}N_2O_4$: C, 62.77; H, 7.19. Found: C, 62.91; H, 7.05. (12) Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.54; H, 5.83. Found: C, 54.35; H, 5.53. (13) Anal. Calcd for $C_{12}H_{16}O_7$: C, 52.96; H, 5.88. Found: C, 53.02; H, 5.75. (14) Anal. Calcd for $C_{13}H_{18}O_8$: C, 51.68; H, 5.96. Found: C, 51.45; H, 6.03. (15) Recrystallized from $CHCl_3$/hexane. Anal. Calcd for $C_{11}H_{18}N_2O_6$: C, 48.17; H, 6.62; N, 10.21. Found: C, 48.05; H, 6.62; N, 10.29. (16) Recrystallized from $CHCl_3$/hexane. Anal. Calcd for $C_{12}H_{20}N_2O_7$: C, 47.39; H, 6.58. Found: C, 47.70; H, 6.49. (17) Recrystallized from Et_2O/hexane. Anal. Calcd for $C_{13}H_{22}N_2O_8$: C, 46.73; H, 6.58. Found: C, 46.59; H, 6.72. (18) Recrystallized from $CHCl_3$/hexane. Anal. Calcd for $C_{14}H_{25}N_3O_6$: C, 46.93; H, 8.14. Found: C, 47.05; H, 8.34. (19) E. Bullock, A. W. Johnson, E. Markam, and K. B. Shaw (*J. Chem. Soc.* **1958**, 1430) report a 70% yield with $NaOC_2H_5$ as the catalyst. Similarly, we obtained a 95% yield of the 3-acetyl-5-oxohexanoate from methyl acrylate and 2,4-pentanedione with Ni(acac)$_2$ as catalyst. The physical properties and spectral data agreed with those reported by R. Chong and P. S. Clezy (*Aust. J. Chem.* **1967**, *20*, 123). (20) V. Boekelheide and S. Rothchild (*J. Am. Chem. Soc.* **1949**, *71*, 879) report a 16% yield with $NaOC_2H_5$ as the catalyst. Using Ni(acac)$_2$ as the catalyst and running the reaction for 20 h at reflux with no solvent gave a 20% yield of product plus a 34% yield of 5-(2-pyridyl)-2-pentanone, which was the major product isolated by Boekelheide and Rothchild. (21) Three products were obtained in this reaction. In addition to the monoaddition product (Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.95; H, 5.49. Found: C, 66.03; H, 5.23) which was separated by column chromatography on silica gel with $CHCl_3$ elution, elution with $CH_3OH/CHCl_3$ (5/95) gave a 14% yield of I, mp 199–200 °C. Anal. Calcd for $C_{25}H_{22}N_2O_6$: C, 67.28; H, 4.93. Found: C, 67.51; H, 5.02. The cis isomer was obtained in 4% yield; mp 205–206 °C. Anal. Found: C, 67.19; H, 4.78.

preparation and isolation of nitro olefins are under way. under way. Scheme II seems reasonable since 3-acetyl-4-(2-furyl)-3-buten-2-one[8] is produced in 43.0% yield by refluxing a solution of 2,4-pentanedione and 2-furfuraldehyde in dioxane with 1% Ni(acac)$_2$ for 72 h. Attempts at Ni(acac)$_2$-catalyzed addition of nitroalkanes to 3-acetyl-4-(2-furyl)-3-buten-2-one are in progress.

Since β-keto esters and β-diesters are important classes of compounds for construction of complex molecules, we deemed it important to show whether Ni(acac)$_2$ would also catalyze their Michael additions. Indeed, as Table I shows, this reaction can be extended to the β-keto ester ethyl acetoacetate, the β-keto amide *N,N*-diethylacetoacetamide, and the β-diester diethyl malonate. These reactions then seem to be quite general, and further work to optimize conditions and establish the reaction scope is in progress. Some limitations have been found. For example, dimethyl fumarate, diethyl maleate, and mesityl oxide did not react with any of the four β-dicarbonyls investigated under similar conditions.

To our knowledge, the only other work on transition-metal-catalyzed carbon–carbon bond formation via the Michael reaction is that of Saegusa and co-workers[9] and Trost and co-workers.[10] In contrast to Ni(acac)$_2$, Saegusa's copper(I) salts activate the olefin Michael-acceptor component as do Trost's palladium(II) π-allyls, whereas Ni(acac)$_2$ activates the Michael donor.

In conclusion, Ni(acac)$_2$ is a convenient Michael catalyst (a pressure vessel was needed only to contain the two volatile olefins); it is neutral[11] and gives good to excellent yields. Moreover, the workup conditions necessitate no neutralizations and extractions as is the case with strongly basic catalysts. Often the product crystallizes directly from the reaction mixture or can be distilled therefrom. Consequently, it should provide facile entry into a host of new Michael adducts of potentially high synthetic utility.

Experimental Section

All of the reactions were run in essentially the same manner. The following are exemplary.

Entry 1 (Table I). A dry glass pressure flask is charged with 10 mL (0.10 mol) of 2,4-pentanedione (Aldrich spectrograde), 7.7 g (0.11 mol) of methyl vinyl ketone, 257 mg (1.0 mol %) of Ni(acac)$_2$ (dried in vacuo at 100 °C), and 10 mL of *p*-dioxane (spectrograde, dried over molecular sieves). The sealed flask was immersed in a water bath maintained at 85 °C for 18 h. Evaporation of the *p*-dioxane gave an oily product (17.1 g, 96% yield by ^{1}H NMR analysis) suitable for most subsequent reactions. For a higher purity product, the Ni(acac)$_2$ catalyst is first removed by filtration chromatography (short plug of silica gel, chloroform eluent). Evaporation of solvent and distillation gave 16.1 g of very pale yellow 3-acetylheptane-2,6-dione (90% yield). Conditions for the other reactions are given in Table I.

Entry 20 (Table I). A solution containing 50 g (0.5 mol) of 2,4-pentanedione, 52.5 g (0.5 mol) of 2-vinylpyridine, and 0.5 g of Ni(acac)$_2$ in 50 mL of benzene was refluxed for 12 h. The reaction flask was fitted with a modified Dean–Stark trap and 46 mL of benzene removed. A ^{1}H NMR spectrum of the remaining mixture indicated that the reaction was about 50% complete. The Ni(acac)$_2$ was removed by filtration chromatography (short plug of silica gel, CHCl$_3$ eluent) and the residue distilled under vacuum. After the removal of 15 mL of 2-vinylpyridine at 50–60 °C (15 mm), there was obtained 47 g (45.8%) of pale yellow liquid product, bp 120–123 °C (0.15 mm).

All compounds were characterized by elemental analyses (Table I) (Chemalytics, Inc.), infrared (Table I), ^{1}H NMR (Table II, Supplementary Material), and mass spectroscopy and compared to authentic samples where possible. The purification of reagents and instruments used to obtain spectroscopic data have been described elsewhere.[4]

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Registry No. 1, 29214-57-1; 2, 35490-05-2; 3, 4761-26-6; 4, 72709-58-1; 5, 72725-71-4; (±)-6, 72709-59-2; 7, 72709-60-5; 8, 72709-61-6; 9, 72709-62-7; (±)-10, 71639-13-9; 11, 72709-63-8; (*E*)-12, 72709-64-9; (*E*)-13, 72709-65-0; (*Z*)-13, 72709-66-1; (*E*)-14, 72709-67-2; (*Z*)-14, 72709-68-3; 15, 72709-69-4; 16, 72709-70-7; 17, 72709-71-8; 18, 72709-72-9; 19, 2832-10-2; 20, 72709-73-0; 21, 72709-74-1; I, 72709-75-2; 2,4-pentanedione, 123-54-6; ethyl 3-oxobutanoate, 141-97-9; diethyl propanedioate, 105-53-3; *N,N*-diethyl-3-oxobutanamide, 2235-46-3; 3-oxo-1-butene, 78-94-4; 1,4-diphenyl-2-butene-1,4-dione, 4070-75-1; (2-nitroethenyl)benzene, 102-96-5; dimethyl butynedioate, 762-42-5; diethyl diazenedicarboxylate, 1972-28-7; ethyl acrylate, 140-88-5; 2-ethenylpyridine, 100-69-6; 1-phenyl-1*H*-pyrrole-2,5-dione, 941-69-5; benzaldehyde, 100-52-7; 2-furfuraldehyde, 98-01-1; 3-acetyl-4-(2-furyl)-3-buten-2-one, 4728-04-5; Ni(acac)$_2$, 3264-82-2.

Supplementary Material Available: Table II, the ^{1}H NMR spectral data for the products listed in Table I (4 pages). Ordering information is given on any current masthead page.

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[8] Midorikawa, H. (*Bull. Chem. Soc. Jpn.* **1954**, *27*, 213) reports a 64% yield of 3-acetyl-4-(2-furyl)-3-buten-2-one with piperidine as the catalyst.

[9] Saegusa, T.; Ito, Y.; Tomita, S.; Kinoshita, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 496. Typical yields are 72–86%.

[10] Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407 and succeeding papers. Typical yields are 90–100%.

[11] Since 2,4-pentanedione is only very slightly acidic (pK_a = 9; ref 6, p 494), our nonaqueous conditions are only slightly acidic.