Rhodium(II) Acetate and Nafion-H Catalyzed Decomposition of *N*-Aryldiazoamides. An Efficient Synthesis of 2(3*H*)-Indolinones

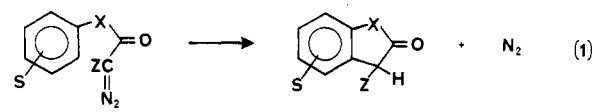
Michael P. Doyle,* Michael S. Shanklin, Hoan Q. Pho, and Surendra N. Mahapatro

Department of Chemistry, Trinity University, San Antonio, Texas 78284

Received August 19, 1987

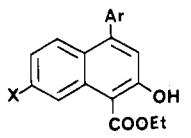
N-Aryldiazoamides undergo facile intramolecular aromatic substitution to form 2(3*H*)-indolinones in high yield when these reactions are performed in the presence of a catalytic amount of rhodium(II) acetate. Diazoacetamides react smoothly at room temperature in dichloromethane, whereas the corresponding less reactive diazoacetoacetamides respond in refluxing benzene. A meta methoxy substituent directs substitution solely to its para position, but a meta methyl substituent offers virtually no selectivity for substitution. *N*-α-Naphthyldiazoacetamide undergoes exclusive intramolecular substitution at the β-position. The perfluororesinsulfonic acid Nafion-H also catalyzes the decomposition of *N*-aryldiazoacetamides, but not *N*-aryldiazoacetoacetamides, and yields of 2-indolinones are even greater than those obtained with rhodium carboxylate catalysis even though higher reaction temperatures are required to initiate decomposition.

Rhodium(II) acetate is widely known to be an effective catalyst for the decomposition of diazo compounds,[1] and an increasing number of chemical syntheses are based on this catalytic methodology. Their success is derived, at least in part, from the generation of electrophilic metal carbenes whose reactivities and selectivities in cyclopropanation reactions,[2] ylide generation and rearrangement,[3] and carbon–hydrogen insertion reactions[4] have been amply demonstrated. Far less attention has been given to catalytic methods for electrophilic aromatic substitution by diazo compounds (eq 1) even though acid-catalyzed

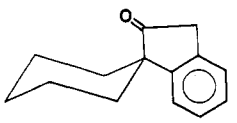


(1)

cyclization reactions of unsaturated diazo carbonyl compounds are well established.[5] Taylor and Davies have shown that rhodium(II) acetate catalyzed decomposition of selected 5-aryl-2-diazo-3-oxopent-4-enoates resulted in the formation of 4-aryl-2-hydroxy-1-naphthoates (1) in high



1



2

yield,[6] and Durst and co-workers have described the preparation of 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxides in low to moderate yields from α-diazo-β-arylmethanesulfonyl esters with the use of the same catalyst.[7] Saba has explored the use of copper(II) hexafluoroacetylacetonate for intramolecular aromatic substitution of representative 1-diazo-3-(aryloxy)-2-propanones to 3-oxo-3,4-dihydro-2*H*-1-benzopyrans,[8] and others have examined substitution into heterocyclic rings with copper[9] or rhodium(II) acetate[10] catalysts. More recently, Nakatani reported the synthesis of 2-indanone **2** in 98% yield by $Rh_2(OAc)_4$-catalyzed cyclization although, in the simplest case, 2-indanone was produced in only 42% yield,[11] and Taber has provided an example of the use of an analogous α-diazo-β-keto ester to achieve the synthesis of 1-carbethoxy-2-indanone in 76% yield.[4] Alkyl substitution at the benzylic carbon of the diazo ketones derived from phenylacetic acids or their corresponding acetoacetonate esters facilitated competitive aliphatic carbon–hydrogen insertion. Only a few examples of acid-promoted intramolecular aromatic substitution of diazo ketones have been reported,[12] and these usually occurred in low yield.

To further explore the general feasibility of catalytic methods for intramolecular aromatic substitution by diazo compounds, we have prepared a series of *N*-aryldiazoamides and investigated their cyclization to 2-indolinones. As expected, rhodium(II) acetate is a highly effective catalyst for this transformation, but common Lewis acids such as $BF_3{\cdot}OEt_2$ are not. However, the perfluorinated ion-exchange polymer Nafion-H[13] (Du Pont Co.) also promotes cyclization, and this resin exhibits substantial promise as the catalytic reagent of choice for electrophilic aromatic substitution reactions involving diazo carbonyl compounds.

Results and Discussion

N-Aryldiazoacetoacetamides **3** were prepared from the corresponding secondary amines and diketene[14] followed by diazo transfer by use of methanesulfonyl azide.[15] Base-promoted deacylation[16] produced the corresponding

(1) (a) Doyle, M. P. *Acc. Chem. Res.* **1986**, *19*, 348. (b) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (c) Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75.
(2) (a) Doyle, M. P.; Loh, K.-L.; DeVries, K. M.; Chinn, M. S. *Tetrahedron Lett.* **1987**, *28*, 833. (b) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petinoit, N.; Teyssie, Ph. *J. Org. Chem.* **1980**, *45*, 695. (c) Callot, H. J.; Metz, F. *Tetrahedron* **1985**, *41*, 4495.
(3) (a) Doyle, M. P.; Griffin, J. H.; Chinn, M. S.; van Leusen, D. *J. Org. Chem.* **1984**, *49*, 1917. (b) Doyle, M. P.; Tamblyn, W. H.; Bagheri, V. *Ibid.* **1981**, *46*, 5094. (c) Pirrung, M. C.; Werner, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 6060. (d) Roskamp, E. J.; Johnson, C. R. *Ibid.* **1986**, *108*, 6062.
(4) Taber, D. F.; Ruckle, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7686.
(5) Burke, S. D.; Grieco, P. A. *Org. React. (N.Y.)* **1979**, *26*, 361.
(6) Taylor, E. C.; Davies, H. M. L. *Tetrahedron Lett.* **1983**, *24*, 5453.
(7) Hrytsak, M.; Etkin, N.; Durst, T. *Tetrahedron Lett.* **1986**, *27*, 5679.
(8) Saba, A. *Synthesis* **1984**, 268.
(9) Jefford, C. W.; Zaslona, A. *Tetrahedron Lett.* **1985**, *26*, 6035.
(10) Storflor, H.; Skramstad, J.; Nordenson, S. *J. Chem. Soc., Chem. Commun.* **1984**, 208.
(11) Nakatani, K. *Tetrahedron Lett.* **1987**, *28*, 165.
(12) (a) Newman, M. S.; Eglinton, G.; Grotta, H. M. *J. Am. Chem. Soc.* **1953**, *75*, 349. (b) Johnson, D. W.; Mander, L. N. *Aust. J. Chem.* **1974**, *27*, 1277.
(13) (a) Waller, F. J. In *Polymeric Reagents and Catalysts*; Fort, W. T., Ed.; ACS Symposium Series No. 308, American Chemical Society: Washington, DC, 1986; p 42. (b) Olah, G. A.; Iyer, P. S.; Prakash, G. K. S. *Synthesis* **1986**, 513.
(14) Clemens, R. J. *Chem. Rev.* **1986**, *86*, 241.
(15) Taber, D. F.; Ruckle, R. E., Jr.; Hennessy, M. J. *J. Org. Chem.* **1986**, *51*, 4077.
(16) Doyle, M. P.; Dorow, R. L.; Terpstra, J. W.; Rodenhouse, R. A. *J. Org. Chem.* **1985**, *50*, 1663.

0022-3263/88/1953-1017$01.50/0

Table I. Synthesis of 2(3*H*)-Indolinones by Rhodium(II) Acetate Catalyzed Decomposition of *N*-Aryldiazoamides

diazo compd	Ar	R[a]	solvent[b]	2(3*H*)-indolinone	Z	yield,[c] %
4a	C_6H_5	Me	CH_2Cl_2	**5**	H	86
4b	C_6H_5	Ben	CH_2Cl_2	**6**	H	87
4c	o-$CH_3C_6H_4$	Et	CH_2Cl_2	**7**	H	86
4d	2,3-$(CH_3)_2C_6H_3$	Et	CH_2Cl_2	**8**	H	98
4e	m-$CH_3C_6H_4$	Et	CH_2Cl_2	**9**	H	85
4f	3,4-$CH_2(O)_2C_6H_3$	Et	CH_2Cl_2	**10**	H	90
4g	α-naphthyl	Et	CH_2Cl_2	**11**	H	98
3a	C_6H_5	Me	C_6H_6	**5**	CH_3CO	86
3b	C_6H_5	Ben	C_6H_6	**6**	CH_3CO	80
3d	2,3-$(CH_3)_2C_6H_3$	Et	C_6H_6	**8**	CH_3CO	84
3e	m-$CH_3C_6H_4$	Et	C_6H_6	**9**	CH_3CO	85
3f	3,4-$CH_2(O)_2C_6H_3$	Et	C_6H_6	**10**	CH_3CO	67
3g	α-naphthyl	Et	C_6H_6	**11**	CH_3CO	70

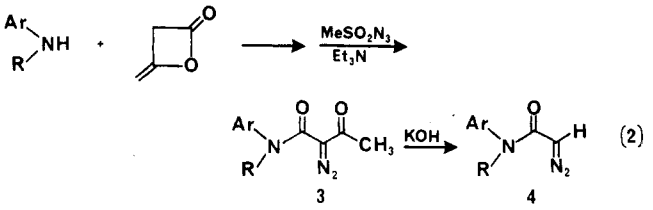
[a] Me = methyl, Ben = benzyl, Et = ethyl. [b] Reactions in dichloromethane were performed at room temperature; those in benzene were performed at reflux temperature. [c] Isolated weight yield of the purified product.

Table II. Selectivity in Aromatic Substitution Reactions

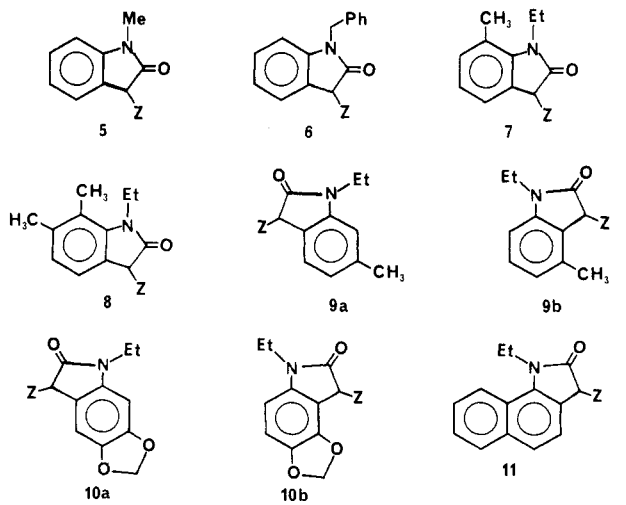
diazo compd	catalyst	temp, °C	solvent	2(3*H*)-indolinone	Z	yield, %	**a/b**
4e	$Rh_2(OAc)_4$	22	CH_2Cl_2	**9**	H	85	1.0
4e	$Rh_2(OOCC_3F_7)_4$	22	CH_2Cl_2	**9**	H	91	1.7
4e	$Rh_2(NHCOCH_3)_4$	22	CH_2Cl_2	**9**	H	72	1.2
4e	Nafion-H	61	$CHCl_3$	**9**	H	92	1.0
4e	Nafion-H	40	CH_2Cl_2	**9**	H	96	1.0
3e	$Rh_2(OAc)_4$	79	C_6H_6	**9**	CH_3CO	85	2.0
3e	Nafion-H	92	$PhCH_3$	**9**	CH_3CO	92	1.1
3e	none[a]	92	$PhCH_3$	**9**	CH_3CO	90	1.1
4f	$Rh_2(OAc)_4$	22	CH_2Cl_2	**10**	H	90	11.3
4f	Nafion-H	61	$CHCl_3$	**10**	H	95	3.8
4f	Nafion-H	40	CH_2Cl_2	**10**	H	98	5.2
3f	$Rh_2(OAc)_4$	79	C_6H_6	**10**	CH_3CO	85	9.0
3f	Nafion-H	92	$PhCH_3$	**10**	CH_3CO	89	4.0
3f	none[a]	92	$PhCH_3$	**10**	CH_3CO	89	4.0
3f	Nafion-H	79	C_6H_6	**10**	CH_3CO	90	4.3
3f	none[a]	79	C_6H_6	**10**	CH_3CO	88	4.2

[a] Reaction times were identical with those for reactions performed in the presence of Nafion-H and monitored throughout the course of the transformation.

N-aryldiazoacetamides (**4**, eq 2) in high yields. These compounds can be stored for long periods of time without noticeable decomposition.

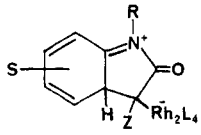


Rhodium(II) acetate catalyzed decomposition of **4** proceeded smoothly in dichloromethane at room temperature to form 2(3*H*)-indolinones (**5**–**11**, Z = H) in exceptionally high yields (Table I). *N*-Methyl, -ethyl, and -benzyl amides were compatible with these transformations. The acetyl derivatives **3** were stable to $Rh_2(OAc)_4$ at room temperature and required refluxing benzene for rapid decomposition to 3-acetyl-2(3*H*)-indolones (**5**–**11**, Z = CH_3CO). Neither the reactants nor the products inhibited the catalytic activity of rhodium(II) acetate, and no special reaction[17] or handling techniques were required. Products from aliphatic carbon–hydrogen insertion, analogous to those reported by Nakatani,[11] were not observed nor were those from intermolecular reactions with benzene.



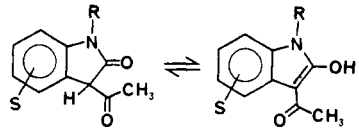
Selectivity in these aromatic substitution processes is indicated by products from reactions of **3** and **4** possessing *m*-tolyl (**e**), 3,4-(methylenedioxy)phenyl (**f**), and 1-naphthyl (**g**) groups. Rhodium(II) acetate catalyzed decomposition of *N*-*m*-tolyldiazoamides resulted in two products, **9a** and **9b**, with **9a**/**9b** equal to 1.0 (Z = H) and 2.0 (Z = CH_3CO), respectively. However, **11** was the sole product from the catalytic decomposition of the *N*-1-naphthyldiazoamides, and **10a** (Z = H) was obtained with exceptional selectivity from the *N*-[3,4-(methylenedioxy)phenyl] derivative. Both **10a** and **10b** were formed from the rhodium acetate catalyzed decomposition of **3f** in a 90:10 ratio. Clearly, the electronic effects of strong electron donating aromatic substituents are important determinants of product selectivity. Changing the catalyst from $Rh_2(OAc)_4$ to $Rh_2(OOCC_3F_7)_4$ or $Rh_2(NHCOCH_3)_4$[2a] produces a change in the **9a**/**9b** ratio (Table II), which is consistent with rhodium catalyst involvement during electrophilic addition to the aromatic ring (**12**).[18]

(17) Doyle, M. P., van Leusen, D.; Tamblyn, W. H. *Synthesis* **1981**, 787.



12

Infrared and NMR spectral data demonstrate that 3-acyl-2-indolinones exist in their tautomeric form, **13b**, except when steric congestion inhibits the required planarity of the heterocyclic ring. Thus, the acetyl derivatives



13a 13b

of **5**, **6**, **8**, **9a**, **10a**, **10b**, and **11** exist preferentially as the 3-acyl-2-hydroxyindole tautomer, whereas **9b** has the 3-acyl-2-indolinone structure. Evidence for **13b** consists of their hydroxyl stretching frequency, the absence of the methine proton at position 3 by ^1H NMR analysis, the nearly constant chemical shift of the acyl methyl group (δ 2.56–2.39), and ^{13}C NMR spectral data (see the Experimental Section), which for **9** adequately define the structural differences between the two tautomeric forms. Whereas **9a** (X = CH_3CO) exhibits low-field resonances at δ 172 and 171 for C-2 and the carbonyl carbon of the 3-acetyl substituent, these same signals are observed at δ 199 and 170, respectively, for **9b** (X = CH_3CO). Furthermore, **9a** (X = CH_3CO) produces only three ^{13}C aliphatic resonances below δ 100 whereas **9b** (X = CH_3CO) shows four signals with the methine C-3 at δ 61. Relief of steric congestion between the 3-acetyl substituent and the 4-methyl substituent in **9b** is the obvious cause of this tautomeric reversal. Similar influences are not observed for 2-indolinones having a 7-methyl substituent or by **10b** in which an oxygen atom is substituted at the 4-position.

The use of $BF_3{\cdot}OEt_2$ to promote intramolecular electrophilic addition was also examined, but this Lewis acid was considerably less effective than $Rh_2(OAc)_4$. Nearly 2.0 molar equiv of $BF_3{\cdot}OEt_2$ was required for complete decomposition of the diazo compound, and mixtures of products often resulted even when reactions were performed at or below 0 °C. Crude **9** (Z = H) was obtained in 70% yield as a mixture of isomers (**9a**/**9b** = 4.8), but **11** (Z = H) was isolated in only 20% yield following purification.

Nafion-H proved to be an exceptionally suitable alternative to $Rh_2(OAc)_4$ for intramolecular aromatic substitution of diazoacetamides **4**. Although these reactions were slow at room temperature, they proceeded rapidly and smoothly in refluxing chloroform with the use of catalytic amounts of the acid resin. Product yields were comparable or superior to those obtained with $Rh_2(OAc)_4$ catalysis (Table III), but isolation of the 2(3*H*)-indolinone products was simpler.

The catalytic nature of Nafion-H in these reactions was demonstrated by comparative studies of diazoacetamide decomposition with and without added Nafion-H. For the decomposition of **4f** in the presence of 100 mg of Nafion-H per mmol of the diazoacetamide at the temperature of refluxing dichloromethane, 58% of **10a,b** was formed after 14 h, and 42% of the reactant remained. In the absence of Nafion-H, only 4% of **10a,b** was produced after 14 h, and only unreacted starting material remained. By 35 h, 91% of **10a,b** had formed in the Nafion-H-promoted reaction, but only 13% of **10a,b** was produced in the uncatalyzed decomposition, the residual amount being due solely to unreacted **4f**. At 47 h, no trace of the reactant remained in the Nafion-H-catalyzed reaction, but 83% of **4f** was left from the uncatalyzed decomposition. Thus, the Nafion-H-catalyzed decomposition of **4f** was more than 15 times faster than the uncatalyzed decomposition. Similar results were obtained with **4e** in refluxing dichloromethane, but decomposition occurred over a longer time period. Decomposition rates were faster in refluxing chloroform for reactions performed in the presence and absence of the acid resin, but the catalytic activity of Nafion-H was evident even under these conditions.

Diazoacetoacetamides **3**, which required higher temperatures in reactions catalyzed by $Rh_2(OAc)_4$ than did diazoacetamides **4**, were stable to Nafion-H in refluxing chloroform but underwent intramolecular substitution within 6 h at 92 °C in toluene. However, uncatalyzed decomposition also occurred at this temperature and at a comparable rate. Nafion-H appears to marginally influence the rate for decomposition of **3**. This may be a steric phenomenon whereby **3** are prevented access to the protonic region of the resin that is immersed in a fluorocarbon backbone[13a] whereas the structurally less demanding diazoacetamides **4** are not. However, the relative stability of **3** toward electrophilic addition may also account for these observations. In any case, **4** exhibits significantly greater reactivity toward electrophilic reactions than does **3**.

The selectivities for formation of **9a** and **10a** in Nafion-H-catalyzed decompositions of the corresponding diazoamides were generally less than those achieved with rhodium(II) catalysts, but they were the same as those observed from uncatalyzed decompositions (Table II), even though precautions were taken to ensure that the glassware and solvents did not contain traces of acid. The reaction temperature has little effect on selectivity.

Nafion-H is being employed as an effective catalyst for a growing list of electrophilic reactions,[13] but this is the first example of its use to catalyze the decomposition of diazo compounds. The ease with which 2(3*H*)-indolinones are formed in high yield suggests that Nafion-H is the catalyst of choice for electrophilic aromatic substitution reactions of *N*-aryldiazoacetamides. However, rhodium carboxylates offer greater selectivity in those cases where two indolinone products can be formed.

Experimental Section

General Methods. ^1H NMR spectra were obtained on either a Varian VXR-300 or EM-360L spectrometer; chemical shifts are reported in δ units with tetramethylsilane as the internal standard. Infrared spectra were recorded on an IBM IR/32 FT spectrometer, and mass spectra were obtained with the Hewlett-Packard 5995C GC/MS system operated at 70 eV. Analytical gas chromatographic analyses were performed on a Hewlett-Packard 5890A capillary GC with use of either or both SP-2330 or methylsilicone columns. Elemental analyses were pefformed by Texas Analytical Laboratories, Inc. Rhodium(II) acetate was prepared from rhodium trichloride;[19] rhodium(II) perfluorobutyrate[20] and rhodium(II) acetamide[21] were synthesized by acetate displacement from stock rhodium(II) acetate according to established procedures and

(18) Alternative reaction intermediates such as norcaradienes have been considered, but they involve the introduction of considerable ring strain. Intermediate **12** offers the most direct explanation for reactivity/selectivity observed in this transformation.

(19) Rampel, G. A.; Legzdins, P.; Smith, H.; Wilkinson, G. *Inorg. Synth.* **1972**, *13*, 90.

(20) Drago, R. S.; Long, F. R.; Cosmano, R. *Inorg. Chem.* **1982**, *21*, 2196.

(21) Ahsan, M. Q.; Bernal, I.; Bear, J. L. *Inorg. Chem.* **1986**, *25*, 260. The composition of rhodium acetamide was greater than 95% $Rh_2(NHCOCH_3)_4$ after chromatography according to ^1H NMR analysis (single absorption at δ 2.10 in CD_3CN).

Table III. Synthesis of 2(3*H*)-Indolinones by Nafion-H Catalyzed Decomposition of *N*-Aryldiazoamides

diazo compd	Ar	R[a]	solvent[b]	2(3*H*)-indolinone	Z	yield,[c] %
4b	C_6H_5	Ben	$CHCl_3$	6	H	90
4d	2,3-$(CH_3)_2C_6H_3$	Et	$CHCl_3$	8	H	97
4e	*m*-$CH_3C_6H_4$	Et	$CHCl_3$	9	H	92
4f	3,4-$CH_2(O)_2C_6H_3$	Et	$CHCl_3$	10	H	95
4g	α-naphthyl	Et	$CHCl_3$	11	H	96
3a	C_6H_5	Me	$PhCH_3$	5	CH_3CO	92
3e	*m*-$CH_3C_6H_4$	Et	$PhCH_3$	9	CH_3CO	90
3f	3,4-$CH_2(O)_2C_6H_3$	Et	$PhCH_3$	10	CH_3CO	89
3g	α-naphthyl	Et	$PhCH_3$	11	CH_3CO	90

[a] Me = methyl, Ben = benzyl, Et = ethyl. [b] Reactions in chloroform were performed at reflux; those in toluene were performed at 92 °C. [c] Isolated weight yield of the purified product.

purified by subsequent and sequential soxhlet extractions with dichloromethane and methanol. Nafion-H was obtained commercially and ordinarily used without prior treatment, but reactivation of this acid resin was achieved by standard procedures.[13] Methanesulfonyl azide was prepared from methanesulfonyl chloride and sodium azide.[22] Solvents were dried and distilled prior to use.

Synthesis of 2-Diazo-3-oxobutanamides (3). General Procedure. Diketene (1.2 equiv) in anhydrous tetrahydrofuran was added dropwise over a 30-min period to a 2 M solution of the secondary amine in THF. The resulting solution was heated at reflux for 3 h and, after cooling, was poured into a saturated ammonium chloride solution and extracted twice with ether. The combined ether solution was washed with brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The crude product, obtained in 70–90% yield, was employed in the diazo transfer step without further purification.

Methanesulfonyl azide (33 mmol) in 20 mL of anhydrous acetonitrile was added over a 30-min period to a solution of the 3-oxobutanamide (25 mmol) and triethylamine (27 mmol) in 35 mL of dry acetonitrile. The resulting solution was continuously stirred for 14 h at room temperature after which time 50 mL of water was added, and the resulting mixture was extracted twice with 50-mL portions of ether. The combined ether extract was washed with 10% aqueous sodium hydroxide and brine, and the ether solution was then dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude product was chromatographed on a column of neutral alumina with use of 4:1 hexane/ether as the eluent. Yields are reported for the diazo transfer process.

***N*-Methyl-*N*-phenyl-2-diazo-3-oxobutanamide (3a).**[23] Yield: 86%. ^1H NMR ($CDCl_3$, 60 MHz): δ 7.5–7.0 (m, Ph), 3.37 (s, CH_3N), and 2.48 (s, CH_3CO). IR (neat): 2112 (C=N_2) and 1646 (C=O) cm^{-1}.

***N*-Benzyl-*N*-phenyl-2-diazo-3-oxobutanamide (3b).** Yield: 90%. ^1H NMR ($CDCl_3$, 60 MHz): δ 7.5–6.8 (m, PhN), 7.23 (s, Ph), 4.94 (s, CH_2N), and 2.52 (s, CH_3CO). IR (KBr): 2128 (C=N_2) and 1639 (C=O) cm^{-1}.

***N*-Ethyl-*N*-(2,3-dimethylphenyl)-2-diazo-3-oxobutanamide (3d).** Yield: 81%. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.21 (d of d, *J* = 7.5, 1.5 Hz, 1 H), 7.16 (t, *J* = 7.5 Hz, 1 H), 6.97 (d of d, *J* = 7.5, 1.5 Hz, 1 H), 4.01 (d of q, *J* = 13.5, 7.2 Hz, 1 H), 3.49 (d of q, *J* = 13.5, 7.5 Hz, 1 H), 2.53 (s, CH_3CO), 2.31 (s, CH_3), 2.14 (s, CH_3), and 1.20 (t, *J* = 7.2 Hz, CH_3). IR (CCl_4): 2115 (C=N_2) and 1642 (C=O) cm^{-1}.

***N*-Ethyl-*N*-*m*-tolyl-2-diazo-3-oxobutanamide (3e).** Yield: 92%. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.30 (t, *J* = 7.8 Hz, 1 H) 7.16 (d, *J* = 7.8 Hz, 1 H), 6.98 (s, 1 H), 6.97 (d, *J* = 7.8 Hz, 1 H), 3.82 (q, *J* = 7.1 Hz, CH_2N), 2.51 (s, CH_3CO), 2.37 (s, CH_3), and 1.18 (t, *J* = 7.1 Hz, CH_3). IR (neat): 2125 (C=N_2) and 1644 (C=O) cm^{-1}.

***N*-Ethyl-*N*-[3,4-(methylenedioxy)phenyl]-2-diazo-3-oxobutanamide (3f).** Yield: 91%. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.81 (d, *J* = 8.8 Hz, 1 H), 6.68–6.63 (m, 2 H), 6.04 (s, CH_2), 3.77 (q, *J* = 7.2 Hz, CH_2), 2.51 (s, CH_3CO), and 1.17 (t, *J* = 7.2 Hz, CH_3). IR (neat): 2109 (C=N_2) and 1642 (C=O) cm^{-1}.

***N*-Ethyl-*N*-α-naphthyl-2-diazo-3-oxobutanamide (3g).** Yield: 93%. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.94–7.88 (m, 1 H), 7.84–7.31 (m, 5 H), 7.22 (d, *J* = 8.2 Hz, 0.4 H), 6.60 (d, *J* = 7.5 Hz, 0.6 H), 4.24 (d of q, *J* = 13.5, 7.1 Hz, 1.2 H), 3.56 (d of q, *J* = 13.5, 7.1 Hz, 0.8 H), 2.53 (s, CH_3CO), and 1.40 (t, *J* = 7.1 Hz, CH_3). IR (CCl_4): 2110 (C=N_2) and 1650 (C=O) cm^{-1}.

Synthesis of Diazoacetamides (4). General Procedure. To a vigorously stirred solution of the 2-diazo-3-oxobutanamide (20 mmol) in 20 mL of acetonitrile was added 15 mL of 16% aqueous potassium hydroxide dropwise over a 20-min period, and the mixture was maintained at room temperature for 14 h. Following the addition of 20 mL of water, the resulting mixture was extracted twice with 100-mL portions of ether. The combined ether extract was washed with brine, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The crude product was purified by column chromatography on neutral alumina with a 5:1 hexane/ether eluent.

***N*-Methyl-*N*-phenyldiazoacetamide (4a).**[23] Yield: 82%. ^1H NMR ($CDCl_3$, 60 MHz): δ 7.6–7.1 (m, Ph), 4.53 (s, CHN_2), and 3.30 (s, CH_3N). IR (neat): 2109 (C=N_2) and 1624 (C=O) cm^{-1}.

***N*-Benzyl-*N*-phenyldiazoacetamide (4b).** Yield: 88%. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.4–7.2 (m, 8 H), 7.07–7.01 (m, 2 H), 4.95 (s, CH_2), and 4.63 (s, CHN_2). IR (KBr): 2104 (C=N_2) and 1614 (C=O) cm^{-1}. Mp: 56–58 °C. Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.71; H, 5.18. Found: C, 71.70; H, 5.20.

***N*-Ethyl-*N*-*o*-tolyldiazoacetamide (4c).** Yield: 80%. ^1H NMR ($CDCl_3$, 60 MHz): δ 7.4–7.0 (m, 4 H), 4.26 (s, CHN_2), 4.17 (d of q, *J* = 7, 13 Hz, 1 H), 3.38 (d of q, *J* = 7, 13 Hz, 1 H), 2.26 (s, CH_3), and 1.15 (t, *J* = 7 Hz, CH_3). IR (CCl_4): 2110 (C=N_2) and 1640 (C=O) cm^{-1}.

***N*-Ethyl-*N*-(2,3-dimethylphenyl)diazoacetamide (4d).** Yield: 82%. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.18 (d of d, *J* = 7.8, 1.8 Hz, 1 H), 7.14 (t, *J* = 7.8 Hz, 1 H), 6.96 (d of d, *J* = 7.8, 1.8 Hz, 1 H), 4.28 (s, CHN_2), 4.09 (d of q, *J* = 14.0, 7.1 Hz, 1 H), 3.38 (d of q, *J* = 14.0, 7.1 Hz, 1 H), 2.33 (s, CH_3), 2.15 (s, CH_3), and 1.14 (t, *J* = 7.1 Hz, CH_3). IR (neat): 2105 (C=N_2) and 1623 (C=O) cm^{-1}.

***N*-Ethyl-*N*-*m*-tolyldiazoacetamide (4e).** Yield: 91%. ^1H NMR ($CDCl_3$, 60 MHz): δ 7.3–6.8 (m, 4 H), 4.40 (s, CHN_2), 3.80 (q, *J* = 7 Hz, CH_2), 2.37 (s, CH_3), and 1.13 (t, *J* = 7 Hz, CH_3). IR (neat): 2105 (C=N_2) and 1624 (C=O) cm^{-1}.

***N*-Ethyl-*N*-[3,4-(methylenedioxy)phenyl]diazoacetamide (4f).** Yield: 82%. ^1H NMR ($CDCl_3$, 60 MHz): δ 6.9–6.5 (m, 3 H), 6.04 (s, CH_2), 4.44 (s, CHN_2), 3.72 (q, *J* = 7 Hz, CH_2), and 1.08 (t, *J* = 7 Hz, CH_3). Mp: 93–95 °C dec. IR (neat): 2108 (C=N_2) and 1624 (C=O) cm^{-1}.

***N*-Ethyl-*N*-α-naphthyldiazoacetamide (4g).** Yield: 75%. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.95–7.82 (m, 3 H), 7.62–7.52 (m, 2 H), 7.50 (d of d, *J* = 7.8, 7.3 Hz, 1 H), 7.35 (d, *J* = 7.3 Hz, 1 H), 4.27 (d of q, *J* = 13.6, 7.2 Hz, 1 H), 4.16 (s, CHN_2), and 3.55 (d of q, *J* = 13.6, 7.2 Hz, 1 H). IR (KBr): 2111 (C=N_2) and 1613 (C=O) cm^{-1}.

Rhodium(II) Acetate Catalyzed Decomposition of Diazoacetamides (4). A solution containing 1.0 mmol of the diazoacetamide in 5 mL of dry dichloromethane was added dropwise over 30 min to a mixture of 4.0 mg of rhodium(II) acetate (1.0 mol percent) in 10 mL of dichloromethane, and the solution was stirred at room temperature for 1 h. The mixture was then filtered through neutral alumina, and the solvent was removed under reduced pressure. The same procedure was employed for Rh_2-

(22) Boyer, J. H.; Mack, C. H.; Goebel, W.; Morgan, L. R., Jr. *J. Org. Chem.* **1959**, *24*, 1051.

(23) Franich, R. A.; Lowe, G.; Parker, J. *J. Chem. Soc., Perkin Trans. 1*, **1972**, 2034.

$(OOCC_3F_7)_4$- and $Rh_2(NHOCH_3)_4$-catalyzed reactions. Products obtained by this procedure were generally chromatographically pure.

Nafion-H Catalyzed Decomposition of Diazoacetamides (4). A solution containing 1.0 mmol of the diazoamide in 5 mL of anhydrous chloroform was added dropwise over 30 min to a mixture of 100 mg of Nafion-H (ca. 10 mol % SO_3H) in 10 mL of refluxing chloroform. The resulting mixture was heated at reflux under nitrogen overnight. After cooling, the solution was filtered by gravity, and the solvent was removed under reduced pressure. Reactions performed in refluxing dichloromethane also occurred, but they required longer times to reach completion (24 h for **4b**).

1-Methyl-2-indolinone (5). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.27 (t, J = 7.8 Hz, 1 H), 7.22 (d, J = 7.8 Hz, 1 H), 7.02 (t, J = 7.8 Hz, 1 H), 6.80 (d, J = 7.8 Hz, 1 H), 3.48 (s, CH_2), and 3.19 (s, CH_3N). IR (KBr): 1708 (C=O) cm^{-1}. MS: m/e 148 (7, M + 1), 147 (68, M), 118 (100), 91 (21), 89 (10). Mp: 88–89 °C (lit.[19] 87–88 °C).

1-Benzyl-2-indolinone (6). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.30 (s, Ph), 7.25 (d, J = 7.4 Hz, 1 H), 7.17 (t, J = 7.4 Hz, 1 H), 7.00 (t, J = 7.4 Hz, 1 H), 6.72 (d, J = 7.4 Hz, 1 H), 4.92 (s, CH_2Ph), and 3.63 (s, CH_2). IR (neat): 1710 (C=O) cm^{-1}. MS: m/e 224 (6, M + 1), 223 (37, M), 194 (5), 132 (8), 92 (8), 91 (100). Mp: 50–52 °C. Anal. Calcd for $C_{15}H_{13}NO$: C, 80.72; H, 5.82; N, 6.28. Found: C, 80.70; H, 5.85; N, 6.26.

1-Ethyl-7-methyl-2-indolinone (7). ^1H NMR ($CDCl_3$, 60 MHz): δ 7.4–6.9 (m, 4 H), 4.07 (q, J = 7 Hz, CH_2), 3.50 (s, CH_2), 2.54 (s, CH_3), and 1.28 (t, J = 7 Hz, CH_3). IR (CCl_4): 1722 (C=O) cm^{-1}. Mp: 46–48 °C. Anal. Calcd for $C_{11}H_{13}NO$: C, 75.43; H, 7.43; N, 8.00. Found: C, 75.46; H, 7.46; N, 8.00.

1-Ethyl-6,7-dimethyl-2-indolinone (8). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.96 (d, J = 7.4 Hz, 1 H), 6.84 (d, J = 7.4 Hz, 1 H), 4.02 (q, J = 7.1 Hz, CH_2), 3.42 (s, CH_2), 2.40 (s, CH_3), 2.30 (s, CH_3), and 1.28 (t, J = 7.1 Hz, CH_3). IR (neat): 1705 (C=O) cm^{-1}. MS: m/e 190 (8, M + 1), 189 (53, M), 174 (20), 160 (22), 146 (100), 131 (22), 91 (19). Mp: 75–76 °C. Anal. Calcd for $C_{12}H_{15}NO$: C, 76.19; H, 7.93; N, 7.41. Found: C, 76.19; H, 7.98; N, 7.43.

1-Ethyl-6-methyl-2-indolinone (9a). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.11 (d, J = 7.4 Hz, 1 H), 6.83 (d, J = 7.4 Hz, 1 H), 6.66 (s, 1 H), 3.75 (q, J = 7.2 Hz, CH_2), 3.45 (s, CH_2), 2.38 (s, CH_3), and 1.26 (t, J = 7.2 Hz, CH_3). MS: m/e 176 (12, M + 1), 175 (91, M), 160 (21), 132 (100), 117 (29), 105 (26), 91 (25).

1-Ethyl-4-methyl-2-indolinone (9b). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.18 (t, J = 7.5 Hz, 1 H), 6.85 (d, J = 7.5 Hz, 1 H), 6.68 (d, J = 7.5 Hz, 1 H), 3.76 (q, J = 7.2 Hz, CH_2), 3.38 (s, CH_2), 2.25 (s, CH_3), and 1.25 (t, J = 7.2 Hz, CH_3). MS: m/e 176 (8 M + 1), 175 (61, M), 160 (18), 132 (100), 117 (20), 105 (8), 91 (14), IR **9a,b** (neat): 1710 (C=O) cm^{-1}. Anal. Calcd for $C_{11}H_{13}NO$: C, 75.43; H, 7.43; N, 8.00. Found: C, 75.44; H, 7.45; N, 8.01.

1-Ethyl-5,6-(methylenedioxy)-2-indolinone (10a). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.77 (s, 1 H), 6.44 (s, 1 H), 5.92 (s, CH_2), 3.70 (q, J = 7.2 Hz, CH_2), 3.42 (s, CH_2), and 1.23 (t, J = 7.2 Hz, CH_3). IR (KBr): 1713 (C=O), 844, 812 cm^{-1}. MS: m/e 206 (13, M + 1), 205 (100, M), 190 (10), 176 (37), 162 (61), 132 (49), 91 (10). Mp: 134–135 °C. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 66.37; H, 5.42; N, 6.81.

1-Ethyl-4,5-(methylenedioxy)-2-indolinone (10b). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.72 (d, J = 8.1 Hz, 1 H), 6.26 (d, J = 8.1 Hz, 1 H), 5.95 (s, CH_2), 3.73 (q, J = 7.0 Hz, CH_2), 3.47 (s, CH_2), and 1.18 (t, J = 7.0 Hz, CH_3). MS: m/e 206 (12, M + 1), 205 (94, M), 190 (10), 176 (13), 162 (40), 132 (100), 91 (10).

1-Ethylbenzo[*g*]indolin-2-one (11). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.20 (d, J = 8.4 Hz, 1 H), 7.87 (d, J = 8.4 Hz, 1 H), 7.57 (d, J = 8.0 Hz, 1 H), 7.50 (d of quin, J = 8.0, 0.8 Hz, 2 H), 7.39 (d, J = 8.0 Hz, 1 H), 4.32 (q, J = 7.2 Hz, CH_2), 3.66 (s, CH_2), and 1.46 (t, J = 7.2 Hz, CH_3). IR (CCl_4): 1726 (C=O) cm^{-1}. MS: m/e 212 (15, M + 1), 211 (100, M), 196 (15), 183 (15), 182 (40), 168 (83), 127 (17). Mp: 134–135 °C. Anal. Calcd for $C_{14}H_{13}NO$: C, 79.62; H, 6.16; N, 6.63. Found: C, 79.61; H, 6.22; N, 6.62.

Rhodium(II) Acetate Catalyzed Decomposition of 2-Diazo-3-oxobutanamides (3). A solution containing 1.0 mmol of the 2-diazo-3-oxobutanamide in 5 mL of dry benzene was added dropwise over 30 min to a mixture of 4.0 mg of rhodium(II) acetate (1.0 mol percent) in 10 mL of refluxing benzene. The resulting solution was heated at reflux under nitrogen for 3 h. After cooling, the solution was filtered through neutral alumina, and benzene was removed under reduced pressure.

Nafion-H Catalyzed Decomposition of 2-Diazo-3-oxobutanamides (3). A solution containing 1.0 mmol of the diazoacetoacetamide in 5 mL of dry toluene was added dropwise over 30 min to a mixture of 100 mg of Nafion-H (ca. 10 mol % SO_3H) in 10 mL of toluene maintained at 92 °C. The resulting mixture was heated at this temperature for 12 h. After cooling, the solution was filtered by gravity, and the solvent was removed under reduced pressure. Reactions performed in refluxing benzene also occurred, but they required approximately 40 h to reach completion.

1-Methyl-3-acetyl-2-indolinone (5). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.37 (d, J = 7.6 Hz, 1 H), 7.23 (d of t, J = 7.6, 1.1 Hz, 1 H), 7.11 (d of t, J = 7.6, 1.1 Hz, 1 H), 6.95 (d, J = 7.6 Hz, 1 H), 3.35 (s, CH_3N), and 2.46 (s, CH_3CO). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 172.82, 170.95, 138.85, 125.15, 122.17, 122.04, 119.62, 108.31, 101.69, 25.58, and 20.23. IR (neat): 3436 (O—H) and 1661 (C=O) cm^{-1}. MS: m/e 190 (14, M + 1), 189 (100, M), 174 (85), 171 (50), 147 (22), 143 (20), 118 (21), 91 (27). Mp: 105–106 °C. Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.85; H, 5.83; N, 7.41. Found: C, 69.78; H, 5.81; N, 7.38.

1-Benzyl-3-acetyl-2-indolinone (6). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.39 (d of d, J = 6.8, 1.7 Hz, 1 H), 7.34–7.21 (m, C_6H_5), 7.10 (d of quin, J = 6.8, 1.7 Hz, 2 H), 6.86 (d of d, J = 6.8, 1.7 Hz, 1 H), 5.06 (s, CH_2), and 2.49 (s, CH_3CO). IR (KBr): 3434 (O—H) and 1657 (C=O) cm^{-1}. Mp: 119–120 °C. Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.88; H, 5.71; N, 5.23.

1-Ethyl-3-acetyl-6,7-dimethyl-2-indolinone (8). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.13 (d, J = 7.8 Hz, 1 H), 6.92 (d, J = 7.8 Hz, 1 H), 4.17 (q, J = 7.1 Hz, CH_2), 2.48 (s, CH_3), 2.43 (s, CH_3), 2.35 (s, CH_3), and 1.33 (t, J = 7.1 Hz, CH_3). IR (neat): 3440 (O—H) and 1654 (C=O) cm^{-1}. MS: m/e 232 (19, M + 1), 231 (100, M), 216 (26), 213 (30), 198 (27), 189 (24), 188 (21), 146 (63). Mp: 86–87 °C. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.65; H, 7.46; N, 6.03.

1-Ethyl-3-acetyl-6-methyl-2-indolinone (9a). Convenient separation of the two isomers was achieved on silica gel with a Chromatotron with hexane/ethyl acetate (2:1). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.23 (d, J = 7.6 Hz, 1 H), 6.89 (d, J = 7.6 Hz, 1 H), 6.78 (s, 1 H), 3.86 (q, J = 7.2 Hz, CH_2), 2.40 (s, CH_3CO), 2.40 (s, CH_3), and 1.30 (t, J = 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 171.70, 170.82, 138.07, 135.17, 122.50, 119.68, 119.53, 109.24, 101.75, 34.14, 21.70, 20.10, and 13.22. IR (neat): 3416 (O—H) and 1705 (C=O) cm^{-1}. MS: m/e 218 (2, M + 1), 217 (11, M), 175 (100), 160 (36), 130 (16), 91 (12).

1-Ethyl-3-acetyl-4-methyl-2-indolinone (9b). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.24 (t, J = 7.9 Hz, 1 H), 6.89 (d, J = 7.9 Hz, 1 H), 6.73 (d, J = 7.9 Hz, 1 H), 4.45 (s, CH), 3.82–3.70 (m, CH_2), 2.24 (s, CH_3CO), 2.16 (s, CH_3), and 1.27 (t, J = 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 199.48, 170.27, 143.68, 135.52, 129.10, 124.47, 122.53, 106.19, 60.84, 35.18, 27.94, 18.56, and 12.58. IR (neat): 1705 (C=O) and 1661 (amide) cm^{-1}. MS: m/e 218 (14, M + 1), 217 (100, M), 202 (45), 199 (45), 184 (29), 175 (26), 132 (46), 130 (20), 91 (19). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.79; H, 6.91; N, 6.41.

1-Ethyl-3-acetyl-5,6-(methylenedioxy)-2-indolinone (10a). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.90 (s, 1 H), 6.57 (s, 1 H), 5.94 (s, CH_2), 3.84 (q, J = 7.1 Hz, CH_2), 2.39 (s, CH_3CO), and 1.29 (t, J = 7.1 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 171.42, 170.57, 145.55, 143.05, 132.40, 114.87, 102.25, 101.40, 100.97, 92.14, 34.43, 20.11, and 13.25. IR (CCl_4): 3400 (O—H) and 1676 (C=O) cm^{-1}. MS: m/e 248 (15, M + 1), 247 (100, M), 230 (13), 229 (78), 214 (27), 205 (16), 176 (13), 162 (15). Mp: 132–133 °C. Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.66. Found: C, 63.12; H, 5.34; N, 5.62.

1-Ethyl-3-acetyl-4,5-(methylenedioxy)-2-indolinone (10b). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.70 (d, J = 8.1 Hz, 1 H), 6.40 (d, J = 8.2 Hz, 1 H), 5.98 (s, CH_2), 3.85 (q, J = 7.2 Hz, CH_2), 2.58 (s, CH_3CO), and 1.29 (t, J = 7.2 Hz, CH_3). MS: m/e 248 (16, M + 1), 247 (100, M), 230 (6), 229 (18), 214 (8), 205 (13), 176 (6), 162 (32).

3-Acetoxy-1-ethylbenzo[*g*]indolin-2-one (11). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.22 (d, J = 8.5 Hz, 1 H), 7.88 (d of d, J = 8.5, 1.4 Hz, 1 H), 7.61 (s, 2 H), 7.51 (d of t, J = 8.5, 1.4 Hz, 1

H), 7.42 (d of t, J = 8.5, 1.4 Hz, 1 H), 4.44 (q, J = 7.2 Hz, CH_2), 2.56 (s, CH_3), and 1.50 (t, J = 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 175.08, 170.74, 132.49, 131.24, 129.39, 129.35, 126.04, 124.22, 122.63, 121.00, 120.90, 118.49, 101.90, 36.82, 20.73, and 14.78. IR (KBr): 1650 (C=O) cm^{-1}. MS: m/e 254 (18, M + 1), 253 (100, M), 235 (38), 220 (16), 188 (10), 168 (18), 167 (11). Mp: 139.5-140.5 °C. Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.86; H, 5.95; N, 5.45.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation for this work and for partial funding for the mass spectrometer and NMR spectrometers employed in these investigations. Partial funding for the high-field NMR spectrometer was also obtained from the Keck Foundation. We thank the Johnson Matthey Co. for their loan of rhodium(III) chloride.

Registry No. **3a**, 38118-69-3; **3b**, 112482-66-3; **3d**, 112482-67-4; **3e**, 112482-68-5; **3f**, 112482-69-6; **3g**, 112482-70-9; **4a**, 38118-70-6; **4b**, 112482-71-0; **4c**, 112482-72-1; **4d**, 112482-73-2; **4e**, 112482-74-3; **4f**, 112482-75-4; **4g**, 112482-76-5; **5** (Z = H), 61-70-1; **5** (Z = Ac), 59624-50-9; **6** (Z = H), 7135-32-2; **6** (Z = Ac), 112482-84-5; **7** (Z = H), 112482-77-6; **8** (Z = H), 112482-78-7; **8** (Z = Ac), 112482-85-6; **9a** (Z = H), 112482-79-8; **9a** (Z = Ac), 112482-86-7; **9b** (Z = H), 112482-80-1; **9b** (Z = Ac), 112482-87-8; **10a** (Z = H), 112482-81-2; **10a** (Z = Ac), 112482-88-9; **10b** (Z = H), 112482-82-3; **10b** (Z = Ac), 112482-89-0; **11** (Z = H), 112482-83-4; **11** (Z = Ac), 112482-90-3; Ph_2NH, 122-39-4; PhNHMe, 100-61-8; PhNHBen, 103-32-2; Me-*o*-C_6H_4NHEt, 94-68-8; 2,3-$Me_2C_6H_3NHEt$, 41115-23-5; Me-*m*-C_6H_4NHEt, 102-27-2; 3,4-$CH_2(O_2)C_6H_3NHEt$, 32953-14-3; $MeSO_2N_3$, 1516-70-7; α-naphthyl-NHEt, 118-44-5; diketene, 674-82-8.

Metal-Metal Exchange of α-Metallo Ketones. Novel Formation of α-Acyl Anion and α-Keto Carbonium Ion Equivalents from (Aryl)phenacyl Tl^{III}, Pb^{IV}, and Hg^{II} Systems

Robert M. Moriarty,* Raju Penmasta, Indra Prakash, and Alok K. Awasthi

Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

Received April 8, 1987

The novel class of α-metallo ketones $RCOCH_2Tl^{III}$tolyl$(OCOCF_3)$ where R = phenyl, substituted phenyl, thienyl, pyridinyl, and *tert*-butyl have been synthesized and characterized by ^1H NMR and ^{13}C NMR. These compounds serve as anion equivalents in the $TiCl_4$-mediated aldol condensation. Metal-metal exchange with iodosylbenzene or lead tetraacetate leads to α-nucleophilic substitution derived from the formal α-keto carbonium ion equivalent. The corresponding p-$CH_3OC_6H_4COCH_2Pb^{IV}C_6H_4OCH_3$-$p$-$(OCOCH_3)_2$ and $(p$-$CH_3OC_6H_4COCH_2)_2Hg^{II}$ analogues were synthesized and shown to likewise behave as either enolate anion or α-keto carbonium ion equivalents upon metal-metal exchange with Ti^{IV}, Pb^{IV}, or I^{III}. The importance of this work is that the range of reactivity of α-metallo ketones may be selectively adjusted by metal-metal or metal-metalloid exchange.

α-Metallo ketones, also known as α-metalloacyl systems, $-MCH_2CO-$, have been well studied for group IVA acylsilanes, acylgermanes, and acylstannanes.[1] Carbon to oxygen rearrangement is a primary process for these compounds. In the cases of silicon[2] and tin[1b,3] both isomers have been studied separately. Among group IIB elements α-mercurio ketones have been used in the aldol condensation.[4] Even though Hg(II) can show redox behavior, $-HgCR_2CO-$ acts as an anion equivalent. Hypervalent iodine can occur in systems of the type $-MCH_2CO-$ where M = I^{III} as in $RCOCH_2I^{III}C_6H_5X$[5] and $(RCO)_2C^{-+}IC_6H_5$;[6] however, in these cases the invariable course of chemical reaction is reductive elimination of $C_6H_5I^{I}$ with overall nucleophilic substitution at carbon. The chemistry of organoiodine(III) compounds such as $C_6H_5I^{III}X_2$ is similar to that of $Pb^{IV}X_4$,[7] $Tl^{III}X_3$,[8] and $Hg^{II}X_2$,[9] the common reactivity pattern is reductive elimination, i.e., $Pb^{IV} \rightarrow Pb^{II}$, $Tl^{III} \rightarrow Tl^{I}$, and $Hg^{II} \rightarrow Hg^0$ with Pb^{IV} being the most easily reduced (-1.6 V) and Hg^{II} the least easily reduced (-0.92 V). Pursuant to these formal relationships we synthesized the α-metallo ketones corresponding to these three redox metals, namely, $RCOCH_2M(OCOR)_n(Ar)$, where M = Tl^{III}, Pb^{IV}, and Hg^{II}, **2a-f**, **3**, and **4**, respectively, with the objective of comparing their chemistry with that of the related $RCOCH_2I^{III}C_6H_5X$ mentioned above. We now report

(1) (a) For a review, see: Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 96. The term "β-ketometalloid" used by Brook in this chapter is acknowledged to be confusing. In a conventional organic chemical designation a β-keto metalloid would be thought of as $-MCH_2CH_2COR$ while emphasis on the metal atom accounts for the β-keto metalloid nomenclature. (b) Odic, Y.; Pereyre, M. *J. Organomet. Chem.* **1973**, *55*, 273.

(2) (a) The stereochemistry of this process in the case of β-keto silanes has been studied in Brook et al. Brook, A. G.; Mac Rae, D. M.; Limburg, R. W. *J. Am. Chem. Soc.* **1967**, *89*, 5493. (b) Lutsenko, I. F.; Baukov, Y. I.; Dudukina, O. V.; Kramarova, E. N. *J. Organomet. Chem.* **1968**, *11*, 35. (c) Matsuda, I.; Sato, S.; Hattori, M.; Izumi, Y. *Tetrahedron Lett.* **1985**, *26*, 3215.

(3) (a) Pereyre, M. "Recherches sur les Reactions d'Hydures Organostanniques avec des Systêmes non Sature", Dissertation, Bordeaux, 1965, p 133. (b) Pereyre, M.; Bellegarde, B.; Mendelsohn, J.; Valade, J. *J. Organomet. Chem.* **1968**, *11*, 97.

(4) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1982**, *104*, 2323.

(5) For a discussion of this intermediate, see: Moriarty, R. M.; Prakash, O.; Duncan, M. P. *Synthesis* **1985**, 943.

(6) These compounds, called iodonium ylides, react with HX to yield the protonated form which reacts further with X^- with the reductive elimination of C_6H_5I. For a discussion of the protonolysis of iodinanes with Brønsted acids, see: Koser, G. F. In *The Chemistry of Functional Groups*, Supplements D; Patai, S.; Rappaport, S., Eds.; Wiley: New York, 1983; Chapter 18, pp 790-792.

(7) (a) For a comparison of iodosobenzene with $Pb(OAc)_4$, see: Bunton, C. A. In *Oxidations in Organic Chemistry*, Part A, Wiberg, K. B., Ed.; Academic Press: New York and London, 1965; pp 367-433. (b) Reference 7a, Criegee, R., 1965; pp 278-365.

(8) McKillop, A., Taylor, E. C. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: England, 1982; Vol. 7, pp 465-513.

(9) Negishi, E. *Organometallics in Organic Synthesis*; John Wiley and Sons: New York, 1980; Vol. 1, pp 455-479.

0022-3263/88/1953-1022$01.50/0