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Direct Synthesis of Anilides from Nitroarenes

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Nitroaromatic compounds are readily reduced to arylamines by a number of reagents [e.g., Fe, Sn, Sn(II), Zn, Ti(III)]. However, only a few methods are available for their direct conversion to the anilides, e.g., catalytic hydrogenation in the presence of acid anhydrides, and reaction with acyl tetracarbonylferrates.[1] We wish to report a new method for this latter transformation.

Despite conspicuousness of the reducing ability of low-valent molybdenum, the property has, until recently, rarely been exploited in organic synthesis. Aside from our own effort,[2] we are aware of only one report[3] on the use of complex salts of molybdenum for deoxygenation of sulfoxides. As molybdenum(II) species[4] are conveniently prepared by heating $Mo(CO)_6$ with carboxylic acids, we considered it worthwhile to examine the synthetic utility of the system. From various experiments performed, it has been shown that nitroarenes are converted to anilides directly.

$$ArNO_2 \xrightarrow{Mo(CO)_6,\ RCOOH} RCONHAr$$

Since arylamines undergo acylation on heating with carboxylic acids, it can be inferred that the amines, either in the free or metalated state, are the intermediates of our reaction. Dimeric products such as azoarenes have neither been detected nor isolated. In fact, these compounds are convertible to anilides also.[5]

It should be emphasized that the reagent combination is a rather mild reducing system. For example, it can be used to reduce a nitro group in the presence of an olefinic linkage which cannot be achieved by catalytic hydrogenation. To illustrate this point, 4-nitrostilbene was subjected to our experimental conditions. 4-Acetaminostilbene[6] was isolated. Most other functional groups such as alcohols, ketones, esters, acids, amides, nitriles, and sulfones are stable toward the Mo(II) reagents.

Table I. Reductive Acylation of Nitroarenes

Nitroarene	Anilide	Yield, %
$PhNO_2$ 98-95-3	PhNHAc 103-84-4	55
	PhNHCOEt 620-71-3	62
	$PhNHCOPr^n$ 1129-50-6	63
m-$MeC_6H_4NO_2$ 99-08-1	m-MeC_6H_4NHAc 537-92-8	68
p-$MeOC_6H_4NO_2$ 100-17-4	p-$MeOC_6H_4NHAc$ 57-66-1	85
p-$AcC_6H_4NO_2$ 100-19-6	p-AcC_6H_4NHAc 2719-21-3	46
p-$O_2NC_6H_4CH{=}CHPh$ 4003-94-5	p-$AcNHC_6H_4CH{=}CHPh$ 18559-97-2	50

Experimental Section

General Procedure for Reductive Acylation of Nitroarenes. A mixture of a nitroarene (5 mmol) and molybdenum hexacarbonyl (2.64 g, 10 mmol) in a carboxylic acid (5 mL) was heated under nitrogen at 120 °C for 20 h. The sublimed $Mo(CO)_6$ was returned to the liquid phase during reaction by occasional swirling. The cooled reaction mixture was neutralized with dilute ammonia and extracted with ether (three 50-mL portions), and the extracts were dried and evaporated to give a solid product, which was recrystallized and identified by comparison with an authentic sample.

Registry No.—$Mo(CO)_6$, 13939-06-5; acetic acid, 64-19-7; propionic acid, 79-09-4; butyric acid, 107-92-6.

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Alkylation of 1,5-Dimethoxy-1,4-cyclohexadiene. A Convenient Synthesis of 2-Alkyl- and 2-Alkenyl-1,3-cyclohexanediones

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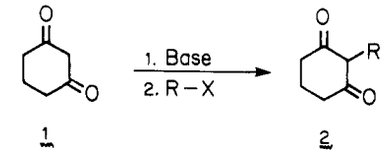
In connection with another research problem in our laboratory, we required a series of 2-alkyl- and 2-alkenyl-1,3-cyclohexanediones (**2**). The preparation of this type of compound via direct alkylation of the parent 1,3-cyclohexanedione (**1**) is reasonably efficient with reactive alkylating reagents

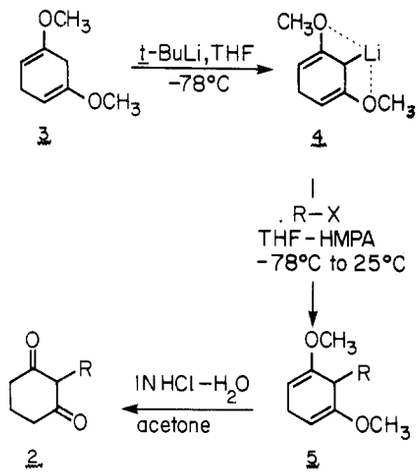


1 **2**

such as methyl iodide[1] and allylic[2,3] or benzylic halides.[2] However, with less reactive alkylating agents, the reaction is generally sluggish. For example, alkylation of **1** with 1-bromobutane[3] and 4-iodo-1-butene[4] afforded the corresponding alkylated products **2** [R = $(CH_2)_3CH_3$ and $(CH_2)_2CH{=}CH_2$, respectively] in very poor yield (<11%).[5] We report herein an efficient and experimentally convenient method which avoids this problem. The method involves two simple steps: the alkylation of 1,5-dimethoxy-1,4-cyclohexadiene (**3**)[7,8] and the acid-catalyzed hydrolysis of the resultant products **5**.

The dimethoxy compound **3** was converted into the corresponding organolithium derivative by treatment with t-BuLi in THF at −78 °C. On the basis of competing inductive and

resonance effects associated with the two methoxy groups in **3**, one might expect the allylic protons at C-6 to be more acidic than those at C-3. Furthermore, lithiation at C-6 would undoubtedly be facilitated by initial association of the lithium of *t*-BuLi with the oxygen atoms of the two methoxy groups, and it thus seems reasonable to propose that the lithiated



species can be conveniently represented by structure **4**.[9] In any case, successive addition of HMPA (slightly more than 1 equiv) and alkylating agent to the solution of the lithiated intermediate resulted in smooth and efficient formation of the corresponding alkylated compounds **5**. In each case, it was clear from GLC and spectral analyses of the product that the alkylation was very highly regioselective, since no isomeric products could be detected.

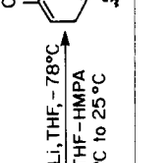
A number of different reagents and procedures were investigated in connection with the conversion of the alkylated products **5** into the corresponding 1,3-cyclohexanediones **2**. Eventually it was found that this hydrolysis could be conveniently and efficiently accomplished by treatment of **5** with dilute hydrochloric acid in acetone. However, the reaction was clean and high yielding only if precautions were taken to carefully exclude oxygen from the reaction mixture. Thus, prior to use, both the acetone and dilute hydrochloric acid were thoroughly purged with a stream of nitrogen, and the hydrolyses were carried out under an atmosphere of nitrogen. If these precautions were not followed, the products obtained were seriously discolored and the yields were considerably diminished.

A summary of the results appears in Table I.

Experimental Section

1,5-Dimethoxy-1,4-cyclohexadiene (3). Ammonia (700 mL, freshly distilled from sodium metal) was collected in a three-necked, 1-L flask equipped with a dry-ice condenser, an all-glass mechanical stirrer, and an addition funnel. Sodium metal (30.0 g, 1.3 mol) was added over a period of about 30 min while the ammonia was vigorously stirred, and the resultant dark blue solution was stirred for an additional 30 min. A solution of *m*-dimethoxybenzene (32.7 g, 0.237 mol) in a mixture of anhydrous ether (100 mL) and anhydrous ethanol (62.5 g, 1.36 mol) was added slowly over a period of 2 h. The mixture was stirred for an additional 1.5 h. The reaction mixture was quenched by careful addition of 75 mL of 1:1 ethanol–water, followed by water until a colorless mixture was obtained. The condenser and addition funnel were removed from the flask and the ammonia was allowed to evaporate. The remaining mixture was diluted with brine (700 mL) and thoroughly extracted with a 1:1 mixture of ether and petroleum ether (bp 30–60 °C). The combined extracts were washed with brine and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure, followed by distillation of the remaining oil, afforded 31.5 g (95%) of 1,5-dimethoxy-1,4-cyclohexadiene (**3**) as a clear colorless oil: bp 56 °C (0.55 Torr) [lit. bp 95 °C at (18 Torr)[7]]; IR (film) ν_{max} 3090, 3010, 2960, 2925, 2850, 1690, 1665, 1590, 1440, 1390, 1360, 1230, 1200, 1140, 1005, 920, 885, 760 cm^{-1}; ^1H NMR

Table I. Synthesis of 2-Alkyl- and 2-Alkenyl-1,3-cyclohexanediones[a]



t-BuLi, equiv	Alkylating agent (Equiv)	Registry no.	HMPA, equiv	Yield of 5, %[b]	Registry no.	Distillation temp[c] of 5, °C (Torr)	Yield of 2, %[d]	Registry no.	Mp of 2, °C: Obsd[e]	Mp of 2, °C: Lit.
1.09	$CH_3(CH_2)_3I$ (1.30)	542-69-8	1.33	99	63588-95-4	80–85 (0.4)	96	18456-90-1	116–117	115–116[f] 112–113[g]
1.11	$CH_2{=}CH(CH_2)_2Br$ (1.31)	5162-44-7	1.17	99	63588-96-5	55–60 (0.1)	95	56459-16-6	95–96	95–97.5;[h] 92.5–93.5[g]
1.09	$CH_3(CH_2)_4I$ (1.09)	628-17-1	1.02	96	63588-97-6	60–67 (0.25)	95	63589-01-5	91–95	
1.11	$C_6H_5CH_2CH_2Br$ (1.11)	103-63-9	1.33	99	63588-98-7	110–117 (0.25)[i]	93	62264-41-9	149–150	147–148[j]
1.09	$(CH_3)_2C{=}CH(CH_2)_2Br^k$ (1.10)	2270-59-9	1.04	98	63588-99-8	60–65 (0.25)	93	63589-02-6	117–120	
1.08	$(CH_3)_2C{=}CH(CH_2)_3I^l$ (1.04)	63588-94-3	1.04	88	63589-00-4	65–70 (0.08)	94	63589-03-7	87–89	
1.11	CH_3I (1.08)	74-88-4	1.08	98	25435-93-2	40–45 (0.2)[m]	65	1193-55-1	205–208 dec	208–210[n] dec

[a] All products reported in the table showed expected spectral properties. All new compounds gave satisfactory C, H analyses (within ±0.3% of calculated values). [b] Isolated yield, based on **3**. [c] Air-bath temperature (uncorrected) of bulb-to-bulb distillation. [d] Isolated yield based on **5**. [e] Melting points are uncorrected and were measured on a Fischer–Johns melting point apparatus. [f] Reference 3. [g] Reference 6. [h] Reference 4. [i] Lit.[8] bp 163–164 °C (2 Torr). [j] Reference 8. [k] M. Julia, S. Julia, and R. Guegan, *Bull. Soc. Chim. Fr.*, 1072 (1960). [l] M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 1789 (1957). [m] Lit. bp 65–67 °C (3 Torr): A. J. Birch and R. A. Russell, *Aust. J. Chem.*, **24**, 1975 (1971). See also I. Alfaro, W. Ashton, L. D. McManus, R. C. Newstead, K. L. Rabone, N. A. J. Rogers, and W. Kernick, *Tetrahedron*, **26**, 201 (1970). [n] Reference 1.

($CDCl_3$) δ 2.66–2.86 (unresolved m, 4 H, allylic protons), 3.47 (s, 6 H, methoxy protons), 4.58 (br t, 2 H, vinylic protons, $J \approx 3$ Hz).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.74; H, 8.80.

The following procedures, describing the preparation of compounds **5** (R = $CH_2CH_2CH{=}CH_2$) and **2** (R = $CH_2CH_2CH{=}CH_2$), are typical.

3-(Δ^3-Butenyl)-2,4-dimethoxy-1,4-cyclohexadiene (5, R = $CH_2CH_2CH{=}CH_2$). To a solution of *t*-BuLi[10] (1.11 equiv) in cold (−78 °C) THF (80 mL) was added 1.98 g of 1,5-dimethoxy-1,4-cyclohexadiene (**3**) and the resultant solution was stirred at −78 °C for 1 h. HMPA (1.17 equiv, freshly distilled from $LiAlH_4$) was added and stirring was continued for an additional 10 min. Addition of 4-bromo-1-butene (1.31 equiv, freshly filtered through a short column of neutral alumina) resulted in an immediate change in the color of the reaction mixture (maroon to light brown). The reaction mixture was allowed to warm to room temperature, diluted with 50 mL of brine, and then trice extracted with 50-mL portions of pentane. The combined pentane extracts were washed twice with brine and dried over anhydrous $MgSO_4$. Removal of the solvent, followed by distillation (air-bath temperature 55–60 °C, 0.1 Torr) of the resultant light brown oil, afforded 1.71 g (99%) of 3-(Δ^3-butenyl)-2,4-dimethoxy-1,4-cyclohexadiene: IR (film) ν_{max} 3090, 3020, 2950, 2925, 2850, 1690, 1660, 1640, 1610, 1450, 1390, 1320, 1300, 1140, 1020, 985, 955, 900, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70–2.02 (unresolved m, 4 H, $-CH_2CH_2CH{=}CH_2$), 2.66–3.04 (unresolved m, 3 H, C-3 and C-6 protons), 3.50 (s, 6 H, methoxy protons), 4.68 (t, 2 H, C-1 and C-5 protons, J = 4 Hz), 4.76–5.06 (unresolved m, 2 H, $-CH{=}CH_2$), 5.56–6.02 (unresolved m, 1 H, $-CH{=}CH_2$).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.00; H, 9.38.

2-(Δ^3-Butenyl)-1,3-cyclohexanedione (2, R = $CH_2CH_2CH{=}CH_2$). To a solution of compound **5** (R = $CH_2CH_2CH{=}CH_2$) (0.52 g) in acetone (12 mL, spectrograde, previously purged with a stream of N_2 for 15 min) was added, with vigorous stirring, 1 N hydrochloric acid (4 mL, previously purged with a stream of N_2 for 15 min). The resultant solution was stirred for 1 h. The acetone was removed under reduced pressure, the residue was diluted with 10 mL of brine, and the mixture was then extracted four times with 10-mL portions of CH_2Cl_2. The combined extracts were dried over anhydrous magnesium sulfate. Removal of the solvent afforded 0.42 g (95%) of 2-(Δ^3-butenyl)-1,3-cyclohexanedione as a white crystalline solid. This material was shown by GLC analysis to be >98% pure,and exhibited IR and ^1H NMR spectra which were essentially identical with those of an analytical sample obtained by recrystallization from benzene–heptane: mp 95–96 °C (lit. mp 95–97.5 °C[4], 92.5–93.5 °C[6]); UV (C_2H_5OH) λ_{max} 262 mm (ϵ 1.56 × 10^4); IR ($CHCl_3$) ν_{max} 3570, 3500–2600 (broad), 1715, 1695, 1615, 1370, 1170, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74–2.28 (m, 4 H), 2.28–2.76 (m, 6 H), 3.45 (t, 1/6 H, C-2 proton of diketo tautomer, J = 5 Hz), 4.84–5.16 (unresolved m, 2 H, $-CH{=}CH_2$), 5.62–6.12 (unresolved m, 1 H, $-CH{=}CH_2$).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.27; H, 8.45.

Acknowledgments. Financial support from the National Research Council of Canada is gratefully acknowledged.

Registry No.—**3**, 37567-78-5; *m*-dimethoxybenzene, 151-10-0.

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(10) A commercially available (Ventron) solution of *t*-BuLi in *n*-pentane was employed.

Aliphatic Diazo Ketones. A Modified Synthesis Requiring Minimal Diazomethane

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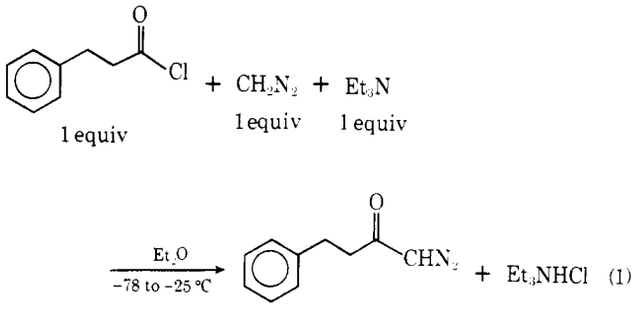
The common practice of employing excess diazomethane to scavenge HCl during the preparation of α-diazo ketones from acid chlorides and diazomethane[1] works extremely well in most instances but does not lend itself to the efficient use of isotopically labeled diazomethane or of other diazoalkanes. To circumvent this problem, Newman[2] and Berenbom[3] independently developed an alternative procedure for preparing α-diazo ketones from aromatic acid chlorides using 1 molar equiv of diazomethane in the presence of triethylamine at 0 °C. Under the same conditions, however, aliphatic acid chlorides bearing α-hydrogen atoms give only low yields of impure products,[2] presumably as a consequence of competing ketene formation and subsequent side reactions.[4]

In connection with a ^{13}C-labeling study, we had need to prepare the diazo ketone derived from 3-phenylpropanoyl chloride using minimal diazomethane and found that this can be accomplished simply by carrying out the reaction with triethylamine present at lower temperatures than usual (eq 1). A stoichiometric ratio of reagents gives optimal yields of



the diazo ketone based on diazomethane (see Table I). By comparison, the conventional procedure,[1] using 2 equiv of diazomethane, gives a much lower yield of product based on diazomethane (49.6%), albeit in a somewhat higher state of purity (95.2% by N_2 evolution, 90.1% by NMR). Chromatography on silica gel provides a means of separating and identifying the minor by-products formed during the reaction in eq 1 (see Experimental Section); however, the crude product proved satisfactory for subsequent copper-catalyzed cyclization.[5]

Table I lists several other aliphatic diazo ketones prepared by this method. Ketene formation competes successfully only in those cases with especially acidic α-hydrogens; phenylacetyl chloride, for example, gives an 85% yield of 2- and 3- phenylcyclobutanone under these reaction conditions,[6] presumably via phenyl ketene and phenylcyclopropanone.[7]

Experimental Section

1-Diazo-4-phenyl-2-butanone. Dry triethylamine[8] (11.1 mL, 0.08 mol) was added to 350 mL of an anhydrous ethereal solution of diazomethane[9] (0.08 mol) under nitrogen in a baked-out 1-L Morton flask fitted with a mechanical stirrer, a dropping funnel, and a low-temperature thermometer. The solution was cooled to − 78 °C (dry ice/acetone), and 11.8 mL of 3-phenylpropanoyl chloride[10] (0.08 mol) in 40 mL of anhydrous ether[8] was added dropwise with vigorous stirring over 25 min. A thick slurry formed during the addition.[11] The reaction mixture was stirred an additional 15 min at −78 °C and then for 1 h at −25 to −20 °C (dry ice/H_2O/$CaCl_2$).[12] During the course of the