Integrated Chemical Process: One-Pot Aromatization of Cyclic Enones by the Double Elimination Methodology**

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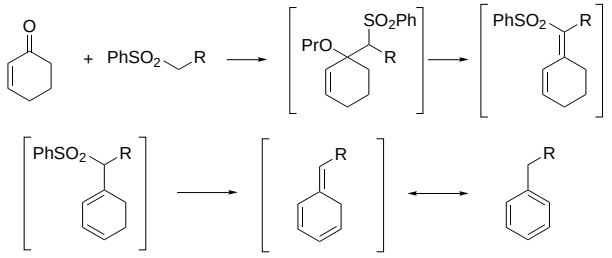
The aromatization of non-benzenoid compounds has attracted a great deal of attention for a long time. Although dehydrogenation of cyclic alkanes or alkenes is the most common way, this method requires severe reaction conditions and yields are not always satisfactory.[1] Trimerization of ketones, which is of synthetic interest in terms of the availability of starting materials, also suffers from low yields.[2] In contrast to these classical technologies, the recent progress in organometallic chemistry has given rise to a great deal of innovation. Trimerization of acetylenes proved to be versatile[3] although the regiochemistry is not easy to control in the intramolecular versions.[4] The [4+2] cycloaddition was widely employed as well for constructing benzene frameworks. The reaction of cyclopentadienones with acetylenes is the oldest, but still quite popular, method.[5] More recently the cycloaddition of cyclopentadienones[6] or furans[7] with olefins followed by oxidation was put forth. The reaction of 1,3-dienes with quinone also led to aromatic compounds after oxidation of the cycloadducts.[8] A number of intramolecular [4+2] cycloaddition protocols that use $\alpha,\beta,\gamma,\delta$-unsaturated heterocumulenes appeared.[9] Moreover, the intermolecular version between vinylallenes and acetylenes was reported to furnish regiocontrolled alkylbenzenes.[10] Despite these sophisticated technologies there still exists a strong need for practical methods.

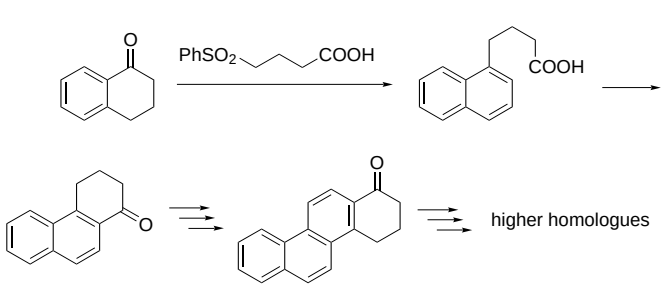
We earlier disclosed a one-pot procedure for arriving at dienes and acetylenes under the concept "integrated chemical process".[11] In this procedure the dienic or acetylenic moieties are generated in one pot through the aldol-type coupling of sulfones with aldehydes followed by a double elimination reaction. The present study stemmed from the idea of using cyclohexenones as the carbonyl substrates as depicted in Scheme 1. The following problems had to be solved to realize this procedure: 1) the addition of α-sulfonyl carbanions should be specific to provide the 1,2-adducts without 1,4-adducts, 2) the tertiary alcohol in the resulting aldolates should be efficiently trapped with a protecting group, and 3) the double elimination of the sterically demanding β-substituted sulfones should proceed smoothly. We report here that these problems can be readily overcome and thus a new, practical version of aromatization is advanced that consists of simple manipulations only.



Scheme 1. Concept for the aromatization of cyclohexenones.

The operation is quite simple (see experimental section). Sequential treatment of sulfone **2** with BuLi, enone **1**, PhCOCl, and *t*BuOK (5 equivalents) furnishes the desired aromatic compounds **3** in good yields (Table 1). In addition to simple alkyl groups such as methyl, ethyl, and *n*-hexyl, those bearing an acid-sensitive group can also be incorporated (entries 1–7). Notably, crotyl sulfone **2d** also works to afford 1-butenylbenzene, though the yield is modest (entry 8). A variety of cyclohexenones undergo smooth aromatization. α-Tetralones and their higher homologues can also be employed to arrive at polycyclic aromatic hydrocarbons (entries 9–14). It should be noted that the primary alkyl groups are incorporated on the aromatic rings with complete regiocontrol, which is a great advantage over the Friedel–Crafts reaction. The Friedel–Crafts reaction exhibits poor regioselectivity, and alkyl groups are incorporated in branched forms even if primary alkyl halides were subjected to the reaction. More seriously, the degree of alkylation is difficult to control: polyalkylation predominates over monoalkylation because the alkylation products are more reactive than their precursors. Our method is entirely free from such problems and thus allowed us to prepare various new polyalkylated aromatic compounds that are not easy to obtain by conventional methods.[12]

Next, we were intrigued by the development of a procedure for polycyclic aromatic hydrocarbons, which are the targets of current interest as new materials.[13] The use of ω-carboxy sulfones leads to α-tetralones or their higher homologues and the iteration of this procedure, in principle, results in annulation of aromatic skeletons (Scheme 2). First, we employed sulfones with a carboxyl or its ester group at the γ-position but the reaction of their anions with ketones failed to give the desired aldol products. However, we found an alternative, convenient procedure with regard to ω-acetal sulfones **4**. Treatment of **4** with **1** as described above accomplished the one-pot aromatization to give **5** (Table 2). Then, treatment of **5** with OXONE (potassium peroxomonosulfate) in THF/H_2O resulted in both deprotection and oxidation of the acetal to



Scheme 2. Synthetic route to polycyclic aromatic compounds.

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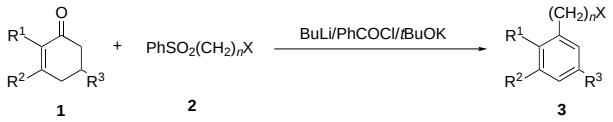
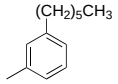
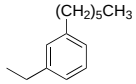
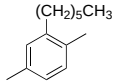
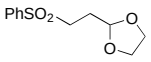
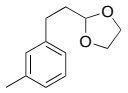
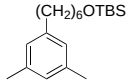
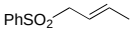
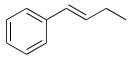
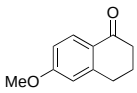
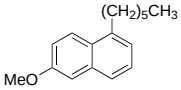
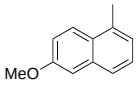
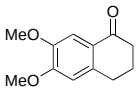
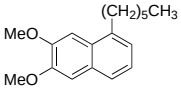
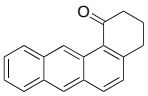
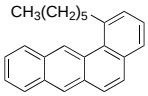
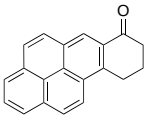
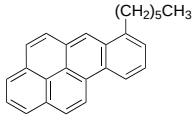
Table 1. One-pot synthesis of aromatic compounds from cyclic enones.[a]



Entry	1		2	3		Yield [%]
1		(**1a**)	$PhSO_2(CH_2)_5CH_3$ (**2a**)		(**3a**)	75
2		(**1b**)	**2a**		(**3b**)	72
3		(**1c**)	**2a**		(**3c**)	69
4		(**1d**)	**2a**		(**3d**)	84
5		(**1e**)	**2a**		(**3e**)	79
6		**1b**	 (**2b**)		(**3f**)	78
7		**1d**	$PhSO_2(CH_2)_6OSiMe_2tBu$ (**2c**)		(**3g**)	72
8		**1a**	 (**2d**)		(**3h**)	59
9		(**1f**)	**2a**[c]		(**3i**)	82
10		(**1g**)	**2a**		(**3j**)	74
11		**1g**	$PhSO_2CH_3$		(**3k**)	76
12		(**1h**)	**2a**		(**3l**)	79
13		(**1i**)	**2a**[d]		(**3m**)	78
14		(**1j**)	**2a**		(**3n**)	88

[a] Reaction conditions: a) **2** (1.2 mmol), BuLi (1.1 mmol), THF, −78 °C, 30 min; b) **1** (1 mmol), PhCOCl (1.5 mmol), −78 °C → RT, 3 h; c) *t*BuOK (5 mmol), reflux, 3 h. [b] Yield of isolated product after column chromatography. [c] **2a** (1.4 mmol), BuLi (1.2 mmol). [d] **2a** (1.3 mmol), BuLi (1.2 mmol).

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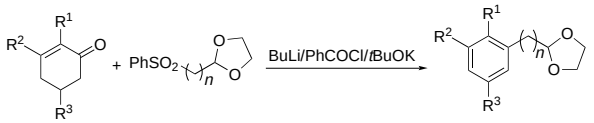
Table 2. One-pot synthesis of aromatic compounds substituted by an acetal-bearing alkyl chain.[a]



1 4 5

Entry	1	4	n	5	R^1	R^2	R^3	Yield [%][b]
1	**1a**	**4a**	3	**5a**	H	H	H	92
2	**1b**	**4a**	3	**5b**	H	Me	H	83
3	**1d**	**4a**	3	**5c**	H	Me	Me	83
4	**1f**	**4a**[c]	3	**5d**		$-(CH)_4-$	H	55
5	**1a**	**4b**	2	**5e**	H	H	H	78
6	**1b**	**4b**	2	**5f**[d]	H	Me	H	78
7	**1d**	**4b**	2	**5g**	H	Me	Me	67
8	**1f**	**4b**[c]	2	**5h**		$-(CH)_4-$	H	60
9	**1a**	**4c**	4	**5i**	H	H	H	62

[a] Reaction conditions are identical to those described in Table 1. [b] Yield of isolated product after column chromatography. [c] **4a** (1.4 mmol), BuLi (1.2 mmol). [d] **5f** = **3f** in Table 1.

directly furnish carboxylic acids **6** (Table 3).[14] Exposure of **6** to trifluoromethanesulfonic acid (TfOH) provided the desired ketones **7** in quantitative yields (Table 3). Methyl-substituted derivatives as well as nonsubstituted aromatics are smoothly obtained (Table 3, entries 1–4). Further synthetic utility is apparent from the synthesis of five- and seven-membered ketones (Table 3, entries 5–9) besides the six-membered ones. Notably, no regioisomer was detected in the six-membered ketone of the monomethyl compound (Table 3, entry 2) whereas two regioisomers emerged with the five-membered ketones (Table 3, entry 6). The similar difference of the selectivity was observed in the cyclization of the naphthalene derivatives (Table 3, entries 4 and 8).

In summary, a variety of aromatic hydrocarbons bearing multiple alkyl substituents is accessible with perfect regiocontrol in one pot starting from cyclohexenones and their aromatic analogues. The present methodology can be further extended to the synthesis of polycyclic aromatic hydrocarbons. The drawbacks encountered in the Friedel–Crafts reaction are completely cleared up since the reaction proceeds under basic conditions. A somewhat similar strategy was put forth with regard to the Reformatsky reaction of α-tetralones.[15] This procedure, however, involves dehydrogenation under drastic conditions, and results in modest yields. Obviously, the double elimination enables the generation of the carbon–carbon double bonds more easily. Each reaction in the respective three steps (aldol-type coupling, benzoylation, and double elimination) demands no special or drastic conditions. As a result of the mildness and practicality, the present protocol will find wide applications for the synthesis of aromatic compounds that are otherwise difficult to obtain.

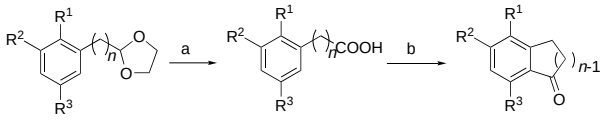
Experimental Section

BuLi (690 μL, 1.6 M solution in hexanes, 1.1 mmol) was added to a solution of **4a** (307 mg, 1.2 mmol) in THF (5 mL) at −78 °C. The solution was stirred for 30 min, and then **1a** (96 mg, 1.0 mmol) and PhCOCl (174 μL, 1.5 mmol) were added. The reaction mixture was warmed up to room temperature and stirred for 3 h. Then, *t*BuOK (562 mg, 5 mmol) was added and the reaction mixture was heated under reflux for 3 h. The reaction was quenched with aqueous ammonium chloride. The mixture was extracted with diethyl ether and the organic layer was dried (Na_2SO_4). Evaporation and column chromatography of the residue on silica gel (hexane/EtOAc 95/5) furnished **5a** (177 mg, 92%).

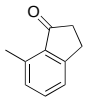
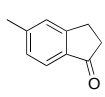
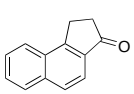
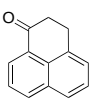
A suspension of OXONE (6.46 g, 10.5 mmol) in H_2O (10 mL) was added to a solution of **5a** (672 mg, 3.5 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at room temperature for 12 h and then a mixture of H_2O/EtOAc added. The organic layer was washed with brine and dried (Na_2SO_4). The residue obtained by evaporation was subjected to column chromatography on silica gel (hexane/EtOAc 70/30) to furnish **6a** (564 mg, 98%).

A solution of **6a** (164 mg, 1 mmol) in TfOH (1 mL) was stirred at 5 °C → room temperature over 2 h. Crushed ice was added slowly and the reaction mixture was extracted with diethyl ether. The organic layer was

Table 3. Cyclization of **5**.



5 6 7

Entry	5	n	6	Yield [%][c]	7	R^1	R^2	R^3	Yield [%][c]
1	**5a**	3	**6a**	98	**7a**	H	H	H	98
2	**5b**	3	**6b**	97	**7b**	H	Me	H	97
3	**5c**	3	**6c**	94	**7c**	H	Me	Me	99
4	**5d**	3	**6d**	95	**7d**	$-(CH)_4-$		H	99
5	**5f**	2	**6f**	96	**7e**	H	H	H	99
6	**5g**	2	**6g**	93	**7f**+**7f′**	 (**7f**)	 (**7f′**)		99[d]
7	**5h**	2	**6h**	82	**7g**	H	Me	Me	94
8	**5i**	2	**6i**	98	**7h**+**7h′**	 (**7h**)	 (**7h′**)		97[e]
9	**5j**	4	**6j**	79	**7i**	H	H	H	93

[a] OXONE (3 equiv), THF/H_2O, 0 °C → RT, 12 h. [b] In TfOH, 5 °C → RT, 2 h. [c] Yield of isolated product after column chromatography. [d] **7f**:**7f′** = 1:1. [e] **7h**:**7h′** = 5:1.

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washed sequentially with aqueous $NaHCO_3$, water, and brine, and dried (Na_2SO_4). The residue obtained by evaporation was subjected to column chromatography on silica gel (hexane/EtOAc 90/10) to furnish **7a** (144 mg, 98%).

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Electronic Communication in C_4-Bridged Binuclear Complexes with Paramagnetic Bisphosphane Manganese End Groups

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Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

Binuclear metal complexes $[L_nMC_xML_n]$ bridged by linear unsaturated carbon chains are of exceptional interest as building blocks for new one-dimensional materials.[1] Electronic and optical properties of the molecular precursors, such as metal–metal interactions in mixed-valent compounds and electron delocalization and conjugation within the carbon chain, are important for the prediction and optimization of bulk properties of polymeric materials, such as nonlinear optical (NLO) properties,[2] electrical conductivity,[3] or cooperative magnetic effects.[4] Most complexes found in the literature possess an even number of carbon atoms in the chain ($x = 2$,[5] 4,[6] ≥ 6[7]), a few also an uneven number ($n = 3$,[8] 5[9]). The metal centers usually have a d^8/d^8, d^6/d^6, d^5/d^6, or d^5/d^5 electron configuration.[10] Paramagnetic complexes are supposed to be more polarizable, as their SOMO/LUMO gaps are usually small—an important prerequisite, for example, for NLO properties.[2] We report the syntheses, properties, and solid-state structures of the paramagnetic binuclear Mn^{II} compound **1** (dmpe = 1,2-bis(dimethylphosphanyl)ethane) and of its one- and two-electron oxidation products $\mathbf{1}^+$ and $\mathbf{1}^{2+}$, respectively.

$[I(dmpe)_2Mn{-}C{\equiv}C{-}C{\equiv}C{-}Mn(dmpe)_2I]$ **1**

According to Scheme 1 the green d^5 low-spin Mn^{II} complex **1** is obtained from [MeCpMn(dmpe)I][18a] and half an equivalent of bis(trimethylstannyl)-1,3-butadiyne in the presence of DMPE in 70% yield. The low-spin character of **1** is shown by ^{1}H PNMR spectroscopy: the resonances of the methyl and methylene protons of the DMPE ligand appear in a typical region for low-spin $[Mn^{II}(dmpe)_2]$ complexes (Figure 1).[11]

The linear dependence of the signal positions on the temperature points to Curie–Weiss behavior in the measured temperature range from $-90\,^\circ$C to $25\,^\circ$C. As theoretically predicted for the isolobal complex $[Cp(CO)_2Mn{-}C{\equiv}C{-}C{\equiv}C{-}Mn(CO)_2Cp]$[12] and confirmed by our density functional theory (DFT) calculations on the model complex $[I(PH_3)_4Mn{-}C{\equiv}C{-}C{\equiv}C{-}Mn(PH_3)_4I]$, **1** has a triplet ground state (Figure 2).[13]

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