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ORGANOMETALLIC COMPOUNDS IN ORGANIC SYNTHESIS. AN EQUIVALENT OF AROMATIC NUCLEOPHILIC SUBSTITUTION BY REACTIONS OF TRICARBONYLCYCLOHEXADIENYLIUMIRON SALTS WITH O-SILYLATED ENOLATES: A NOVEL ARYLATION IN THE 2-POSITION OF CARBONYL COMPOUNDS.

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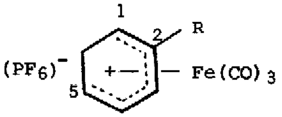
Summary: Tricarbonylcyclohexadienyliumiron salts are synthetically equivalent to specifically substituted phenyl cations.

More extensive ability to form carbon-carbon bonds with aromatic rings would enlarge the scope of useful synthetic methods.[1] Nucleophilic substitution of aryl halides by carbon nucleophiles requires the presence of o- and/or p-substituents with electron withdrawing character (e.g. NO_2), or complexation of the aromatic ring with groups like $Cr(CO)_3$.[2] The former is limited by the need to introduce and remove the activating groups, while in the case of the latter, the reactivity is a function of the leaving group,[3] F > Cl > I (*cf.* aromatic nucleophilic substitutions).[4] For the π-benzene-chromium tricarbonyl complex, the range of carbanions is limited to carbon acids of pK_a = 25 or higher.[5] Other methods have limitations to generality: benzyne processes[6] because of regioselectivities which make some patterns inaccessible (e.g. o-OMe or p-OMe), and reactions of ketone enolates with photogenerated aryl radicals ($S_{RN}1$ mechanism)[7] where ketones employable are restricted in structures; e.g. enolates derived from secondary ketones give only poor yields.

Some indirect arylation processes are now shown to be possible based on nucleophilic reactions with substituted tricarbonylcyclohexadienyliumiron salts, in conjunction with subsequent processes of removal of the complexing group and dehydrogenation. The cations can therefore be regarded as stabilized products of the regiospecific addition of a proton to the substituted benzene. Many of the starting materials can be obtained by the reduction of substituted benzenes followed by complexing and other processes.[8]

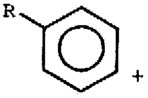
The description of reagents in terms of synthetic equivalents[9] and latent functionalities[10] is useful in drawing attention to their potential in terms immediately obvious to the synthetic organic chemist. One example in this context is the 2-substituted cation (1, R = alkyl, e.g. Me) which because of its mesomeric nature is equivalent to both (2) and (3) to the extent that reaction occurs with a nucleophile at the 1-position or the 5-position. Methods for controlling alternative courses of such reactions will be discussed later.[11]

A more regiospecific case is (1, R = OMe) where it is well known[12] that reaction of anionoid reagents is directed to the 5-position making it the equivalent of (2, R = OMe) when completed by a dehydrogenation process. An alternative sequence of iron-removal and hydrolysis makes (1, R = OMe) as a protected enol-ether derivative, the equivalent of the C-4 cation of 2-cyclohexenone (4) (a vinylogous enolonium ion[13]), which has obvious potentialities in synthesis including the generation of other substituted aryl rings.



(1)

R = alkyl or OMe



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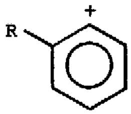

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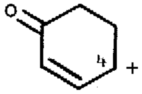

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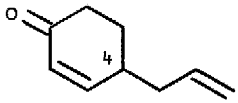


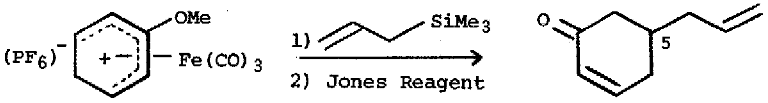
(5)

Anionoid reagents leading to new C-C bonds which have been shown to react with cations of this type are of many structural types: thermodynamic enols from ketones and 1,3-dicarbonyls, enamines, derivatives of boron, cadmium, zinc, copper, allylsilanes[14], trimethylsilyl enol ethers from ketones[15] and 1,2-bis(trimethylsiloxy)-1-cycloalkenes.[16]

The scope of the arylation process is now shown to include reaction with O-silylated enolates from acyclic ketones, aldehydes, esters and lactones (Table 1).

The expected alkylation products were obtained in yields from about 70% to 94%, following the procedure already noted.[15] The cyclohexa-1,3-dienes can be obtained by removal of $Fe(CO)_3$ with excess $Me_3NO \cdot 2H_2O$ in DMA at 60-90° (60-90%), thus opening further synthetic possibilities. Dehydrogenation of the diene with DDQ leads to 2-aryl carbonyl compounds by an overall process which represents a novel and rather direct α-arylation procedure for ketones, aldehydes, esters and lactones. It is more general than other recently described methods, applicable only to ketones, which involve: (1) 1,4-conjugate additions of organomagnesium or cuprates to tosylazo-ene[17] ("enolonium synthon"[17,18]), 1,2-carbonyl transposition of Friedel-Crafts acylation products[19] or coupling of organocuprates with 2-(phenylthio)-allylic acetates[20] and (2) nickel catalyzed arylation which works well only with lithium ester enolates.[21]

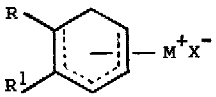
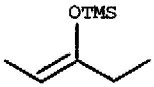
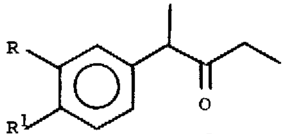
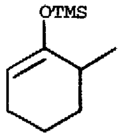
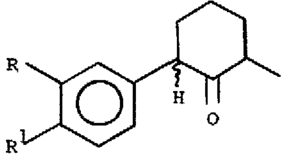
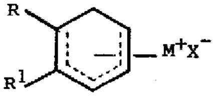
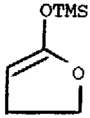
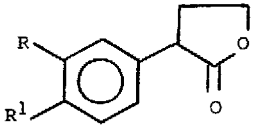
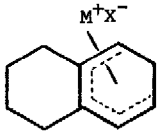
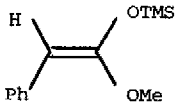
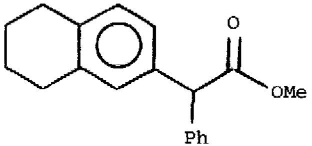
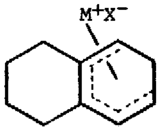
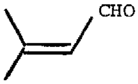
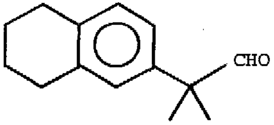
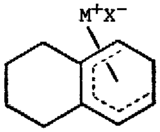
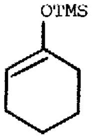
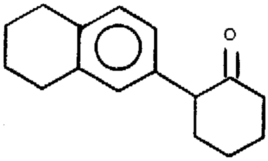
An example of (1, R = OMe) as an equivalent of (4) is shown by its reaction with allyl trimethylsilane[22] and removal of $Fe(CO)_3$ (Ce^{IV}, AcOH, room temp.) to give the known[23] (5) (63%) uncontaminated by its more stable isomer the 3,4-ene. Likewise, 3-methoxy cation (6) gave 5-(2-propenyl)-2-cyclohexen-1-one [7, 60%, $\delta_H(CCl_4)$, 6.90 (m), 6.0-4.9 (m), 2.6-1.9 (m); $\nu_{max.}$ 1685 cm^{-1}].



(6) (7)

Structures of all compounds in Table 1 are fully supported by spectral data (NMR, IR, Mass).

TABLE 1

SALTS	TMS ENOL ETHERS	2-ARYLCARBONYLS	YIELDS
			52%
			59%
			34%
			60%
			74%
			68%

M = Fe(CO)$_3$, X = PF$_6$
R = CO$_2$Me, R^1 = Me

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