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PHASE TRANSFER CATALYZED TERT-ALKYLATIONS OF CYCLOPENTADIENE AND INDENE: INDICATIONS FOR SET PROCESSES [1)]

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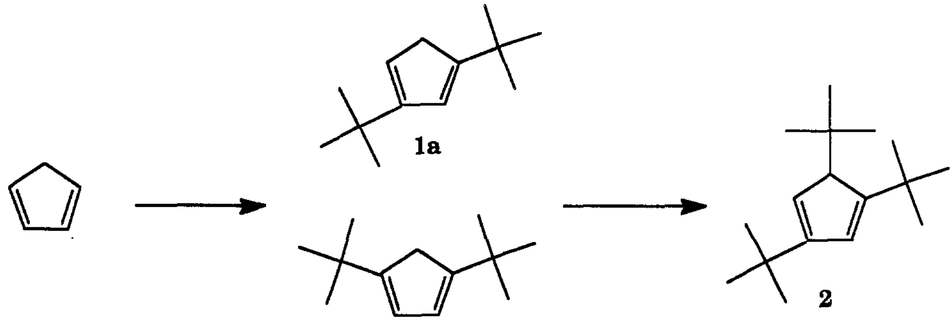
Abstract: *Scope and mechanism of the PTC tert-alkylation of cyclopentadienide anion have been investigated. On the side of the anion, the reaction is limited to cyclopentadiene and indene, whereas many tertiary as well as secondary and primary alkylating agents can be employed. Hexamethylcyclopentadiene 8, for instance, is available easily. Tert-alkylations of this type are more effective if 4,4'-bipyridinium salts are present in addition to a phase transfer catalyst. The reactions involve probably an initial single electron transfer (SET) step.*

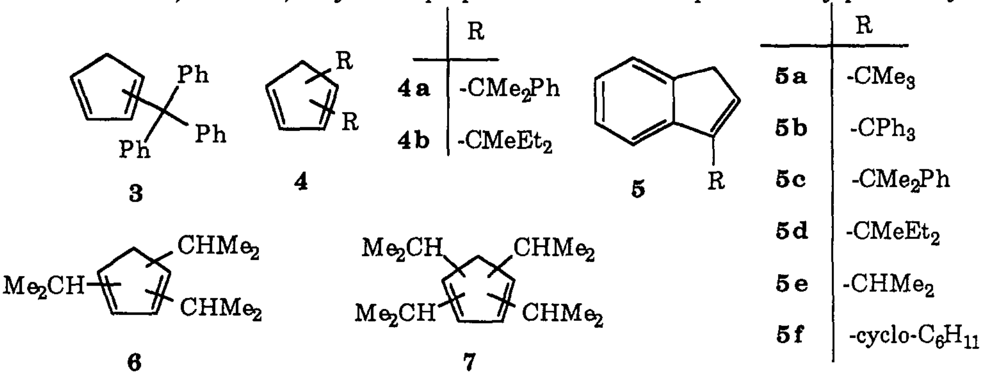
Base catalyzed phase transfer catalytical alkylations with tert-alkyl halides were thought to be impossible because of intervening elimination.[2] A 1990 report by Venier and Casserly on the tert-butylation of cyclopentadiene[3] came as a surprise therefore. The present study is concerned with mechanism and scope of this reaction.

In our hands, conversion of cyclopentadiene with tert-butyl bromide, 50% KOH, and Aliquat 336 as a catalyst [4] gives 44% yield of a 4 : 1 mixture of **1a** and **1b**. Under these conditions no trisalkylation occurs. The somewhat differing results reported earlier [3] could not be reproduced. Synthesis of 1,3,5-tri-tert-butylcyclopentadiene is possible using a large excess of tert-butyl bromide and sodium hydride/ benzo-15-crown-5 as base system in THF (4 days at 60°C ; 33% yield).



Scheme 1

The same reaction with indene yields only 3-tert-butylindene (**5 a**; 85%) and no bis-product. Fluorene, on the other hand, cannot be transformed at all in this way. Other representative tert-alkyl bromides give also products with cyclopentadiene and indene : trityl bromide, 2-bromo-2-phenylpropane, and 3-bromo-3-methylpentane, but not 1-bromoadamantane. Tritylation of cyclopentadiene as well as all reactions with indene lead to mono-alkylation only (compounds **3**, **5 b-d**), whereas in the other cases bis-substitution compounds (**4 a,b**) are found. Variation of the leaving group in tert-butyl halides gives the following yields under identical conditions: Cl, 4% **1** ; Br, 44 % 1; I, 56 % 1. Secondary halides can also be applied, and compounds **5 e,f** and **6** , **7** are obtained; **6** and **7** as position isomer mixtures (Scheme 2). Except for **4a, b, 5 c, d, f** [5], all compounds are known from the literature. As a rule, however, they were prepared in a more complicated way previously .[6]



	R
4a	$-CMe_2Ph$
4b	$-CMeEt_2$

	R
5a	$-CMe_3$
5b	$-CPh_3$
5c	$-CMe_2Ph$
5d	$-CMeEt_2$
5e	$-CHMe_2$
5f	-cyclo-C_6H_{11}

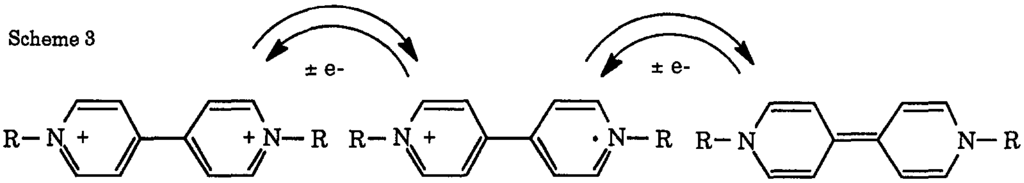
Scheme 2

The PTC method cannot be used to tert-butylate the following substrates under these conditions: pyrrole, indole, benzimidazole, succinimide, phthalimide, nitromethane, phenyl acetonitrile, phenylacetylene, and di-tert-butyl malonate.

Single electron transfer (SET) processes in seemingly simple S_N2 reactions have found much attention in the last few years.[7,8,9] Whereas such reactions were first observed mostly with aromatic and aliphatic nitro compounds, later investigations showed that they may play a role in many substitutions. In the present context it is especially noteworthy that the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine can also be tert-butylated.[10] Furthermore, a careful investigation of the single electron transfer rate constants between the derived radical anion and some alkyl halides revealed that tert-butyl bromide reacts almost 1000 times faster than 1-bromoadamantane.[8] Thus, the unexpected tert-alkylations as well as the failure of our reaction with bromoadamantane and the yield improvements with chloride to iodide leaving groups may indicate the following mechanism, which is analogous to one proposed in the literature:[9] $[cp^-] + R_3C\text{-}X \rightarrow \{ [cp^\cdot]\ R_3C^\cdot\ X^- \} \rightarrow cp\text{-}CR_3 + X^-$. Here $[cp^-]$ and $[cp\cdot]$ denote the cyclopentadienide anion and radical.

It occurred to us that rate and yield of the reaction might be improved by the presence of a redox catalyst which oxidizes [cp·] and which is reduced back by an intermediate radical. To probe this further, the tert-butylation of cyclopentadiene was conducted in the presence of redox systems. Experiments with $FeCl_3$, $K_3[Fe(CN)_6]$, $FeCp_2FeCl_4$, and Fe-porphyrins gave polymerizations. Therefore, a redox carrier was selected which is more amenable to PTC conditions. It is well known that 4,4'-bipyridinium salts (viologens, **V**) are useful single electron transfer agents:

Scheme 3

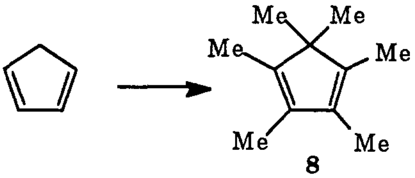


Va R = Me **Vb** R = Hex **V***

When the cyclopentadiene / tert-butylbromide / (10 mol-%) Aliquat reaction is performed at room temperature, no **1a,b** is obtained. In the additional presence of 1.2 mol-% **Vb**, however, 27 % yield are found under identical conditions. Conceivably, **V** could act both as a phase transfer and redox catalyst at the same time. A control reaction with **Vb** but *without Aliquat* gave no **1**. Only a fivefold increase of the concentration of **Vb** brought about a 9% yield of **1**. At elevated temperatures, concentrations of **V** as high as that of Aliquat 336 give extensive tarring. Thus, the main action of **V** must be of redox nature. As can be seen from Table 1, both **Va** and **Vb** accelerate the conversions, the more lipophilic **Vb** being somewhat better. As might be expected, a leveling-off the beneficial effects of **V** is found at long reaction times and with those conversions that give fair yields already under standard conditions.

Table 1. Alkylations of Cyclopentadiene in the Presence and Absence of **Va** and **Vb** (10 mmol alkene, 50 mmol tert-alkylhalide, 400 mmol 50% KOH, 1 mmol Aliquat 336, 0.12 mmol **Va,b**)

Halide	Reaction Time(min) Conditions	Yield (%) in Presence of only Aliquat	Aliquat + **Va**	Aliquat+**Vb**
tert-BuCl	75 at 60°,45 at 100°	3		31
tert-BuBr	210 at 20°	0		27
	20 at 60°	7	17	21
	40 at 60°	29	31	44
	60 at 60°	45	48	56
	80 at 60°	49	52	59
	100 at 60°	54	56	62
$Ph-CMe_2Br$	75 at 60°,45 at 100°	34		54
Et_2MeCBr	75 at 60°,45 at 100°	41		55



Scheme 4

8

Further experiments were conducted to methylate cyclopentadiene aiming at **8** as the ultimate product.[10] It turned out that fair yields (55-65% [11]) can be realized only if sodium hydride is used as a base. Here the best PT catalyst is benzo-15-crown-5. Using methyl iodide, the yield is improved by the presence of **V**. If , however, dimethyl sulfate is the alkylating agent, the presence of **V** does not make any difference.

We suggest that noteable improvements by viologen presence in otherwise ineffective conversions can be explained best by the intervention of a somewhat different SET process: $[cp^{-}] + [X^{-}\ \mathbf{V}^{++}\ X^{-}] \dashrightarrow [cp^{\cdot}\ \mathbf{V}^{+\cdot}\ X^{-}] + X^{-}$; $[cp^{\cdot}\ \mathbf{V}^{+\cdot}\ X^{-}] + R_3C\text{-}X \dashrightarrow cp\text{-}CR_3 + [X^{-}\ \mathbf{V}^{++}\ X^{-}]$.

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4. Technical methyl-trioctylammonium chloride. - General reaction conditions: 10 mmol cyclopentadiene or indene, 50 mmol alkyl bromide (no extra solvent) , 400 mmol 50% aqueous KOH, and 1mmol catalyst are heated for 75 min. at 60 ° C and then 45 min. at 100 ° C under nitrogen. The mixture is cooled, diluted with petroleum ether (b.p.40-60°C), and separated. The aqueous layer is extracted with more petroleum ether, and the combined organic phases are dried, concentrated, washed over silica gel, and distilled.**1a,b**: with tert-butyl bromide, b.p. (0.3 Torr) 60°C; lit.-b.p.[3] (40 Torr) 100-105°C; yield 44 %.
5. **4a**, **b** and **5c**, **d**, **f** were characterized by NMR spectroscopy and analyzed correctly. **4a** : prepared using the general conditions from cumyl bromide, b.p.(0.3 Torr) 180°C; 34% yield.- **4b** : under the general conditions from 3-bromo-3-methylpentane, b.p.(3 Torr) 135°C; 41% yield.- **5c** : using the general conditions from indene and cumyl bromide, b.p. (0.8 Torr) 130°C; 65% yield.- **5d**: similarly with 3-bromo-3-methylpentane, b.p.(3 Torr) 120°C; 70% yield.- **5f**: similarly with cyclohexyl bromide, b.p. (0.3 Torr) 80°C; 85% yield.
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11. Optimal conditions for MeI: 10 mmol cyclopentadiene, 1 mmol benzo-15-crown-5, 0.1 mmol **Vb**, 150 mmol NaH, 192 mmol MeI, 25 ml THF heated and stirred at 60°C for 4 days under nitrogen. Yield 65%; b.p. (14 Torr) 61°C; Lit.-b.p.[10] (12 Torr) 59°C.

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