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Triazatriangulenium Cations: Highly Stable Carbocations for Phase-Transfer Catalysis

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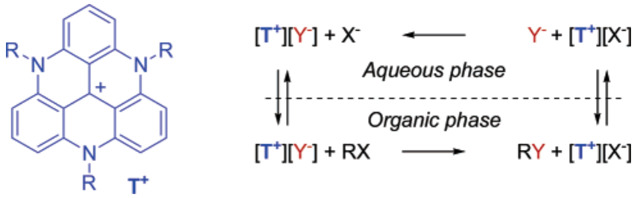
ABSTRACT



Highly stable triazatriangulenium carbocations, of pK_{R+} higher than 20, can be used as novel phase-transfer catalysts for several classical organic reactions, their intrinsic stability in strongly basic and nucleophilic conditions rendering this novel use feasible.

Since the pioneering work of Makosza almost 40 years ago[1] and the extensive study of Starks in the early 1970s,[2] phase-transfer catalysis (PTC) has become a topic of great interest belonging, nowadays, to the burgeoning fields of organocatalysis and green chemistry.[3,4]

PTC allows reactions to proceed through active transport by small molecules (in substoichiometric amount) of reactive polar reagents from one phase to another and has many advantages over other catalytic (and stoichiometric) processes: simple reaction procedure, safe, inexpensive, environmentally friendly reagents, absence of anhydrous solvents, ease of scale-up, and (most often) metal-free conditions.

Many PTC-mediated processes are performed under strongly basic and nucleophilic conditions. As such, the small organic molecules that are used as phase-transfer catalysts need to be stable under these strenuous conditions. If most polyethers as well as cationic nitrogen- and phosphorus-based catalysts fit the case, it is not so for usual carbocations. These moieties, although interesting due to their charge and the subsequent solubility of their salts in both aqueous and organic phases,[5] are general electrophiles reacting with strong bases and nucleophiles to form neutral adducts by addition, elimination, or fragmentation reactions.[6] Carbocations have, per se, not been used as catalysts for PTC purposes, and it was questionable whether they would ever be.

Reports have however indicated that highly stable carbenium ions can be prepared.[7] Recently, a new class of such derivatives have been described that make use of the reaction of tris(2,6-dimethoxyphenyl)carbenium ion **1** with primary alkylamines to form a variety of very stable carbocations

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[4] Yadav, G. D. *Top. Catal.* **2004**, *29*, 145−161. Yadav, G. D.; Lande, S. V. *Adv. Synth. Catal.* **2005**, *347*, 1235−1241. Yadav, G. D.; Desai, N. M. *Org. Process. Res. Dev.* **2005**, *9*, 749−756.

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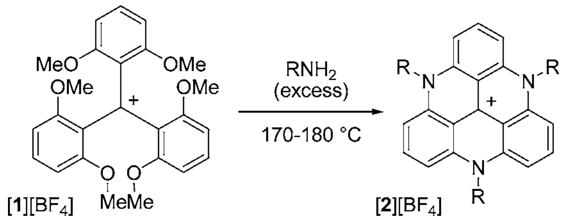
and triazatriangulenium ions of type **2** in particular (Scheme 1).[8,9] We thus wondered whether the high chemical stability of moieties **2**—translated in quantitative terms by a highly positive pK_{R+} value ($\geq$20)—was sufficient to permit their use as phase-transfer catalysts. Herein, we report that it is indeed the case as several classical PTC reactions can be mediated by these carbenium ions, with their efficiency being compared to that of tetrabutylammonium (as its bromide salt, TBAB) and/or 18-crown-6 (18-C-6).

Scheme 1. One-Step Synthesis of Triazatriangulenium Salts, [**2a**][BF$_4$]−[**2d**][BF$_4$]



2a	R = (CH$_2$)$_2$OH	41%
2b	R = (CH$_2$)$_2$CH$_3$	40%
2c	R = (CH$_2$)$_5$CH$_3$	44%
2d	R = (CH$_2$)$_7$CH$_3$	44%

As the efficacy of a phase-transfer catalyst often depends on its partition ability between aqueous and organic phases and, hence, on its hydrophilicity/lipophilicity, several triazatriangulenium cations were prepared, **2a**−**2d**, bearing alkyl side chains of various lengths and polar/apolar character (R = CH$_2$CH$_2$OH, *n*-Pr, *n*-Hex, and *n*-Oct, respectively; Scheme 1). These triazatriangulenium ions were synthesized by the simple reaction of salt [**1**][BF$_4$] with the corresponding primary amines in excess at elevated temperatures (170−180 °C).[10] Purification of the resulting salts, [**2a**][BF$_4$]−[**2d**][BF$_4$], was better afforded by crystallization (e.g., CH$_3$CN/Et$_2$O or MeOH), although the necessity to perform the purification steps several times afforded analytically pure samples in reduced yields (40−44%, Scheme 1).

To check the lack of reaction of the carbenium ions under strongly basic and nucleophilic conditions and thus the viability of the PTC approach, care was taken to select test reactions that would associate, as ion pairs along the mechanistic pathways, carbenium ions **2** with reactive bases (e.g., OH$^-$) and nucleophiles (e.g., OOH$^-$, enolates). Three reactions fitting this description (a β-keto ester alkylation, an alkene epoxidation, and an olefin dichlorocarbene addition) were selected for the study along with a synthetically useful alkene aziridination.

The generation of tertiary and quaternary centers by C−C bond-forming reactions is of great importance for the synthesis of natural and unnatural products.[11] For this reason, the alkylation of (α-substituted) β-keto esters has been strongly studied. This reaction is amenable to PTC using strongly basic conditions and a biphasic mixture of solvents (e.g., 50% KOH, toluene/water, or CH$_2$Cl$_2$/water). The alkylation of methyl-1-oxo-2-indanecarboxylate **3** by benzyl bromide to afford α,α'-disubstituted β-keto ester **4** was chosen as a particular example. Halogenated solvents (CHCl$_3$, CH$_2$Cl$_2$) were selected as organic phases because of the high solubility of salts [**2b**][BF$_4$]−[**2d**][BF$_4$] in these media, with compound [**2a**][BF$_4$] being, on the contrary, highly soluble in water. The results are reported in Table 1.

Significantly, salts [**2b**][BF$_4$]−[**2d**][BF$_4$] behaved as effective catalysts; no reaction was observed in their absence or in the presence of [**2a**][BF$_4$]. Whereas salt [**2b**][BF$_4$] gave slightly lower yields of **4** than TBAB, compounds [**2c**][BF$_4$] and [**2d**][BF$_4$] gave similar and better results, respectively. With the latter salt, yields could be increased using longer reaction times (3 vs 1 h). Lower catalyst loading (5 mol %) was amenable. As far as solvent effects are concerned, biphasic CH$_2$Cl$_2$/H$_2$O conditions were better overall than CHCl$_3$/H$_2$O conditions.[12]

In the case of **2a**, the effective partitioning of the carbenium ion in the aqueous layer prohibits any reaction of its hydroxide salt with **3** in the organic layer. The difference in the reactions performed in the presence of salts [**2b**][BF$_4$]−[**2d**][BF$_4$] is probably due to an increased lipophilicity of the cations. The more lipophilic the carbenium ion is, the better catalyst it is for this reaction.

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(9) Triazatriangulenium cations are related to the historically important class of trioxatriangulene derivatives. For references on these moieties and on azadioxa and diazaoxo derivatives as well, see: Martin, J. C.; Smith, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 2252−2256. Lofthagen, M.; Chadha, R.; Siegel, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 8785−8790. Lofthagen, M.; Siegel, J. S. *J. Org. Chem.* **1995**, *60*, 2885−2890. Andresen, T. L.; Krebs, F. C.; Larsen, M.; Thorup, N. *Acta Chem. Scand.* **1999**, *53*, 410−416. Krebs, F. C. *Tetrahedron Lett.* **2002**, *44*, 17−21. Krebs, F. C.; Spanggaard, H.; Rozlosnik, N.; Larsen, N. B.; Jorgensen, M. *Langmuir* **2003**, *19*, 7873−7880.

(10) Cations **2a**−**2d** result from the nucleophilic aromatic substitutions (S$_N$Ar) of all six methoxy substituents of **1** by nitrogen-containing moieties; see refs 8c and 8d.

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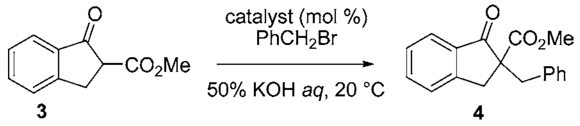
(12) The lower yield in CHCl$_3$ might be the result of a side reaction, that is, the attack of the solvent by the hydroxyde anion associated with the carbenium ion **2**.

Table 1. PTC Alkylation of Methyl-1-oxo-2-indanecarboxylate



entry	catalyst[a]	mol %	solvent	time (h)	yield (%)[b]
1	none		CH_2Cl_2	19	0
2	TBAB	10	$CHCl_3$	1	60
3	TBAB	10	CH_2Cl_2	1	50
4	[**2a**][BF_4]	10	$CHCl_3$	1	0
5	[**2a**][BF_4]	10	CH_2Cl_2	1	0
6	[**2b**][BF_4]	10	$CHCl_3$	1	40
7	[**2b**][BF_4]	10	CH_2Cl_2	1	55
8	[**2c**][BF_4]	10	$CHCl_3$	1	60
9	[**2c**][BF_4]	10	CH_2Cl_2	1	65
10	[**2d**][BF_4]	10	$CHCl_3$	1	70
11	[**2d**][BF_4]	10	CH_2Cl_2	1	85
12	[**2d**][BF_4]	1	CH_2Cl_2	3	35
13	[**2d**][BF_4]	2	CH_2Cl_2	3	60
14	[**2d**][BF_4]	5	CH_2Cl_2	3	92[c]
15	[**2d**][BF_4]	10	CH_2Cl_2	3	99

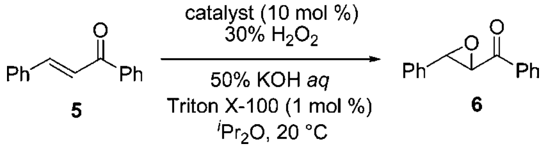
[a] Unless otherwise specified, the reaction was carried out with **3** (29 mg, 150 μmol), catalyst (10 mol %), benzyl bromide (22 μL, 180 μmol), and mesitylene (21 μL, 150 μmol), in a mixture of 50% KOH aq (42 μL, 750 μmol) and halogenated solvent (1 mL). [b] Yield measured by ^1H NMR spectroscopy using mesitylene as an internal reference. [c] 85% isolated yield of **4**.

After this example, the ability of carbenium ions **2** to perform under strongly basic and nucleophilic conditions was tested further in the context of the epoxidation of *trans*-chalcone **5**. For this reaction, a variety of biphasic or triphasic conditions are known using, as stoichiometric oxidants, sodium/potassium hypochlorite, hydrogen peroxide, alkyl hydroperoxide, combinations of urea and H_2O_2, sodium perborate or percarbonate, as well as trichloroisocyanuric acid.[13] Recently, an effective protocol was developed using a cocatalytic amount of surfactant.[14] These are the conditions (H_2O_2 (10 equiv), 50% KOH aq, $^iPr_2O/H_2O$, TRITON X-100 (1 mol %)) that were used to test the efficiency of salts [**2a**]-[BF_4]–[**2d**][BF_4] as catalysts. Results are summarized in Table 2.

Interestingly, all four salts [**2a**][BF_4]–[**2d**][BF_4] behaved as catalysts. Whereas salts [**2a**][BF_4]–[**2c**][BF_4] gave slightly lower yields of epoxide **6** than TBAB, compound [**2d**][BF_4] gave better results (44 vs 35% isolated yields); this example demonstrates further the general aptitude of carbenium ions **2** to act as phase-transfer catalysts for reactions performed under strongly basic and nucleophilic conditions.

Having showed that liquid/liquid PTC reactions can be mediated by carbenium ions **2**, a solid/liquid PTC protocol was tested in the context of a cyclopropanation of styrene **7**.[15] Previously, Nomura and collaborators have reported a procedure of this type to generate *gem*-dichlorocyclopropane **8** (Table 3).[16] The results of the reactions (KOH powder (5.0 equiv), $CHCl_3$ (5.0 equiv), CH_2Cl_2/H_2O) in the presence of salts [**2a**][BF_4]–[**2d**][BF_4] are reported in Table 3 and are compared with those of TBAB and 18-C-6 as catalysts.

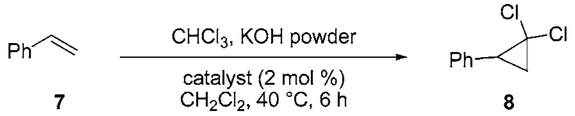
Table 2. PTC Epoxidation of *trans*-Chalcone[a]



entry	catalyst	time (h)	Triton X-100	conversion (%)[b]	yield (%)[c]
1	no	18	yes	0	0
2	TBAB	17	yes	45	35
3	[**2a**][BF_4]	17	yes	21	16
4	[**2b**][BF_4]	17	yes	27	23
5	[**2c**][BF_4]	17	yes	26	22
6	[**2d**][BF_4]	17	yes	50	44

[a] Aqueous H_2O_2 (30%, 270 μL; 2.4 mmol) and 50% KOH aq (27 μL, 0.24 mmol) were added to a mixture of chalcone **5** (50 mg, 0.24 mmol), catalyst (10 mol %), naphthalene (0.24 mmol, reference), and Triton X-100 (1 mol %) in diisopropyl ether (0.8 mL). [b] Conversion was determined by HPLC analysis (Nucleosil 50-5, hexane/*i*PrOH 99:1, 0.5 mL min^{-1}, 23 °C, λ 230 nm; t_R 5.05 min (naphthalene), 6.6 min (*trans*-chalcone **5**), 7.3 min (epoxide **6**)). [c] Isolated yields after flash chromatography (SiO_2, hexane/EtOAc 9:1, R_f 0.22).

Table 3. PTC Addition of Dichlorocarbene to Styrene[a]



entry	catalyst	equiv of $CHCl_3$/KOH	conversion (%)[b]	yield (%)[b]
1	no	5.0	12	10
2	18-C-6	5.0	100	>95[c]
3	TBAB	5.0	100	100
4	[**2a**][BF_4]	5.0	16	16
5	[**2b**][BF_4]	5.0	28	27
6	[**2c**][BF_4]	5.0	27	27
7	[**2d**][BF_4]	5.0	26	26
8	no	20.0	20	18
9	[**2b**][BF_4]	20.0	70	68[d]

[a] To a stirred CH_2Cl_2 (305 μL) solution of styrene (70 μL, 0.60 mmol) with powdered KOH (171 mg, 3.0 mmol, 5 equiv), catalyst (2 mol %), and mesitylene (73.2 mg, 85 μL, 0.6 mmol) was added $CHCl_3$ (3.0 mmol, 244 μL, 5 equiv) dropwise at 40 °C. [b] Conversions and yields determined by ^1H NMR using mesitylene as an internal reference. [c] 90% isolated yield obtained by distillation on a 10 mmol scale of starting material **7**. [d] 65% isolated yield obtained by distillation on a 10 mmol scale of starting material **7**.

In this case, salts [**2a**][BF_4]–[**2d**][BF_4] performed less efficiently than 18-C-6 or TBAB. Using 5.0 equiv of $CHCl_3$

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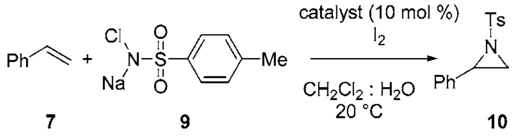
and KOH powder as reagents and a standard reaction time of 6 h, a maximum yield of 27% was obtained for **8** in the reactions catalyzed by the carbenium ions and essentially quantitative reactions were obtained using TBAB or 18-C-6. Whereas salts [**2a**][BF_4]−[**2d**][BF_4] could compete effectively with TBAB or 18-C-6 in liquid/liquid PTC reactions, slower kinetics hamper their efficiency in this solid/liquid protocol. As far as we can tell (NMR, UV), there is no catalyst decomposition or deactivation in the crude reaction mixture. The lower rates may then be due to a poor extraction of OH^- from the surface of the powdered KOH by the carbenium ions **2**. To compensate this effect, a larger excess of reagents can be used. For instance, a decent yield of **8** (70%) can be afforded if 20 equiv of $CHCl_3$/KOH powder is used.

Finally, a synthetically useful PTC alkene aziridination reaction was tested in the presence of carbenium ions **2** as catalysts. The effective protocol developed by Minakata and Komatsu,[17] that is, the PTC reaction of olefins with a mixture of Chloramine-T (**9**) and diiodine, was used, and the results are summarized in Table 4. With styrene **7** as the substrate, a standard reaction time of 5 h, and 10 mol % of carbenium ions or TBAB as catalysts, aziridine **10** was afforded in low to moderate yields. Salts [**2c**][BF_4] and TBAB were the two best phase-transfer agents this time. As the mild conditions of the reaction did not lead to any decomposition of the reagents or products, higher conversions and yields (80−85%) were easily afforded by extending the reaction time to 15 and 24 h with salts TBAB and [**2c**][BF_4], respectively.

Table 4. PTC Aziridination of Styrene by Chloramine-T/I_2[a]



entry	catalyst	time (h)	conversion (%)[b]	yield(%)[c]
1	no	5	5	3
2	TBAB	5	37	30
3	[**2a**][BF_4]	5	7	5
4	[**2b**][BF_4]	5	9	7
5	[**2c**][BF_4]	5	28	23
6	[**2d**][BF_4]	5	20	16
7	TBAB	15	95	80
8	[**2c**][BF_4]	24	∼100	85

[a] Reaction conditions: at room temperature, styrene (49 μL, 0.43 mmol), chloramine-T (60 mg, 0.21 mmol), catalyst (10 mol %), iodine (5.4 mg, 0.021 mmol), and phenanthrene (7.6 mg, 0.043 mmol) were stirred in CH_2Cl_2/H_2O (1:1, 1.3 mL). [b] Conversion was determined by HPLC analysis (Nucleosil 50-5, hexane, 0.5 mL min^{-1}, 23 °C, λ 254 nm; t_R 6.19 min (styrene), 7.99 min (phenanthrene)). [c] Yield of isolated product **10** after column chromatography (SiO_2, hexane/EtOAc 9:1, R_f 0.26).

In conclusion, experimental data indicate that PTC reactions can be performed using chemically robust carbenium ions as phase-transfer catalysts. This is an interesting development in this field of organocatalysis as highly stable [4]helicenium ions can be readily synthesized and resolved;[18] these derivatives are then possible nonracemic reagents for enantioselective PTC processes.[19]

Acknowledgment. We are grateful for financial support of this work by the Swiss National Science Foundation and the State Secretariat for Education and Research.

Supporting Information Available: Synthesis and spectral characterization of novel salts [**2a**][BF_4] and [**2c**][BF_4]. This material is available free of charge via the Internet at http://pubs.acs.org.

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