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FULL PAPER

Syntheses of Phosphonium Salts from Phosphines and Carbenium: Efficient CO_2 Fixation and Phase-Transfer Catalysts

Aslam C. Shaikh,[a] José M. Veleta,[a] Jan Bloch,[b] Hannah J. Goodman,[a] and Thomas L. Gianetti,*[a]

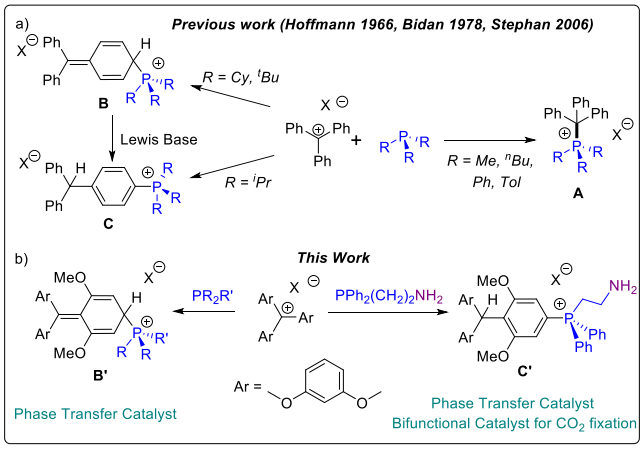
Abstract: A new library of phosphonium salts has been synthesized from the reaction of tris-(2,6-dimethoxyphenyl)carbenium with different phosphines. The resultant phosphoninum salts work as efficient phase transfer catalysts for the alkylation of 1,3-dicarbonyl compounds. One compound, a bifunctional phosphonium salt prepared from tris-(2,6-dimethoxyphenyl)carbenium and an aminophosphine, was also found to be an efficient catalyst for CO_2 fixation reactions with epoxides under mild conditions.

Introduction

Quaternary phosphonium salts[1] are used in a variety of organic transformations. They are used as Wittig reagents, Lewis acid organocatalysts, ionic liquids, and anti-cancer agents.[2] Further applications include asymmetric catalysis, drug delivery, and phase-transfer catalysis precursors.[3] Phase-transfer catalysis (PTC) is a process widely used in laboratory synthesis and in industry. Recent developments in PTC involve tetraamino-phosphonium salts, along with other cationic systems (imidazolium, triazolium, cyclopropenium, etc.).[4] Most practical syntheses of quaternary phosphonium salts are limited to either phosphine arylation/alkylation[5] or coupling reactions of an aryl halide (alkyl/Ar-X) with a triarylphosphine (Ar_3P). Another extensively studied transformation that uses bifunctional quaternary ammonium and phosphonium salts is the synthesis of cyclic carbonates using epoxides and CO_2.[6] These processes have also been studied using KI−tetraethylene glycol complexes, transition metals, and cationic polymer systems.[7] Considering their diverse range of applications, it is desirable to develop novel synthetic approaches to quaternary phosphonium salts.

Trityl[8] cation and its analogues have played significant roles in a variety of stoichiometric and catalytic reactions,[9] in material science, and in cell-imaging studies.[10] Several groups have used the Lewis acidity of these carbeniums to form quaternary phosphonium adducts (Scheme 1a),[11] and in 2006 Stephan and coworkers reported their crystal structures.[12] Insight into the reactivity of these compounds was provided from Bidan and Genies' conclusion that the steric demands of the phosphine determine the course of the reaction.[10d] They further determined that small phosphines bind these moieties at the carbon cation center (compound **A**, Scheme 1a), while sterically demanding phosphines undergo nucleophilic aromatic substitution (S_NAr) at the *para* position (compounds **B** - **C**, Scheme 1a). They also showed that the isomerization of cyclohexadienyl isomer **B** to the phenyl isomer **C** is Lewis base-catalyzed. This phosphine–trityl interaction was further explored by Stephan in 2014 and Berionni in 2017 with the design of new Frustrated Lewis Pairs (FLP), in which tritylium ions act as Lewis acids and phosphines act as Lewis bases.[13],[14] However, other than FLP reactivity, trityl phosphonium compounds remain largely unexplored for applications in organic synthesis. To the best of our knowledge, the reactivity between derivatives of trityl cation and phosphines to form novel quaternary phosphonium ions has not yet been reported (Scheme 1b). Of the compounds that make up the triaryl carbenium family, tris-(2,6-dimethoxyphenyl)carbenium[15] has received increasing interest since it was first published in 1964.[10,16] Notably, Lacour *et al.* reported the direct coupling of this triaryl carbenium ion with indoles and anilines that proceed via nucleophilic attack at the *para* position,[17] similarly to the reactivity observed in isomer **B** (Scheme 1a).

Herein, we report the reaction of tris-(2,6-dimethoxyphenyl)carbenium with alkyl/aryl phosphines (PMe_3, $PPhMe_2$, PPh_2R, with R = CH_3, $(CH_2)_2NH_2$)). This results almost exclusively in S_NAr at the *para* position of the carbenium moiety, leading to the formation of cyclohexadiene isomer **B′** regardless of the phosphine used (Scheme 1b). Aromaticity is rapidly reformed in the isomer **C′** by amine-catalyzed tautomerization.[11a] Both phosphonium isomers **B′** and **C′** were found to be efficient phase transfer catalysts. We also report the synthesis of a bifunctional aminoethyl–phosphonium cation **5** and its application as a catalyst for CO_2 fixation.



Scheme 1. Reactivity of phosphine towards trityl cation.

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Supporting information for this article is given via a link at the end of the document. CCDC 1984242 contain the supplementary crystallographic data for this paper

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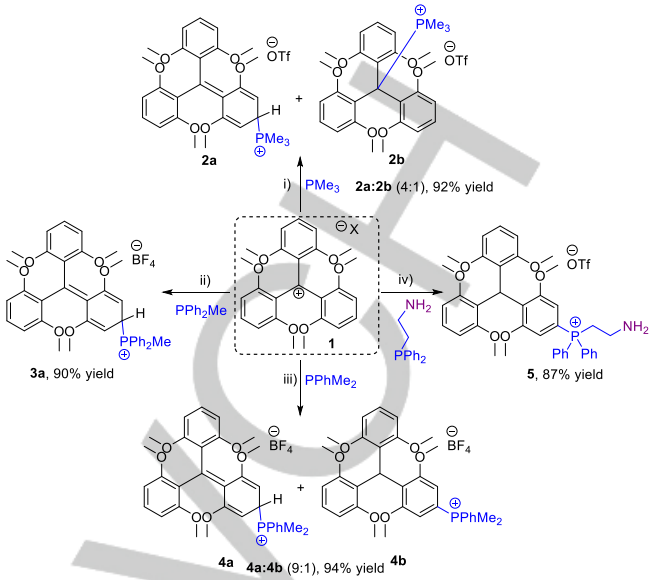
Results and Discussion

Synthesis and characterization of phosphonium salts: The addition of trimethylphosphine to a solution of tris(2,6-dimethoxyphenyl)methylium triflate in CH_2Cl_2 at room temperature yields a colorless, crystalline, air-stable mixture of phosphonium salts **2a** and **2b** in 92% yield (Scheme 2i). The ^{31}P NMR spectrum indicates the formation of two phosphonium species in 4:1 ratio (Figure S1). The major isomer **2a** has a ^{31}P chemical shift of 35 ppm, while the minor isomer **2b** resonates at 56 ppm. The $\{^1H\}^{31}P$ NMR spectrum for **2a**, reveals that the phosphorous is strongly coupled to several hydrogens, while the phosphorous in **2b** possesses much weaker coupling. ^1H NMR spectroscopy shows that the minor isomer **2b** has C_3 symmetry (Figure S2), based on comparison to the D_3 symmetry of **1**. The loss of the C_2 rotation axis is shown by the presence of two asymmetrical methoxy groups presenting two distinct proton signals. The retention of the principal C_3 axis of rotation suggests that the phosphorous is bound to the central carbon of the carbenium scaffold. On the other hand, the ^1H NMR spectrum of **2a** shows C_s symmetry, suggesting that PMe_3 attacked another position of carbenium **1**. The 2 sets of correlated protons in a 2:1 ratio at 4.30 ppm (dd, $^3J_{P\text{-}H}$ = [4-6] Hz, $^3J_{H\text{-}H}$ = 5.4 Hz, 2H) and 3.75 ppm (dt, $^2J_{P\text{-}H}$ = 25.2 Hz, $^3J_{H\text{-}H}$ = 5.4 Hz, 1H) suggest that PMe_3 attacked at the *para* position of one aromatic ring. Thermal treatment and variable temperature NMR spectroscopy analysis did not show interconversion between **2a**–**2b** or affect their relative ratio. Only thermal decomposition and formation of an untraceable mixture of products was observed after several hours.

Interestingly, this reactivity is different from prior reports of interactions between PMe_3 and trityl cation,[11] which provided exclusive formation of the symmetric isomer **A** (*vide supra*). DFT calculations of **1** and trityl cation show that, even though **1** has a larger number of electron donating groups, the lowest unoccupied molecular orbital (LUMO) of both molecules has a larger distribution of the wavefunction on the central carbon (Figure 1). This suggests that differences in reactivity are mostly controlled by steric hindrance imposed by the methoxy groups. The upfield ^{31}P NMR chemical shift of **2b** compared to **2a** (56 ppm and 35 ppm, respectively, Figure S1) supports this claim of larger positive charge at the central carbon. It is conceivable, then, that increasing the cone angle and steric bulk of the phosphine should result in quantitative formation of the *para* product. Unlike the trityl cation, treatment of tris(2,6-dimethoxyphenyl)methylium cation with triphenylphosphine failed to yield the phosphonium salt. Free PPh_3 and **1** were observed in solution, which can be rationalized by the fact that **1** is less Lewis acidic than the unsubstituted trityl cation. However, using sterically demanding and stronger σ-donor phosphines (diphenylmethyl or phenyldimethyl) led to the formation of **3a** and **4a** (Scheme 2ii-iii). These products were crystallized from CH_2Cl_2/hexanes and isolated in good yield (90% and 94%, respectively). The ^1H NMR spectrum of complexes **3a-4a** indicates C_s symmetry with 2 sets of correlated protons in a 2:1 ratio at 4.66 ppm (t, $^3J_{H\text{-}H}$ = 5.4 Hz, 2H) and 4.35 ppm (dt, $^2J_{P\text{-}H}$ = 25.3 Hz, $^3J_{H\text{-}H}$ = 5.3 Hz, 1H) for **3a** (Figure S4) and at 4.45 ppm (t, $^3J_{H\text{-}H}$ = 5.5 Hz, 2H) and 4.97 ppm (dt, $^2J_{P\text{-}H}$ = 24.3 Hz, $^3J_{H\text{-}H}$ = 5.2 Hz, 1H) for **4a** (Figure S6). Both ^{31}P NMR signals for these phosphoniums are characteristic of the formation of the cyclohexadiene scaffold as observed in **2a** (Figure S6, S9).



Scheme 2. Synthesis of phosphonium salts.[a] Unless otherwise noted, all reactions were carried out on a 1 mmol scale using **1**, 1.2 mmol phosphine in 5 mL of CH_2Cl_2 for 5 min at rt.[b] Isolated yields are given; (X = BF_4, OTf).

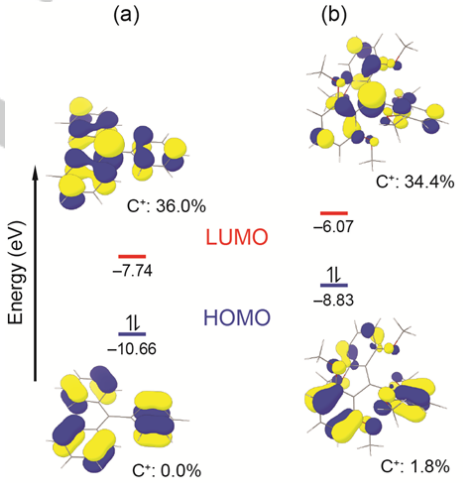


Figure 1. Molecular orbitals of (**a**) triphenylcarbenium and (**b**) tris(2,6-dimethoxyphenyl)methylium cations. Contribution of the carbocation center for each MO was obtained from the normalized wavefunction after geometry optimization and frequency calculations. Contour surface diagrams of the MOs are shown at a 0.04 isovalue.

Interestingly, conversion to the cyclohexadiene moiety was not quantitative when $PPhMe_2$ was used. Careful analysis of both ^1H and ^{31}P NMR spectra reveals the formation of about 15% of a minor isomer **4b** (Figure S7 and S9). The ^{31}P NMR spectrum of this minor phosphonium isomer resonates at 21 ppm, 5 ppm upfield from **4a**. The slight upfield shift suggests that **4b** has a more electropositive phosphonium moiety. In the ^1H NMR spectrum, isomer **4b** has a singlet at 6.53 ppm (1H) and a doublet at 6.81 ppm (d, $^3J_{P\text{-}H}$ = 14.8 Hz, 2H) assigned to the central sp^3-hybridized methyl proton and the two aromatic protons *ortho* to the phosphonium group. These values are consistent with previously reported values for $HC(Ar)_3$ (6.38 ppm for methine, Ar = 2,6-dimethoxyphenyl)[17] and for $HC(p\text{-}^iPr_3PC_6H_4)Ph_2$) (5.69 ppm methine).[11] These results support proton transfer from the

para position to the carbon center along with aromatization of the ring, which is similar to the isomerization observed during the reaction between trityl cation and P^iPr_3 (scheme 1, compound **C**).[11]

The major phosphonium isomer **2a** was recrystallized from CH_2Cl_2/hexanes. Its structure was confirmed by single crystal X-ray diffraction, which showed the formation of a dissymmetric phosphonium salt from phosphine attack at the less sterically hindered *para* position of **1** (Figure 2). The alternating short/long C-C bond distances of the ring and the short C4-C7 bond distance support the presence of a dearomatized cyclohexadiene system. The P1-C1 bond distance of 1.835 Å is within the normal range for phosphonium–carbon bonds (1.8–1.9 Å).[18] The steric hindrance imposed by the methoxy groups is evident by the distortion observed around the C7=C4 double bond, and a dihedral angle of about 17° is observed.

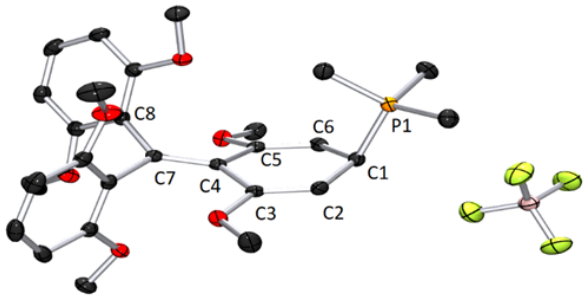
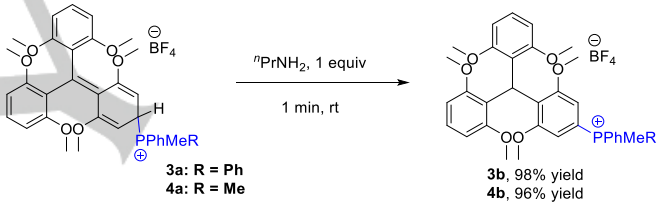


Figure 2. Ortep diagram of **2a**. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond distances (A): P1–C1 = 1.8348(16); C1–C2 = 1.498(2); C2–C3 = 1.342(2); C3–C4 = 1.482(2); C4–C5 = 1.484(2); C5–C6 = 1.339(2); C6–C1 = 1.497(2); C4–C7 = 1.357(2). Selected angles (°): C5-C4-C7-C8 = 17.1.

Seeking inspiration from the formation of **2-4,** a bifunctional phosphonium salt (**5**) was targeted and synthesized by reacting **1** with 2-(diphenylphosphenyl)ethan-1-amine at rt for 5 min (Scheme 2iv). Crystallization from CH_2Cl_2/hexanes afforded pale pink microcrystalline material in 87% yield. The ^1H and ^{31}P NMR spectra of **5** show characteristic signals for the triaryl moieties (with two pairs of methoxies) and for the $P(Ph_2)CH_2CH_2NH_2$ unit (^{31}P at 23 ppm, two methylene sets coupled to ^{31}P, and a broad singlet for NH_2) in a 2:1 ratio. These data suggest low C_s symmetry, supporting phosphine attack at the *para* position (Figure S18-S24). However, the ^1H and $\{^1H\}^{13}C$ NMR spectra are not consistent with the signature observed for the phosphonium salts **2a, 3a** and **4a**. Instead, the ^1H NMR spectra of **5** resembles that of the minor isomer **4b** (Scheme 2iii) and compound **C** (Scheme 1), which both undergo hydrogen transfer and aromatization. The proton beta to the phosphorous moiety resonates at 7.06 ppm (compared to 4-5 ppm for **2-4**) and only exhibits coupling to the phosphorous (d, $^3J_{P\text{-}H}$= 8.2 Hz, 2H), which supports the presence of an aromatic, not olefinic, proton. The methine proton resonates at 6.49 ppm as a singlet with no ^{31}P or ^1H coupling (compared to the doublet of triplets between 3.5–4.5 ppm for **2-4**), further supporting hydrogen atom transfer from the cyclohexadiene moiety to the central carbon (see ESI). The $\{^1H\}^{13}C$ NMR and ^1H–^{13}C HSQC spectroscopy analysis of **5** reveals that the methine proton is bound to a singlet carbon that resonates at 31.18 ppm (Figure S15, S19). This contrasts with the doublet observed for the carbon bound to the methine proton in **2a**-**4a** (δ = 35.04 ppm for **2a**, 86.41 ppm for **3a**, and 41.43 ppm for **4a**), supporting isomerization.

Two pathways can be proposed for hydrogen atom transfer and aromatization of the cyclohexadiene moiety: 1) intramolecular [1,5] sigmatropic shift, or 2) base-assisted tautomerization. Thermal treatment of cycohexadiene isomers **3a** or **4a** did not lead to isomerization and hydrogen transfer to form **3b** and **4b**. Additionally, PPh_2Me and PPh_2R (R = $CH_2CH_2NH_2$) have similar cone angle and σ-donor ability.[19] Therefore, quantitative isomerization observed in **5** cannot be rationalized by electronic and steric properties of the phosphine. Furthermore, when the cyclohexadienyl isomers **3a** and **4a** were treated with 1.0 equivalents of $^nPrNH_2$, immediate formation of the aryl isomers **3b** and **4b** was observed (see Scheme 3 and Figure S10-S17). This results suggests that isomerization occurs via base-assisted tautomerization, which is consistent with the work of Bidan and Genies on trityl cation.[10d] The stronger basicity of $PPhMe_2$ (pKa = 6.50) relative to PPh_2Me (pKa = 4.57)[18, 20] explains the formation of minor isomer **4b** from $PPhMe_2$, while the amine group of $PPh_2CH_2CH_2NH_2$ promotes quantitative tautomerization to form **5**.



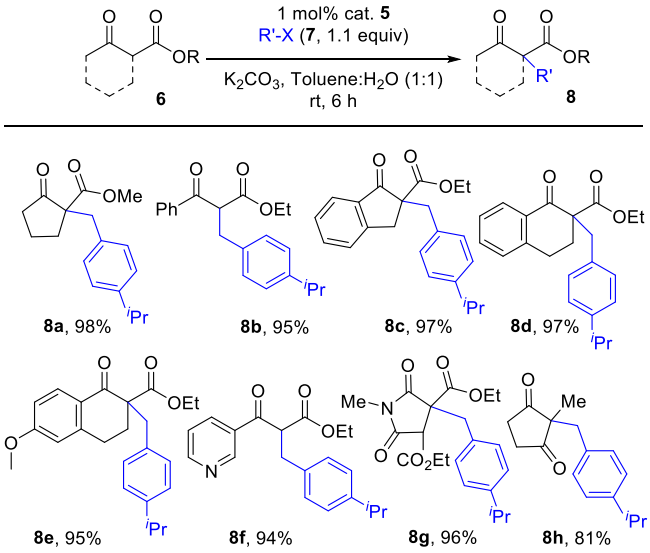
Scheme 3. Base-catalyzed tautomerization of **3a-4a** to **3b-4b**.

The phosphonium salts **2-5** were investigated as catalysts for phase-transfer alkylation.[21] The reaction between β-ketoester (**6a**) and alkyl bromide (**7**) in the presence of base and the phosphonium salts (1 mol%) in toluene/H_2O (1:1 mixture) yielded the desired product **8** (See Table 1 and SI). Of the phosphonium salts screened, **5** gave the highest yield (**8a** in 98% yield). The scope of the phase-transfer alkylation reaction was further investigated under optimized reaction conditions (Table 1). Several β-ketoesters were screened that produced alkylation products **8b**-**8h** in good to excellent yield (81-98%). This reaction was performed on a gram scale to produce **8a**, which was isolated in 92% yield.

Bifunctional catalyst, species containing both a cationic and protic fucntionality, are known to catalyse the chemical fixation of carbon dioxide (CO_2) using epoxide for production of cyclic carbonates under 1 atm of CO_2.[7],[22] The bifunctional phosphonium **5** was found to be a very efficient catalyst for this transformation. After optimizating reaction conditions,[23] 1 mol% of **5** and 10 mol% of NaI under CO_2 in chlorobenzene at 100 °C for 12 h yielded formation of the desired cyclic carbonate in 92% yield with >99% conversion. A series of substituted epoxides (**9b**–**9g**) performed efficient CO_2 fixation to yield the corresponding desired carbonates (**10b**–**10g**) in good to excellent yields (83–92%, Table 2). The reactions with 1,2-disubstituted epoxide **9h** proceeded slowly to give cyclic carbonate **10h**. Raising the

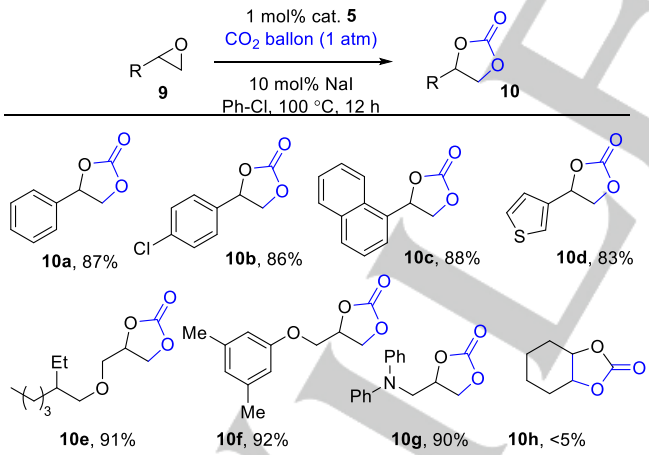
temperature to 120 °C did not significantly alter the rate of the reaction.

Table 1. Substrate scope for phase-transfer alkylation reaction[a,b]



[a]Unless otherwise noted, all reactions were carried out on a 0.50 mmol scale using **6**, 0.55 mmol **7**, cat **5** (1 mol%), 1.1 equiv. K_2CO_3, 2 mL toluene:H_2O (1:1) for 6 h. See Supporting Information for details.[b] Isolated yields are given.

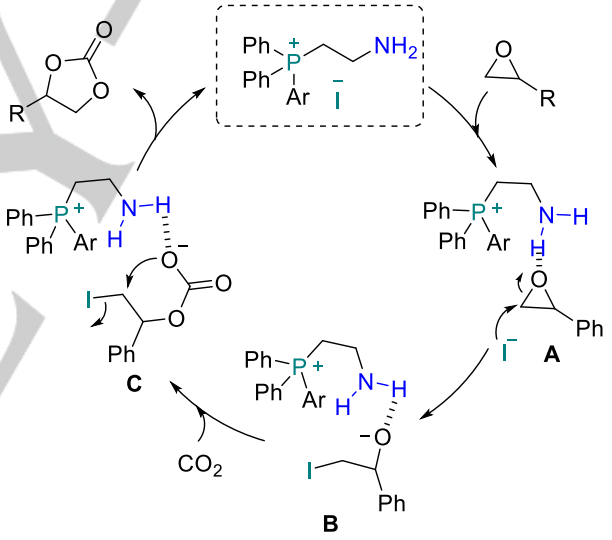
Table 2. Substrate scope for CO_2 fixation.[a,b]



[a]Unless otherwise noted, all reactions were carried out on a 1.0 mmol scale using **9**, 0.01 mmol NaI, 1 mol% cat **5**, 2.7 mL chlorobenzene at 100 °C for 12 h (See ESI).[b] Isolated yields are given.

Frustrated Lewis pairs (FLPs) are well known to promote a large variety of organic transformations.[24] However, no catalytic CO_2 fixation was observed when the triaryl cation **1** was used in the presence of PPh_3, thus ruling out the involvement of an FLP-type mechanism (entry 1, Table S4).

It is established in relevant literature that the bifunctional nature of catalysts is required to promote CO_2 fixation with epoxides.[7,22] It has been proposed that, on one hand, epoxide acitivation and CO_2 insertion are both facilitated by hydrogen bonding to the protic part of the catalyst.[22a-b] On the other hand, the cationic nature of the catalyst promotes ring opening by bringing the halide anion in close proximity to the activated epoxide.[25] Under optimized conditions, abscence of catalyst, or when compounds **3b, 4b,** or PPh_3 are used instead of **5**, little to no conversion was observed, supporting the need for a hydrogen bonding interaction (entry 2-5, Table S4). Furthermore, no conversion was observed in this reaction with $^{n}PrNH_2$ or $PPh_2(CH_2)_2NH_2$ alone (entry 6-7, Table S4), or with **5** (that contains a triflate counterion) in the absence of NaI (Entry 8, Table S4). Trace amounts of product were formed when 1 mol% of **3b** and 1 equiv. $^{i}PrNH_2$ was used (entry 9, Table S4). Finally, by monitoring the ^{1}H NMR spectrum of the reaction between the epoxide **9** and either **3b** or **5** in C_6D_5Br, in the presence of NaI, revealed that ring opening only ocurred with the bifunctional molecule **5** (Figure S25-S26). These observations are consistent with the need for an ion pair in close proximity to the hydrogen bond activated epoxide.



Scheme 4. A plausible mechanism for CO_2 fixation reaction.

Based on our mechanistic studies and previous reports,[7, 22, 25] we propose a plausible catalytic cycle for the CO_2 fixation in Scheme 4. The epoxide (**9**) is activated via hydrogen bonding with the amino group of aminoethyl–phosphonium cation (intermediate **A**). The activated epoxide intermediate **A** then undergoes nucleophilic attack from an iodide anion to form intermediate **B**. The reactive alkoxide in intermediate **B** attacks CO_2 to yield intermediate **C**, which affords cyclic carbonate (**10**) upon intramolecular ring closure.

Conclusions

A variety of phosphines were reacted with *tris*-(2,6-dimethoxyphenyl)carbenium to yield novel phosphonium salts, which were characterized by ^{1}H NMR, ^{31}P NMR, ^{1}H-^{13}C HSQC, and {^{1}H}^{13}C NMR spectroscopy, along with single crystal X-ray

crystallography. The steric hindrance imposed by the methoxy groups was rationalized as the cause for differences in reactivity between trityl cation and *tris*-(2,6-dimethoxyphenyl). These new phosphonium salts were found to be efficient catalysts for phase-transfer alkylation reactions. Finally, the synthesis of a bifunctional phosphonium salt was reported as well as its catalytic application in the synthesis of industrially significant cyclic carbonates by CO_2 fixation. Because of the efficiency of this catalyst system, it is worth further investigation for application to other synthetic aims.

Experimental Section

General considerations

The syntheses of phosphonium salts were carried out in oven dried vials or reaction vessels with magnetic stirring inside a N_2 filled glove box. Solvents were dried by passing them through an alumina column on a solvent purification system, then stored under molecular sieves. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringes. Most of the catalytic experiments were performed on the bench and monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plates was visualized under UV light at 254 nm. Further visualization was achieved by staining with *p*-anisaldehyde solution and heating. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in hexanes and flushed with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump. All chemicals and solvents were purchased from Sigma Aldrich, Fisher Scientific, Oakwood or VWR. Commercially obtained reagents were used without further purification. Compound **1** was prepared according to Laursen's report. [26]

I. Synthetic procedures for synthesis of 2-5

I.1 Reaction between tris(2,6-dimethoxyphenyl)methylium trifluoro- methanesulfonate (1) and PMe_3: To a stirred solution of **1** (500 mg, 1.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added trimethylphosphine (91 mg, 1.2 mmol, 1.2 equiv). The solution was stirred at rt for 5 min. After addition of the amine precursor, the reaction mixture immediately changed color from violet to colorless. The product was precipitated by addition of Et_2O (10 mL), filtered off, and washed with Et_2O (2 x 5 mL). Finally, the product was crystallized from layering diethyl ether on the product dissolved in acetonitrile to yield pure **2a**/**2b** as colourless crystals (0.595 g, 92% yield).

I.2 Reaction between tris(2,6-dimethoxyphenyl)methylium trifluoro-methanesulfonate (1) and PPh_2Me: To a stirred solution of **1** (501 mg, 1.0 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added methyldiphenylphosphine (222 mg, 1.2 mmol, 1.2 equiv). The solution was stirred at rt for 5 min. After addition of the amine precursor, the reaction mixture color immediately changed from deep to pale purple. The product was precipitated by addition of hexanes (5 mL), filtered, and washed with hexanes (2 x 5 mL). Finally, the product was crystallized by layering hexanes over a CH_2Cl_2 solution to yield pure **3a** as light purple microcrystalline material (0.690 g, 96% yield).

I.3 Reaction between tris(2,6-dimethoxyphenyl)methylium trifluoro-methanesulfonate (1) and $PPhMe_2$: In a glove box, dimethylphenylphosphane (222 mg, 1.2 mmol, 1.2 equiv) was added to a stirred solution of **1** (501 mg, 1.0 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL). The solution was stirred at ambient temperature for 5 min. After addition of the amine precursor, the reaction mixture color immediately changed violet to purple. The product was precipitated by addition of hexanes, filtered, and washed with hexanes. Finally, it was precipitated by adding twofold of hexanes to the CH_2Cl_2 solution, and further crystalized by slow diffusion of a hexane layer into a DCM solution containing the product, yielding **4a**/**4b** as colourless microcrystalline powder (0.610 g, 94% yield).

I.4 Representative procedure for amine mediated conversion of 3a/4a to 3b/4b: To a stirred solution of **3a** (200 mg, 0.28 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added $^nPrNH_2$ (17 mg, 1.0 mmol, 1.0 equiv) and the solution was stirred at ambient temperature for 5 min. After addition of the amine precursor, the reaction mixture color immediately changed from violet to light red. The product was precipitated with addition of hexanes, filtered, and washed with hexanes. Finally, it was crystallized by adding twofold of Et_2O to the CH_2Cl_2 solution yielding pure **3b** as red solid (0.192 g, 96% yield).

I.5 Reaction between tris(2,6-dimethoxyphenyl)methylium trifluoro-methanesulfonate (1) and $NH_2CH_2CH_2PPh_2$: In a glove box, 2-(diphenylphosphaneyl)ethan-1-amine (229 mg, 1 mmol, 1.0 equiv) was added to a stirred solution of **1** (570 mg, 1 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) and stirred at ambient temperature for 5 min. After addition of the amine precursor, the reaction mixture color immediately changed from purple to wine red. The product was precipitated by addition of Et_2O, filtered, and washed with Et_2O. Finally, it was crystallized by adding twofold of diethyl ether to the acetonitrile solution, yielding pure compound **5** as pink powder (0.840 g, 87% yield).

II.1 Representative Procedure for phase-transfer alkylation reaction: To a stirred solution of **6a** (0.5 mmol, 1.0 equiv) and cat. **5** (1 mol%) in toluene (1 mL) and aq. K_2CO_3 solution (1 ml, 1M) was added *p*-^{i}Pr benzyl bromide (1.1 equiv). The reaction mixture was stirred for 12 h and monitored by TLC. After complete conversion, the residue was diluted with water (5 ml) and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude reaction mixture was purified by flash chromatography on silica gel using Hexane/EtOAc in a 4:1 ratio.

II. 2 Representative procedure for CO_2 fixation reaction: In a 25 mL Schlenk flask, a mixture of styrene oxide **9a** (120 mg, 1 mmol), catalyst **5** (8 mg, 0.01 mmol, 1 mol %), sodium iodide (17.0 mg, 0.10 mmol, 10 mol %), and chlorobenzene (2.7 ml, 0.3 M) was heated at 100 °C for 12 h under a CO_2 atmosphere (1 atm, using a balloon). After cooling to room temperature, the reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1−3:1 as the eluent) to afford cyclic carbonate **10a** (142 mg, 92% yield, 4.95 mmol; Rf = 0.24 in hexane/EtOAc = 3:1).

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Keywords: triarylcarbenium • phosphonium • bifunctional catalyst •CO_2 fixation • phase-transfer catalysis

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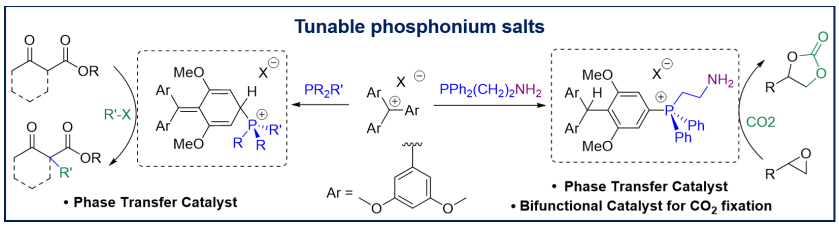

A new library of phosphonium salts has been synthesized from the reaction tris-(2,6-dimethoxyphenyl)carbenium with different phosphines. All of these phosphoninum salts were efficient phase transfer catalysts for alkylation of 1,3 dicarbonyl compounds. One compound, a bifunctional phosphonium salt prepared from tris-(2,6-dimethoxyphenyl)carbenium and an aminophosphine, was found to be an efficient catalyst for CO_2 fixation reactions with epoxides under mild conditions.

Phosphonium Salts

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Page No. – Page No.

Syntheses of Phosphonium salt from Phosphines and carbenium: Efficient CO_2 Fixation and Phase-Transfer Catalysts