Cyclopropanation of styrenes and stilbenes using lithiomethyl trimethylammonium triflate as methylene donor

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Contents
1. Experimental details ........................................................................................................................ 3
   1.1 Notes on the influence of transition metal contamination on the methylenation. ................... 3
   1.2 General Procedures .................................................................................................................. 3
   1.3 nBuLi solution in hexane ........................................................................................................ . 4
   1.4 Tetramethylammonium triflate (1a) ........................................................................................ 4
   1.5 Tetramethylammonium triflimide (1c) .................................................................................... 4
   1.6 Tetramethylammonium pivalate (1d) ...................................................................................... 4
   1.7 Preliminary attempts to cyclopropanate olefins with soluble lithiomethyl trimethylammonium reagents derived from several tetramethylammonium salts. ............................. 5
   1.8 Cyclopropanation of olefins with soluble lithiomethyl trimethylammonium reagents ........... 5
       1.8.1 General procedure ........................................................................................................... 5
       1.8.2 Cyclopropylbenzene (7a) ................................................................................................ 5
       1.8.3 1-cyclopropyl-4-methylbenzene (7b) ............................................................................. 5
       1.8.4 1-(tert-butyl)-4-cyclopropylbenzene (7c) ....................................................................... 6
       1.8.5 1-cyclopropyl-4-methoxybenzene (7d) .......................................................................... 6
       1.8.6 1-cyclopropyl-3-methoxybenzene (7e) .......................................................................... 6
       1.8.7 4-fluoro-1-cyclopropyl-benzene (7f) ............................................................................... 6
       1.8.8 Attempted cyclopropanation of 4-nitrostyrene (5g) ........................................................... 6
       1.8.9 trans-1,2-diphenylcyclopropane (7h) ............................................................................. 6
       1.8.10 trans-1-(4-methoxyphenyl)-2-phenylcyclopropane (7j) ................................................. 7
       1.8.11 Attempted cyclopropanation of cyclohexene (5k) ........................................................... 7
   1.9 Kinetic measurements ............................................................................................................. 7
       1.9.1 Monitoring of the reaction of N-C ylide 2 with styrene 5c ............................................. 7
       1.9.2 Competition experiments ............................................................................................... 10
   2. References ..................................................................................................................................... 11
   3. NMR Spectra of the synthesized cyclopropanes .......................................................................... 12
       3.1 Cyclopropylbenzene (7a) .................................................................................................. 12
       3.2 1-cyclopropyl-4-methylbenzene (7b) ................................................................................. 13
3.3  1-(tert-butyl)-4-cyclopropylbenzene (7c) ................................................................. 14
3.4  1-cyclopropyl-4-methoxybenzene (7d) ................................................................. 15
3.5  1-cyclopropyl-3-methoxybenzene (7e) ................................................................. 16
3.6  4-fluoro-1-cyclopropyl-benzene (7f) ................................................................. 17
3.7  *trans*-1,2-diphenylcyclopropane (7h), from *trans*-stilbene. ...................................... 19
3.8  *trans*-1,2-diphenylcyclopropane (7h), from *cis*-stilbene. ....................................... 20
3.9  *trans*-1-(4-methoxyphenyl)-2-phenylcyclopropane (7i) ........................................... 21
1. Experimental details

1.1 Notes on the influence of transition metal contamination on the methylenation.

In early methylenation attempts low and variable yields were obtained. After careful examination of the possible causes it was noted that even traces (ppm level) of transition metals in the reaction mixture degraded the lithiomethyl trimethylammonium reagent, with concomitant formation of ethylene and trimethylamine, therefore reducing the efficiency of the methylenation. As a preventive measure all the materials were thoroughly purified and all the glassware was cleaned rigorously (see below). It was noted that commercially available stir bars, coated with Teflon, are susceptible to corrosion by the used cleaning methods, and were an important source of contamination. It was then decided to construct glass coated stir bars which allowed for a very rigorous exclusion of metals in our system. All the tetramethylammonium salts can be easily prepared and/or purified by recrystallisation from distilled solvents to achieve sub-ppm levels of metals, as measured by ICP-MS. A self-made \( n \)BuLi solution (see procedure below) was also used to guarantee that all possible sources of trace metals were controlled. It was later recognized that the minimal trace metals present in commercial \( n \)BuLi (Aldrich) were not detrimental for the methylenation. All the experiments reported in this paper were performed using commercial \( n \)BuLi, however our method to prepare this reagent is described below.

1.2 General Procedures

Note: All glassware in which cyclopropanation reactions were performed, or substrates were synthesized, including the self-made glass stir-bars were cleaned consecutively in a base bath to remove all organics and then with \textit{aqua regia} to ensure that no traces of transition metals were present. Finally, rinsing of the glassware was performed with HPLC grade deionised water.

All reactions were conducted under an Ar or \( \text{N}_2 \) atmosphere using standard Schlenk or glove-box techniques.

Flash column chromatography was performed over Silica gel 60, 70-230 mesh (Merck). Concentration of solutions was conducted using a rotary evaporator. \( ^1 \text{H}, ^{13} \text{C} \) and \( ^{19} \text{F} \) NMR spectra were recorded at 300 or 400 MHz (Bruker AV300 or AV400 spectrometers) with CDCl\(_3\) or CD\(_3\)OD as solvent. Chemical shifts were determined relative to the residual solvent peaks (CHCl\(_3\), \( \delta = 7.26 \) for hydrogen atoms, \( \delta = 77.0 \) for carbon atoms; CD\(_3\)OD \( \delta = 3.31 \) for hydrogen atoms, \( \delta = 49.0 \) for carbon atoms) or were not corrected (\( ^{19} \text{F} \)). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was performed on a Finnigan Focus CG with a Zebron ZB-5MS, 30m*0.25 mm column using a flame ionization detector. GC-MS was performed on a Thermo-Finnigan Trace GC [SN17479]-MS[SN20015483] equipped with a Zebron ZB-5MS, 30m*0.25mm column using electron impact ionization (70 eV). Electrospray ionization (ESI) MS analysis was performed on a Thermo Finnigan TSQ Quantum. Recycling HPLC system (GPC: LC-9101 Japan Analytical Industry Co. Ltd., JAIGEL-1H, mobile phase: CHCl\(_3\)) was used for size exclusion chromatography (SEC).

Anhydrous THF was distilled from Na/benzophenone under \( \text{N}_2 \) prior to use. Anhydrous hexane was distilled from NaK alloy under \( \text{N}_2 \) prior use.

Tetramethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (1b) was synthesised as previously reported.\(^1\)

\( n \)BuLi (1.6 M in hexane), \textit{trans}-stilbene (5h), 4-fluorostyrene (5f), 3-methoxystyrene (5e), lithium ribbon (99.9% trace metals basis), anhydrous 1-chlorobutane (99.5%) and deuterium oxide were purchased from Sigma-Aldrich. Styrene (5a), cyclohexene (5j) and undecane were purchased from Fluka. 4-\textit{tert}-butylstyrene (5c) and 4-nitrostyrene (5g) were purchased from TCI-Deutschland. 4-methoxystyrene (5d) and 4-methoxy-\textit{trans}-stilbene (5i) were purchased from ABCR. 4-methystyrene (5b) was purchased from Acros Organics. Unless otherwise stated all bought chemicals were used as received.
1.3 nBuLi solution in hexane.
Under argon, lithium ribbon (2.65 g, 0.3828 mol, 4 eqv.) was placed in a 100 mL Schlenk flask. (Note: lithium ribbon was cut into smaller pieces using a ceramic knife to avoid metal contamination). Anhydrous, distilled n-hexane (70 mL, or enough to cover all the lithium ribbon) was added. Finally, distilled 1-chlorobutane (10 mL, 0.0957 mol, 1 eqv.) was added to the reaction mixture. The Schlenk flask was placed in a sonication apparatus and a reflux condenser was attached to the flask. A blast shield was used to cover the apparatus and the reaction mixture was sonicated for 8 h. During the sonication process the mixture heats up enough to ensure a slow reflux. The mixture is allowed to settle for a period of 2 to 5 hours. A metal-free filtration device is prepared fusing an HPLC grade plastic filter to a wide (2.5 mm) Teflon cannula using a heat gun. This filter is dried overnight in an oven prior to use. The mixture is filtrated under argon using the described device into a Schlenk flask fitted with a Young-type stopper. Filtration is slow and might take several hours, clogging is problematic especially if the filter has not been thoroughly dried. The resulting clear, colourless solution is finally titrated to determine the nBuLi concentration. By this method concentrations of about 1.0 M of nBuLi in hexane were typically obtained. This solution can be stored in a refrigerator without major changes in concentration for a period of at least 3 months.

1.4 Tetramethylammonium triflate (1a)
Salt 1a was prepared following the previously reported procedure.1 A 250 mL round bottom flask equipped with stir bar under air, was charged with tetramethylammonium chloride (2.2020 g, 20.09 mmol, 1 equiv) and 100 mL methanol. In another flask under air, silver trifluoromethanesulfonate (5.1622 g, 20.09 mmol, 1 equiv) was dissolved in 50 mL methanol. The AgOTf solution was added to the NMe4Cl solution under constant stirring. After 10 minutes the suspension was filtered to remove AgCl, and the solution was concentrated under reduced pressure. The crude salt was then recrystallised from anhydrous iso-propanol: the crude NMe4 OTf was dissolved in iPrOH (approximately 60 mL per gram of salt), after keeping the solution at -20 °C for 20 h the crystals were filtered off, and rinsed with a small amount of chilled iPrOH. The product was dried under high vacuum (5x10⁻² mbar) for 16 h. 3.7824 g (84%) of 1a was obtained as non-hygroscopic white powder. Elemental analysis: Found: C, 26.95; H, 5.33; N, 6.22; F, 25.72; S, 14.29. Calc. for C3H12NO3F3S: C, 26.90; H, 5.42; N, 6.27; F, 25.53; S, 14.37 %. ¹H NMR (400 MHz, CD3OD) δ 3.21-3.18 (m, 12H); ¹³C NMR (101 MHz, CD3OD) δ 123.3 (t, J(C-F) = 319 Hz), 55.9 (t, J(C-N) = 4 Hz); ¹⁹F NMR (376 MHz, CD3OD) δ -76.2.

1.5 Tetramethylammonium triflimide (1c)
The salt was prepared following a reported procedure.2 The salt was recrystallised twice from CH2Cl2 and dried under high vacuum before use.

Elemental Analysis: Found: C, 20.39; H, 3.41; N, 7.92. Calc. for C6H12F6N2O4S2: C, 20.34; H, 3.41; N, 7.91. ¹H NMR (400 MHz, MeOD) δ 4.78 – 4.72 (m, 12H). ¹³C NMR (101 MHz, MeOD) δ 121.2 (q, J(C-F) = 320 Hz), 55.9 (t, J(C-N) = 4 Hz). ¹⁹F NMR (376 MHz, MeOD) δ -80.70.

1.6 Tetramethylammonium pivalate (1d)
The salt was synthesised analogously to tetramethylammonium benzoate.3 Tetramethylammonium hydroxide (4 mL of a 25% solution in methanol, 10.96 mmol) and pivalic acid (1.12 g, 10.96 mmol) and 25 mL of methanol were stirred in a round bottom flask at 40 °C for 16h. After reaction the solvent was removed using a rotary evaporator. The white solid obtained was sonicated three times with portions of 20 mL of diethylether followed by decantation. The solid was then dried overnight using high vacuum (1x10⁻³ mbar). Yield: 1.81 g (94%) Elemental analysis (highly hygroscopic solid): Found: C, 59.79; H, 12.11; N, 7.23. Calc. for C9H21NO2: C, 61.68; H, 12.08; N, 7.99. ¹H NMR (400 MHz, MeOD) δ 3.20 – 3.19 (m, 12H), 1.13 (s, 9H); ¹³C NMR (101 MHz, MeOD) δ 187.3, 55.9 (t, J(C-N) = 4 Hz). ¹⁹F NMR (376 MHz, MeOD) δ -80.70.
1.7 Preliminary attempts to cyclopropanate olefins with soluble lithiomethyl trimethylammonium reagents derived from several tetramethylammonium salts.
A dried 50 mL Schlenk flask equipped with a glass coated stir bar and a glass stopper under Ar, was charged with a tetramethylammonium salt (0.35 mmol of 1a, 1b, 1c or 1d). The salt was suspended in anhydrous THF (10 mL) and undecane (50 µL) was added as internal standard. The flask was cooled down to 0 ºC in an ice-water bath. nBuLi (0.20 mL, 1.6 M, 0.33 mmol) was added to the suspension and the flask was completely closed using the glass stopper and the Schlenk tap to prevent any gas exchange. The reaction mixture was stirred for 30 minutes at 0 ºC. Then under an Ar counterflow at 0 ºC, neat styrene 5a was added (34 µL, 0.30 mmol). The flask was then again fully closed and the stirring was continued for 5 h during which the temperature was allowed to slowly reach room temperature. A sample of 0.50 mL of reaction mixture was diluted with 1.00 mL pentane and filtered through a small amount of silica. The filtrate was then directly analysed by GC-FID. The concentration of the starting material and product are obtained by interpolation in previously measured calibration curves.

1.8 Cyclopropanation of olefins with soluble lithiomethyl trimethylammonium reagents
1.8.1 General procedure
A dried 50 mL Schlenk flask equipped with a glass coated stir bar and a glass stopper under Ar, was charged with NMe₄ OTf (390 mg, 1.74 mmol). The salt was suspended in anhydrous THF (20 mL) and the flask was cooled down to 0 ºC in an ice-water bath. nBuLi (1.00 mL, 1.6 M, 1.60 mmol) was added to the suspension and the flask was completely closed using the glass stopper and the Schlenk tap to prevent any gas exchange. The reaction mixture was stirred for 30 minutes at 0 ºC. Then under an Ar counterflow at 0 ºC, the olefin substrate was added (between 1.16 and 1.45 mmol, for 1.4 to 1.1 equiv ylide to olefin ratios) either neat, or alternatively if the substrate is solid, dissolved in 2 mL of anhydrous THF. The flask was then again fully closed and the stirring was continued for 16 h during which the temperature was allowed to slowly reach room temperature. Then the reaction mixture was diluted with 30 mL of H₂O and transferred to a separation funnel. 20 mL of pentane was used to rinse the Schlenk flask and perform the first extraction of the aqueous phase. The aqueous phase was further extracted using pentane (2x 20 mL). The combined organic extracts were washed with H₂O (4x 20 mL) and brine (10 mL), dried using MgSO₄, filtered and the solvent was concentrated under reduced pressure. The crude material was then purified by column chromatography on silica gel.

1.8.2 Cyclopropylbenzene (7a)
Styrene (170 µL, 1.48 mmol) (5a) was used as substrate. 7a was purified by column chromatography using pentane as eluent. 147.8 mg of 7a (71% yield) was obtained as a colorless oil.

All experimental data were in agreement with reported data. ⁴

1.8.3 1-cyclopropyl-4-methylbenzene (7b)
4-methylstyrene (192 µL, 1.45 mmol) (5b) was used as substrate. 7b was purified by column chromatography using pentane as eluent. 179.7 mg of 7b (93% yield) was obtained as a colorless oil.

All experimental data were in agreement with reported data. ⁵
1.8.4 1-(tert-butyl)-4-cyclopropylbenzene (7c)
4-tert-butylstyrene (263 µL, 1.45 mmol) (5c) was used as substrate. 7c was purified by column chromatography using pentane as eluent. 202.8 mg of 7c (80% yield) was obtained as a colorless oil.

All experimental data were in agreement with reported data. 5

1.8.5 1-cyclopropyl-4-methoxybenzene (7d)
4-methoxystyrene (197 µL, 1.45 mmol) (5d) was used as substrate. 7d was purified by column chromatography using pentane as eluent. 189.5 mg of 7d (88% yield) was obtained as a colorless oil.

All experimental data were in agreement with reported data. 6

1.8.6 1-cyclopropyl-3-methoxybenzene (7e)
3-methoxystyrene (157 µL, 1.16 mmol) (5e) was used as substrate. 7e was purified by column chromatography using pentane as eluent. 132.8 mg of 7e (77% yield) was obtained as a colorless oil.

All experimental data were in agreement with reported data. 7

1.8.7 4-fluoro-1-cyclopropyl-benzene (7f)
4-fluorostyrene (139 µL, 1.16 mmol) (5f) was used as substrate. During workup a polymer precipitated. Initial GC analysis of the soluble organics showed a complex mixture consisting of approximately 37% of the desired product and several other compounds. The product was identified by GC-MS and NMR spectroscopy of the mixture (See the spectra and GC traces, see pages 16 and 17). Isolation of this compound was not attempted. The mass of the obtained product mixture after workup was 70.9 mg. Yield of the product can be estimated as 26.2 mg (16% yield).

1.8.8 Attempted cyclopropanation of 4-nitrostyrene (5g)
4-nitrostyrene (174 µL, 1.16 mmol) (5g) was used as substrate. During workup a polymer precipitated. SEC analysis of this material confirmed its polymeric nature. No remaining material was found in the organic phase after extraction.

1.8.9 trans-1,2-diphenylcyclopropane (7h)
Trans-stilbene (210 mg, 1.16 mmol) (5h) was used as substrate. 7h was purified by column chromatography using pentane/ethyl acetate 95/5 as eluent. 207.2 mg of 6e (92% yield) was obtained as an off-white solid.

All experimental data were in agreement with reported data. 9

Alternatively, reaction of cis-stilbene (207 µL, 1.16 mmol) (5i) affords 221.3 mg of 7h (98% yield).
1.8.10 *trans*-1-(4-methoxyphenyl)-2-phenylcyclopropane (7j)

4-methoxy-*trans*-stilbene (245 mg, 1.16 mmol) (5j) was used as substrate. 7j was purified by column chromatography using pentane/ethyl acetate 90/10 as eluent. 190.6 mg of 7j (73% yield) was obtained as a white solid.

![Chemical Structure](image)

All experimental data were in agreement with reported data. 10

1.8.11 Attempted cyclopropanation of cyclohexene (5k)

Cyclohexene (118 µL, 1.16 mmol) (5k) was used as substrate. NMR analysis of the crude product after workup showed unreacted starting material and no sign of norcarenne (7k).

1.9 Kinetic measurements

1.9.1 Monitoring of the reaction of N-C ylide 2 with styrene 5c

![Chemical Reaction](image)

**Scheme S1**

*Method*

A dried 50 mL Schlenk flask equipped with a glass coated stir bar and a glass stopper under Ar, was charged with NMe₄OTf (196 mg, 0.88 mmol). The salt was suspended in anhydrous THF (20 mL) and 100 µL of undecane was added as internal standard. The flask was then cooled down to 0 °C in an ice-water bath. nBuLi (0.50 mL, 1.6 M, 0.81 mmol) was added to the suspension and the flask was completely closed using the glass stopper and the Schlenk tap to prevent any gas exchange. The reaction mixture was stirred for 30 minutes at 0 °C. The first sample was now taken (see sampling procedure). Then under an Ar counterflow at 0 °C, the styrene substrate 5c was added (1.48 mL, 8.14 mmol, 10 equivalents) as quickly as possible (t=0). The reaction mixture was sampled over time following the sampling procedure described below.

*Sampling procedure*

Under Ar counterflow an aliquot of approximately 200 µL of reaction mixture was taken and poured quickly over 0.7 mL of D₂O. Pentane (2 mL) was added to the quenched sample and the vial was shaken vigorously for 30 seconds. The organic phase was separated in a GC vial and analyzed by GC-FID. A small portion of the aqueous phase was diluted approximately 200 times with methanol for analysis by ESI-MS.

The absolute concentration of the neutral organic materials in the organic phase was determined by extrapolation in previously measured calibration curves using authentic materials with undecane as internal standard.

Under the assumption that there were no sources of acidic protons under the described reaction conditions all "N(CH₃)₄⁺ (m/z = 74) ions must have come from the excess of 1a employed in the reaction, i.e. tetramethylammonium salt that was not deprotonated by nBuLi, and therefore can be used as self-reference since its concentration should not change during the course of the experiment.
After quenching the reaction mixture with D\textsubscript{2}O the part of the ammonium that was deprotonated (lithium coordinated N-C ylide 2\textit{a}) and still has not reacted is deuterated \textsuperscript{15}N(CH\textsubscript{3})\textsubscript{3}(CH\textsubscript{2}D) (m/z = 75). Using ESI-MS it is possible to determine the isotopic composition of the ammonium ions for all of the samples. Using the first measurement, done \textit{before} the substrate is added, as calibration it is possible to assess the concentration of reagent 2\textit{a} at the time of quenching by simple interpolation.

The intensity of the peak at m/z = 74 is measure as the area under the peak. The intensity of the peak at m/z = 75 is the area under the peak minus 4.9\% of the area of peak m/z 74 accounting for the natural abundance of deuterium.

\textbf{Figure S1.} Typical isotope patterns recorded from quenched samples at different times, normalized for intensity of peak at m/z = 74.

\textit{Data analysis}

The absolute concentration of 2\textit{a} and 7\textit{c} can be plotted against time to produce graphs like figure S2. Using the least squares method, the decay of 2\textit{a} and the formation of 7\textit{c} are fitted to the equations $[\text{2a}] = A_0 e^{-k_1 t}$ and $[\text{7c}] = A'_0 (1 - e^{-k_1 t})$ respectively. The confidence intervals for the fitted parameters $A_0$ and $k_1$ were determined using the Bootstrap method\textsuperscript{11} of iterative resampling and refitting for 1000 times. The real value for the fitted parameter is considered to lie between +/- 2 standard deviations (\sigma) (approximately 95\% confidence) from the mean of the produced set of values.
Figure S2. Typical plot of absolute concentrations of 2 and 6 with their corresponding best fits.

Figure S3. Typical outcome of the Bootstrap method.
Table S1. Fit parameters for the reaction of 2a with 4-tert-butylstyrene 5c

<table>
<thead>
<tr>
<th>Repetition</th>
<th>Formation of cyclopropane 7c ($A_0$ (M) $2\sigma$ $k_1$ (s$^{-1}$) $2\sigma$)</th>
<th>Consumption of 2a ($A_0$ (M) $2\sigma$ $k_1$ (s$^{-1}$) $2\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.22E-02 1.90E-03 1.23E-03 2.79E-04</td>
<td>2.44E-02 3.77E-03 8.12E-04 2.29E-04</td>
</tr>
<tr>
<td>2</td>
<td>2.37E-02 1.87E-03 1.11E-03 2.24E-04</td>
<td>2.76E-02 4.54E-03 7.78E-04 1.89E-04</td>
</tr>
<tr>
<td>3</td>
<td>2.44E-02 1.77E-03 1.04E-03 1.88E-04</td>
<td>3.08E-02 1.98E-03 6.67E-04 6.29E-05</td>
</tr>
</tbody>
</table>

The values obtained for both the pre-exponential factor $A_0$ and the first order kinetic constant $k_1$ for the two curves are in good agreement, supporting the hypothesis of a consecutive set of irreversible reactions where the nucleophilic attack of 2a on the styrene 5c is rate limiting.

1.9.2 Competition experiments

Following the method described by Harper et al., a series of competition experiments were performed. In order to avoid interferences with the stabilisers added to the styrenes all of the substrates were dried over CaH$_2$ and distilled under reduced pressure. A stock solution was prepared containing the substrates styrene 5a (100 µL, 0.869 mmol), 3-methoxystyrene 5e (100 µL, 0.739 mmol), 4-methoxystyrene 5d (450 µL, 3.34 mmol) and 4-tert-butyldimethane 5c (600 µL, 3.32 mmol) as well as undecane (100 µL, 0.474 mmol) as internal standard in 4 mL anhydrous THF.

A dried 50 mL Schlenk flask equipped with a glass coated stir bar and a glass stopper under Ar, was charged with NMe$_4$OTf (80 mg, 0.36 mmol). The salt was suspended in anhydrous THF (10 mL). The flask was then cooled down to 0 °C in an ice-water bath. nBuLi (0.20 mL, 1.6 M, 0.33 mmol) was added to the suspension and the flask was completely closed using the glass stopper and the Schlenk tap to prevent any gas exchange. The reaction mixture was stirred for 20 minutes at 0 °C. Under Ar counterflow 1.00 mL of the stock solution is quickly added to the reaction mixture and the flask is closed again. After 20 minutes stirring at 0 °C the reaction is quenched by addition of 0.20 mL of methanol. A sample of 0.50 mL is taken and diluted with 1.0 mL of pentane. The sample is filtered through celite to remove the precipitated ammonium salt. The filtrate is analyzed by GC-FID.

The absolute concentrations of the styrenes before and after reaction (with respect to undecane) are obtained by extrapolation in previously measured calibration curves. Following equation (1) one can obtain the ratio of the rates as function of the ratio of the concentrations.

$$
\frac{k_x}{k_y} = \frac{\ln \left( \frac{S_x}{S_x,t=0} \right)}{\ln \left( \frac{S_y}{S_y,t=0} \right)} \quad (1)
$$

Table S2. Concentration in mmol of styrenes per mmol of undecane before and after reaction.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Before$^1$</th>
<th>Rep. 1</th>
<th>Rep. 2</th>
<th>Rep. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-H 5a</td>
<td>1.98</td>
<td>1.53</td>
<td>1.49</td>
<td>1.46</td>
</tr>
<tr>
<td>3-MeO 5e</td>
<td>1.81</td>
<td>1.23</td>
<td>1.21</td>
<td>1.18</td>
</tr>
<tr>
<td>4-MeO 5d</td>
<td>7.32</td>
<td>7.22</td>
<td>7.24</td>
<td>7.26</td>
</tr>
<tr>
<td>4-tBu 5c</td>
<td>7.28</td>
<td>6.74</td>
<td>6.76</td>
<td>6.79</td>
</tr>
</tbody>
</table>

$^1$ All reactions were performed using the same stock solution over a period of less than 24 hours. All experiments are referenced to this initial composition.
Table S3. Values of $k_X/k_H$ obtained from data in table S2 using equation (1)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\sigma$ parameter$^{13}$</th>
<th>Rep. 1</th>
<th>Rep. 2</th>
<th>Rep. 3</th>
<th>Average</th>
<th>$2\sigma$ $^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-H 5a</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>3-MeO 5g</td>
<td>0.115</td>
<td>0.18</td>
<td>0.14</td>
<td>0.15</td>
<td>0.16</td>
<td>0.02</td>
</tr>
<tr>
<td>4-MeO 5f</td>
<td>-0.268</td>
<td>-1.29</td>
<td>-1.41</td>
<td>-1.57</td>
<td>-1.42</td>
<td>0.14</td>
</tr>
<tr>
<td>4-iBu 5c</td>
<td>-0.197</td>
<td>-0.52</td>
<td>-0.58</td>
<td>-0.63</td>
<td>-0.58</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Figure S4. Hammett plot for the cyclopropanation of several styrenes with lithiomethyl trimethylammonium triflate.

2. References


$^2$ Standard deviation
3. NMR Spectra of the synthesized cyclopropanes

The NMR spectra shown below are from samples synthesised by reaction of the parent styrene or stilbene with lithiomethyl trimethylammonium triflate as described previously. It is possible that minimal amounts of starting material or solvents used for purification are present in the samples.

3.1 Cyclopropylbenzene (7a)

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.27–7.23 (m, 2H), 7.16–7.10 (m, 1H), 7.09–7.04 (m, 2H), 1.88 (s, 3H). δ 8.5, 7.3 (s, 1H), 6.99–6.93 (m, 2H), 5.72–5.64 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 159.83, 145.91, 139.36, 118.24, 111.60, 110.74, 55.28, 15.63, 9.37.
3.2 1-cyclopropyl-4-methylbenzene (7b)
3.3 1-(tert-butyl)-4-cyclopropylbenzene (7c)
3.4 1-cyclopropyl-4-methoxybenzene (7d)

$\text{H NMR (400 MHz, Chloroform-$d$):}$ 7.07 - 7.02 (m, 2H), 6.87 - 6.82 (m, 2H), 3.81 (s, 3H), 1.89 (m, 7 + 8, 5.1 Hz, 1H), 0.96 - 0.89 (m, 2H), 0.68 - 0.61 (m, 2H).

$\text{C NMR (101 MHz, CDCl$_3$):}$ 167.71, 135.99, 135.97, 113.89, 55.43, 14.74, 8.64.
3.5 1-cyclopropyl-3-methoxybenzene (7e)

$\text{O}$

- D (6d) 5.63
- A (s) 3.80
- B (d) 7.17
- C (m) 6.69
- E (t) 1.88
- F (m) 0.95
- G (m) 0.79

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.71 (t, $J = 7.8$ Hz, 1H), 6.72–6.66 (m, 2H), 4.63 (dd, $J = 3.5$, 1.7 Hz, 1H), 3.80 (s, 3H), 1.88 (m, $J = 4.4$, 5.1 Hz, 1H), 1.56–0.80 (m, 2H), 0.74–0.66 (m, 2H).

$^1$C NMR (100 MHz, CDCl$_3$): δ 159.83, 145.91, 129.36, 118.24, 111.49, 110.74, 55.28, 15.63, 9.37.
3.6 4-fluoro-1-cyclopropyl-benzene (7f)

$^1$H NMR of the mixture obtained after workup

CG-FID trace of the mixture obtained after workup
CG-MS trace of the mixture obtained after workup
3.7 *trans*-1,2-diphenylcyclopropane (7b), from *trans*-stilbene.
3.8 *trans*-1,2-diphenylcyclopropane (7h), from *cis*-stilbene.
3.9 *trans*-1-(4-methoxyphenyl)-2-phenylcyclopropane (7i)