Design of a Novel Cyclopropane Donor Bis(trimethylsilylmethyl)cyclopropane and Its Electron Transfer Reactions

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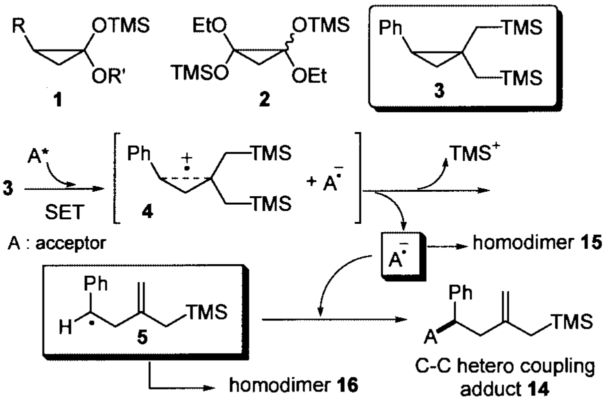
A novel donor of SET reactions, 1,1-bis(trimethylsilylmethyl)-2-phenylcyclopropane (BTCP), was designed to function as a homoallylic 1-phenyl-3-(trimethylsilylmethyl)-3-butenyl radical (**5**). Thus, non-irradiated reaction of BTCP with DDQ or chloranil gave a six-membered cyclic compound, which corresponds to a Diels–Alder adduct of 3-trimethylsilylmethyl-1,3-butadiene derived from BTCP. The photoinduced electron transfer reaction of BTCP with ketones afforded the C–C coupling products of **5** in high yields.

Utilization of cyclopropanes as three-carbon synthons for carbon–carbon bond forming reactions has been extensively studied. In parallel, their donor character was found and requirements of enforcing that nature have been unveiled in the study of electron transfer reactions.[1] In the course of study on cyclopropanone mixed acetals **1**[2] and **2**[3] which, upon oxidative electron transfer conditions, form substituted β-carbonyl radicals by loss of silyl groups, we found that these donors inevitably introduce oxygen groups (carbonyl) to the C–C bonded products, that are sometimes undesirable.

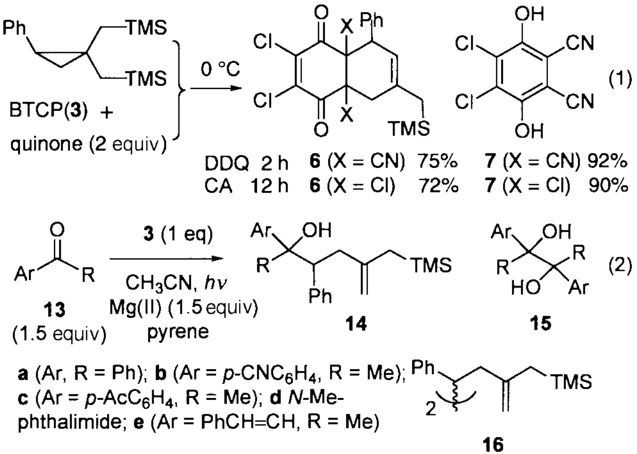
To eliminate the oxygen-functionality from cyclopropane donors, we expected that trimethylsilylmethyl group (abbreviated as $TMSCH_2$) will function as a non-*O*-type donating substituent under the single electron transfer (SET) conditions[4] and, hence, designed 1,1-bis(trimethylsilylmethyl)-2-phenylcyclopropane (BTCP, **3**) as the appropriate donor. Indeed, the mixed DFT/SCF-calculations [HF/6-311++G(3df,2p)//B3LYP/6-311+ G(d,p)] of cyclopropanes bearing silyloxy and silylmethyl substituents on the ring indicate that the silylmethyl group increases the HOMO energy even more than the silyloxy group does. An additional silylmethyl substituent leads to a further significant elevation of the HOMO energy. Further detailed theoretical investigations in this field are in progress.[5] Thus, the order in substituents for increasing the HOMOs is Ph > $TMSCH_2$ ≈ TMSO > MeO. After confirming these substituent effects, the utilization of **3** for C–C bond forming reactions also intrigued us because of its non-oxygenic functionality (Scheme 1).



Scheme 1.

Cyclopropane **3** was prepared by the coupling reaction of dichlorostyrene with $TMSCH_2MgCl$[6] to give 3-TMS-2-TMS-CH_2-1-Ph-propene, followed by the Simmons–Smith reaction.[7]

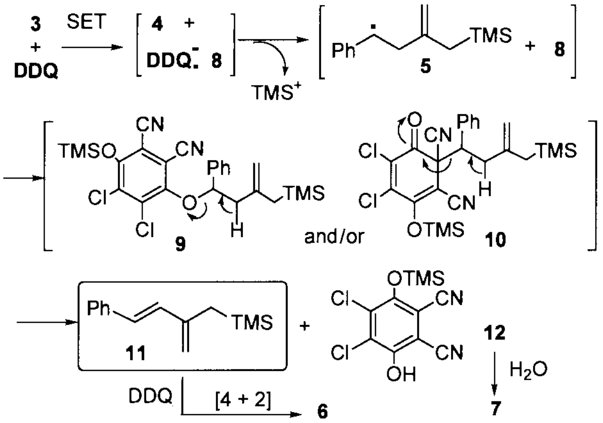
Non-irradiated reaction of **3** with typical acceptor 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 1.1 eq to **3**) in THF at 0 °C afforded cycloadduct 2,3-$(Cl)_2$-9,10-$(CN)_2$-5-Ph-7-$TMSCH_2$-1,4,5,8,9,10-hexahydronaphthalene-1,4-dione (**6**, X = CN, 20%) and hydroquinone **7** (65%) (Scheme 2, eq 1). When 2 equiv moles of DDQ was used, product yields were improved to 75% for **6** and 92% for **7**. A similar reaction with chloranil also produced cycloadduct **6** (X = Cl, 72%) provided that more drastic conditions were adopted (82 °C, 12 h in CH_3CN). The solvent effect, which was observed by changing THF to a much stronger dipolar aprotic solvent CH_3CN,[2b] indicates that a polar transition state consisting of paired ion radicals is involved instead of a concerted process. Thus, the cycloaddition reaction seems to have proceeded sequentially first via a SET mechanism followed by the Diels–Alder reaction of intermediate diene **11** to give **6**.[8]



Scheme 2.

The most plausible pathway for this cycloaddition is depicted in Scheme 3. First, a SET reaction between **3** and DDQ generates an ion radical pair [**4** + **8**], where **4** eliminates TMS^+ cation to produce $TMSCH_2$-substituted homoallyl radical **5**. Coupling between **5** and **8** produces either C–O or C–C bonded linear adduct **9** and/or **10**[9], that undergo elimination of hydroquinone **12** to give diene **11**. Diene **11**, presumably being as reactive as the Danishefski diene,[10] reacts with intact DDQ to produce [4+2] cycloadduct **6**.

The unique donor nature of **3** further attracted us to extending its utility to the construction of other C–C frameworks.



Scheme 3.

Indeed, the photo-induced electron-transfer reaction (PET) of **3** with carbonyl compounds (Scheme 2, eq 2) enabled the bonding with allylsilyl or homoallyl moieties (Scheme 1). Thus, the PET reaction of **3** with benzophenone (**13a**) in the presence of Mg(II) salt[11] produced C–C bonded product **14** (18%) though in low yield. To improve the yield, pyrene (0.1 equiv) which has been known as a redox photocatalyst in PET reactions[12] was added. Consequently, the yield was improved (37%) together with the increase in the yield of radical homodimer **16** (28%) of radical **5**. Hence, pyrene[13] was used in every experiment thereafter.

Under the high dilution conditions, however, expected improvement in the yield of **14**[14] was not observed. This indicates that an initially formed radical ion pair in a cage [**4** + ketyl radical] may spontaneously collapse in a polar solvent to stabilized solvent-separated radical ion pair [**4**] + [ketyl radical], which, after the removal of silyl cation, finally undergoes the coupling to give **14**, **15** and **16** (Scheme 1). Therefore, product ratios are more or less statistically controlled and not influenced by the substrate concentration.

The effect of Mg^{2+} is clear. With increase in the molar equivalence of Mg^{2+} from 1 to 1.5, the yield of **14** increased from 3 to 47%. This indicates that the concentration of homoallyl radical **5** increases in parallel to that of ketyl radical–Mg^{2+} complex. The role of pyrene as a photocatalyst is also evidenced. It functions as a redox catalyst to generate radical ion **4** (or radical **5**) and the ketyl radical. Acetylbenzonitrile (**13b**), diacetylbenzene (**13c**), *N*-methylphthalimide (**13d**), and benzalacetone (**13e**) also underwent the similar C–C bond forming reactions with **3** via the PET process. To be noted is that these ketones reacted with **3** as effectively as benzophenone (**13a**) leading to the C–C bonded products.

In conclusion, the present study has unveiled that $TMSCH_2$ group on a cyclopropane ring plays a role of endowing the ring with donor character at both ground state and excited state reactions, the effect being comparable to, or even more than that of TMSO as predicted on theoretical basis. Further study on both theoretical and experimental bases will widen the versatile profile of the $TMSCH_2$ group.

References and Notes

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5 All geometries were optimised and characterized as real minima (via second derivative calculation) using Becke's hybrid density functional B3LYP method with the 6-311+G(d,p) or 6-31G(d) basis sets. The orbital energies were taken from a SCF-population analysis on the HF/6-311++G(3df,2p) level of theory. All calculations were carried out using the GAUSSIAN98 package of programs.[15] Relative HOMO energies of substituted cyclopropanes vs parents cyclopropane are [eV]: 0.475 for 1-H_3SiO-, 0.846 for 1-H_3SiCH_2-, 1.079 for 1,1-$(H_3SiCH_2)_2$-, 1.338 for (*E*)-1,2-$(H_3SiCH_2)_2$-cyclopropane.

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8 Similarly, **3** reacted with TCNE under non-irradiated conditions to afford a five-membered [2+3]cycloadduct. Sequential profile of the reaction was difficult to be proven by the stereochemical analysis of the adduct.

9 Similar types of C–O and C–C bonded intermediates were reported for the reaction of **1** (ref 2b).

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14 High dilution was effective in the PET reaction of **2** with ketones (ref 3).

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