An Air-Stable Alkene-Derived Organic Radical Cation

Rahul Kumar, Shubhadeep Chandra, Mithilesh Kumar Nayak, Arijit Singha Hazari, Benedict J. Elvers, Carola Schulzke,* Biprajit Sarkar,* and Anukul Jana*

ABSTRACT: Alkenes are known to undergo oxidation to radical cations and dications. The radical cations are often highly reactive and not stable under air. Herein, we report the synthesis, isolation, characterization, and molecular structure determination of the \( \text{E-diamino tri-substituted alkene} \) as a synthons for the synthesis of \( \text{A} \) through one-electron oxidation. The \( \text{E-diamino tri-substituted alkene} \) was synthesized by the two-electron reduction of \( \text{N,N',1,2-propylene-bridged bis-2-phenyl-pyrrolinium cation} \). Under two-electron oxidation, alkene \( \text{B} \) transforms to cation \( \text{C} \) involving a double carbocation rearrangement.

INTRODUCTION

Organic open-shell compounds such as radicals and radical ions (cations or anions) comprise an important class of compounds due to their various applications from synthetic chemistry 1 to various branches of materials science. 2 However, most organic radicals and radical ions are highly reactive toward an open atmosphere and must be handled under inert atmosphere conditions, which restricts their utilization. 2 The design and synthesis of air-stable radicals and radical ions are therefore generally attractive but challenging. Gomberg reported already in 1900 the first isolable triphenyl methyl radical, 3 which is stable in air both in the solid state and in solution. The access to this compound was facilitated from \( \text{E-diamino tri-substituted alkene} \). Under two-electron oxidation, alkene \( \text{B} \) transforms to cation \( \text{C} \) involving a double carbocation rearrangement.

RESULTS AND DISCUSSION

The colorless crystalline solid salt of the \( \text{N,N',1,2-propylene-bridged bis-2-phenyl-pyrrolinium cation} \) was synthesized through three sequential one-pot reactions of corresponding bis-immine 1 with lithium diisopropylamide (LDA), isobutylenes oxide, and triflic anhydride (Scheme 2). 23 The \( ^1 \text{H NMR} \) spectrum of compound 2 exhibits two doublets of doublets at \( \delta = 4.38 (J_{\text{HH}} = 13.9 \text{ Hz and } J_{\text{HH}} = 3.9 \text{ Hz}) \) and \( 3.69 (J_{\text{HH}} = 13.9 \text{ Hz and } J_{\text{HH}} = 13.2 \text{ Hz}) \) ppm for the two magnetically

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non-equivalent protons of the CH$_2$ motif in the bridge. The salt is soluble in acetonitrile and stable in an open atmosphere. The cyclic voltammogram of 2 exhibits the appearance of two fairly close-lying sequential one-electron redox waves at $E_{1/2} = -1.52$ and $-1.74$ V vs Fc/Fc$^+$ (Figure 1, left), which are very similar to those of corresponding N,N'-ethylene-bridged bis-2-phenyl-pyrrolinium cation IX (Scheme 2, inset, $E_{1/2} = -1.50$ and $-1.71$ V vs Fc/Fc$^+$).\textsuperscript{19c} The differential pulse voltammetry (DPV) experiment confirms the two-sequential one-electron redox process. The differences in the cathodic and anodic peak current of the reduction processes at lower scan rates indicate the possibility of the 1,3-hydrogen shift following the EC mechanism.

The chemical reduction of 2 with two equivalents of KC$_8$ in THF leads to the formation of 3 in 57% yield (Scheme 2). The $^1$H NMR spectrum of compound 3 exhibits a singlet at $\delta = 5.27$ ppm for the CH resonance of the C=C=CH$_3$ bridge unit and two singlets at $\delta = 4.01$ and 3.64 ppm for the two magnetically non-equivalent Ph-CH units. The formation of compound 3 was further confirmed unambiguously by single-crystal structure determination (Figure 1, center). The C1–C2 bond distance is 1.341(2) Å, which is longer than that in the corresponding two-electron reduced compound of IX (1.332(2) Å).\textsuperscript{19c} Compound 3 is soluble in hexane and toluene.
It is reasonable to assume that the reduction of 2 to 3 with two-equivalents of KC₈ proceeds through the initial formation of radical cation [4], which is subsequently reduced to biradical [5] bearing two CAAC-based radical motifs, the latter of which then selectively abstracts hydrogen atoms from the CH and CH₂ moieties in the N,N'-1,2-propylene-bridge (Scheme 2). The one-electron reduced product [4] was studied with UV–vis-spectroelectrochemical experiments. The formation of the radical cation upon one-electron reduction is accompanied by the appearance of new bands in the visible regions at λ_max = 345 and 485 nm (Figure 1, right).

To investigate the reverse reactions (formation of 2 from 3), 3 was oxidized electrochemically as well as chemically. The cyclic voltammogram of 3 exhibits two-sequential one-electron oxidation waves at E_{1/2} = −0.37 and −0.62 V vs Fc/Fc⁺ (Figure S15).

Accordingly, the chemical oxidation of 3 with one equivalent and two equivalents of AgOTf leads to the formation of radical cation 6 (75%) and dication 2 (51%), respectively (Scheme 2).

The formation of radical cation 6 (not [4], notably) was confirmed by electron paramagnetic resonance (EPR) spectroscopy (Figure 2, left). It displays a well-resolved, isotropic EPR spectrum with a g-value of 2.0044 at 295 K. The spectrum was simulated with high accuracy by considering hyperfine couplings to two equivalent ^14N nuclei (a(^14N) = 20.37 MHz) and three non-equivalent sets of ^1H nuclei (a(^1H) = 17.47 (2H), 13.17 (1H), and 18.69 (3H) MHz). Theoretical calculations show the spin density to be predominantly located on the central N–C–C=N motif (Figure S19).

Formation of radical cation 6 was further confirmed through its solid-state molecular structure determined with single-crystal X-ray structural analysis (Figure 2, center). The C1–C2 bond distance is 1.341 (2) Å, which is the same as that of the starting alkene 3 (1.341 (2) Å), indicating no change in the alkene bond length after one-electron oxidation. This could be most likely due to the crystal packing. However, in the case of corresponding N,N'-ethylene-bridge, the small changes of the C–C bond length of the alkene motif were observed from 1.332 (2) to 1.358 (5) Å upon one-electron oxidation. The dihedral angle of the central N–C–C=N motif is 5.26 (20)°, substantially larger than that in 3 (1.58 (11)°) (Table 1). Compound 6 exhibits absorbances in the UV–vis at λ_max(ε) = 381 (1495) and 255 (8780) nm (L mol⁻¹ cm⁻¹).

On the other hand, the formation of dication 2 from the oxidation of 3 most likely proceeds through the double carboxation of the starting alkene 3 (measured at a scan rate of 10 mVs⁻¹) (right).
(Scheme S1). The calculated energy difference $\Delta E(2-[\sigma])$ was found to be $-24.25 \text{ kcal/mol}$ (Table S5).23

When handling single crystals of 6 for the crystallographic experiment, its potential stability in air was noted. To verify this observation, a time-dependent UV-vis-spectroscopic study of an air-exposed THF solution of 6 was carried out (Figure 2). Most surprisingly, the radical species 6 is stable in solution even after 48 h while dissolved in THF and exposed to air.

In conclusion, the first air-stable tri-substituted alkene-derived radical cation was synthesized by one-electron oxidation employing an E-diamino tri-substituted alkene as a synthons. Because the applied procedures are controllable and reliable, we anticipate that the reported observations will motivate and facilitate the design and synthesis of further air-stable alkene-derived radical cations with varied substituents, which will ultimately lead to the utilization in a range of potential applications and therefore an entire research field well worth pursuing.

EXPERIMENTAL SECTION

General Considerations. All experiments (unless otherwise stated) were carried out under an N$_2$ atmosphere using standard Schlenk techniques or in a PL-HE-2GB Innovative Technology glovebox. Hexane, pentane, diethyl ether, THF, and toluene were dried with a PS-MD-5 Innovative Technology solvent purification system or common drying solvent technique. KC$_8$ was synthesized according to the literature procedure.24 All other chemicals were purchased commercially (1,2-diaminopropane, Sigma-Aldrich; isopropyl phenyl ketone, TCI Chemicals; potassium, Sigma-Aldrich; graphite, Sigma-Aldrich; isobutylene oxide, TCI Chemicals; triflic anhydride, TCI Chemicals; LDA, Hychem Laboratories; AgOTf, Sigma-Aldrich; isobutylene oxide, TCI Chemicals; LDA, Hychem Laboratories; AgOTf, Sigma-Aldrich) and used as received. Benzene-d$_6$ and acetonitrile-d$_3$ were dried and distilled over potassium under argon. Chloroform-d$_1$ and acetonitrile-d$_3$ were dried and distilled over CaH$_2$ under argon. NMR spectra were recorded on a BrukerNanoBay 300 MHz NMR spectrometer. $^1$H and $^{13}$C{H} NMR spectra were referenced to the peaks of residual protons of the deuterated solvent ($^1$H) or the deuterated solvent itself ($^{13}$C). $^{19}$F{H} NMR spectra were referenced to external tol-C$_6$F$_5$. UV−vis spectra were acquired with a Jasco V-670 spectrometer using quartz cells with a path length of 0.1 cm. Elemental analyses were performed on a PerkinElmer Analyzer 240. Melting points were determined in closed NMR tubes under a nitrogen atmosphere and were uncorrected. A Bruker Daltonics microTOF-Q instrument was used for electron spray mass spectrometry. All reported ESI-MS data were recorded in positive operating mode. UV−vis−NIR spectroelectrochemical measurements were recorded on a J&M TIDAS spectrometer instrument by using an optical transparent thin layer electrochemical (OTTLE) cell.15 Cyclic voltammograms were recorded in 0.1 M NBu$_4$PF$_6$/CH$_3$CN solutions using a three-electrode configuration (glassy carbon working, Pt wire counter electrodes, and Ag reference) with a Metrohm Autolab potentiostat. The ferrocene/ferroenium (Fc/Fc$^+$) couple served as the internal reference. The UV−vis−SEC EPR spectra at X-band frequency (ca. 9.5 GHz) were obtained with a Magnetech MS-5000 bench top EPR spectrometer equipped with a rectangular TE 102 cavity. The measurements were carried out in synthetic quartz glass tubes. The spectral simulations were performed using MATLAB 9.8.0.1323502 (R2020a) and an EasySpin 5.2.28 toolbox.26

Synthesis of 1. Isobutyrophenone (30.0 mL, 200.0 mmol) and catalytic amounts of p-toluenesulfonic acid monohydrate (200.0 mg, 1.05 mmol) were added to a 250 mL Schlenk flask and stirred for half an hour at room temperature. Then, toluene (100.0 mL) and 1,2-diaminopropane (8.5 mL, 100.0 mmol) were added. The resulting mixture was refluxed using a Dean−Stark apparatus for 2 h at 100 °C and for 10 h at 180 °C. Subsequently, toluene and all the volatiles were removed by vacuum distillation. Compound 1 was separated at 180 °C and 0.5 Torr as a colorless liquid. Density: 0.942 g/mL. Yield: 30.4 g (91%). $^1$H NMR (CDCl$_3$, 25 °C, 300 MHz): $\delta$ = 7.39−7.29 (m, 6H, Ar-H), 7.09−7.02 (m, 4H, Ar-H), 3.59−3.53 (m, 1H, CH$_2$CHCH$_2$), 3.27 (dd, 1H, J$_{HH}$ = 12.7 Hz, J$_{HF}$ = 7.4 Hz, H$_z$, CH$_2$CHCH$_2$), 3.15 (dd, 1H, J$_{HH}$ = 12.7 Hz, J$_{HF}$ = 5.6 Hz, H$_z$, CH$_2$CHCH$_2$). 2.78−2.69 (sept, 2H, J = 6.9 Hz, CH(CH$_3$)$_2$), 1.10−1.04 (m, 12H, CH(CH$_3$)$_3$), 0.95−0.93 (d, 3H, J = 6.4 Hz, CH$_3$) ppm. $^{13}$C{H} NMR (CDCl$_3$, 25 °C, 75 MHz): $\delta$ = 175.87, 174.59, 138.36, 138.11, 128.08, 127.91, 127.49, 127.36, 126.99, 126.90, 59.75, 57.49, 39.27, 39.03, 20.26, 20.19, 20.02, 19.94 ppm.

Synthesis of 2. LDA solution (44.0 mmol) in THF (2 M) was added to a Et$_2$O solution of 1 (6.6 g, 7 mL, 19.7 mmol in 60.0 mL of Et$_2$O) at 0 °C, and the reaction mixture was slowly allowed to warm up to room temperature. Then, the resulting reaction mixture was stirred for 8 h at room temperature, and afterward, all solvents and volatiles were removed under vacuum. Then, 200 mL of Et$_2$O was added followed by the dropwise addition of isobutylene oxide (3.8 mL, 44.0 mmol) at 0 °C. The resulting reaction mixture was allowed to warm up to room temperature. After that, the reaction mixture was stirred at room temperature for another 12 h. Subsequently, trifluoromethane sulfonic anhydride (7.4 mL, 44.0 mmol) was added dropwise at −78 °C. The reaction mixture was allowed to slowly reach room temperature and stirred for another 5 h. Then, the resulting solution was filtered and the residue was washed 5 times with 10 mL of DCM. The resulting residue was dissolved in CH$_3$CN, and slow diffusion of Et$_2$O led to the desired compound 2 as colorless crystals, suitable for single-crystal X-ray diffraction analysis. The crystals were filtered and washed with diethyl ether. Yield: 2.93 g (20%). M.P.: >200 °C. 

$^1$H NMR (CD$_2$CN, 25 °C, 300 MHz): $\delta$ = 7.79−7.56 (m, 7H, Ar-H), 7.46−7.36 (m, 3H, Ar-H), 4.38 (dd, 1H, J$_{HH}$ = 13.9 Hz, J$_{HM}$ = 3.9 Hz, CH$_2$CH$_2$CH$_2$), 4.06−3.93 (m, 1H, CH$_2$CH$_2$CH$_2$), 3.69 (dd, 1H, J$_{HM}$ = 13.9 Hz, J$_{HH}$ = 13.2 Hz, CH$_2$CH$_2$CH$_2$), 2.28−2.20 (m, 4H, (CH$_3$)$_2$CH$_2$CH$_2$), 1.55 (br, 3H, CH$_3$), 1.44 (s, 3H, CH$_3$), 1.31 (s, 9H, CH$_3$), 1.28 (br, 3H, CH$_3$), 1.24 (s, 3H, CH$_3$), 1.22 (s, 3H, CH$_3$), 1.21 (s, 3H, CH$_3$) ppm. $^{13}$C{H} NMR (CD$_2$CN, 25 °C, 75 MHz): $\delta$ = 199.21 (C$_{iminium}$), 199.09 (C$_{iminium}$), 133.91 (Ar-C), 133.41 (Ar-C), 131.07 (Ar-C), 130.17 (Ar-C), 129.92 (Ar-C), 127.89 (Ar-C), 127.66 (Ar-C), 127.08 (Ar-C), 126.73 (Ar-C), 126.57 (Ar-C), 124.19 (Ar-C), 119.94 (Ar-C), 81.10 (C$_{CH_3}$), 79.77 (C$_{CH_3}$), 52.24 (C$_{CH_3}$), 51.92 (C$_{CH_3}$), 49.72 (CH$_2$CH$_2$CH$_2$), 47.90 (CH$_2$CH$_2$CH$_2$), 28.15 (CH$_2$), 27.54 (CH$_2$), 27.44 (CH$_3$), 27.20 (CH$_3$), 27.01 (CH$_3$), 26.77 (CH$_3$), 26.70 (CH$_3$), 19.94 (CH$_3$) ppm. $^{19}$F{H} NMR (CD$_2$CN, 25 °C, 282 MHz): $\delta$ = −79.24 ppm. Elemental analysis calcd (%) for C$_{33}$H$_{44}$F$_6$N$_6$O$_6$S$_2$: C, 53.36; H, 5.97; N, 3.77; found: C, 53.75; H, 6.07; N, 3.77. HRMS (ESI-TOF) m/z: [M$^+$/2 calcd for C$_{33}$H$_{44}$F$_6$N$_6$O$_6$S$_2$: 843.3649; found: 843.3661. 
Synthesis of 3. Compound 2 (1.41 g, 1.89 mmol) and KC₈ (641 mg, 4.75 mmol) were added to a 100 mL Schlenk flask inside the glovebox, and 50 mL of THF was added through a cannula at −78 °C. The reaction solution became initially green and then colorless. After 6 h of stirring, all the volatiles were removed under vacuum and the resulting residue was extracted with 50 mL of hexane. Evaporation of the solvent under reduced pressure led to the isolation of the desired product 3 as a white solid. A concentrated hexane solution of the compound at room temperature led to the formation of single crystals suitable for single-crystal X-ray diffraction analysis. Yield: 512 mg (57%). M.P.: 177−179 °C. ¹H NMR (CD₂Cl₂, 25 °C, 300 MHz): δ = 7.21−7.18 (m, 6H, Ar-H), 7.13−7.08 (m, 4H, Ar-H), 5.27 (s, 1H, CH=CHCH₃), 4.01 (s, 1H, Ar-CH), 3.64 (s, 1H, Ar-CH), 1.82 (s, 3H, CH=CHCH₃), 1.61−1.58 (s, 2H, CH₂), 1.54 (s, 2H, CH₂), 1.11 (s, 3H, CH₃), 0.98 (s, 6H, CH₃), 0.95 (s, 3H, CH₃), 0.94 (s, 3H, CH₃), 0.80 (s, 3H, CH₃), 0.76 (s, 3H, CH₃), 0.74 (s, 3H, CH₃) ppm. ¹³C(¹H) NMR (CD₂Cl₂, 25 °C, 75 MHz): δ = 140.86 (Ar-C), 140.44 (Ar-C), 140.29 (Ar-C), 131.84 (Ar-C), 129.42 (Ar-C), 128.89 (Ar-C), 128.32 (Ar-C), 127.68 (Ar-C), 127.53 (Ar-C), 126.88 (CH₃C=C), 126.84 (CH₃C=CH), 78.70 (Ar-CH), 73.24 (Ar-CH), 62.59(CH₃), 60.57 (CH₃), 56.05 (C(CH₃)₃), 55.57 (C(CH₃)₂), 40.12 (C(CH₃)₂), 39.79 (C(CH₃)₂), 31.75 (CH₃), 30.43 (CH₃), 28.86 (CH₃), 27.99 (CH₃), 27.37 (CH₃), 26.50 (CH₃), 25.77 (CH₃), 23.36 (CH₃), 16.79 (CH₃C=C) ppm. Elemental analysis calcd (%) for C₃₁H₄₄N₂: C, 83.73; H, 9.97; N, 6.30; found: C, 82.99; H, 9.94; N, 6.20. HRMS (ESI-TOF) m/z: [M + H]+ calcd for C₃₁H₄₄N₂: 444.3582; found: 445.3545.

Synthesis of 6. THF (5 mL) was added to a 25 mL Schlenk flask containing 3 (140 mg, 0.31 mmol) and silver trflate (72.0 mg, 0.28 mmol) at room temperature with stirring inside the glovebox. Immediately, the formation of metallic silver was observed as evidenced by its black color. After 2 min of stirring, the reaction mixture was allowed to stand for 10 min to sediment metallic silver. The supernatant solution was taken out using a glass pipette and the orange-red liquor, it was kept again at −78 °C for a second crop of crystals. Colorless crystals of 6 were obtained after 12 h. Yield: 33 mg (51%).

Air Stability Experiment of 6 by Solution-State UV−Vis Spectroscopy. First, we prepared the stock solution of 6 (a 10 mL volumetric flask containing 10 mL of THF solution in 10 mg of 6 (0.0168 mmol)) inside the glovebox. The stock solution unexposed to air was investigated with UV−Vis absorption. The maximum absorption wavelengths appeared at 255 and 381 nm. After that, the stock solution was taken out of the glovebox and well exposed to an open air atmosphere for 5 min. Subsequently, the time-dependent electronic absorption experiments were carried out at 5 min, 10 min, 1 h, and then in intervals up to 48 h.

1:2 Reaction of 3 and AgOTf. A THF solution of 3 (45 mg, 0.101 mmol in 10 mL of THF) was added dropwise to a THF solution of silver trflate (65 mg, 0.252 mmol in 10 mL of THF) at room temperature through a cannula under stirring. Immediately, the formation of metallic silver was observed as evidenced by its black color. After stirring the reaction mixture for 30 min, it was allowed to stand for 10 min to sediment metallic silver. Then, the supernatant solution was taken out, concentrated to about 5 mL, and kept at −30 °C with pentane diffusion for crystallization. Colorless crystals of 2 were obtained after 12 h. Yield: 33 mg (51%).
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