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CERIUM(IV) AMMONIUM NITRATE–MEDIATED OXIDATION OF MONO-ARYL-SUBSTITUTED METHYLENECYCLOBUTANES: A CONVENIENT METHOD FOR THE SYNTHESIS OF SPIROCYCLOBUTYL-1,2-DIOXETHANES

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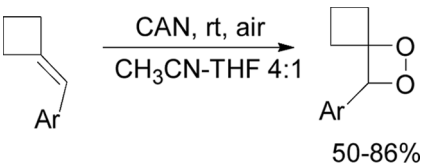
GRAPHICAL ABSTRACT



Abstract *Cerium(IV) ammonium nitrate (CAN)-mediated oxidation of methylenecyclobutanes was investigated. Compared with the similar reactions of methylenecyclopropanes, the reaction products were quite different. Instead of the desired ring-enlarged product cyclopentanones, a cyclobutyl ring-intact product, spirocyclobutyl-1,2-dioxethane, was obtained. The structures of these spiroheterocycle-containing compounds are interesting, and the reactions are potentially valuable in both organic synthesis and mechanism research.*

Keywords CAN; 1,2-dioxetane; methylenecyclobutane; oxidation; spiro compound

During the past decade, highly activated small organic molecules have attracted much attention, and their novel reactions have been widely investigated. These include methycyclopropanes (MCPs),[1] vinylidenecyclopropanes (VCPs),[2] allenes,[3] cyclopropyl allenes.[4] Because of their high intramolecular ring strain or cumulated carbon–carbon double bonds, these compounds have high reactivity and therefore can undergo a series of interesting reactions under mild conditions with high selectivity, providing convenient methods for the construction of many useful organic skeletons. Hence, they are all useful building blocks in organic synthesis. Containing a four-membered carbon ring and an exocyclic double bond, the molecular structure of methylenecyclobutanes (MCBs) are very similar to that of MCPs.[5] Therefore,

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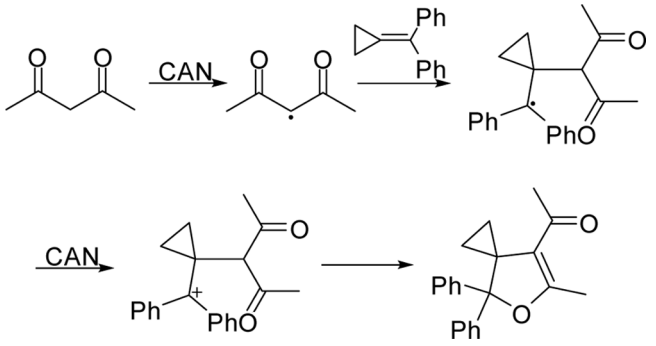
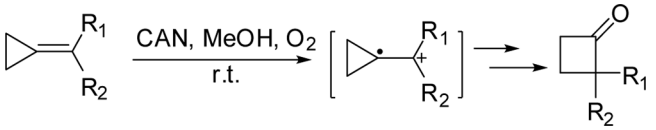


Scheme 1. CAN-promoted reactions of MCPs with 1,3-dicarbonyl compounds.

MCBs may undergo a series of reactions like MCPs. Recently, the novel reactions of MCBs have also been reported in the literature.[6]

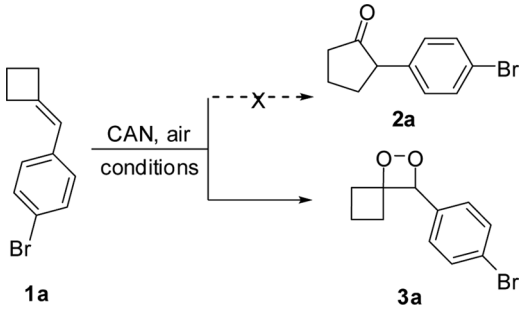
Cerium(IV) ammonium nitrate (CAN) is a good single-electron-transfer (SET) reagent in organic synthesis. In the field of MCPs, CAN-mediated reactions have been widely investigated, providing novel entry to many useful organic compounds.[7] CAN-mediated oxidative additions of MCPs with 1,3-dicarbonyl compounds provide a convenient method for the synthesis of spirocyclopropyl dihydrofurans. In this reaction, CAN first reacts with 1,3-dicarbonyl anions through the SET mechanism to generate the corresponding intermediate carbon-free radicals, which then react with MCPs (Scheme 1).[7c,7d] In 2006, Nair and coworkers reported that the direct reaction of CAN with MCPs in the presence of oxygen led to cyclobutanones (Scheme 2),[7b] which are also useful building blocks in both organic synthesis and drug design.[8] Encouraged by these works, we became interested in the exploration of CAN-mediated reactions. Herein, we report our recent interesting findings in the CAN-mediated oxidation of MCBs.

We initially chosen MCB **1a** as the model starting compound and examined its CAN-mediated oxidations under different conditions. When **1a** and CAN were stirred in methanol or ethanol under air, no desired ring-enlarged product **2a** was observed and a series of unidentified complexes were obtained (Table 1, entries 1 and 2). Interestingly, when the reaction was carried out in tetrahydrofuran (THF), a spiroheterocycle-containing product, **3a**, was obtained in 15% yield (Table 1, entry 3). Further screening demonstrated that the yield of **3a** could be enhanced in CH_3CN-THF (4:1) mixed solvent at room temperature (Table 1, entry 7). The structure of compound **3a** was confirmed by analytical spectra as well as the literature.[9] In the ^1H NMR spectrum, the disrupt alkyl peaks (chemical shifts: 1.35–2.61 ppm)



Scheme 2. CAN-promoted SET reactions of MCPs.

Table 1. CAN-mediated oxidation of MCBs under different conditions[a]



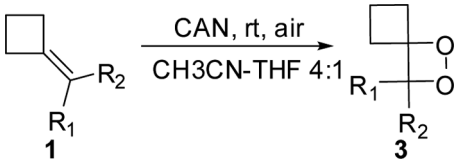
Entry	Solvent	Temp.	Time (h)[b]	Yield of **3a** (%)[c]
1	MeOH	rt	6	0[d]
2	EtOH	rt	10	0[d]
3	THF	rt	5	15
4	CH_3CN–THF (1:1)	rt	4	31
5	CH_3CN–THF (2:1)	rt	3	38
6	CH_3CN–THF (3:1)	rt	3	46
7	CH_3CN–THF (4:1)	rt	3	51
8	CH_3CN–THF (4:1)	40 °C	1	30
9	CH_3CN–THF (4:1)	60 °C	1	Trace[d]

[a]Reaction conditions: **1a** (0.3 mmol) and CAN (0.6 mmol) were stirred in 1 mL of solvent under different conditions.
[b]The reaction was monitored by TLC (eluent: petroleum ether).
[c]Isolated yields.
[d]Unidentified complexes were observed.

indicate the asymmetric cyclobutyl structure with different substituents on its two sides.[1d] The single peak at 6.36 ppm indicated the proton of the carbon adjacent to the O-O group, as the literature reported.[9a] In infrared (IR) spectrum, the absorption at 1074 cm^{-1} indicated the O-O structure. In the mass spectrum, the fragments at 71 (16) and 185 (95) are cyclobutanone $[M + H^+]$ and 4-bromobenzaldehydes $[M + H^+]$, respectively. Since literature contains reports of thermolysis of 1,2-dioxethanes generating aldehydes or ketones,[9b] the existence of these two fragments in the mass spectrum confirmed the spirocyclobutyl-1,2-dioxethane structural unit.

Containing a spirocyclobutyl ring and a dioxetane structure unit, spirocyclobutyl-1,2-dioxethanes **3** may have potential value in organic synthesis.[6,10] Therefore, we next examined the application scope of this reaction. A series of MCBs **1** were employed to synthesize the corresponding spirocyclobutyl-1,2-dioxethane **3**. The experimental results are listed in Table 2. When monosubstituted MCBs were employed, the corresponding spirocyclobutyl-1,2-dioxethanes **3** could be smoothly obtained (Table 2, entries 1–7). The product yields are especially good when MCBs with alkyl groups on their aryl ring were employed (Table 2, entries 6 and 7). However, only a series of unidentified complexes were obtained when disubstituted MCBs

Table 2. Synthesis of spirocyclobutyl-1,2-dioxethanes **3**[a]

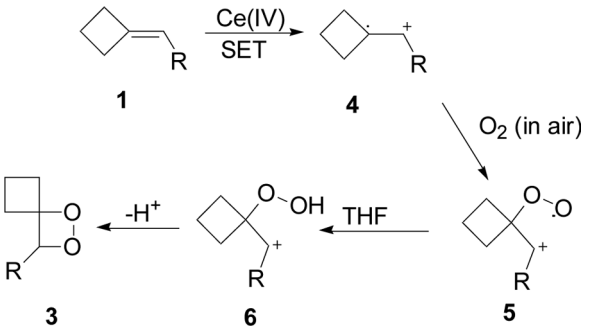


Entry	R^1, R^2	Yield of **3** (%)[b]
1	*p*–BrC_6H_4, H (**1a**)	51 (**3a**)
2	C_6H_5, H (**1b**)	60 (**3b**)
3	*o*–BrC_6H_4, H (**1c**)	56 (**3c**)
4	*p*–ClC_6H_4, H (**1d**)	50 (**3d**)
5	*m*–ClC_6H_4, H (**1e**)	64 (**3e**)
6	*p*-MeC_6H_4, H (**1**)	72 (**3f**)
7	*p*-$Bu^tC_6H_4$, H (**1g**)	86 (**3g**)
8	C_6H_5, C_6H_5 (**1h**)	Trace[c]
9	C_6H_5, Me (**1i**)	Trace[c]

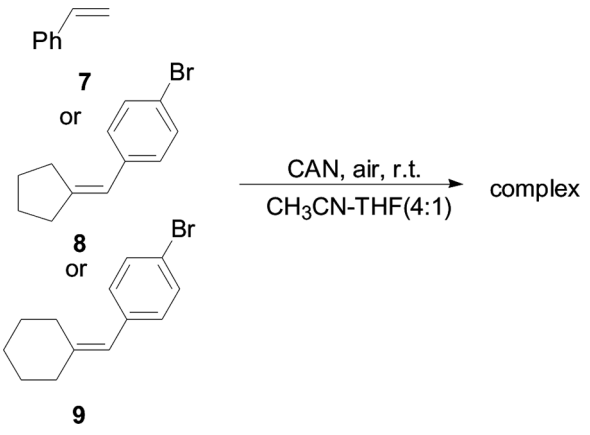
[a]Reaction conditions: **1** (0.3 mmol), CAN (0.6 mmol), CH_3CN (0.8 mL), and THF (0.2 mL), and the reactions were carried out in air at room temperature.
[b]Isolated yields.
[c]Unidentified complexes were observed.

were employed (Table 2, entries 8 and 9). The products spirocyclobutyl-1,2-dioxethanes are not very stable and should be kept in a refrigerator. When they are stored for a long time, traces of decomposition products, cyclobutanone or aldehydes, might be observed in ^{1}H NMR spectra.

Based on these experimental results as well as literature reports, we supposed the probable mechanisms. The initial CAN-mediated SET reaction of MCBs **1** furnished the intermediate radical cation **4**.[7b] It is reasonable that **4** could be oxidized to **5** by trapping molecular oxygen in air. After capturing a proton from THF,[11] the peroxide free radical **5** was transformed to **6**, which then led to the final product **3** (Scheme 3).[12]



Scheme 3. Probable mechanisms.



Scheme 4. CAN-promoted oxidation of other olefins.

We then tried to expand the application scope of this interesting reaction by employing some other kinds of olefins. The experimental results showed that the cyclobutyl ring in the substrate is necessary. When styrene **7**, methylenecyclopentane **8**, or methylenecyclohexane **9** was employed, no desired product was obtained (Scheme 4).

In conclusion, the reaction products of MCBs' CAN-mediated oxidations are quite different from those of MCPs. Instead of the ring-enlarged cyclopentanones, cyclobutyl ring-intact products spirocyclobutyl-1,2-dioxethanes were obtained. The structures of these spiroheterocycle-containing compounds are interesting and potentially valuable in organic synthesis. This CAN-mediated SET reaction might provide an oxidation of olefins with air and therefore have some successive applicable value in future.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker Avance (600-MHz) spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were recorded on a Bruker Avance (150-MHz) spectrometer in $CDCl_3$. IR spectra were recorded on a Shimadzu IR-408 spectrometer. Electron-impact mass spectrometry (EIMS) studies were run on a HP 5989B mass spectrometer. Elemental analysis was recorded on a Carlo Erba 1106 elemental analysis instrument.

Typical Procedure for the Preparation of 3

A solution of MCBs **1** (0.3 mmol) in CH_3CN (0.8 mL) and THF (0.2 mL) was added to a Schlenk tube containing 0.6 mmol of CAN. The mixture was stirred in air, and the reaction was monitored by thin-layer chromatography (TLC; eluent: petroleum ether). When the reaction terminated, 5 mL of water were added, and the mixture was extracted by ether (5 mL) three times. The combined organic layer was dried with anhydrous Na_2SO_4, and then the solvent was evaporated under

vacuum. The residue was purified by preparative TLC (eluent: petroleum ether–EtOAc 16:1) and gave the corresponding product **3**.

Data

Compound 3a. A colorless oil. IR (film): 2961, 1641, 1302, 1281, 1251, 1108, 1074, 1012, 981, 840 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 1.35–1.40 (m, 1H), 1.90–1.94 (m, 1H), 2.32–2.38 (m, 1H), 2.44–2.50 (m, 2H), 2.59–2.61 (m, 1H), 6.36 (s, 1H), 7.31–7.59 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 14.0, 28.7, 29.7, 81.7, 87.8, 124.0, 128.5, 132.2, 132.3 ppm; MS (EI) m/z (%): 254 (1) [M^+], 185 (95) (p-$BrC_6H_4CHO + H^+$), 183 (100), 71 (16) ($C_4H_6O + H^+$). Anal. calcd. for $C_{11}H_{11}BrO_2$: C, 51.79; H, 4.35. Found: C, 52.12; H, 4.11.

Compound 3b. A colorless oil. IR (film): 2962, 1640, 1498, 1455, 1281, 1091, 978, 849, 751, 702 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 1.28–1.30 (m, 1H), 1.85–1.89 (m, 1H), 2.34–2.36 (m, 1H), 2.43–2.53 (m, 2H), 2.63–2.65 (m, 1H), 6.42 (s, 1H), 7.44 (s, 5H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 13.9, 28.5, 29.9, 82.4, 88.1, 126.9, 129.0, 129.7, 133.2 ppm; MS (EI) m/z (%): 176 (2) [M^+], 105 (100) ($C_6H_5CHO + H^+$), 71 (7) ($C_4H_6O + H^+$). Anal. calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.70; H, 6.63.

Compound 3c. A colorless oil. IR (film): 2962, 1644, 1471, 1429, 1300, 1282, 1029, 979, 845, 753 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 1.36–1.43 (m, 1H), 1.91–1.94 (m, 1H), 2.40–2.49 (m, 2H), 2.58–2.69 (m, 2H), 6.92 (s, 1H), 7.29–7.68 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 14.5, 28.5, 30.2, 80.7, 88.6, 124.3, 128.1, 128.2, 131.1, 133.1, 133.7 ppm; MS (EI) m/z (%): 255 (1) [$M^+ + 1$], 185 (95) (p-$BrC_6H_4CHO + H^+$), 183 (100), 71 (16) ($C_4H_6O + H^+$). Anal. calcd. for $C_{11}H_{11}BrO_2$: C, 51.79; H, 4.35. Found: C, 51.60; H, 4.67.

Compound 3d. A colorless oil. IR (film): 2962, 1704, 1643, 1597, 1493, 1302, 1281, 1093, 1015, 983, 942, 838 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 1.35–1.40 (m, 1H), 1.90–1.93 (m, 1H), 2.34–2.38 (m, 1H), 2.44–2.51 (m, 2H), 2.59–2.62 (m, 1H), 6.38 (s, 1H), 7.37–7.43 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 13.9, 28.7, 29.7, 81.7, 87.8, 128.2, 129.3, 129.5, 130.9 ppm; MS (EI) m/z (%): 210 (2) [M^+], 141 (32) (p-$ClC_6H_4CHO + H^+$), 139 (100), 71 (9) ($C_4H_6O + H^+$). *Anal.* calcd. for $C_{11}H_{11}ClO_2$: C, 62.72; H, 5.26. Found: C, 63.01; H, 5.22.

Compound 3e. A colorless oil. IR (film): 2962, 1643, 1576, 1477, 1433, 1299, 1282, 1087, 986, 846, 784, 753 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 1.37–1.40 (m, 1H), 1.91–1.94 (m, 1H), 2.33–2.39 (m, 1H), 2.43–2.53 (m, 2H), 2.60–2.64 (m, 1H), 6.37 (s, 1H), 7.31–7.43 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 14.0, 28.7, 29.8, 81.5, 87.8, 125.1, 127.0, 130.0, 130.3, 135.1, 135.3 ppm; MS (EI) m/z (%): 210 (3) [M^+], 141 (31) (m-$ClC_6H_4CHO + H^+$), 139 (100), 71 (29) ($C_4H_6O + H^+$). Anal. calcd. for $C_{11}H_{11}ClO_2$: C, 62.72; H, 5.26. Found: C, 62.55; H, 5.58.

Compound 3f. A colorless oil. IR (film): 2960, 1641, 1515, 1424, 1299, 1281, 1252, 1087, 975, 851, 758 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 1.28–1.33 (m, 1H), 1.85–1.88 (m, 1H), 2.32–2.45 (m, 2H), 2.40 (s, 3H), 2.49–2.53 (m, 1H),

2.61–2.65 (m, 1H), 6.39 (s, 1H), 7.23–7.33 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 13.9, 21.3, 28.5, 29.9, 82.5, 88.2, 126.8, 129.6, 130.1, 139.7 ppm; MS (EI) m/z (%): 190 (1) [M^+], 120 (8) (p-MeC_6H_4CHO), 119 (100), 71 (2) ($C_4H_6O + H^+$). Anal. calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.51; H, 7.08.

Compound 3g. A colorless oil. IR (film): 2965, 2907, 2871, 1642, 1515, 1463, 1423, 1366, 1281, 1252, 1126, 1109, 979, 851, 750 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.19–1.25 (m, 1H), 1.25 (s, 9H), 1.76–1.80 (m, 1H), 2.25–2.37 (m, 2H), 2.43–2.56 (m, 2H), 6.34 (s, 1H), 7.27–7.36 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 13.9, 28.5, 29.9, 31.2, 34.8, 82.4, 88.3, 125.8, 126.7, 130.0, 152.8 ppm. MS (EI) m/z (%): 162 (25) (p-$Bu^tC_6H_4CHO$), 147 (100), 71 (2) ($C_4H_6O + H^+$). Anal. calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.22; H, 8.54.

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