OXIDATIVE DEAROMATIZATION: SYNTHESIS OF FUNCTIONALIZED BICYCLO[2.2.2]OCTENONES, SIGMATROPIC SHIFT IN EXCITED STATE, AND RADICAL-INDUCED CLEAVAGE OF CYCLOPROPANE RING

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GRAPHICAL ABSTRACT

Abstract Synthesis of novel bicyclo[2.2.2]octenones endowed with a β,γ-enone system in which γ-carbon is substituted with an electron-withdrawing group from simple aromatics is described. Oxa-di-pi-methane reaction of bicyclo[2.2.2]octenones to functionalized bicyclo[3.3.0]octanes and their transformation to bicyclo[3.2.1]octane framework are also presented.

Keywords Diels–Alder reaction; oxa-di-pi-methane rearrangement; pericyclic reaction; photochemistry

INTRODUCTION

Rapid creation of structural, functional, and stereochemical complexity is one of the most important aspects of synthesis design and development of methods. Cascade reactions and multicomponent reactions are often employed to achieve this objective.[1] In addition, chemistry of reactive species generated by oxidative dearomatization of phenols has played a very important role in developing methods for efficient generation of molecular complexity and has proved to be a powerful method for synthesis of a diverse array of molecular architecture.[2–4]

Functionalized bicyclo[2.2.2]octanes such as 1 (Fig. 1) endowed with a β,γ-enone chromophore are versatile intermediates for the synthesis of a diverse array
of molecular architectures and serve as precursors for many complex natural products.\[5\] This is presumably due to their propensity toward various types of regio- and stereoselective reactions by virtue of their rigid structure and interaction among functional groups. For example, bicyclo[2.2.2]octane of type 1 having a $\beta,\gamma$-enone chromophore undergoes two unique photoreactions such as 1,2-acyl shift (oxa-di-$\pi$-methane rearrangement) and 1,3-acyl shift upon triplet and singlet excitation respectively, as a consequence of homo-conjugation between carbonyl group and olefinic moiety.\[6–9\]

In view of this and our continuing interest in synthesis and photoreaction of $\beta,\gamma$-enone, we considered exploring the photochemical reaction of bicyclo[2.2.2]octenones of type 2 (Fig. 1) in which the C=C moiety is also conjugated with ester function in addition to homo-conjugation with the CO group and examine the effect of additional conjugation on the photochemical reaction.

We report herein an efficient synthesis of compounds of type 2 via a tandem oxidative dearomatization of aromatic precursor 5 and cycloaddition with ethyl acrylate, and results of photoreactions of compound 2 to diquinanes such as 3 and radical-induced transformation to bicyclo[3.2.1]octanes 4 (Fig. 1).

**RESULTS AND DISCUSSION**

Conceptually, the desired bicyclo[2.2.2]octenones of type 2 may be prepared by cycloaddition of cyclohexa-2,4-dienes of type 1 (Fig. 2) with acrylate. However, cyclohexa-2,4-diene such as 1 are not easily accessible as these are keto-tautomer of the corresponding phenols. Therefore, we considered employing 6,6-spiroepoxycyclohexadienones such as 6 that may be generated in situ from the aromatic precursor of type 5 via oxidative dearomatization.

To realize our objective, a simple preparation of $o$-hydroxymethyl phenols 5a,b was required. The compound 5a was prepared by hydroxymethylation of
t-butyl-4-hydroxy benzoate 7a that was readily prepared from p-hydroxybenzoic acid following a reported procedure.\[^{[10]}\] Thus, treatment of 7a with aqueous NaOH and HCHO at 55 °C\[^{[11a]}\] gave monohydroxymethylated compound 5a in moderate yield. The precursor 5b is known in the literature and it was prepared in two steps involving reaction of methyl-4-hydroxy benzoate with phenyl boronic acid followed by treatment with H₂O₂.\[^{[11b]}\] However, we prepared compound 5b by hydroxymethylation of methyl-4-hydroxybenzoate 7b (Scheme 1). Though the yields of hydroxymethylated products 5a,b are on the low side, the experimental procedure is simple and can be repeated in a routine manner to generate significant quantities.

After having prepared the aromatic precursors 5a,b we set out to explore oxidative dearomatization and cycloaddition. At the outset, however, we were aware that oxidative dearomatization of phenols having an electron-withdrawing group is relatively difficult. Thus, a solution of o-hydroxymethylated ester 5a in acetonitrile containing ethyl acrylate was oxidized with aqueous NaIO₄ following a procedure developed earlier in our group,\[^{[12]}\] and the reaction mixture was stirred at ambient temperature for 48 h. Indeed, usual workup and chromatography of the product mixture gave the endo-adduct 9a in good yield (62%) along with the known aldehyde 8a\[^{[13]}\] as a minor product. The adduct 9a is formed as a result of in situ generation of spirocyclohexa-2,4-dienone 6a followed by a regio- and stereoselective cycloaddition with ethyl acrylate, in a tandem fashion (Scheme 2).

Structure of adduct 9a was deduced from the following spectral features and further confirmed with the help of a single-crystal structure determination. Thus, IR spectrum of 9a showed characteristic absorption bands at 1732 and 1712 cm⁻¹.

![Scheme 1. Preparation of aromatic precursors.](image-url)
for the carbonyl groups. $^1$H NMR (400 MHz) spectrum of adduct displayed signals at $\delta$ 7.06 (dd, $J_1 = 6.4$ Hz, $J_2 = 1.8$ Hz, 1H) for the $\beta$-proton of $\beta,\gamma$-enone group. The methylene protons of the oxirane moiety displayed highly characteristic signals at $\delta$ 3.11 (part of an AB system, $J_{AB} = 6.2$ Hz, 1H) and 2.93 (part of an AB system, $J_{AB} = 6.2$ Hz, 1H) and methylene protons of ester group and methyl group were observed at $\delta$ 4.15 (q, $J = 7.1$ Hz, 2H) and 1.26 (t, $J = 7.1$ Hz, 3H) respectively. The presence of olefinic proton, oxirane group, and carboethoxy group clearly indicated that cycloaddition had occurred. Further, signals were shown at $\delta$ 3.86 (dd, $J_1 = 6.4$ Hz, $J_2 = 2.2$ Hz, 1H), 3.21–3.15 (m, 2H), 2.44 (partly merged ddd, $J_1 = 13.3$ Hz, $J_2 = 10.5$ Hz, $J_3 = 2.6$ Hz, 1H), 2.02 (ddd, $J_1 = 13.3$ Hz, $J_2 = 5.2$ Hz, $J_3 = 2.9$ Hz, 1H), 1.50 (s, 9H) due to other protons. The $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 9a exhibited signals at $\delta$ 203.2, 172.1 for the carbonyl carbons of CO group present in the bridge and ester group respectively. Olefinic carbons appeared at $\delta$ 162.5 and 140.4. In addition, signals were shown at $\delta$ 135.4, 81.9, 61.7, 57.3, 53.2, 51.2, 40.6, 37.8, 28.2, 25.8, and 14.2 for other carbons. These spectral features clearly suggested the gross structure of the adduct. However, the endo-stereochemistry of the carboethoxy group and stereochemical orientation of the oxirane ring was not readily discernible. Hence, a single-crystal x-ray structure determination was undertaken that confirmed this formulation (Fig. 3).

Similarly, oxidative dearomatization of the substrate 5b in the presence of ethyl acrylate gave the adduct 9b in moderate yield along with aldehyde 8b (Scheme 2). The structure of 9b was deduced from its spectral characteristics and comparison with spectral features of 9a. Though, the oxidative dearomatization–cycloaddition led to adducts 9a,b in good to moderate yields, the generation of molecular complexity from simple aromatic precursor is noteworthy. It may be mentioned that functionalized bridged bicyclic compounds of type 9a,b are not easily accessible otherwise.
The presence of contiguous keto-epoxide functionality in adducts 9a,b provided opportunity for selective manipulation of the oxirane ring. Thus treatment of 9a with Zn-NH₄Cl in aqueous methanol at ambient temperature furnished the β-hydroxymethyl ketone 11a (as a mixture of syn-anti isomers) in excellent yield along with minor amounts of 10a (Scheme 3). The compound 10a was formed as a result of deoxygenation of the oxirane ring. Subsequent oxidation of 11a by Jones’s reagent followed by decarboxylation of the resulting β-ketoacid furnished the desired chromophoric system 2a. Similarly, adduct 9b was also reduced with Zn-NH₄Cl, which gave 10b and 11b, the latter as a major product. Oxidation of 11b followed by decarboxylation gave the desired bicyclic compound 2b endowed with a β,γ-enone chromophore.

The IR spectrum of compound 2a showed an absorption band at 1732 cm⁻¹ for carbonyl group. ¹H NMR (400 MHz) spectrum displayed signals at 7.00 (dd, \( J_1 = 6.6 \text{ Hz}, J_2 = 1.8 \text{ Hz} \)) for the β-proton of β,γ-enone group. In addition, signals were observed at \( \delta 4.13 \) (q, \( J = 7.1 \text{ Hz}, 2\text{H} \)), 3.68 (dd, \( J_1 = 6.6 \text{ Hz}, J_2 = 2.1 \text{ Hz}, 1\text{H} \)), 3.63–3.59 (m, 1H), 3.04–3.00 (m, 1H), 2.13–2.04 (m, 3H), 1.93–1.88 (m, 1H), 1.50 (s, 9H), 1.24 (t, \( J = 7.1 \text{ Hz}, 3\text{H} \)) for other methine, methylene, and methyl protons. The ¹³C NMR (100 MHz, CDCl₃) spectrum of compound 2a exhibited signals at \( \delta 209.3, 172.6 \) for the carbonyl carbons of ketone and ester group respectively. Signals for olefinic carbons were observed at \( \delta 163.2, 142.2 \). Other signals were

Figure 3. Crystal structure of adduct 9a.
shown at δ 134.9, 81.3, 61.4, 52.0, 39.8, 38.9, 31.7, 29.4, 28.2, and 14.3 (total 14 carbons). The compound 2b also exhibited similar spectral features.

After having prepared bicyclo[2.2.2]octenones 2a,b in which the ene-moiety is also conjugated with ester group in addition to its homoconjugation with the CO group, their photochemical reaction was explored. The photochemical reactions of β,γ-enones have stimulated interest for long time,[6] which has increased recently because of its synthetic potential.[7–9] As we have mentioned earlier, rigid β,γ-enones undergo 1,2-acyl shift (oxa-di-pi-methane reaction) and 1,3-acyl shift upon triplet and singlet (1S) excitation, respectively. Though these two types of reactions are quite characteristic of the excited state, it often controlled by structural features and the presence of functional group in the chromophoric system, in a subtle fashion.[6a,6b] While photoreaction of a number of bicyclo[2.2.2]octanes endowed with β,γ-enone chromophore has been examined,[6,7] only a few examples of photoreaction of bicyclo[2.2.2]octenones having an electron-withdrawing substituent at the γ-carbon of β,γ-enone moiety have been studied.[8a,8b]

Keeping this in mind, we first examined the sensitized photoreaction of compound 2a. Thus, a solution of 2a in acetone (both solvent as well as sensitizer) was irradiated in a Pyrex immersion well with a mercury vapor lamp (125 W, Bajaj) for 1 h. Removal of solvent followed by chromatography of photolysate furnished the product 3a in excellent yield, as a result of an efficient 1,2-acyl shift or oxa-di-pi-methane rearrangement (Scheme 4). Similar irradiation of substrate 2b also led to a smooth reaction and furnished the diquinane 3b as a result of 1,2-acyl shift.

The structure of both the products was deduced from their spectral features and comparison with spectral data of their precursor. Thus, the IR spectrum of

![Scheme 3. Synthesis of compounds 2a,b.](image-url)
compound 3a showed an absorption band at 1731 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) spectrum exhibit signals at $\delta$ 4.18 (q, $J = 7.1$ Hz, 2H), 3.40 (dd, $J_1 = 9.1$ Hz, $J_2 = 5.9$ Hz, 1H), 2.82–2.76 (merged multiplet, 2H), 2.68 (dd, $J_1 = 18.2$ Hz, $J_2 = 9.1$ Hz, 1H), 2.59 (d, $J = 10.1$ Hz, 1H), 2.45–2.36 (m, 1H), 1.94 (dd, $J_1 = 12.1$ Hz, $J_2 = 6.4$ Hz, 1H), 1.85 (d, $J = 18.2$ Hz, 1H), 1.46 (s, 9H), 1.27 (t, $J = 7.1$ Hz, 3H). The aforementioned signals and lack of signal due to olefin proton in the proton NMR spectrum clearly suggested that 1,2-acyl shift had occurred during the photoreaction. The structure was also corroborated with the $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum as it displayed characteristic signal
at δ 211.2 that indicated the presence of CO group in a five-membered ring. It further displayed resonances at δ 173.2, 169.9 for CO group of ester moieties in addition to signals at δ 81.7, 61.3, 50.6, 47.0, 46.2, 45.1, 43.4, 40.2, 37.7, 28.1, and 14.2 for other carbons. The photoproduct 3b also exhibited similar spectral characteristics.

To explore the possibility of a 1,3-acyl shift, the photoreaction of chromophoric systems 2a,b in an excited singlet (1S) was also examined. Thus, a solution of 2a in benzene was irradiated in a Pyrex immersion well with a mercury vapor lamp for 1 h (Scheme 4). However, no photoreaction was observed and starting material was recovered. Irradiation for extended time period also did not lead to any reaction. The substrate 2b was also found to be unreactive and did not give any 1,3-acyl shift product. While it is difficult to rationalize the unreactivity of 2a,b toward the 1,3-acyl shift upon direct excitation, it may be due to the presence of an electron-withdrawing group at the γ-carbon of β,γ-enone moiety as similar systems without such groups are known to undergo 1,3-acyl shift upon direct excitation. [6,7]

Subsequently, the photoproducts 3a,b were subjected to reductive cleavage of the cyclopropane ring. Thus, initially, tricyclic compound 3a was treated with H2/Pd-C both at atmospheric pressure and at 147 psi. However, no reaction was observed. Then, it was treated with Bu3SnH-AIBN in refluxing benzene. Chromatography of the reaction mixture gave the compound 4a as a sole product (a single stereoisomer) in excellent yield (93%) a result of highly regio- and stereoselective cleavage of the internal cyclopropane bond. The reaction of 3b with Bu3SnH-AIBN also gave the compound 4b containing the bicyclo[3.2.1]octane ring system in excellent yield. Interestingly, products of type 13 that may form as a result of cleavage of peripheral cyclopropane bond were not obtained (Scheme 5).

Structures of both the products 4a,b were clearly revealed from their spectral features, particularly 13C NMR spectrum. Thus, IR spectrum of 4a showed an absorption band at 1722 cm−1. 1H NMR spectrum (400 MHz, CDCl3) displayed signals at δ 4.12 (q, J = 7.1 Hz, 2H), 3.02–2.98 (m, 1H), 2.94–2.86 (m, 2H), 2.82–2.75 (m, 2H), 2.66 (dd, J1 = 9.5 Hz, J2 = 5.6 Hz, 1H), 2.38–2.23 (m, 2H), 2.20–2.12 (m, 1H), 1.86 (dd, J1 = 13.9 Hz, J2 = 9.5 Hz, 1H), 1.48 (s, 9H), 1.25 (t, J = 7.1 Hz, 3H).

13C NMR spectrum (100 MHz, CDCl3) exhibited a characteristic signal at δ 210.4 that suggested presence of carbonyl group in a six-membered ring. Carbonyl carbons of ester groups showed signals at δ 175.3 and 171.2. In addition, signals were shown at δ 81.4, 61.1, 49.1, 46.5, 45.9, 45.8, 40.8, 36.8, 33.7, 28.3, and 14.3. The 13C NMR spectrum in Attached Proton Test (APT) mode revealed the presence of only four methylene carbons at δ 61.1, 45.9, 45.8, and 33.7, which confirmed the structure 4a and ruled out other possibilities such as 13a. The compound 4b also exhibited similar spectral features. Though the products 4a,b were single diastereoisomer, the exact stereochemical orientation of the COOR group at the methano- bridge was not easily discernible from aforementioned spectral characteristic.

CONCLUSION

We have described oxidative dearomatization of o-hydroxymethyl phenols having an electron-withdrawing group to spiroepoxycyclohexa-2,4-dienes and their cycloaddition with ethyl acrylate leading to bicyclo[2.2.2]octenones. Manipulation of adducts led to desired chromophoric systems that upon oxa-di-pi-methane
reaction gave tricyclic compound having a diquinane framework. Cleavage of the cyclopropane ring of photoproducts gave functionalized bicyclo[3.2.1]octanes.

EXPERIMENTAL

IR spectra were recorded on a Nicolet Impact 400 FT-IR. $^1$H NMR and $^{13}$C NMR spectra were recorded on either Bruker 400-MHz or Bruker 500-MHz instruments. The samples were dissolved in CDCl$_3$ with tetramethylsilane (TMS) as internal standard. High-resolution mass spectrometry (HRMS) were recorded on a Maxis Impact Bruker mass spectrometer. Melting points were determined on a Veego apparatus of Buchi type. All organic extracts were dried over anhydrous Na$_2$SO$_4$. Reactions were monitored with thin-layer chromatography (TLC), and spots were visualized with I$_2$ vapor. Column chromatography was performed using SRL/Thomas Baker silica gel (60–120 and 100–200 mesh) with elution using petroleum ether (bp 60–80°C) and EtOAc mixes.

**General Procedure for Oxidative Dearomatization of 5a,b**

A solution of NaIO$_4$ in water was added dropwise to a stirred solution of the compounds 5a,b and ethyl acrylate in acetonitrile at 0°C, and the reaction mixture was stirred at ambient temperature for 48 h. Acetonitrile was evaporated under reduced pressure, and the residue was diluted with water and extracted with ethyl acetate. The organic extract was combined, washed with brine, and dried over anhydrous Na$_2$SO$_4$. Solvent was removed under reduced pressure and the product was chromatographed on silica gel.

**6-tert-Butyl 8-ethyl 3-oxospiro[bicyclo[2.2.2]oct[5]ene-2,2’-oxirane]-6,8-dicarboxylate (9a).** The reaction of compound 5a (2.00 g, 8.93 mmol) with ethyl acrylate (7 mL, excess) and NaIO$_4$ (6.00 g, 28.00 mmol) in aqueous acetonitrile followed by workup and chromatography [elution with petroleum ether/ethyl acetate (70:30)] gave the desired adduct 9a as a colorless solid (1.77 g, 62%), mp 104–106°C. $R_f = 0.5$ petroleum ether/EtOAc (70:30). IR $\nu_{\text{max}}$: 1732, 1712 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.06 (dd, $J_1 = 6.4$ Hz, $J_2 = 1.8$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.86 (dd, $J_1 = 6.4$ Hz, $J_2 = 2.2$ Hz, 1H), 3.21–3.15 (m, 2H), 3.11 (part of an AB system, $J_{AB} = 6.2$ Hz, 1H), 2.93 (part of an AB system, $J_{AB} = 6.2$ Hz, 1H), 2.44 (partly merged ddd, $J_1 = 13.3$ Hz, $J_2 = 10.5$ Hz, $J_3 = 2.6$ Hz, 1H), 2.02 (ddd, $J_1 = 13.3$ Hz, $J_2 = 5.2$ Hz, $J_3 = 2.9$ Hz, 1H), 1.50 (s, 9H), 1.26 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 203.2, 172.1, 162.5, 140.4, 135.4, 81.9, 61.7, 57.3, 53.2, 51.2, 40.6, 37.8, 28.2, 25.8, 14.2. HRMS (ESI): $m/z$ [M+Na]$^+$ calcd. for C$_{17}$H$_{22}$NaO$_6$: 345.1309; found: 345.1306.

Crystal data of compound 9a: C$_{17}$H$_{22}$O$_6$, $M = 322.36$, triclinic, space group P-1 (#2), $a = 6.636$ (4) Å, $b = 9.419$ (6) Å, $c = 13.627$ (8) Å, $\alpha = 92.616$ (10)$^\circ$, $\beta = 99.969(12)^\circ$, $\gamma = 93.654(9)^\circ$, $V = 835.8$ (9) Å$^3$, $D_c = 1.281$ g/cm$^3$, $Z = 2$, $F(000) = 344.00$, size: 0.45 $\times$ 0.20 $\times$ 0.09 mm$^3$, wavelength = 0.71070 Å, GoF = 0.885, absorption coefficient = 0.965 cm$^{-1}$, total/unique reflections = 8828/2929 [R(int) = 0.0950], $T = 100$ K, 20 range = 5.0 to 50.0$^\circ$, final $R[I > 2\sigma(I)]$: $R_1 = 0.0567$, $wR_2 = 0.1604$, $R$ (all data): $R_1 = 0.0854$, $wR_2 = 0.1604$. Crystallographic data has been deposited.
with Cambridge Crystallographic Data Centre, CCDC no. 1004667. Copy of the data can be obtained, free of charge, on application to CCDC. E-mail: Deposit@ccdc.cam.ac.uk

**General Procedure for Photoreaction of 2a,b**

Ketones 2a,b were dissolved in acetone and degassed by passing nitrogen. They were then irradiated with a mercury vapor lamp (125 W, Bajaj) under nitrogen. Solvent was evaporated, and residue was chromatographed on silica gel.

**1-(tert-Butoxycarbonyl)-7-exo-(ethoxycarbonyl)tricyclo[3.3.0.0^{2,8}]octane-3-one (3a).** Irradiation of ketone 2a (0.100 g, 0.34 mmol) in acetone (100 mL) followed by removal of solvent and chromatography [elution with petroleum ether/ethyl acetate (70:30)] gave compound 3a as a liquid (0.064 g, 64%) [Rf = 0.5 petroleum ether/EtOAc (70:30)]. IR νmax: 2979, 1731 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 4.18 (q, J = 7.1 Hz, 2H), 3.40 (dd, J₁ = 9.1 Hz, J₂ = 5.9 Hz, 1H), 2.82–2.76 (merged multiplet, 2H), 2.68 (dd, J₁ = 18.2 Hz, J₂ = 9.1 Hz, 1H), 2.59 (d, J = 10.1 Hz, 1H) 2.45–2.36 (m, 1H), 1.94 (dd, J₁ = 12.1 Hz, J₂ = 6.4 Hz, 1H), 1.85 (d, J = 18.2 Hz, 1H), 1.46 (s, 9H), 1.27 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 211.2, 173.2, 169.9, 81.7, 61.3, 50.6, 47.0, 46.2, 45.1, 43.4, 40.2, 37.7, 28.1, 14.2. HRMS (ESI): m/z [M + Na]⁺ calcd. for C₁₆H₂₂NaO₅: 317.1351; found: 317.1359.

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**SUPPORTING INFORMATION**

Full experimental details and ¹H and ¹³C NMR spectra can be accessed on the publisher’s website.

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