Pergamon

Tetrahedron 58 (2002) 3229–3234

TETRAHEDRON

Oxidative fragmentation of 1-aryl-1-cycloalkenes using cerium(IV) ammonium nitrate (CAN): some novel observations

Vijay Nair,* Sreeletha B. Panicker, Siji Thomas, V. Santhi and Sindhu Mathai

Organic Chemistry Division, Regional Research Laboratory (CSIR), Trivandrum 695 019, India

This paper is dedicated with warm personal regards and best wishes to Professor Gilbert Stork on the occasion of his 80th birthday

Received 20 August 2001; revised 6 February 2002; accepted 28 February 2002

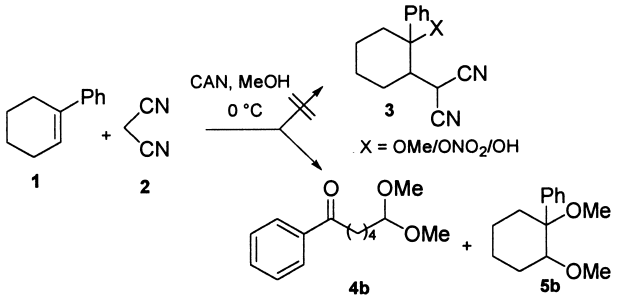
Abstract—1-Phenyl-1-cycloalkenes undergo oxidative fragmentation in presence of CAN in methanol, affording 1,*n*-dicarbonyl compounds as the major products along with 1,2-dimethoxycycloalkanes. The reaction under deoxygenated conditions afforded the latter in good yields. In the presence of azide ion, fragmentation leading to the corresponding cyanoketones was observed whereas with sulfinate only the 1-methoxy-2-sulfonyl cycloalkanes were formed. © 2002 Published by Elsevier Science Ltd.

1. Introduction

Carbon–carbon bond forming reactions mediated by radicals have found general acceptance in organic synthesis during the last two decades, largely due to a paradigm shift consequent on Stork's demonstration that radical methodology offers a powerful and unique alternative to ionic reactions in complex carbocyclic constructions.[1] The use of one-electron oxidants such as Ce(IV) reagents in the generation of carbon centered radicals and the addition of the latter to alkenes was introduced independently by Heiba and Dessau.[2] Subsequent investigations carried out by a number of groups have shown that cerium(IV) ammonium nitrate (CAN) is an excellent one electron oxidant for various synthetic transformations;[3] special mention may be made of the work by Baciocchi and co-workers on CAN mediated carbon–carbon bond formation.[4]

In recent years, we have been interested in the addition of carbon centered radicals generated by CAN to various alkenes. A detailed investigation carried out in this area has shown that CAN is a superior reagent vis a vis $Mn(OAc)_3$ in intermolecular reactions and the CAN induced addition of various 1,3-dicarbonyl compounds such as dimedone and acetylacetone to alkenes offers a convenient method for the synthesis of dihydrofuran derivatives.[5] The CAN mediated addition of dimethylmalonate to styrene in methanol led to a mechanistically fascinating reaction yielding 2-oxo-2-phenylethylpropanedioic acid dimethylester as the major product.[6] During the course of this work, we were intrigued by the possibility of CAN mediated oxidative addition of malononitrile to alkenes; malononitrile is an active methylene compound (pK_a 11.2) comparable to dimethyl malonate (pK_a 12.7). With this objective, a methanolic solution of 1-phenyl-1-cyclohexene and malononitrile was treated with a solution of CAN in the same solvent. In the event, no addition of malononitrile to phenylcyclohexene occurred; instead the latter underwent a smooth oxidative fragmentation to afford the mono acetal of 5-benzoylpentanaldimethyl acetal and 1,2-dimethoxy-1-phenylcyclohexane (Scheme 1). It may be noted that a similar fragmentation has been reported electrochemically by Ojibin et al.[7]

Although the expected reaction did not occur, the fragmentation of the alkene was quite interesting and therefore we decided to pursue this novel reaction. In particular, the reaction appeared very useful for the synthesis of 1,*n*-dicarbonyl compounds, which are key intermediates in the synthesis of various heterocyclic compounds. A preliminary report of this work has been published.[8] In view of its synthetic potential and the mechanistic implications, we studied this reaction in some detail and the complete results are presented here.

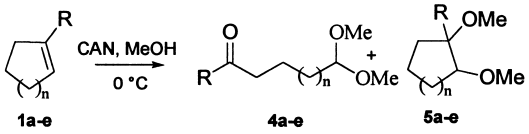


Scheme 1.

Keywords: oxidative fragmentation; cycloalkenes; dicarbonyl compounds.

* Corresponding author. Tel.: +91-471-490406; fax: +91-471-491712; e-mail: gvn@csrrltrd.ren.nic.in

0040–4020/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0040-4020(02)00261-2



1a, n = 1, R = Ph, **4a** (48%), **5a** (20%)
1b, n = 2, R = Ph, **4b** (69%), **5b** (18%)
1c, n = 3, R = Ph, **4c** (56%), **5c** (32%)
1d, n = 4, R = Ph, **4d** (45%), **5d** (37%)
1e, n = 2, R = 1-Nphth, **4e** (72%), **5e** (0%)

Scheme 2.

2. Results and discussion

As already reported,[8] studies were initiated by treating a methanolic solution of 1-phenyl-1-cyclohexene with a solution of CAN in methanol at 0°C. A facile reaction occurred and the absence of the starting material after 30 min indicated the completion of the reaction. The products **4b** and **5b** were isolated in 69 and 18% yields, respectively (Scheme 2). In order to explore the scope of the reaction, a number of aryl cycloalkenes were treated with CAN in methanol. The results are summarized in the following scheme

When 1-naphthyl-1-cyclohexene was treated with a methanolic solution of CAN, the expected fragmentation occurred and the product was obtained in 72% yield; surprisingly no dimethoxy compound was isolated in this case (entry 4, Table 1). 1-Phenyl-3,4-dihydronaphthalene 6 under the usual reaction conditions afforded the keto acetal **7** and the dimethoxycompound **8** in 35 and 30% yields, respectively (Scheme 3).

Although the mechanistic details of the reaction are not fully understood a rationalization involving the intermediacy of a cation radical may be invoked to account for the formation of the products (vide infra for a detailed discussion).

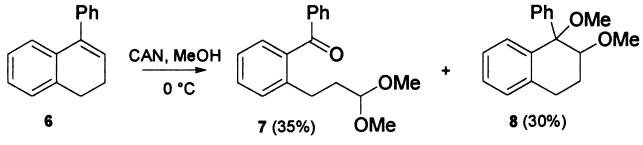
2.1. Reaction of phenylcycloalkenes under deoxygenated conditions

The mechanism for the fragmentation of phenylcycloalkenes (vide infra) invokes the participation of oxygen in the reaction. It is then reasonable to assume that in the absence of oxygen the benzylic radical may undergo further oxidation to the cation which in turn will be quenched by methanol leading to the dimethoxy compound. In order to verify these assumptions, the reactions were done under deoxygenated conditions. Interestingly, when phenylcyclohexene was treated with CAN in dry methanol in an argon atmosphere, the dimethylether **5b** was formed as the major product (72% yield). Only a trace amount of the fragmentation product was observed. The reaction under deoxygenated conditions has been studied with other phenylcycloalkenes also and the results are presented in Table 1.

Table 1. Reaction of phenylcycloalkenes with CAN in methanol under deoxygenated conditions

Entry	Alkene	Product	Yield (%)
1	**1a**	**5a**	72
2	**1b**	**5b**	72
3	**1c**	**5c**	80
4	**1d**	**5d**	69
5	**6**	**8**	65

Reaction conditions: CAN, dry MeOH, argon, 1 h, 0°C.



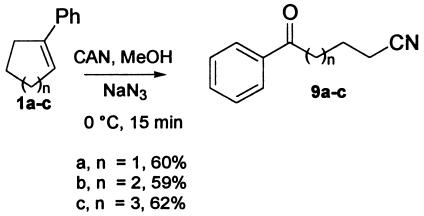
Scheme 3.

2.2. Reactions of cycloalkenes in presence of azide and sulfinate ions

In view of our recent observation of facile CAN mediated oxidative addition of azide and sulfinate to styrenic double bonds it was of interest to examine the reaction of CAN with arylcycloalkene in presence of these anions.[9] Interestingly, while the above work was in progress, a photochemical cleavage of phenyl cycloalkenes with azide in the presence of copper ions in an atmosphere of oxygen affording the corresponding keto nitriles was reported.[10]

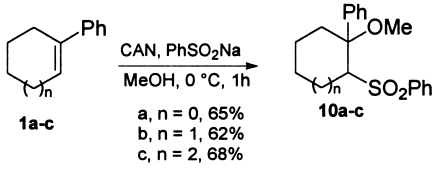
An experiment was carried out in which a mixture of phenylcyclohexene, sodium azide and methanol was treated with CAN at ice temperature. As expected, the keto-nitrile was obtained. Similar reactivity was observed in the case of phenylcyclopentene and phenylcycloheptene (Scheme 4).

Subsequent to the above studies, we attempted the addition of sulfinate in presence of CAN. Narasaka has extensively studied the addition of sulfinate radical to electron rich olefins using CAN and other Ce(IV) reagents.[11] Phenylcyclohexene on treatment with CAN and phenylsulfinic acid sodium salt in methanol, led to the formation of the addition product **10** (Scheme 5). Interestingly, no fragmentation product was observed in this case. Phenylcyclopentene and phenylcycloheptene also gave similar results,



a, n = 1, 60%
b, n = 2, 59%
c, n = 3, 62%

Scheme 4.



a, n = 0, 65%
b, n = 1, 62%
c, n = 2, 68%

Scheme 5.

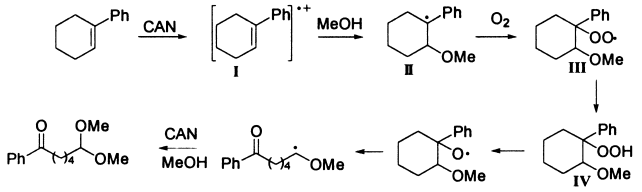
when treated with phenylsulfinic acid sodium salt and CAN in methanol.

2.3. Mechanistic aspects

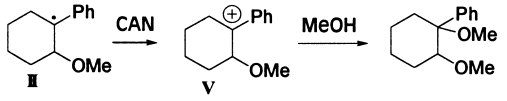
Mechanistically it is not clear if all the above reactions follow the same pathway; the initial event, however may be considered to be the formation of the cation radical **I** from the arylcycloalkene. The involvement of the latter in further transformations may be invoked to explain the formation of the different products. Reaction of **I** with methanol can lead to the benzylic radical **II** which can trap molecular oxygen leading to a peroxyradical **III** and the latter can abstract hydrogen from the solvent to form the hydroperoxide **IV**. The hydroperoxide can undergo fragmentation and ultimately lead to the keto acetal as outlined in Scheme 6.

Alternatively, the benzylic radical **II** undergoes oxidation to the cation **V** and the latter on quenching by methanol will lead to the formation of the dimethoxy compound (Scheme 7). Exclusive formation of the dimethoxy compound under deoxygeneated conditions indirectly supports this suggestion.

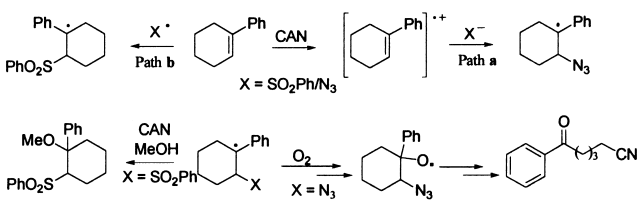
In reactions involving the addition of anions to phenyl cycloalkenes, either a mechanism involving the addition of the anion to the cation radical of phenylcycloalkene leading to a benzylic radical (path a) or the addition of the azide/sulfinate radical generated by the oxidation of the corresponding anion by CAN leading to the benzylic radical (path b) can be conceived. In the case of azide, the benzylic radical traps molecular oxygen forming a hydroperoxide and subsequent transformations of the hydroperoxide lead to the ketonitrile. However in the reaction involving the addition of sulfinate, the benzylic radical undergoes oxidation by CAN, followed by methanol quenching. The absence of fragmentation product in the reaction of sulfinate



Scheme 6.



Scheme 7.



Scheme 8.

may be due to the competing reaction of the latter and/or sulfonyl radical with oxygen. A schematic representation is shown in Scheme 8.

Although it cannot be said with certainty, it is likely that both pathways (a and b) may be operating in these reactions.

In conclusion, we have uncovered some novel reactions of phenyl cycloalkenes in presence of CAN affording products which are of importance both from mechanistic and synthetic standpoints. It is worthy of note that in view of the experimental simplicity and mild reaction conditions, the present method offers a convenient alternative to the existing methods for oxidative fragmentation. Since the products can serve as important intermediates for a variety of compounds, it is conceivable that these reactions will find application in organic synthesis.

3. Experimental

All reactions were carried out in oven dried glassware. Melting points were recorded on Toshniwal or Buchi-530 melting point apparatus and are uncorrected. The IR spectra were recorded on Nicolet Impact 400D FT-IR or Bomem MB series FT-IR spectrophotometers. The NMR spectra were recorded at 300 MHz on a Bruker 300 MHz FT-NMR spectrometer using chloroform-*d* as the solvent. Chemical shifts are reported on δ scale with TMS as the internal standard. Elemental analyses were carried out on a Perkin–Elmer 2400 Series II CHNSO analyser. Products were purified by gravity column chromatography using silica gel (100–200 mesh) in hexane or hexane–ethyl acetate mixtures as eluent. All the solvents were distilled prior to use. CAN used for the reaction was purchased from Aldrich Co. and was used without purification.

3.1. Synthesis of phenylcycloalkenes: general procedure

All the cycloalkenes were prepared from the corresponding cycloalkanones and bromobenzene or bromonaphthalene by Grignard reaction, followed by acid catalyzed dehydration.

3.2. Synthesis of monoacetals of 1,*n*-dicarbonyl compounds from phenyl cycloalkenes: general procedure

To a solution of the phenylcycloalkene (1 mmol) in methanol (10 mL) was added dropwise a solution of CAN (2.3 mmol) in methanol (15 mL) at ice temperature. When the starting material was fully consumed as shown by tlc, the reaction mixture was diluted with water (100 mL) and extracted with dichloromethane (3×30 mL). The combined organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue was subjected to column chromatography on silica gel. Elution with an appropriate mixture of hexane and ethyl acetate afforded the products.

3.3. Synthesis of dimethylethers under deoxygenated conditions: general procedure

To a deoxygenated solution of the phenylcycloalkene (1 mmol) in methanol (10 mL), a deoxygenated solution

of CAN (2.3 mmol) in methanol (15 mL) was added dropwise at ice temperature. When the starting material was fully consumed as shown by TLC, the reaction mixture was diluted with water (100 mL) and extracted with dichloromethane (3×30 mL). The combined organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue was subjected to column chromatography on silica gel. Elution with an appropriate mixture of hexane and ethyl acetate afforded the products.

3.4. Reaction of phenylcycloalkenes with CAN in presence of sodium azide: general procedure

To a solution of the phenylcycloalkene (1 mmol) and sodium azide (1 mmol) in methanol (10 mL) was added dropwise a solution of CAN (2.3 mmol) in the same solvent (15 mL) at ice temperature. On completion, the reaction mixture was diluted with water (50 mL) and extracted with dichloromethane (3×30 mL). The organic extracts were pooled, washed with brine and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue was subjected to column chromatography on silica gel. Elution with an appropriate mixture of hexane and ethyl acetate afforded the products.

3.5. Reaction of phenylcycloalkenes with CAN in presence of phenyl sulfinic acid sodium salt: general procedure

To a solution of the phenylcycloalkene (1 mmol) and phenyl sulfinic acid sodium salt (1 mmol) in methanol (10 mL) was added dropwise a solution of CAN (2.3 mmol) in the same solvent (15 mL) at ice temperature. On completion, the reaction mixture was diluted with water (50 mL) and extracted with dichloromethane (3×30 mL). The organic extracts were pooled, washed with brine and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue was subjected to column chromatography on silica gel. Elution with an appropriate mixture of hexane and ethyl acetate afforded the products.

3.5.1. 4-Benzoylbutanal dimethylacetal (4a)[7] and 1,2-dimethoxy-1-phenylcyclopentane (5a).[12] To a solution of 1-phenyl-1-cyclopentene (144 mg, 1 mmol) in methanol (10 mL) was added a solution of CAN (1.26 g, 2.3 mmol) in methanol (15 mL) at ice temperature and stirred for 30 min. On completion of the reaction, the mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using a mixture of hexane–ethyl acetate (98:2) as eluent afforded 41 mg of **5a** as colorless viscous liquid (20%) and on further elution with hexane–ethyl acetate (95:5) afforded 106 mg of **4a** as colorless viscous liquid (48%).

4a: IR (neat) ν_{max}: 2978, 1742, 1684, 1607, 1364, 1128, 1074, 960 cm^{-1}; ^1H NMR: 7.93–7.90 (m, 2H, Ar*H*), 7.52–7.40 (m, 3H, Ar*H*), 4.38 (t, 1H, CH(O*Me*)$_2$, *J*=5.6 Hz), 3.30 (s, 6H, O*Me*), 3.01 (t, 2H, CH_2, *J*=7 Hz), 1.82–1.63 (m, 4H, CH_2); ^{13}C NMR: 200.51, 136.85, 132.90, 128.51, 127.93, 104.67, 52.51, 38.01, 32.26, 23.53, 21.67.

5a: IR (neat) ν_{max}: 1621, 1508, 1206, 1169, 721 cm^{-1}. ^1H NMR: 7.69–7.28 (m, 5H, ArH), 3.30 (s, 3H, O*Me*), 3.14 (m, 1H, C*H*OMe), 3.09 (s, 3H, O*Me*), 1.67–1.01 (m, 6H, CH_2); ^{13}C NMR: 142.81, 128.14, 127.88, 126.69, 86.24, 80.58, 59.18, 49.04, 36.64, 29.99, 23.16.

3.5.2. 5-Benzoylpentanaldimethylacetal (4b)[7] and 1,2-dimethoxy-1-phenylcyclohexane (5b).[12] To a solution of 1-phenyl-1-cyclohexene (156 mg, 1 mmol) in methanol (10 mL) a solution of CAN (1.26 g, 2.3 mmol) in methanol (15 mL) was added at ice temperature and stirred for 30 min. On completion of the reaction, the mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane–ethyl acetate mixture (98:2) afforded 39 mg of **4b** as colorless viscous liquid (18%) and on further elution using hexane–ethyl acetate mixture (95:5) afforded 162 mg of **5b** as colorless viscous liquid (69%).

4b: IR (neat) ν_{max}: 2959, 1681, 1593, 1482, 1202, 1128, 1067, 960, 703 cm^{-1}; ^1H NMR: 7.94–7.91 (m, 2H, Ar*H*), 7.53–7.43 (m, 3H, Ar*H*), 4.36 (t, 1H, C*H*(OMe)$_2$, *J*=5.4 Hz), 3.29 (s, 6H, O*Me*), 2.90 (t, 2H, CH_2, *J*=7.2 Hz), 1.99–1.39 (m, 6H, CH_2); ^{13}C NMR: 200.15, 137.01, 132.90, 128.55, 127.93, 104.93, 52.75, 38.42, 32.41, 24.34, 24.07.

5b: IR (neat) ν_{max}: 2897, 1647, 1448, 1108, 1202, 1074, 966, 717 cm^{-1}; ^1H NMR: 7.46–7.26 (m, 5H, Ar*H*), 3.15 (s, 3H, O*Me*), 3.06–3.01 (m, 1H, C*H*OMe), 2.98 (s, 3H, O*Me*), 2.10–1.25 (m, 8H, CH_2); ^{13}C NMR: 142.35, 127.73, 127.14, 126.67, 85.92, 80.03, 57.82, 50.12, 31.86, 26.86, 26.52, 24.52, 24.69, 20.92. Anal. Calcd for $C_{14}H_{20}O_2$: C 76.33, H 9.15; Found C 76.12, H 8.97.

3.5.3. 6-Benzoylhexanal dimethylacetal (4c)[7] and 1,2-dimethoxy-1-phenylcycloheptane (5c).[12] To a solution of 1-phenyl-1-cycloheptene (172 mg, 1 mmol) in methanol (10 mL) was added a solution of CAN (1.26 g, 2.3 mmol) in methanol (15 mL) at ice temperature and stirred for 30 min. On completion of the reaction, the mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using a mixture of hexane–ethyl acetate (98:2) as eluent afforded 75 mg of **5c** as colorless viscous liquid (32%) and on further elution with a mixture of hexane–ethyl acetate (95:5) afforded 140 mg of **4c** as colorless viscous liquid (56%).

4c: IR (neat) ν_{max}: 2956, 1681, 1593, 1482, 1450, 1359, 1273, 1091 cm^{-1}; ^1H NMR: 7.96–7.94 (m, 2H, Ar*H*), 7.54–7.42 (m, 3H, Ar*H*), 4.36 (t, 1H, C*H*(OMe)$_2$, *J*=5.5 Hz), 3.31 (s, 6H, O*Me*), 2.97 (t, 2H, CH_2, *J*=7.1 Hz), 1.76–1.25 (m, 8H, CH_2); ^{13}C NMR: 200.15, 137.15, 133.90, 128.67, 128.15, 104.61, 52.79, 38.56, 32.48, 29.29, 24.57, 24.35.

5c: IR (neat) ν_{max}: 2989, 1730, 1632, 1272, 1074, 766, 696 cm^{-1}. ^1H NMR: 7.44–7.23 (m, 5H, Ar*H*), 3.14 (s, 3H, O*Me*), 3.08–3.01 (m, 1H, C*H*OMe), 2.99 (s, 3H, O*Me*), 2.07–1.42 (m, 10H, CH_2); ^{13}C NMR: 144.15, 128.02, 127.62, 127.33, 126.54, 89.57, 82.23, 57.78, 50.91, 33.75, 27.00, 26.21, 23.67, 20.47.

3.5.4. 7-Benzoylheptanal dimethylacetal (4d)[7] and 1,2-dimethoxy-1-phenylcyclooctane (5d).[12] To a solution of

1-phenyl-1-cyclooctene (196 mg, 1 mmol) in methanol (10 mL) was added a solution of CAN (1.26 g, 2.3 mmol) in methanol (15 mL) at ice temperature and stirred for 30 min. On completion of the reaction, the mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using a mixture of hexane–ethyl acetate (98:2) as eluent afforded 84 mg of **5d** as colorless viscous liquid (37%) and on further elution with a mixture of hexane–ethyl acetate (95:5) afforded 118 mg of **4d** as colorless viscous liquid (45%).

4d: IR (neat) ν_{max}: 2987, 1681, 1596, 1442, 1202, 1181, 715 cm^{-1}; ^1H NMR: 7.95–7.92 (m, 2H, Ar*H*), 7.53–7.41 (m, 3H, Ar*H*), 4.34 (t, 1H, C*H*$(OMe)_2$, *J*=5.4 Hz), 3.28 (s, 6H, O*Me*), 2.95 (t, 2H, CH_2, *J*=7.2 Hz), 1.73–1.22 (m, 8H, CH_2); ^{13}C NMR: 199.18, 136.95, 132.63, 128.35, 128.10, 104.25, 52.25, 42.29, 32.21, 29.15, 24.31, 24.05, 20.74.

5d: IR (neat) ν_{max}: 1647, 1448, 1108, 1202, 1074, 966, 717 cm^{-1}. ^1H NMR: 7.46–7.26 (m, 5H, Ar*H*), 3.15 (s, 3H, O*Me*), 3.06–3.01 (m, 1H, C*H*OMe), 2.98 (s, 3H, O*Me*), 2.10–1.25 (m, 12H, CH_2); ^{13}C NMR: 142.35, 127.73, 127.14, 126.67, 85.92, 80.03, 57.12, 31.86, 26.86, 26.52, 24.69, 20.92.

3.5.5. 5-Naphthoylpentanaldimethylacetal (4e). To a solution of 1-naphthyl-1-cyclohexene (208 mg, 1 mmol) in methanol (10 mL) was added a solution of CAN (1.26 g, 2.3 mmol) in methanol (15 mL) at ice temperature and stirred for 30 min. On completion of the reaction, the mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using a mixture of hexane–ethyl acetate (95:5) as eluent afforded 205 mg of **4e** as colorless viscous liquid (72%). IR (neat) ν_{max}: 2942, 1681, 1593, 1482, 1128, 1067, 960, 703 cm^{-1}. ^1H NMR: 8.53 (d, 1H, Ar*H*, *J*=8.2 Hz), 7.94 (d, 1H, Ar*H*, *J*=8.2 Hz), 7.84 (t, 1H, Ar*H*, *J*=8.1 Hz), 7.59–7.45 (m, 4H, Ar*H*), 4.36 (t, 1H, C*H* $(OMe)_2$, *J*=7.5 Hz), 3.30 (s, 6H, O*Me*), 3.05 (t, 2H, CH_2, *J*=7.3 Hz), 2.03–1.42 (m, 6H, CH_2); ^{13}C NMR: 200.15, 137.01, 132.90, 128.55, 127.93, 104.43, 52.75, 38.42, 32.41, 24.34, 24.07. HRMS cald for $C_{18}H_{22}O_3$, 287.1569. Found 287.1579.

3.5.6. 2-(3,3-Dimethoxy) propylbenzophenone (7) and 1,2-dimethoxy-1-phenyl tetralin (8). To a solution of 1-phenyl-3,4-dihydro naphthalene (206 mg, 1 mmol) in methanol (10 mL) was added a solution of CAN (1.26 g, 2.3 mmol) in methanol (15 mL) at ice temperature and stirred. On completion of the reaction, the mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using a mixture of hexane–ethyl acetate (98:2) as eluent afforded 30% of **8** as colorless viscous liquid and on further elution using a mixture of hexane–ethyl acetate (95:5) afforded 99 mg of **7** as colorless viscous liquid (35%).

7: IR (neat) ν_{max}: 2976, 1667, 1596, 1470, 1289, 798 cm^{-1}; ^1H NMR: 7.22–7.17 (m, 9H, Ar*H*), 4.43 (t, 1H, C*H* $(OMe)_2$, *J*=5.5 Hz), 3.16 (s, 6H, O*Me*), 2.65 (m, 2H, CH_2), 1.77 (brs, 2H, CH_2); ^{13}C NMR: 198.07, 140.88, 138.30, 137.88, 130.28, 130.18, 128.70, 128.38, 127.51, 125.34, 103.64, 52.47, 34.27, 28.50; HRMS Calcd for $C_{18}H_{20}O_3$, 284.1412. Found 284.1425.

8: IR (neat) ν_{max}: 1632, 1486, 1438, 1280, 1115 cm^{-1}. ^1H NMR: 7.17–7.04 (m, Ar*H*, 9H), 3.59 (m, 2H, PhCH_2), 3.09 (s, 3H, O*Me*), 3.03 (s, 3H, O*Me*), 2.78 (m, 2H, CH_2), 2.12 (m, 2H, CH_2); ^{13}C NMR: 142.80, 138.73, 136.09, 129.39, 128.78, 127.04, 126.97, 83.49, 80.49, 57.77, 50.83, 26.91, 23.69. HRMS Calcd for $C_{18}H_{20}O_2$, 268.1463. Found 268.1459.

3.5.7. 4-Benzoylbutanenitrile (9a). A solution of CAN (1.26 g, 2.3 mmol) in methanol (15 mL) was added to a solution of 1-phenyl-1-cyclopentene (144 mg, 1 mmol) and sodium azide (65 mg, 1 mmol) in the same solvent (10 mL) at ice temperature and stirred for 30 min. On completion of the reaction, the mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane–ethyl acetate mixture (95:5) afforded 112 mg of **9a** as colorless viscous liquid (60%). IR (neat) ν_{max}: 2932, 2106, 1725, 1447, 1265 cm^{-1}. ^1H NMR: 7.95–7.93 (m, 2H, ArH), 7.59–7.43 (m, 3H, Ar*H*), 3.15 (t, 2H, CH_2, *J*=7 Hz), 2.50 (t, 2H, CH_2, *J*=7 Hz), 2.13–2.04 (m, 2H, CH_2); ^{13}C NMR: 197.74, 136.71, 133.14, 128.64, 127.96, 119.22, 37.27, 25.03, 23.06, 17.18. HRMS Calcd for $C_{11}H_{11}NO$, 174.0841. Found 174.0832.

3.5.8. 5-Benzoylpentanenitrile (9b).[13] A solution of CAN (1.26 g, 2.3 mmol) in methanol (15 mL) was added to a solution of 1-phenyl-1-cyclohexene (156 mg, 1 mmol) and sodium azide (65 mg, 1 mmol) in the same solvent (10 mL) at ice temperature and stirred for about 30 min. On completion of the reaction, the mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane–ethyl acetate mixture (95:5) afforded 115 mg of **9b** (52%). IR (neat) ν_{max}: 2950, 1679, 1449, 1411 cm^{-1}. ^1H NMR: 7.94–7.91 (m, 2H, Ar*H*), 7.43–7.32 (m, 3H, Ar*H*), 3.06 (t, 2H, CH_2, *J*=6.9 Hz), 2.40 (t, 2H, CH_2, *J*=7 Hz), 1.93–1.65 (m, 4H, CH_2); ^{13}C NMR: 197.74, 136.35, 133.26, 128.58, 127.84, 119.09, 36.16, 19.63, 16.47.

3.5.9. 6-Benzoylhexanenitrile (9c). A solution of CAN (1.26 g, 2.3 mmol) in methanol (15 mL) was added to a solution of 1-phenyl-1-cycloheptene (172 mg, 1 mmol) and sodium azide (65 mg, 1 mmol) in the same solvent (10 mL) at ice temperature and stirred for 30 min. On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane–ethyl acetate mixture (95:5) afforded 122 mg of **9c** as colorless viscous liquid (62%). IR (neat) ν_{max}: 2932, 2101, 1725, 1686, 1447, 1336 cm^{-1}; ^1H NMR: 7.94–7.91 (m, 2H, Ar*H*), 7.57–7.42 (m, 3H Ar*H*), 2.98 (t, 2H, CH_2, *J*=7 Hz), 2.35 (t, 2H, CH_2, *J*=6.9 Hz), 1.80–1.57 (m, 4H, CH_2), 1.56–1.52 (m, 2H, CH_2); ^{13}C NMR: 199.12, 136.66, 132.80, 128.38, 127.75, 119.24, 37.74, 28.08, 25.11, 22.96, 16.75; HRMS Calcd for $C_{13}H_{15}NO$, 201.1154. Found 201.1154

3.5.10. 2-Benzenesulfinyl-1-methoxy-1-phenyl-1-cyclopentene (10a). To a solution of the 1-phenyl-1-cyclopentene (144 mg, 1 mmol) and phenyl sulfinic acid sodium salt (164 mg, 1 mmol) in methanol (10 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in the same solvent (15 mL) at ice temperature. On completion, the reaction mixture was diluted with water (50 mL)

and extracted with dichloromethane (3×30 mL). The combined organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue on crystallization using dichloromethane–petroleum ether as solvent afforded the product as colorless crystals (205 mg, 65%), mp 115–117°C. **10a**: IR (neat) ν_{max}: 1632, 1486, 1438, 1280, 1115 cm^{-1}. ^1H NMR: 7.38–6.96 (m, 10H, Ar*H*), 3.81 (uneven doublet, 1H, C*HSO*$_2$*Ph*), 2.78 (s, 3H, O*Me*), 2.74–2.60 (m, 2H, CH_2), 2.46–2.34 (m, 1H, CH_2), 2.18–2.12 (m, 1H, CH_2), 2.02–1.86 (m, 1H, CH_2), 1.83–1.77 (m, 1H, CH_2). ^{13}C NMR: 139.98, 136.29, 131.99, 128. 68, 128.55, 127.93, 127.66, 127.45, 80.76, 76. 58, 48.68, 29.23, 25.01, 20.29. Anal. Calcd for $C_{18}H_{20}O_3S$: C 68.33, H 6.37, S 10.13; Found C 68.28, H 6.62, S 10.23.

3.5.11. 2-Benzenesulfinyl-1-methoxy-1-phenyl-1-cyclohexene (10b). To a solution of the 1-phenyl-1-cyclohexene (156 mg, 1 mmol) and phenyl sulfinic acid sodium salt (164 mg, 1 mmol) in methanol (10 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in the same solvent (15 mL) at ice temperature. On completion, the reaction mixture was diluted with water (50 mL) and extracted with dichloromethane (3×30 mL). The combined organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue on crystallization using dichloromethane–petroleum ether as solvent afforded the product as colorless crystals (229 mg, 70%.), mp 143–145°C. **10b**: IR (KBr) ν_{max}: 1643, 1254, 1232, 1181 cm^{-1}; ^1H NMR: 7.31–7.26 (m, 2H, Ar*H*), 7.16–7.11 (m, 5H, Ar*H*), 7.04–6.96 (m, 3H, Ar*H*), 3.68 (brs, 1H, C*HSO*$_2$*Ph*), 2.94 (m, 1H, CH_2), 2.75 (s, 3H), 2.64 (d, 1H, J=14.1 Hz, CH_2), 2.38–2.27 (m, 1H), 2.08 (d, 1H, J=14.3 Hz, CH_2), 1.90–1.56 (m, 4H, CH_2); ^{13}C NMR: 141.80, 140.34, 131.61, 128.36, 128.18, 127.81, 127.90, 127.04, 77.25, 70.25, 48.22, 25.19, 22.91, 21.21, 20.91. Anal. Calcd for $C_{19}H_{22}O_3S$: C 69.01, H 6.88, S 10.20; Found C 69. 06, H 6.71, S 9.78.

3.5.12. 2-Benzenesulfinyl-1-methoxy-1-phenylcycloheptane (10c). To a solution of the 1-phenyl-1-cycloheptene (172 mg, 1 mmol) and phenyl sulfinic acid sodium salt (164 mg, 1 mmol) in methanol (10 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in the same solvent (15 mL) at ice temperature. On completion, the reaction mixture was diluted with water (50 mL) and extracted with dichloromethane (3×30 mL). The combined organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue on crystalliztaion using dichloromethane–petroleum ether as solvent afforded the product as colorless crystals (233 mg, 68%), mp 148–150°C. **10c**: IR (neat) ν_{max}: 1624, 1431, 1297, 1142, 1067; ^1H NMR: 7.78–7.76 (m, 2H, Ar*H*), 7.52–7.38 (m, 3H, Ar*H*), 7.25–7.18 (m, 5H, Ar*H*), 3.74 (uneven doublet, 1H, C*HSO*$_2$*Ph*), 3.06 (s, 3H, O*Me*), 2.36–2. 04 (m, 5H, CH_2), 1.91–1.53 (m, 5H, CH_2); ^{13}C NMR: 143.64, 142.65, 132.36, 128.91, 128.13, 128.06, 127.18, 126.49, 76.40, 50.49, 35.64, 27.43, 25.59, 24.02, 21.54; Anal. Calcd for $C_{20}H_{24}O_3S$: C 69.73, H 7.02, S 9.31; Found C 70.09, H 7.11, S 9.33.

Acknowledgements

S. B. P., S. T., S. V. and S. M. thank the CSIR, Government of India, New Delhi for Research Fellowships. Thanks are also due to Dr M. Vairamani, Indian Institute of Chemical Technology, Hyderabad for HRMS data, Ms Soumini Mathew for NMR spectral data and Mrs S. Viji for elemental analyses.

References

1. (a) Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. (b) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6765. (c) Stork, G.; Baine, N. H. *Tetrahedron Lett.* **1985**, *26*, 5927.
2. (a) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 524. (b) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 995. (c) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 2888. (d) Heiba, E. I.; Dessau, R. M.; Rodewald, P. G. *J. Am. Chem. Soc.* **1974**, *96*, 7977.
3. For reviews on CAN mediated reactions see: (a) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29. (b) Ho, T. L. *Organic Synthesis by Oxidation with Metal Compounds*; Plenum: New York, 1986 and references cited therein. (c) Imamoto, T. *Lanthanide Reagents in Organic Synthesis*; Academic: London, 1994; p 119. (d) Nair, V.; Mathew, J.; Prabhakaran *J. Chem. Soc. Rev.* **1997**, 127.
4. (a) Baciocchi, E.; Ruzziconi, R. *Synth. Commun.* **1988**, *18*, 1841. (b) Baciocchi, E.; Ruzziconi, R. *J. Org. Chem.* **1986**, *51*, 1645. (c) Baciocchi, E.; Ruzziconi, R. *Gazz. Chim. Ital.* **1986**, *116*, 671.
5. (a) Nair, V.; Mathew, J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 187. (b) Nair, V.; Mathew, J.; Alexander, S. *Synth. Commun.* **1995**, *25*, 3981. (c) Nair, V.; Mathew, J.; Radhakrishnan, K. V. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1487. (d) Nair, V.; Mathew, J.; Nair, L. G. *Synth. Commun.* **1996**, *26*, 4531. (e) Nair, V.; Nair, L. G.; Balagopal, L.; Mathew, J. *Ind. J. Chem.* **2000**, *39B*, 352.
6. Nair, V.; Mathew, J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1881.
7. Ojibin, Y. N.; Ilavoisky, A. I.; Nikishin, G. I. *Russ. Chem. Bull.* **1996**, *45*, 1939 and references cited therein.
8. Nair, V.; Panicker, S. B. *Tetrahedron Lett.* **1999**, *40*, 563.
9. (a) Nair, V.; Nair, L. G.; George, T. G.; Augustine, A. *Tetrahedron* **2000**, *56*, 7607. (b) Nair, V.; George, T. G. *Tetrahedron Lett.* **2000**, *41*, 3199. (c) Nair, V.; George, T. G.; Nair, L. G.; Panicker, S. B. *Tetrahedron Lett.* **1999**, *40*, 1195.
10. Shimizu, I.; Fujita, M.; Nakajima, T.; Sato, T. *Synlett* **1997**, 888.
11. (a) Narasaka, K.; Mochizuki, T.; Hayakawa, S. *Chem. Lett.* **1994**, 1705. (b) Mochizuki, T.; Hayakawa, S.; Narasaka, K. *Bull. Chem. Soc. Jpn* **1996**, *69*, 2317.
12. Ojibin, Y. N.; Ilavoisky, A. I.; Nikishin, G. I. *J. Org. Chem.* **1996**, *61*, 3256–3258.
13. Zbiral, E.; Nestler, G. *Tetrahedron* **1970**, *26*, 2945.