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Divergence in photoinduced electron transfer (PET) reactions: a useful strategy towards identifying route-selectivity in mixed ketones

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ABSTRACT

The work utilized photoinduced electron transfer (PET) reactions to identify the preferred photoreaction route in molecules having juxtaposed α,β and β,γ-enones. Such process directly converted 2-hydroxyimino derivatives of 5-benzoylbicyclo[2.2.2]octenones to the corresponding bicyclo[3.2.1]octane derivatives. First evidence of Type B rearrangement in α,β-enones having acyl substitution at Cγ-position has been depicted in this work. In rigid mixed enones, this has been found to be generally the preferred photoreaction route.

1. Introduction

Recent reports have shown that photoinduced electron transfer (PET) processes are increasingly becoming useful for constructing complex molecules because of their chemo-, regio-, and stereoselectivity.[1] With the emergence of a comprehensive picture of such reactions using amines,[2–4] photochemical reactions involving amines and chromophores like ketones in their triplet excited states, have become one of the much popular methods in organic syntheses. Electron transfer takes place from amine to an electronically excited ketone-acceptor to form radical ions and to avoid the reversible back electron transfer (BET) at this stage polar solvents are used to solvate such ion pairs, which then may eventually undergo different types of reactions depending on the substrates.[5] We have reported applications of such reactions in presence of triethylamine (TEA) to prepare bicyclo[3.2.1]octanones from tricyclo[3.3.0.0^{2,8}]octanones[6] and from bicyclo[2.2.2]octanones[7] and for efficient *trans*-reduction of C=C bonds.[8] In all these cases the molecules contained α,β- as well as β,γ-enones in juxtaposed manner (Fig. 1).

While under PET condition such molecules like **1** underwent one-pot conversion to bicyclo[3.2.1]octanones,[7] on direct irradiation quantitative yields of tricyclo[3.3.0.0^{2,8}]octanones (**2**) were obtained from them (Scheme 1). The **1** to **2** conversion may follow either a Type B rearrangement route from the α,β-enone part or an oxa-di-pi-methane (ODPM) rearrangement route from the β,γ-enone part and till now the preference for either of the routes could not be ascertained conclusively. In the present work we applied PET reactions to ascertain, which of these phototransformation routes is followed in such mixed enones. For this purpose the β,γ-enones in **1a**–**c** have been replaced by hydroxyimino group (**4a**–**c**) and that of **3** was replaced by methylene group (**5**) and the α,β-enone part in **1c**, **d** and **3** have also been replaced by methylene groups (**6a**,**b**, **7**) (Fig. 2).

2. Results and discussion

2.1. Syntheses of 5-benzoyl-2-hydroxyiminobicyclo[2.2.2]oct-5-enes (4a–c)

The 5-benzoylbicyclo[2.2.2]oct-5-en-2-ones (**1a**–**c**) prepared[7] from the respective silyloxyhexa-1,3-dienes and 1-phenylprop-2-yn-1-one (monobenzoylacetylene, MBA), were heated with ~1 equiv

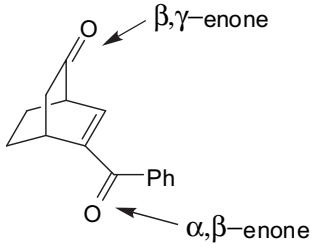

Fig. 1. Model mixed enones.

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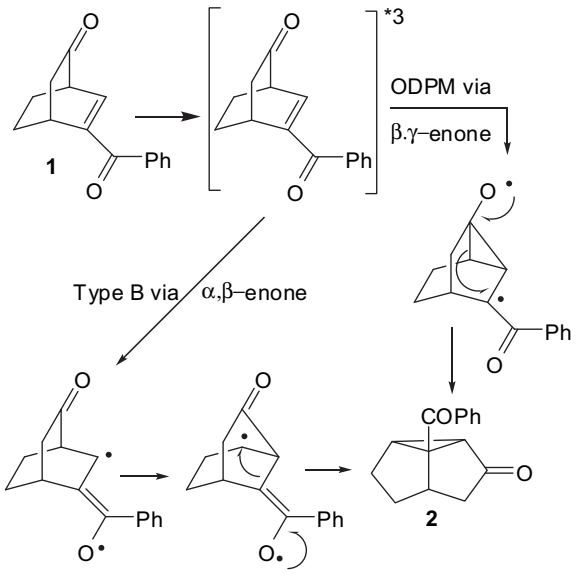


Scheme 1.

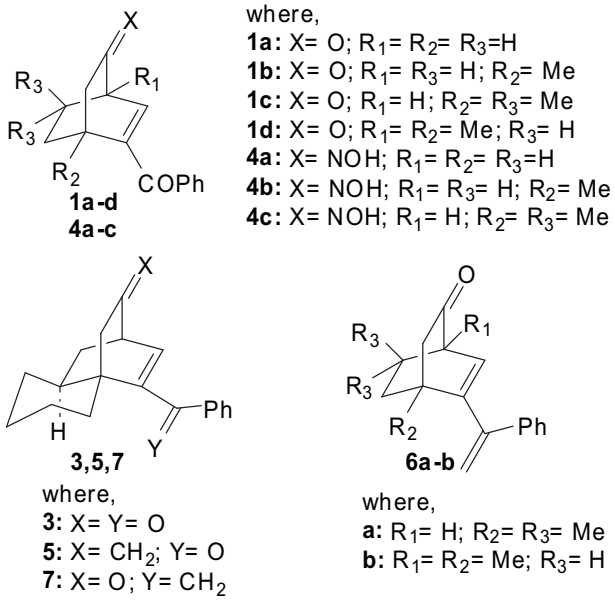
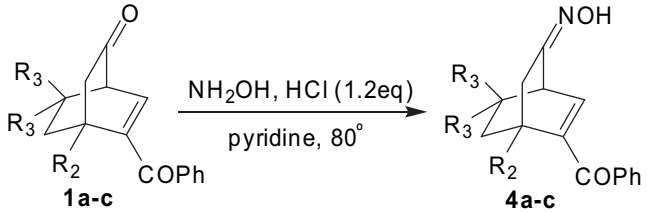


Fig. 2. Enones used for this work.

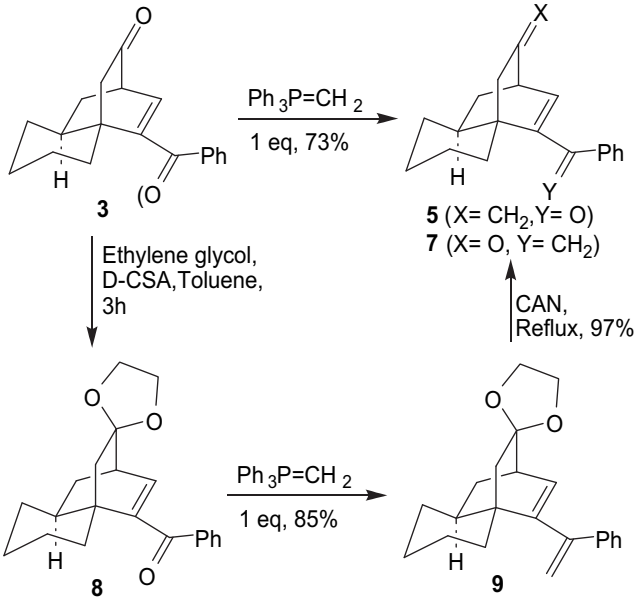
of hydroxylamine hydrochloride in pyridine at 80° to give quantitative yields of the corresponding monooxime derivatives **4a**–**c** (Scheme 2). Interestingly, the hydroxyimino group in the oxime was formed exclusively as the thermodynamically stable *E*-isomer in the products, which on keeping isomerized to mixtures of *E*–*Z* isomers.



Scheme 2.

2.2. Syntheses of 5 and 7

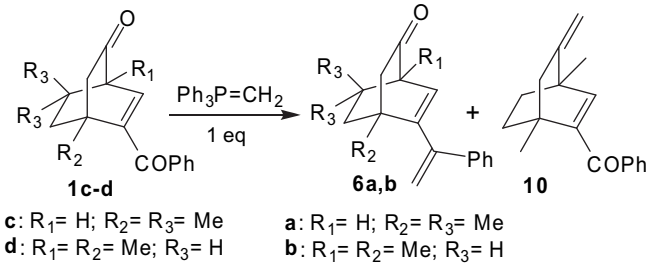
Compound **3**[9] on Wittig reaction using 1 equiv of triphenyl phosphonium methylide following the reported procedure[10] gave **5** selectively (Scheme 3). On the other hand, protection of the bridge-ketone (**8**), gave the wittig product **9**,[10] which on hydrolysis yielded **7** in quantitative quantity (Scheme 3).



Scheme 3.

2.3. Syntheses of 6a,b

Using the same procedure,[10] non-enolizable carbonyls in **1c** and **1d** were olefinated to give **6a** and **6b** in 48% and 41% yields (Scheme 4). These reactions were sluggish presumably because of overall molecular steric congestion and the starting materials were recovered in ~40% yields in both cases.[10] A small amount of **10** (11%) was also obtained from **1d**.



Scheme 4.

2.4. PET reactions of 4a–c

The parent compounds **1a**–**c** on irradiation are known to give corresponding tricyclic derivatives of **2**.[7] However the preferred route to this transformation is not yet very clear (Scheme 1), If such transformation originated from the β,γ-enone part of the molecule, along with the general *E*–*Z* isomerization at the C=N bond[11] the triplet sensitized aza-di-pi-methane (ADPM) rearrangement, as observed in similar bridged systems,[12,13] were also expected to take place giving **11a**–**c** from **4a**–**c** (Scheme 5). When **4a**–**c** were irradiated in benzene, acetonitrile, methanol or acetone, the product was solely from the *E*–*Z* isomerization at C=N bonds in **4a**–**c**. No

trace of the ADPM products **11a**–**c** could be identified from these reactions even on irradiation in presence of sensitizers like acetophenone or benzophenone. In suitable examples, oximes are known to undergo photo-Beckmann rearrangement in methanol[14a–d] or, cyclization via iminyl radicals[14e,f] and no such products could be identified from these reactions. When the irradiation of **4a**–**c** were carried out in presence of TEA at 254 nm as well as at 300 nm, similar to their 2-oxo-analogs **1a**–**c**[7] these compounds also underwent phototransformation to 8-*anti* bicyclo[3.2.1]octane derivatives **12a**–**c** (Scheme 6). The 8-*anti* geometry was confirmed by the X-ray crystallographic picture of **12c** (Fig. 3).[15] Unlike their oxa-counterparts, to accomplish such rearrangements from the oximes **4a**–**c** under comparable reaction conditions, a much longer time of 5–6 h was needed and yields of the rearranged products were also much poor compared to their corresponding oxa-analogs. One of the possible reasons for the inefficiency of these processes in these oximes may be attributed to the dissipation of a major part of the excited state energy via 'free rotor effect' of the C=N bonds leading to the *E*–*Z* isomerization. Similar to the cases of **1a**–**c**,[7] formation of **12a**–**c** may also occur from **4a**–**c** via either of the three routes. In route 'a' the initially formed ketyl radical **A** may undergo bond formation to give **A**′ or, bond migration to give **A**″. In route 'b' similarly the radical ion **B** may undergo bond formation to give **B**′. Both **A**′ and **B**′ then could undergo bond migration followed by back electron transfer (BET) to give **11a**–**c**, which then by PET mediated tandem bond migration could give **12a**–**c** (Scheme 6). But experimentally it has been shown that **11a**–**c** are not formed from **1a**–**c** on irradiation.

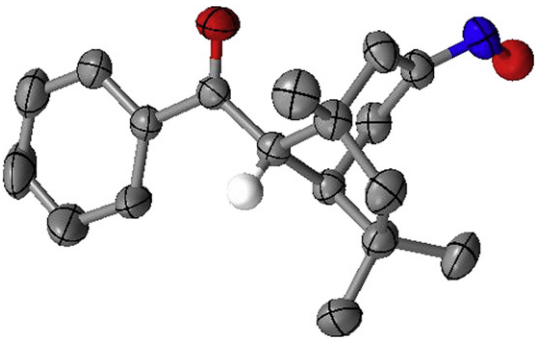
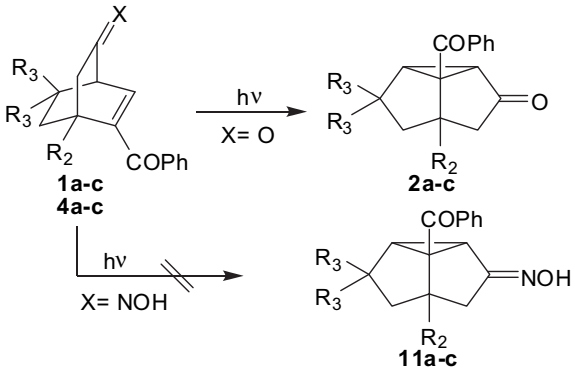


Fig. 3. Molecular structure of **12c** with thermal ellipsoid drawn at the 50% probability level (oxime hydroxyl group is disordered over two positions); color code: C-grey; H-white; O-red.

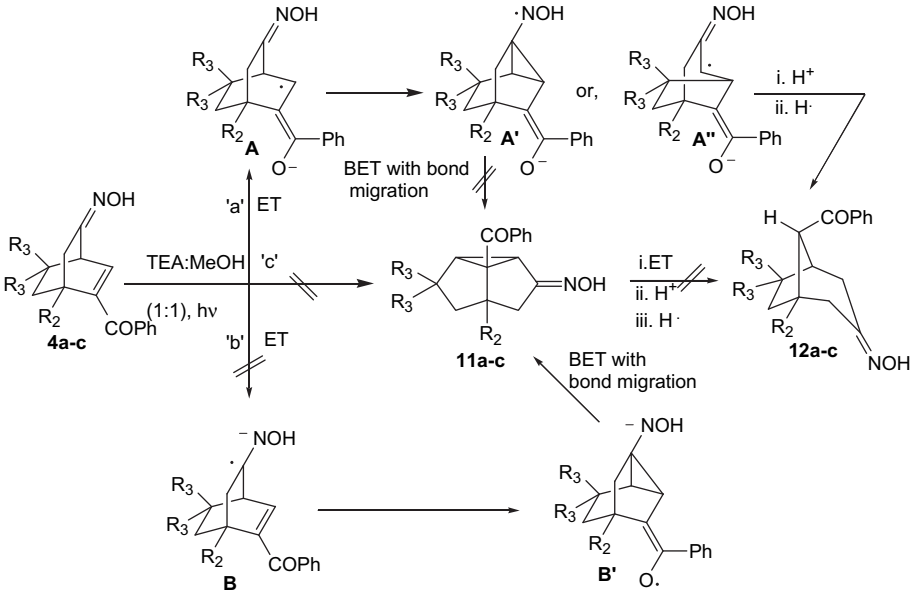
Furthermore, separately prepared **11b** from **2b** (Scheme 5) when subjected to PET reaction in presence of TEA, the product was primarily an *E*–*Z* mixture of the 3-hydroxyimino group along with some unidentified mass and no trace of **12b** was identified from the reaction mixture. On the basis of this observation one can eliminate the intermediacy of **11a**–**c** and hence paths 'b' and 'c' for the conversion of **4a**–**c** to **12a**–**c**. This will then leave only **A**″ as the intermediate, formed from the α,β-enone part by path 'a', towards the formation of the rearranged product **12a**–**c**. These observations would also support our earlier proposition that the conversion of **1a**–**c** to the corresponding bicyclo[3.2.1]octanones follow a similar route.[7] For further confirmation, we carried out the following experiments.



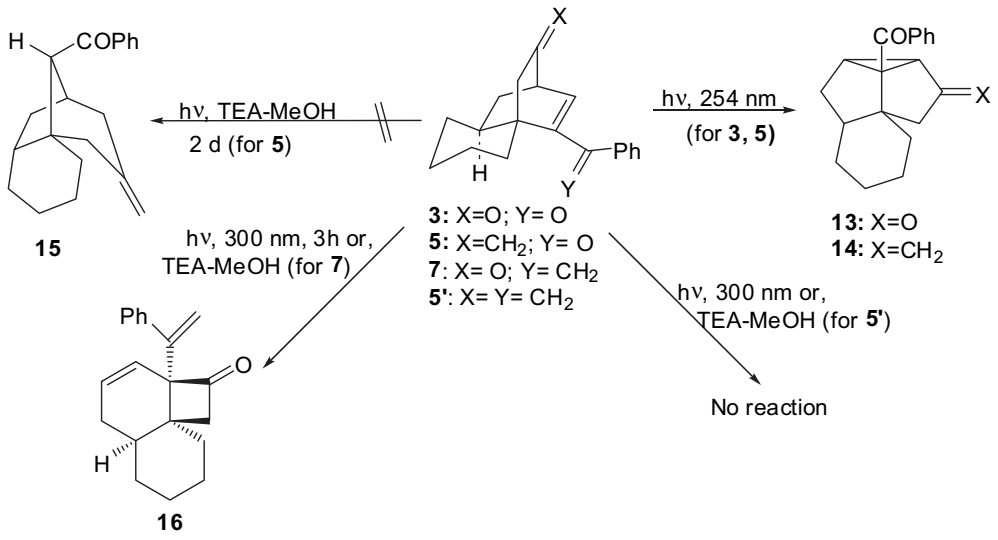
Scheme 5.

2.5. PET reactions of 5, 6a, b and 7

It was known that **3** on direct irradiation gave a quantitative yield of **13** (Scheme 7). On the other hand, when the β,γ-enone part in **3** was replaced by a methylene group (**5**)[9] it becomes an α,β-enone with a vinyl group at C-γ as well as a di-pi-methane system with a 4-keto conjugation. Photoreactivity of this compound was found to be reduced considerably and a prolonged irradiation of 39 h yielded only 46% of the tetracyclic compound **14** (Scheme 7). Quenching of



Scheme 6.



Scheme 7.

the formation of **14** by triplet quenchers like anthracene confirmed the reaction as a triplet one and from the phosphorescence band of **5** at 440 nm showed E_T=65 kcal mol^{-1}. Lifetime of the triplet was found to be 10.6 ms and that suggested an *n*, π* nature of the triplet. This strongly suggested a Type B route for this transformation originated from the α,β-enone moiety. This was further verified from the attempted PET reaction of **5** in presence of TEA. The *exo*-methylene moiety is known to dissipate the triplet energy via a rapid radiationless free rotational decay.[16] This would then compete with the bond migration of the triplet ketyl radicals of **5** formed from its PET reaction with TEA to give **14** or, **15**. In fact, irradiation for 2 days did not bring about any change in **5**, which confirmed the non-involvement of the β,γ-enone part in this rearrangement.

That the β,γ-enone in **3** did not really take part in the PET-rearrangements were further verified from the following reactions.

When the α,β-enone part in **3** was methylated to give **7**, the irradiation experiment for 3 h in acetonitrile yielded a 1,3-acyl shift product **16** in 52% yield (Scheme 7). Quenching experiments showed this to be a triplet reaction however; failure to observe any emission band from **7** could not suggest a probable configuration of the excited state. The structure of **16** was confirmed from its analytical, spectral and X-ray crystallographic structure (Fig. 4).[17] Attempted PET reaction in presence of TEA/MeOH yielded the same product in 65% yields.

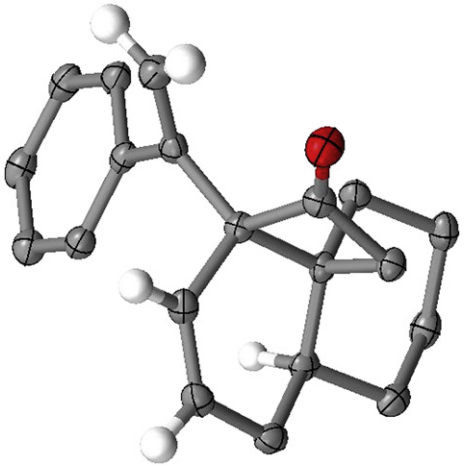
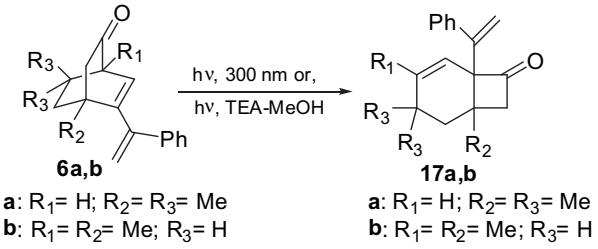


Fig. 4. Molecular structure of **16** with thermal ellipsoid drawn at the 50% probability level; C-grey; H-white; O-red.

When the totally olefinated derivative **5′**, a di-pi-methane system was irradiated, only the starting material was recovered in quantitative yields. This further confirmed the earlier proposition of facile dissipation of the excited energy via a free rotor mechanism of the *exo*-methylene group.

Direct irradiation as well as irradiation in presence of TEA gave the 1,3-acyl shift products **17a**, **b** from **6a**,**b** in 75%, 63%, and 55%, 68% yields, respectively (Scheme 8). Involvement of triplets in direct irradiation was confirmed from quenching experiments. Although in β,γ-enones the 1,3-acyl shifts on irradiation are known generally to take place from the singlet states, the present examples provide some of the less observed 1,3-acyl shifts presumably from the T_1 (*n*, π*) states.[18]



Scheme 8.

All the above-mentioned examples strongly suggest, in mixed enones (α,β- and β,γ-) the reaction route in the excited state originated from the T_1(*n*, π*) states of α,β-enones and thus preferably follow a Type B route instead of an oxa-di-pi-methane route from the β,γ-enone part. Only one example of such Type B rearrangement in non-cyclic system has so far been reported in the literature[19] and the present reactions provide additional examples. The observation also supports our earlier proposition where we had preferred a similar route for the PET-induced transformation of bicyclo[2.2.2]octenones to bicyclo[3.2.1]octanones.[7]

3. Conclusion

With the help of PET reaction we have identified that in a mixed α,β- and β,γ-enone system the photorearrangement route is selectively from the α,β-enone part. We have also confirmed that, Type B rearrangement, so far observed only in cyclohexenones, is a general process for geometrically rigid α,β-enones

and this route predominates over other probabilities in mixed enones. While *exo*-C=C at γ-position of the enone retards the reaction presumably via a 'free rotor effect', C=O can actually facilitates the process. To the best of our knowledge presumably this is the first example of Type B rearrangement having an acyl substitution at C_γ position.

4. Experimental

4.1. General

All melting points were measured in a Gallenkamp melting point apparatus. The IR spectra were recorded on an FTIR-8300 Shimadzu spectrometer. The NMR spectra were recorded in $CDCl_3$ solution and CD_3OD solution at 300 and 500 MHz for ^1H NMR and at 75 and 125 MHz for ^{13}C NMR on a Brucker AC-300 spectrometer and Brucker AC-500 spectrometer, respectively using tetramethylsilane as an internal standard. Elemental analyses were performed with a Heraeus Combustion apparatus or on a 2400 series-II Perkin–Elmer CHN analyzer. High Resolution Mass Spectra (HRMS) were recorded on a Qtof Micro YA263 spectrometer using Electrospray ionization (ESI) technique. UV absorption spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer. Column Chromatography was performed using silica gel (60–120 mesh) under normal pressure. Flash column chromatography was performed using silica gel of mesh 230–400 under nitrogen pressure. Petroleum ether (PE) used was of the boiling range 60–80 °C. Spectral grade solvents were used for recording UV spectra. Triethylamine was dried over KOH. Ether refers to diethyl ether. Irradiation experiments were carried out in a Rayonet Photochemical Reactor using lamps of desired wavelength.

The 5-benzoylbicyclo[2.2.2]oct-5-en-2-ones (**1a**–**d**),[7] tricyclo [3.3.0.02,8]octan-3-one derivatives (**2b**,[7] **13**[20]), methylene derivatives **3**, **5**, **5′**, **6a**, **b**, **9**, **10** and **11**[10] were prepared according to reported procedures.

4.2. Synthesis of hydroxyimino derivative (4a–c, 11b)

A mixture of the starting materials (**1a**–**c**, **2b** 1 mM), and hydroxylamine hydrochloride (1.2 mM) in pyridine (3 mL) was heated at 80 °C (at 55 °C for **2b**) for 10 h stirring under argon atmosphere. The temperature of the reaction was brought down to room temperature. The reaction mixture was extracted with ether and excess pyridine was washed by dilute HCl solution. Then it was washed throughly by saturated $NaHCO_3$ solution and brine and dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was flash chromatographed over a silica gel column.

*4.2.1. 5-Benzoyl-2-hydroxyiminobicyclo[2.2.2]oct-5-ene (**4a**).* A thick liquid was obtained from **1a** (226 mg, 1 mM). Elution of the column with 8% EA in PE gave a thick liquid of **4a** (203 mg, 90%). R_f (8% EA/PE) 0.4, UV (CH_3CN) λ_{max} (nm): 245 (log ϵ 4.3), 340 (3.5); IR: 3259, 2958, 1650, 1597 cm^{-1}. ^1H NMR (300 MHz): δ (ppm) 1.24–2.47 (m, 6H), 3.40–3.44 (m, 1H), 3.57 (br s, 1H), 6.93 (dd, *J* 1 Hz, 1H), 7.43–7.50 (m, 2H), 7.54–7.58 (m, 1H), 7.65–7.74 (m, 2H). ^{13}C NMR (75 MHz): δ (ppm) 23.9 (CH_2), 24.2 (CH_2), 30.3 (CH_2), 30.6 (CH), 38.4 (CH), 128.6 (CH), 129.8 (CH), 132.1 (CH), 144.6 (C), 146.7 (CH), 155.2 (C), 161.0 (C=N), 194.1 (C=O). HRMS (ESI) calcd for $C_{15}H_{15}NO_2Na$: 264.1000; found: $[M+Na]^+$ 264.0998.

*4.2.2. 5-Benzoyl-2-hydroxyimino-4-methylbicyclo[2.2.2]oct-5-ene (**4b**).* An oil was obtained from **1b** (240 mg, 1 mM). Elution of the column with 8% ethyl acetate (EA) in petroleum ether (PE) gave an oil of **4b** (201 mg, 84%). R_f (8% EA/PE) 0.4, UV (CH_3CN) λ_{max} (nm): 325 (log ϵ 1.9); IR 3254, 2931, 1651, 1595 cm^{-1}. ^1H NMR (500 MHz): δ (ppm) 1.43 (s, 3H), 1.58–1.97 (m), 2.32 (d, *J* 18 Hz), 2.42 (d, *J* 18 Hz, 1H), 3.42–3.44 (m, 1 Hz), 6.56 (d, *J* 7 Hz, 1H), 7.35–7.45 (m, 2H), 7.54–7.57 (m, 1H), 7.77–7.78 (m, 2H). ^{13}C NMR (125 MHz): δ (ppm) 22.5 (CH_3), 26.04 (CH_2), 33.30 (CH_2), 38.13 (CH), 38.44 (CH_2), 38.7 (C), 128.49 (CH), 130.07 (CH), 133.05 (CH), 137.76 (C), 138.03 (CH), 148.99 (C), 162.59 (C=N), 195.39 (C=O). HRMS (ESI) calcd for $C_{16}H_{17}NO_2$: 256.1332; found: $[M+H]^+$ 256.1328.

*4.2.3. 5-Benzoyl-2-hydroxyimino-4,7,7-trimethylbicyclo[2.2.2]oct-5-ene (**4c**).* A solid was obtained from **1c** (268 mg, 1 mM). Elution of the column with 8% EA in PE gave a yellow solid of **4c** (241 mg, 90%), mp 98–100 °C. R_f (8% EA/PE) 0.4, UV (CH_3CN) λ_{max} (nm): 247 (log ϵ 2.86); IR: 3277, 2956, 1649, 1597 cm^{-1}. ^1H NMR (500 MHz): δ (ppm) 1.0 (s, 3H), 1.05 (s, 3H), 1.32 (s, 3H), 1.36 (d, *J* 13 Hz, 1H), 1.44 (dd, *J* 13 Hz, 1H), 2.16 (d, *J* 15 Hz, 1H), 2.34 (dd, *J* 15 Hz, 1H), 2.93 (d, *J* 7 Hz, 1H), 6.54 (d, *J* 7 Hz, 1H), 7.46–7.49 (m, 2H), 7.58–7.61 (m, 1H), 7.75–7.77 (m, 2H). ^{13}C NMR (125 MHz): δ (ppm) 20.3 (CH_3), 28.7 (CH_3), 30.0 (CH_3), 35.9 (C), 40.4 (C), 45.0 (CH_2), 47.9 (CH_2), 61.2 (CH), 125.5 (CH), 126.4 (CH), 128.1 (CH), 128.8 (CH), 135.8 (C), 146.5 (C), 155.2 (C=N), 213.7 (C=O). HRMS (ESI) calcd for $C_{18}H_{21}NO_2Na$: 306.1470; found: $[M+Na]^+$ 306.1471.

*4.2.4. 1-Benzoyl-3-hydroxyimino-5-methyltricyclo[3.3.0.0^{2,8}]octane (**11b**).* A thick liquid was obtained from **2b** (240 mg, 1 mmol). Elution of the column with 12% EA in PE gave a thick liquid of **11b** (204 mg, 80%). *Rf* (12% EA/PE) 0.4, UV (CH_3CN) λ_{max} (nm): 287 (log ϵ 3.0); IR: 3257, 2970, 1662, 1597 cm^{-1}. ^1H NMR (500 MHz): δ (ppm) 1.20 (s, 3H), 1.69–1.84 (m, 3H), 2.11 (d, *J* 18 Hz, 1H), 2.27–2.39 (m, 2H), 2.50 (br s 1H), 2.61 (d, *J* 18 Hz, 1H), 7.45–7.50 (m, 2H), 7.56–7.61 (m, 1H), 7.86–7.89 (m, 2H). ^{13}C NMR (125 MHz): δ (ppm) 23.14 (CH_3), 23.85 (CH_2), 35.57 (CH), 39.66 (CH), 45.59 (CH_2), 49.40 (CH_2), 51.90 (C), 54.54 (C), 128.9 (CH), 133.16 (CH), 138.05 (C), 164.01 (C=N), 199.07 (C=O). HRMS calcd for $C_{16}H_{17}NO_2Na$: 278.1157; found $[M+Na]^+$: 278.1156.

4.3. Synthesis of 4-(1-phenylvinyl)-1,5,6,7,8,8a-hexahydro-2*H*-2,4a-ethanonapthalen-10-one (7)

To a well stirred solution of the compound 4′-(1-phenylvinyl)-1′,5′,6′,7′,8′,8a′-hexahydro-2′*H*-spiro[1,3-dioxolane-2,10′-[2,4a]ethanonaapthalene] (**9**, 1 gm, 3.1 mmol) in 20 mL acetonitrile/water mixture (3:1, v/v) cerric ammonium nitrate (CAN) (64 mg, ~10 mol%) was added and the reaction mixture was refluxed for next 1 h. Then it was cooled to room temperature, and was extracted with ether and washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was chromatographed over silica gel column. Elution with 6% EA in PE gave a white solid, which on recrystallization from diethyl ether and petroleum ether (1:8) gave white crystals of 4-(1-phenylvinyl)-1,5,6,7,8,8a-hexahydro-2*H*-2,4a-ethanonapthalen-10-one (**7**, 837 mg, 97%), mp 63–65 °C. R_f (15% EA/PE) 0.5, Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found C, 86.39; H, 7.79; IR: 3035, 1724 cm^{-1}. UV (CH_3CN) λ_{max} (nm): 246 (log ϵ 3.77), 297 (2.48). ^1H NMR (300 MHz) δ (ppm): 1.08–1.38 (m, 7H), 1.57–1.65 (m, 2H), 1.78 (br d, *J* 18 Hz, superimposed with a multiplet 1.75–1.80, 2H), 2.03 (ddd, *J* 12, 9, 3 Hz, 1H), 2.59 (d, *J* 18 Hz, 1H), 3.12–3.15 (m, 1H), 5.04 (s, 1H), 5.36 (s, 1H), 6.14 (d, *J* 6 Hz, 1H), 7.22–7.31 (m, 5H). ^{13}C NMR (75 MHz) δ (ppm): 21.5 (CH_2), 25.7 (CH_2), 30.1 (CH_2), 31.2 (CH_2), 31.4 (CH_2), 37.8 (CH), 39.0 (CH_2), 42.9 (C), 48.9 (CH), 115.0 (CH_2), 124.7 (CH), 126.5 (CH), 127.7 (CH), 128.4 (CH), 140.2 (C), 148.2 (C), 154.9 (C), 212.3 (C=O).

4.4. PET reactions of 4a–c

Methanol solution (5 mL) of the hydroxyimino derivative of bicyclo compound (30 mg) in triethylamine (TEA, 5 mL), was

degassed and then irradiated in desired wavelength. After which the solvents were removed under reduced pressure. The residue was then purified by flash column chromatography to yield the product.

*4.4.1. 8-Benzoyl-3-hydroxyiminobicyclo[3.2.1]octane (**12a**).* Compound **4a** (30 mg, 1 mM) was irradiated at 300 nm wavelength for 5 h. Elution of the column with 10% PE, EA gave a yellow solid of **12a** (4.5 mg, 15%), mp 148–150 °C. R_f (10% EA/PE) 0.4, UV (CH_3CN) λ_{max} (nm): 278 (log ϵ 2.65); IR: 3277, 2956, 1649, 1597 cm^{-1}. ^1H NMR (500 MHz) δ (ppm): 0.407 (m, 2H), 0.97–01.08 (m, 2H), 1.32–1.75 (m, 4H), 3.66 (br s, 1H), 6.58–6.61 (m, 2H), 6.68–6.69 (m, 1H), 7.06–7.07 (m, 2H). ^{13}C NMR (125 MHz) δ (ppm): 24.1 (CH_2), 25.6 (CH_2), 26.7 (CH), 29.4 (CH_2), 31.9 (CH), 43.0 (CH_2), 100.1 (CH), 128.1 (CH), 128.5 (CH), 132.8 (CH), 160.4 (C=N). HRMS (ESI) calcd for $C_{15}H_{17}NO_2Na$ 266.1157; found: $[M+Na]^+$ 266.1156.

Further elution of the column with 10% EA in PE gave unreacted starting material (**4a**, 18 mg, 60%) with superimposible spectra.

*4.4.2. 8-Benzoyl-3-hydroxyimino-1-methylbicyclo[3.2.1]octane (**12b**).* Compound **4b** (30 mg, 1 mM) was irradiated at 300 nm wavelength for 3 h. Elution of the column with 10% PE, EA gave a yellow solid (**12b**, 4.8 mg, 16%), mp 148–150 °C. R_f (10% EA/PE) 0.4, UV (CH_3CN) λ_{max} (nm): 248 (log ϵ 3.7); IR: 3163, 2937, 1662, 1597 cm^{-1}. ^1H NMR (500 MHz): δ (ppm) 1.14 (s, 3H), 1.28–1.63 (m, 2H), 1.86 (d, *J* 15 Hz), 1.97 (d, *J* 15 Hz), 2.02–2.06 (m), 2.66 (hextet, *J* 4 Hz, 1H), 2.97 (d, *J* 16 Hz, 1H), 3.15 (d, *J* 16 Hz, 1H), 3.55 (d, *J* 4 Hz, 1H), 7.48–7.51 (m, 2H), 7.58–7.61 (m, 1H), 7.97–7.98 (m, 2H). ^{13}C NMR (125 MHz): δ (ppm) 24.2 (CH_3), 27.5 (CH_2), 28.2 (CH_2), 37.4 (CH_2), 39.3 (C), 40.1 (CH_2), 42.7 (CH), 55.78 (CH), 127.8 (CH), 128.52 (CH), 132.8 (CH), 138.6 (C), 158.1 (C), 202.7 (C=O). HRMS (ESI) calcd for $C_{16}H_{19}NO_2Na$: 280.1313; found $[M+Na]^+$ 280.1313.

Further elution of the column with 10% EA in PE gave unreacted starting material (**4b**, 15 mg, 50%) with superimposible spectra.

*4.4.3. 8-Benzoyl-3-hydroxyimino-1,6,6-trimethylbicyclo[3.2.1]octane (**12c**).* Compound **4c** (30 mg, 1 mM) was irradiated at 254 nm wavelength for 7 h. Elution of the column with 10% PE, EA gave a white crystal of **12c** (6.0 mg, 20%) R_f (10% EA/PE) 0.4, mp 168–170 °C after crystallization from DCM-PE mixture (1:8). UV (CH_3CN) λ_{max} (nm): 249 nm (log ϵ 4.0); IR: 3281, 2926, 1672, 1595 cm^{-1}. ^1H NMR (500 MHz): δ (ppm) 0.97 (s, 3H), 1.15 (s, 3H), 1.27 (s, 3H), 1.41 (d, *J* 15 Hz, 1H), 1.53 (dd, *J* 15 Hz, 1H), 1.66 (dd, *J* 20 Hz, 1H), 1.98 (d, *J* 15 Hz, 1H), 2.12 (q, *J* 5 Hz, 1H) 3.13 (dd, *J* 15 Hz, 1H), 3.25 (d, *J* 15 Hz, 1H), 3.89 (d, *J* 4 Hz, 1H), 7.48–7.51 (m, 2H), 7.57–7.6 (m, 1H), 7.92–7.94 (m, 2H). ^{13}C NMR (125 MHz): δ (ppm) 23.5 (CH_2), 24.2 (CH_3), 25.0 (CH_3), 32.5 (CH_3), 38.6 (C), 40.2 (CH_2), 43.2 (C), 49.9 (CH), 53.9 (CH_2), 54.9 (CH), 127.7 (CH), 128.5 (CH), 132.7 (CH), 139 (C), 158.4 (C=N), 202.4 (C=O). HRMS (ESI) calcd for $C_{18}H_{23}NO_2Na$: 308.1627; found $[M+Na]^+$ 308.1627.

Further elution of the column with 10% EA in PE gave a solid of unreacted starting material (**4c**, 15 mg, 50%), mp 98–100 °C (mmp 98 °C).

4.5. Irradiation of 5, 6a, 6b, and 7 in solution

A 50 mL solution of the compound in solution was degassed with argon for 10 min and then irradiated at suitable wavelength. Solvent was removed under reduced pressure and the residue was subjected to flash column chromatography.

*4.5.1. 2-Methylenedecahydro-7bH-benzo[g]cyclopropa[cd]pentalen-7b-yl(phenyl)methanone (**14**).* A solution of 10-methylene-1,5,6,7,8,8a-hexahydro-2*H*-2,4a-ethanonapthalen-4-yl(phenyl)methanone (**5**, 139 mg, 0.5 mmol) in dry benzene was irradiated at 254 nm for 39 h. Elution of the column with 2% EA in PE gave **14** (55 mg, 46%) as yellowish thick liquid. R_f (5% EA/PE) 0.5, UV (CH_3CN) λ_{max} (nm): 243 (log ϵ 2.75), 288 (4.01), 320 (2.94); IR: 3053, 2929, 1773, 1614 cm^{-1}. ^1H NMR (300 MHz) δ (ppm): 0.80–1.20 (m, 5H), 1.33–1.53 (m, 4H), 1.86–1.99 (m, 2H), 2.15 (ddd, *J* 9, 6 and 3 Hz, 1H), 2.37 (td, *J* 18 and 3 Hz, 1H), 2.54 (d, *J* 18 Hz, superimposed with another doublet (*J* 9 Hz) at 2.55, total 2H), 4.93 (dd, *J* 3 Hz), 4.99 (dd, *J* 3 Hz), 7.19–7.48 (m, 3H), 7.76–7.79 (m, 2H). ^{13}C NMR (75 MHz) δ (ppm): 22.9 (CH_2), 25.3 (CH_2), 26.7 (CH_2), 27.7 (CH_2), 30.6 (CH), 35.9 (CH_2), 41.2 (CH_2), 44.0 (CH), 54.7 (C), 55.9 (C), 56.2 (CH), 106.5 (CH_2), 128.3 (CH), 128.7 (CH), 132.5 (CH), 138.7 (C), 150.0 (C), 200.3 (C=O). HRMS calcd for $C_{20}H_{22}ONa$: 301.1568; found $[M+Na]^+$: 301.1563.

Further elution of the column with 2% EA in PE gave back **5** (35 mg, 25%) with superimposible spectra.

*4.5.2. 1,3,3-Trimethyl-6-(1-phenylvinyl)bicyclo[4.2.0]oct-4-en-7-one (**17a**).* (i) *In benzene*: A solution of 4,7,7-trimethyl-5-(1-phenylvinyl)bicyclo[2.2.2]oct-5-en-2-one (**6a**, 80 mg, 0.3 mmol) in dry benzene was irradiated at 300 nm for 45 min. Elution of the column with 5% EA in PE gave a yellow thick liquid of **17a** (60 mg, 75%). R_f (10% EA/PE) 0.8, UV (CH_3CN) λ_{max} (nm): 235 (log ϵ 4.1), 310 (2.95); IR: 2956, 1772, 1616 cm^{-1}. ^1H NMR (300 MHz) δ (ppm): 1.06 (s, 3H), 1.18 (s, 3H), 1.37 (d, *J* 15 Hz, 1H), 2.46 (d, *J* 17 Hz, 1H), 3.47 (d, *J* 17 Hz, 1H), 5.32 (d, *J* 1 Hz, 1H), 5.6 (d, *J* 10 Hz, 1H), 5.82 (d, *J* 10 Hz) superimposed with 5.81 (d, *J* 1 Hz) total 2H, 7.23–7.25 (m, 3H), 7.34–7.37 (m, 2H). ^{13}C NMR (75 MHz): 27.6 (CH_3), 28.8 (CH_3), 32.2 (C), 32.9 (CH_3), 34.9 (C), 43.3 (CH_2), 54.2 (CH_2), 71.9 (C), 117.3 (=CH_2), 125.5 (CH), 127.7 (CH), 128.1 (CH), 128.2 (CH), 140.3 (CH), 141.6 (C), 146.3 (C), 208.2 (C=O). HRMS calcd for $C_{19}H_{22}ONa$: 289.1568; found $[M+Na]^+$: 289.1579.

Further elution of the column with same solvent gave back (**6a**, 13 mg, 16%) as colorless semi-solid (superimposable IR spectrum).

(ii) *In acetonitrile*: Follow up of the above mentioned procedure in acetonitrile solution yielded the same compound (**17a**, 58 mg, 72%), which was identified by superimposible spectra.

*4.5.3. 1,4-Dimethyl-6-(1-phenylvinyl)bicyclo[4.2.0]oct-4-en-7-one (**17b**).* (i) *In benzene*: A solution of 1,4-dimethyl-5-(1-phenylvinyl) bicycle[2.2.2]oct-5-en-2-one (**6b**, 90 mg, 0.36 mmol) in dry benzene was irradiated at 300 nm for 40 min. Elution of the column with 3% EA in PE gave a colorless liquid of **17b** (62 mg, 69%). R_f (10% EA/PE) 0.8, UV (CH_3CN) λ_{max} (nm): 238 (log ϵ 4.41), 308 (3.26); IR: 2962, 1766, 1466 cm^{-1}. ^1H NMR (300 MHz) δ (ppm): 0.94 (s, 3H), 1.18–1.34 (m, 1H), 1.47–1.53 (m, 1H), 1.75 (s, 3H), 1.97–2.09 (m, 1H), 2.17 (dd, *J* 18, 6 Hz, 1H), 2.35 (d, *J* 17, 1H), 2.90 (d, *J* 17 Hz, 1H), 5.24 (d, *J* 1 Hz, 1H), 5.30 (s, 1H), 5.76 (d, *J* 1 Hz, 1H), 7.15–7.19 (m, 3H), 7.27–7.30 (m, 2H). ^{13}C NMR (75 MHz) δ (ppm): 24.3 (CH_2), 25.45 (C), 25.49 (CH_3), 27.2 (CH_2), 28.3 (CH_3), 33.5 (C), 51.8 (CH_2), 116.4 (=CH_2), 122.2 (CH), 127.3 (CH), 127.7 (CH), 137.3 (C), 141.4 (C), 146.7 (C), 206.7 (C=O). HRMS calcd for $C_{18}H_{20}ONa$: 275.1412; found $[M+Na]^+$: 275.1413.

Further elution of the column with same solvent gave back (**6b**, 19 mg, 21%) as colorless thick liquid (superimposable IR spectrum).

(ii) *In acetonitrile*: Follow up of the above mentioned procedure in acetonitrile solution yielded the same compound (**17b**, 44 mg, 63%), which was identified by superimposible spectra.

*4.5.4. 2A-(1-phenylvinyl)-5,5a,6,7,8,9-hexahydro-1H-cyclobuta[d]naphthalene-2(2aH)-one (**16**).* A solution of 4-(1-phenylvinyl)-1,5,6,7,8,8a-hexahydro-2*H*-2,4a-ethanonapthalen-10-one (**7**, 139 mg, 0.5 mmol) in dry acetonitrile was irradiated at 300 nm for 3 h. Elution with 2% EA in PE gave **16** (72 mg, 52%) as a white solid, mp 128–130 °C. R_f (5% EA/PE) 0.6, Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.11; H, 8.09; IR: 3053, 3024, 1773 cm^{-1}; UV (CH_3CN) λ_{max} (nm): 239 nm (log ϵ 3.52), 305 nm (2.42). ^1H NMR (300 MHz) δ (ppm):

0.83–0.95 (m, 2H), 1.02–1.33 (m, 3H), 1.45 (ddt, *J* 12, 6, 3 Hz, 1H), 1.60 (brd, *J* 9 Hz, 3H), 1.78 (tdd, *J* 18, 12 and 3 Hz, 1H), 2.3 (td, *J* 18 and 1.2 Hz, 1H), 2.53 (d, *J* 18 Hz, 1H), 2.87 (dd, *J* 18 and 1.2 Hz, 1H), 5.38 (s, 1H), 5.6 (dd, *J* 12 and 3 Hz, 1H), 5.76 (s, 1H), 6.00 (ddd, *J* 12, 6, 3 Hz, 1H), 7.25–7.27 (m, 3H), 7.39–7.42 (m, 2H). ^{13}C NMR (75 MHz) δ (ppm): 22.9 (CH_2), 26.0 (CH_2), 29.5 (CH_2), 29.8 (C), 30.8 (CH_2), 33.7 (CH_2), 33.9 (CH), 39.7 (C), 47.8 (CH_2), 117.5 (CH_2), 127.4 (CH_2), 127.8 (CH), 127.9 (CH), 128.0 (CH), 129.2 (CH_2), 142.0 (C), 145.5 (C), 206.3 (C=O). HRMS calcd for $C_{20}H_{22}ONa$: 301.1568; found 301.1563.

4.6. Irradiation of 6a, 6b, and 7 under PET condition

Methanol solution (5 mL) of the methylene derivatives in triethylamine (TEA, 5 mL), was degassed and then irradiated at 300 nm wavelength for 5 h. After which the solvent was removed under reduced pressure. The residue was then purified by flash column chromatography on silica gel to yield the product.

*4.6.1. 2A-(1-phenylvinyl)-5,5a,6,7,8,9-hexahydro-1H-cyclobuta[d] naphthalene-2(2aH)-one (**16**).* Residue obtained from 4-(1-phenylvinyl)-1,5,6,7,8,8a-hexahydro-2*H*-2,4a-ethanonapthalen-10-one (**7**, 30 mg, 0.1 mmol) on elution with pet ether gave 10 mg of an unidentified decarbonylated compound. Further elution with 4% EA in PE gave a white solid of **16** (20 mg, 68%), identified by superimposible spectra. Further elution of the column with same solvent gave back **7** (3 mg, 10%).

*4.6.2. 1,3,3-Trimethyl-6-(1-phenylvinyl)bicyclo[4.2.0]oct-4-en-7-one (**17a**).* Residue obtained from 4,7,7-trimethyl-5-(1-phenyvinyl) bicyclo[2.2.2]oct-5-en-2-one (**6a**, 30 mg, 0.1 mmol) on elution with pet ether gave 7 mg of an unidentified decarbonylated compound. Further elution with 3% EA in PE gave a yellow thick liquid of **17a** (16.5 mg, 55%), identified by superimposible spectra. Further elution of the column with same solvent gave back **6a** (3 mg, 12%).

*4.6.3. 1,4-Dimethyl-6-(1-phenylvinyl)bicyclo[4.2.0]oct-4-en-7-one (**17b**).* Residue obtained from 1,4-dimethyl-5-(1-phenylvinyl)bicyclo[2.2.2]oct-5-en-2-one (**6b**, 30 mg, 0.1 mmol) on elution with pet ether gave 10 mg of an unidentified decarbonylated compound. Further elution with 3% EA in PE gave a colorless liquid of **17b** (20 mg, 68%), identified by superimposible spectra. Further elution of the column with same solvent gave back **6b** (3 mg, 10%).

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Supplementary data

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References and notes

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15. X-ray single crystal data of a single crystal of **12c** was collected using Mo Kα (λ=0.7107 Å) radiation on an SMART APEX II diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution/refinement were carried out using the software package of SMART APEX. The structure was solved by direct method and refined in a routine manner. The non-hydrogen atoms were treated anisotropically except oxime hydroxyl oxygen atom. The hydroxyl group of oxime moiety was found to be disorderd over two positions and thus treated as two position disorder by FVAR facility of Shelxl-97. The positions of all hydrogen atoms were generated by their idealized geometry and refined using a riding model. Crystal dimension: 0.32×0.24×0.12 mm; T=100(2) K; orthorhombic, space group *P*ca21; a=12.949 (6), b=7.867(4), c=31.438(14) Å; V=3203(2) Å3; Z=8, ρ=1.180 gcm^{-3}; μ=0.076 mm^{-1}; F(000)=1224; $\theta_{min}/\theta_{max}/^{\circ}$=5.76/32.28; R_{int}=0.0810; Range of h, k, l=−19/19, −11/11, −46/46; 45207 reflections collected of which 11066 were unique, 6714 observed [$I>2\sigma(I)$] reflections, 383 parameters were refined; R_1=0.0630, wR_2=0.1776; Goodness of fit on F^2=0.994; CCDC-798095 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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17. Using the above-mentioned instrument and software the single crystal structure of **16** was solved by direct method and refined. The non-hydrogen atoms were treated anisotropically. All hydrogen atoms were located and refined. Crystal dimension: 0.37×0.27×0.18 mm; T=100(2) K; orthorhombic, space group *P*21/c; a=8.9712(7), b=24.4263(19), c=7.1014(6) Å; V=1511.7(2) Å^3; Z=4, ρ_{calcd}=1.223 gcm^{-3}; μ=0.073 mm^{-1}; F(000)=600; $\theta_{min}/\theta_{max}/^{\circ}$=1.67/27.00; R_{int}=0.0458; range of h, k, l=−11/11, −31/31, −9/9; 16250 reflections collected of which 3299 were unique, 2544 observed [$I>2\sigma(I)$] reflections, 278 parameters were refined; R_1=0.0435, wR_2=0.1019; Goodness of Fit on F^2=1.033; CCDC-801061 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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