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Novel reactions of indium reagents with 1,2-diones: a facile synthesis of α-hydroxy ketones

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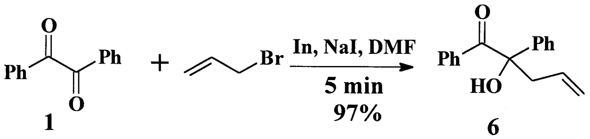
Abstract—Indium mediated reactions of allyl, cinnamyl, propargyl and benzyl bromides, ethyl bromoacetate and ethyl-4-bromocrotonate with 1,2-diones, in the presence of sodium iodide, occur efficiently to afford α-hydroxy keto compounds in excellent yields. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The advent of Barbier[1] and Grignard reactions heralded a new era in organic chemistry. Although generally ignored for a long time, there has been considerable interest in the Barbier reaction vis a vis other organometallic reactions for the formation of carbon–carbon bonds. Recently, indium mediated Barbier reaction of a variety of functional groups such as aldehydes, ketones, anhydrides, acid chlorides, imides, activated alkenes, alkynes, cyclopropenes, imines, enamines etc. has been reported.[2–10] Indium mediated reactions of 1,2-diones, except for the isolated reports on the allylation of azetidinones[11,12] and glyoxals,[13] have remained practically unexplored. Very recently, we reported the indium mediated allylation of 1,2-diones.[14] Subsequently, we have carried out a systematic study of the reactions of organoindium reagents with various 1,2-diones with the objective of devising a convenient synthesis of α-hydroxy carbonyl compounds,[15] the latter being an important class of compounds. The results of our expanded investigations are presented in this paper.

2. Results and discussion

In the first series of experiments, the allylation of 1,2-diones was performed using indium, allyl bromide and sodium iodide. Thus benzil **1** on reaction with allylbromide and using indium in the presence of sodium iodide in dimethyl formamide afforded the corresponding allylated product **6** in 97% yield in 5 min (Scheme 1). In the absence of sodium iodide, the reaction was very slow.



Scheme 1.

The structure of the product was established on the basis of spectroscopic data. The IR spectrum exhibited carbonyl absorption at 1681 cm^{-1} and hydroxyl at 3467 cm^{-1}. The ^1H- and ^{13}C NMR spectra were in good agreement with the expected compound.

Under similar conditions, other 1,2-diones such as biacetyl **2**, acenaphthenequinone **3**, phenanthrenequinone **4**, and isatin **5** afforded corresponding monoallylated products in excellent yields and the results are summarized in Table 1. It is noteworthy that no diallylation occurred when the diones were treated with excess of the allylindium reagent.

Subsequently, we investigated the reaction of cinnamyl bromide with 1,2-diones in the presence of indium. The cinnamylation reactions of phenanthrenequinone and isatin were found to be slow under the above conditions. But under ultrasonication (U. S.) conditions, the reaction proceeded smoothly to afford the corresponding cinnamylated products in good yields. It may be noted that the regioselectivity was not uniform with all the 1,2-dicarbonyls subjected to the cinnamylation. Understandably, regioselectivity depends not only on the nature of allyl bromide but also on the electrophile.[17] The results are summarized in Table 2.

The reaction of propargyl indium complex with 1,2-diones was also found to be facile under conditions described (vide supra); in these cases, both alkyne and allene derivatives were formed in good yields. These isomers, except in the case of phenanthrenequinone, are inseparable by column

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Keywords: indium; diones; α-hydroxy ketones.

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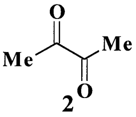
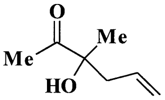
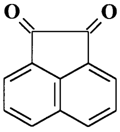
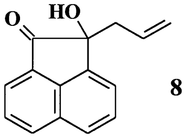
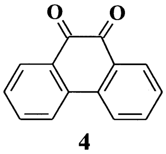
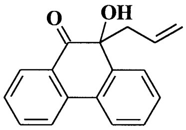
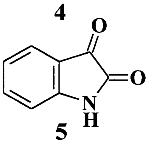
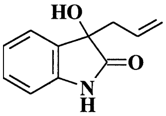
Table 1. Allylation of 1,2-diones

Entry	Diones	Reaction conditions[a]	Product	Yield[b]
1	 **2**	10 min	 **7**	97%
2	 **3**	4 min	 **8**	95%[c]
3	 **4**	2 min	 **9**	95%[c]
4	**4**  **5**	4 min	 **10**	96%

[a] NaI, DMF, rt.

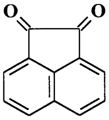
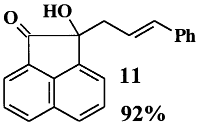
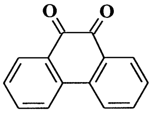
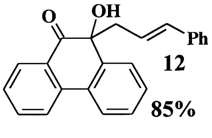
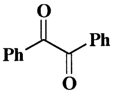
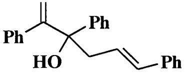
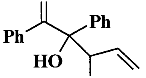
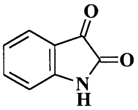
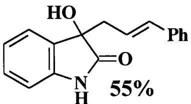
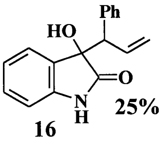
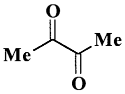
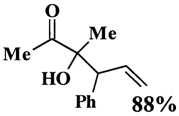
[b] Isolated yield.

[c] The products **8** and **9** were identified by comparison of their physical and spectral data with those of authentic samples.[16]

chromatography. The ratio of the isomers was determined from the ^1H NMR spectra by considering the integration of internal olefinic proton of allene and terminal proton of alkyne. The results are summarized in Table 3.

The benzylation reactions of acenaphthenequinone and phenanthrenequinone were found to be slow under the above conditions. But under ultrasonication conditions, these diones afforded the corresponding benzylated product

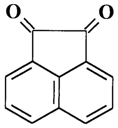
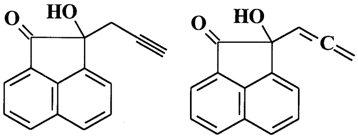
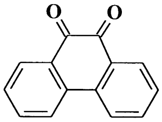
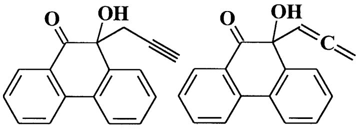
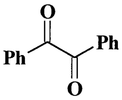
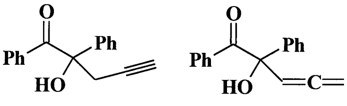
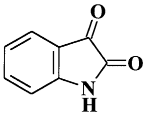
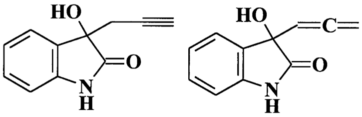
Table 2. Cinnamylation of 1,2-diones

Entry	Diones	Reaction conditions[a]	Products(s), yield(s)
1		4 min	 **11** **92%**
2		U.S.[b], 7 min	 **12** **85%**
3		25 min	 **25%** **13**  **50%** **14**
4		U.S.[b], 25 min	 **55%** **15**  **25%** **16**
5		10 min	 **17** **88%**

[a] In, NaI, DMF.

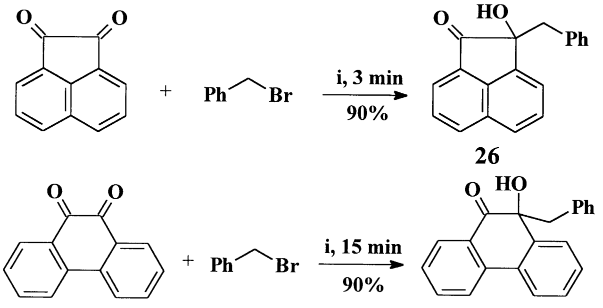
[b] Ultrasonication.

Table 3. Propargylation of 1,2-diones

Entry	Diones	Reaction conditions	Products(s), yield(s)
1		5 min	 **18** **90% (1:1)** **19**
2		3 min	 **20** **99% (13:2)** **21**
3		10 min	 **22** **75% (1:1)** **23**
4		25 min	 **24** **85% (4:1)** **25**

in excellent yields (Scheme 2). Isatin and benzil were found to be unreactive under similar conditions.

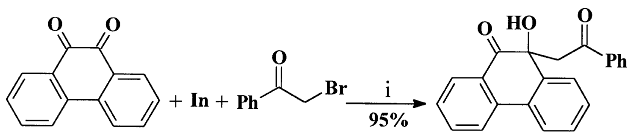
The addition of a metal enolate formed from an α-bromo ketone to a carbonyl compound results in a β-hydroxyketone.[18] It has been reported that phenacyl iodide on reaction with aldehydes in the presence of indium led to aldol products.[19] We have studied the reactivity of phenacyl bromide, ethyl bromoacetate and ethyl-4-bromocrotonate towards 1,2-quinones in the presence of indium. Treatment of phenanthrenequinone with phenacyl bromide and indium did not lead to any products but in the presence of sodium iodide, under ultrasonication conditions, a facile reaction occurred and the aldol **28** was obtained in 95% yield (Scheme 3).



26

27

Scheme 2. i. In, NaI, DMF, U. S.

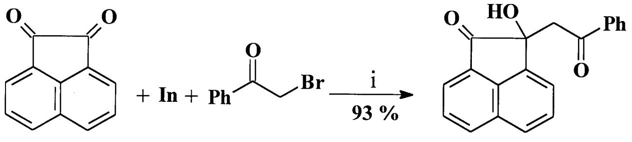


28

Scheme 3. i. NaI, DMF, U. S., rt, 10 min.

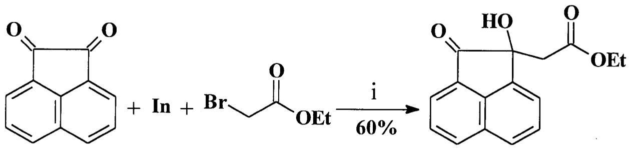
Acenaphthenequinone also afforded the aldol product in very high yield under similar conditions (Scheme 4).

It has been reported that indium can promote Reformatsky reactions of aldehydes to furnish β-hydroxyesters.[20] We have found that acenaphthenequinone on sonication with ethyl bromoacetate and indium in the presence of sodium iodide afforded the corresponding Reformatsky product **30** in 60% yield (Scheme 5).



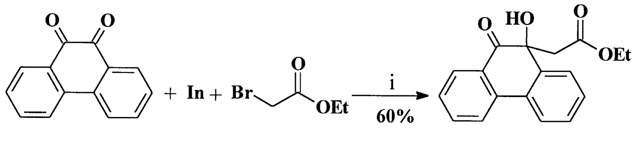
29

Scheme 4. i. NaI, DMF, U. S., rt, 5 min.



30

Scheme 5. i. NaI, DMF, U. S., rt, 6 min.

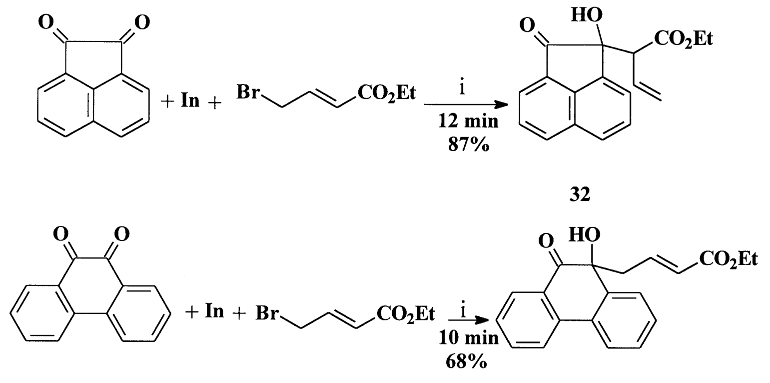


31

Scheme 6. i. NaI, DMF, U. S., 15 min.

Similarly, phenanthrenequinone afforded the β-hydroxy-ester **31** in 60% yield (Scheme 6).

It was found that ethyl bromocrotonate also participates in similar reactions with acenaphthenequinone and phenanthrenequinone leading to the novel γ-keto-β-hydroxy ester **32** and the α-addition product **33**, respectively (Scheme 7).



32

33

Scheme 7. i. NaI, DMF, U. S.

Other substituted allyl organometallics have also been known to exhibit similar contrasting behavior.[21]

3. Conclusion

A variety of organoindium reagents, generated in situ, have been shown to react smoothly with 1,2-diones resulting in a high yield synthesis of β-hydroxy carbonyl compounds. The efficiency of the reaction, short reaction time, mild reaction conditions and high yields of products are clear advantages of the present process vis a vis other comparable organometallic reactions. Thus our investigations have expanded the scope and synthetic potential of indium mediated reactions.

4. Experimental

4.1. General

All reactions were carried out in freshly distilled dimethylformamide. Analytical thin layer chromatography was performed on silica gel TLC plates. Purification by gravity column chromatography was carried out using silica gel (100–200 mesh). Mixtures of ethyl acetate–hexane were used as eluent. All melting points were recorded on a Buchi Meltemp II melting point apparatus and are uncorrected. The IR spectra were recorded on a Bomem MB infrared spectrophotometer. NMR spectra were recorded on a Bruker 300 spectrometer using chloroform-*d* as solvent unless otherwise mentioned. The chemical shifts are given in the δ scale with tetramethylsilane as internal standard.

4.1.1. 1,2-Diphenyl-2-hydroxy-4-penten-1-one 6. A mixture of benzil (0.210 g, 1 mmol), allyl bromide (0.210 g, 1.55 mmol), indium powder (0.120 g, 1.05 mmol) and sodium iodide (0.232 g, 1.55 mmol) in 3 mL dimethyl formamide was stirred at 25°C until completion of the reaction (5 min). The reaction mixture was quenched with a few drops of 1N HCl and extracted with diethyl ether (3×30 mL). The ether layer was washed with water, brine and then dried over anhydrous sodium sulfate. Evaporation of the ether followed by purification of the product by column chromatography on silica gel provided the pure product **6** (0.244 g, 97%) as a colorless solid (mp: 88–90°C). IR (KBr) $\nu_{\max}$: 3467, 3070, 2955, 1681, 1458, 1229, 1007, 946, 710 cm^{-1}. ^{1}H NMR: δ 2.90–2.97 (m, 1H), 3.09–3.16 (m, 1H), 4.09 (s, 1H), 4.98–5.13 (m, 2H), 5.66–5.80 (m, 1H), 7.25–7.73 (m, 10H). ^{13}C NMR: δ 44.06, 81.30, 120.28, 125.50, 127.96, 127.98, 128.76, 130.10, 132.34, 132.57, 134.58, 141.77, 200.44. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.22; H, 6.60.

4.1.2. 3-Methyl-3-hydroxy-5-hexen-2-one 7. Yield (95%), a colorless liquid. IR (neat) $\nu_{\max}$: 3486, 3080, 2980, 1707, 1638, 1426, 1357, 1158, 989, 914 cm^{-1}. ^{1}H NMR: δ 1.37 (s, 3H), 2.21 (s, 3H), 2.44–2.46 (m, 2H), 3.85 (s, 1H), 5.08–5.13 (m, 2H), 5.65–5.79 (m, 1H). ^{13}C NMR: δ 23.94, 24.90, 43.84, 78.62, 118.65, 132.34, 211.42. HRMS: 87.0446 (M^+−allyl) (calcd) 87.0449 (M^+−allyl) (found)

4.1.3. 3-Hydroxy-3-(2-propenyl)-2-indolone 10. Yield (96%), a colorless solid (mp: 150–152°C). IR (KBr) $\nu_{\max}$: 3334, 1720, 1626, 1474, 1189, 922 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.55–2.62 (m, 1H), 2.69–2.76 (m, 1H), 3.43 (s, 1H), 5.07–5.12 (m, 2H), 5.57–5.71 (m, 1H), 6.84–7.35 (m, 4H), 8.43 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 42.80, 77.20, 104.70, 110.14, 120.39, 122.90, 124.42, 129.50, 130.24, 140.21, 179.89. Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.85; N, 7.40. Found: C, 70.18; H, 5.83; N, 7.79.

4.1.4. 1,2-Dihydro-1-hydroxy-1-(3-phenyl-2-propenyl)-2-oxacenaphthene 11. A mixture of acenaphthenequinone

(0.182 g, 1 mmol), cinnamyl bromide (0.305 g, 1.55 mmol), indium powder (0.120 g, 1.05 mmol) and sodium iodide (0.232 g, 1.55 mmol) in 3 mL dimethyl formamide was stirred at 25°C until completion of the reaction (4 min). The usual isolation and purification afforded **11** (0.281 g, 92%) as a colorless solid (mp: 98–100°C). IR (KBr) ν_{max}: 3474, 1695, 1595, 1339, 1195, 970, 746 cm^{-1}. ^{1}H NMR: δ 2.68–2.76 (m, 1H), 2.90–2.97 (m, 1H), 3.40 (brs, 1H), 6.10–6.16 (m, 1H), 6.35 (d, J=15.8 Hz, 1H), 7.13–7.18 (m, 5H), 7.61–8.08 (m, 6H). ^{13}C NMR: δ 42.03, 79.79, 120.98, 122.25, 122.69, 125.36, 126.29, 127.42, 128.32, 128.48, 128.74, 130.67, 132.03, 134.99, 137.05, 139.44, 141.32, 205.17. Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.86; H, 5.44.

4.1.5. 9,10-Dihydro-9-hydroxy-9-(3-phenyl-2-propenyl)-10-oxophenanthrene 12. A mixture of phenanthrenequinone (0.208 g, 1 mmol), cinnamyl bromide (0.305 g, 1.55 mmol), indium powder (0.120 g, 1.05 mmol) and sodium iodide (0.232 g, 1.55 mmol) in 3 mL DMF was ultrasonicated for 7 min. The isolation and purification were done as before to afford **12** (0.276 g, 85%) as a colorless solid (mp: 93–95°C). IR (KBr) ν_{max}: 3474, 1682, 1595, 1445, 1283, 964, 727 cm^{-1}. ^{1}H NMR: δ 2.55–2.70 (m, 2H), 4.10 (s, 1H), 5.89–5.99 (m, 1H), 6.10 (d, J=15.8 Hz, 1H), 7.17–7.93 (m, 13H). ^{13}C NMR: δ 48.63, 80.01, 123.03, 123.30, 124.10, 126.39, 126.44, 127.51, 128.32, 128.53, 128.75, 129.19, 129.36, 134.61, 135.13, 137.13, 137.78, 140.29, 202.88. Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.63; H, 5.58. Found: C, 84.79; H, 5.47.

4.1.6. 1,2,5-Triphenyl-2-hydroxy-4-penten-1-one 13 and 1,2,3-triphenyl-2-hydroxy-4-penten-1-one 14. A mixture of benzil (0.210 g, 1 mmol), cinnamyl bromide (0.305 g, 1.55 mmol), indium powder (0.120 g, 1.05 mmol) and sodium iodide (0.232 g, 1.55 mmol) in 3 mL dimethyl formamide was stirred at 25°C until completion of the reaction (25 min). The usual work up followed by purification of the product afforded α adduct **13** (0.082 g, 25%) as colorless solid; recrystallized from dichloromethane/hexane solvent system (mp: 108–111°C) and γ adduct (0.164 g, 50%) as colorless solid; recrystallized from dichloromethane/hexane solvent system (mp: 112–114°C). From the ^{1}H NMR spectrum, the product **14** was found to be a mixture of *syn* and *anti* isomers in the ratio 1:1.

Spectral data for **13**: IR (KBr) ν_{max}: 3499, 3024, 2912, 1670, 1588, 1445, 1351, 1201, 1126, 1020, 958, 827, 746, 702, 615 cm^{-1}. ^{1}H NMR: δ 3.02–3.09 (m, 1H), 3.24–3.31 (m, 1H), 4.17 (s, 1H), 6.08–6.15 (m, 1H), 6.26 (d, J=15.9 Hz, 1H), 7.18–7.73 (m, 15H). ^{13}C NMR: δ 43.50, 81.93, 123.68, 125.71, 126.42, 127.67, 128.21, 128.62, 129.04, 130.34, 132.81, 134.84, 135.45, 136.95, 142.04, 200.77. Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.11; H, 6.13. Found: C, 84.39; H, 6.25.

Spectral data for **14**: IR (KBr) ν_{max}: 3494, 3058, 3027, 2921, 1676, 1595, 1489, 1446, 1346, 1203, 960, 830, 749, 699 cm^{-1}. ^{1}H NMR: δ 3.83 (s, 1H), 4.10 (s, 1H), 4.58 (d, J=7.5 Hz, 1H), 4.65 (d, J=7.8 Hz, 1H), 4.96–5.17 (m, 4H), 6.11–6.23 (m, 2H), 7.09–7.97 (m, 30H). ^{13}C NMR: δ 54.69, 55.92, 83.61, 84.51, 117.36, 117.92, 125.17, 125.48, 125.72, 125.91, 126.41, 126.80, 126.89, 126.91, 127.09, 127.16, 127.49, 127.89, 128.57, 128.74, 128.82, 128.88, 131.11, 131.14, 133.64, 135.92, 136.10, 199.97, 200.44. Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.11; H, 6.13. Found: C, 84.22; H, 6.37.

4.1.7. 3-Hydroxy-3-(3-phenyl-2-propenyl)-2-indolone 15 and 3-hydroxy-3-(1-phenyl-2-propenyl)-2-indolone 16. A mixture of isatin (0.147 g, 1 mmol), cinnamyl bromide (0.305 g, 1.55 mmol), indium powder (0.120 g, 1.05 mmol) and sodium iodide (0.232 g, 1.55 mmol) in 3 mL DMF was ultrasonicated for 25 min. The usual work up followed by purification of the product afforded **15** (0.145 g, 55%) as colorless solid; recrystallized from dichloromethane/hexane solvent system (mp: 163–166°C) and **16** (0.066 g, 25%) as colorless solid; recrystallized from dichloromethane/hexane solvent system (mp: 160–162°C). The product **16** was found to be a mixture of *syn* and *anti* isomers in the ratio 1:1 as determined by ^{1}H NMR.

Spectral data for **15**: IR (KBr) ν_{max}: 3333, 3274, 1726, 1695, 1470, 1208, 752 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.67–2.74 (m, 1H), 2.86–2.92 (m, 1H), 4.76 (s, 1H), 6.00–6.10 (m, 1H), 6.35 (d, J=15.7 Hz, 1H), 6.85–7.45 (m, 9H), 9.10 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 41.33, 109.55, 121.50, 122.49, 123.80, 125.59, 126.60, 127.84, 128.53, 130.76, 133.52, 136.75, 140.85, 179.27. Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.69; N, 5.27. Found: C, 77.17; H, 5.68; N, 5.51.

Spectral data for **16**: IR (KBr) ν_{max}: 3340, 3267, 1723, 1680, 1475, 1210, 755 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 3.50 (s, 1H), 3.82 (d, J=10.1 Hz, 1H), 5.33 (m, 2H), 6.31 (m, 1H), 6.9–7.25 (m, 9H), 8.10 (s, 1H). ^{13}C NMR (DMSO-d_6): 58.20, 109.75, 119.77, 120.58, 122.46, 125.00, 125.33, 127.07, 127.83, 128.78, 129.01, 129.55, 129.70, 133.81, 136.84, 140.53, 179.04. Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.69; N, 5.27. Found: C, 77.40; H, 5.74; N, 5.50.

4.1.8. 3-Hydroxy-3-methyl-4-phenyl-5-hexen-2-one 17. A mixture of butan-2,3-dione (0.086 g, 1 mmol), cinnamyl bromide (0.305 g, 1.55 mmol), indium powder (0.120 g, 1.05 mmol) and sodium iodide (0.232 g, 1.55 mmol) in 3 mL dimethyl formamide was stirred at 25°C until completion of the reaction (10 min). The isolation and purification were done as before to afford **17** (0.179 g, 88%) as a pale yellow semi-solid. The product was found to be a mixture of *syn* and *anti* isomers in the ratio 1:1 by ^{1}H NMR. IR (neat) ν_{max}: 3467, 3062, 3030, 2980, 1701, 1626, 1451, 1351, 1220, 1145, 1089, 995, 914, 739, 689 cm^{-1}. ^{1}H NMR: δ 1.07 (s, 3H), 1.35 (s, 3H), 2.02 (s, 3H), 2.19 (s, 3H), 3.47 (d, J=9.2 Hz, 2H), 3.92 (brs, 2H), 4.97 (dd, J=13.1, 2.6 Hz, 2H), 5.15 (dd, J=8.3, 1.9 Hz, 2H), 6.05–6.11 (m, 1H), 6.19–6.25 (m, 1H), 7.12–7.35 (m, 10H). ^{13}C NMR: δ 23.71, 23.94, 24.13, 56.79, 57.12, 80.81, 81.02, 116.69, 117.52, 125.70, 126.74, 126.84, 127.99, 128.04, 128.18, 129.33, 136.52, 136.65, 138.89, 139.46, 210.70, 211.27. HRMS: 186.1044 ($M^+ - H_2O$) (calcd) 186.1050 ($M^+ - H_2O$) (found).

4.1.9. 1,2-Dihydro-1-(2-propynyl)-1-hydroxy-2-oxacenaphthene 18 and 1,2-dihydro-1-(prop-1,2-dienyl)-1-hydroxy-2-oxacenaphthene 19. A solution of acenaphthenequinone (0.182 g, 1 mmol), propargyl bromide

(0.179 g, 1.55 mmol), indium powder (0.120 g, 1.05 mmol) and sodium iodide (0.232 g, 1.55 mmol) in 3 mL dimethyl formamide was stirred at 25°C until completion (5 min) of the reaction (TLC). The usual work-up followed by purification of the product by silica gel column using 10% ethyl acetate in hexane as eluent afforded a mixture of alkyne and allene in the ratio 5:2 (0.200 g, 90%) as pale yellow solid. IR (neat) $\nu_{\max}$: 3430, 3374, 3293, 2120, 1944, 1707, 1601, 1495, 1345, 1270, 1164, 1058, 1020, 870, 777, 639 cm^{-1}. ^{1}H NMR: δ 1.93 (t, J=2.4 Hz, 1H), 2.74 (dd, J=16.6, 2.4 Hz, 1H), 2.96 (dd, J=16.6, 2.4 Hz, 1H), 3.18 (s, 1H), 7.67–8.16 (m, 6H). 3.18 (s, 1H), 4.86–4.98 (m, 2H), 5.50–5.55 (m, 1H), 7.67–8.16 (m, 6H). ^{13}C NMR: δ 28.42, 71.73, 77.31, 77.60, 78.07, 79.91, 93.13, 120.82, 121.25, 122.31, 122.50, 125.42, 125.68, 128.26, 128.70, 130.28, 130.53, 131.97, 132.08, 132.35, 138.43, 141.50, 203.11, 212.00. HRMS: 222.0681 (calcd) 222.0679 (found).

4.1.10. 9,10-Dihydro-9-hydroxy-9-(2-propynyl)-10-oxophenanthrene 20 and 9,10-dihydro-9-hydroxy-9-(prop-1,2-dienyl)-10-oxophenanthrene 21. Alkyne **20** (86%) a pale yellow solid; recrystallized from dichloromethane/hexane solvent system (mp: 130–133°C) and allene **21** (13%) a pale yellow solid; recrystallized from dichloromethane/hexane solvent system (mp: 122–125°C).

Spectral data for **20**: IR (KBr) $\nu_{\max}$: 3480, 3293, 3068, 2918, 2123, 1695, 1601, 1451, 1283, 1189, 1102, 1026, 933, 783, 764, 747, 626 cm^{-1}. ^{1}H NMR: δ 2.03 (t, J=2.5 Hz, 1H), 2.56 (dd, J=16.7, 2.3 Hz, 1H), 2.68 (dd, J=16.7, 2.4 Hz, 1H), 4.35 (s, 1H), 7.39–7.42 (m, 3H), 7.68–7.97 (m, 5H). ^{13}C NMR: δ 35.29, 72.69, 79.31, 97.40, 123.06, 127.53, 128.45, 128.55, 129.21, 135.04, 138.86, 200.80. Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.40; H, 4.54.

Spectral data for **21**: IR (KBr) $\nu_{\max}$: 3474, 3068, 1950, 1695, 1595, 1451, 1283, 1195, 1002, 846, 758, 733 cm^{-1}. ^{1}H NMR: δ 4.27 (s, 1H), 4.58–4.72 (m, 2H), 5.22–5.26 (m, 1H), 7.38–7.44 (m, 3H), 7.67–7.96 (m, 5H). ^{13}C NMR: δ 79.35, 97.42, 104.71, 123.07, 123.75, 126.40, 127.75, 128.27, 128.35, 129.13, 129.30, 134.92, 137.57, 138.88, 199.91, 206.95. EIMS m/z: 248 (M^+). Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.01; H, 5.14.

4.1.11. 1,2-Diphenyl-2-hydroxy-4-pentyn-1-one 22 and 1,2-diphenyl-2-hydroxy-3,4-pentadien-1-one 23. Alkyne **22** and allene **23** in the ratio 1:1 in 75% total yield as a pale yellow solid. IR (neat) $\nu_{\max}$: 3453, 3299, 3065, 2922, 2128, 1958, 1678, 1593, 1490, 1444, 1353, 1239, 1119, 1068, 862, 760, 697 cm^{-1}. ^{1}H NMR: δ 2.01 (t, J=2.5 Hz, 1H), 2.89 (dd, J=16.5, 2.4 Hz, 1H), 3.26 (dd, J=16.5, 2.3 Hz, 1H), 4.20 (s, 1H), 4.79–4.96 (m, 3H), 5.94 (t, J=6.6 Hz, 1H), 7.23–7.77 (m, 20H). ^{13}C NMR: δ 31.44, 72.53, 79.32, 79.88, 80.24, 81.39, 95.27, 125.18, 126.72, 128.08, 128.16, 128.28, 128.39, 128.88, 129.00, 129.92, 130.36, 130.70, 132.74, 133.07, 133.51, 134.38, 134.76, 140.46, 141.67, 198.58, 199.01, 207.76. HRMS: 250.0994 (calcd) 250.0987 (found).

4.1.12. 3-Hydroxy-3-(2-propynyl)-2-indolone 24 and 3-hydroxy-3-(prop-1,2-dienyl)-2-indolone 25. Alkyne **24** and allene **25** in the ratio 4:1 in 85% total yield as pale yellow semi-solid. IR (neat) $\nu_{\max}$: 3338, 3301, 3195, 2815, 1956, 1695, 1620, 1471, 1359, 1185, 1110, 749, 643 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 1.99 (t, J=2.6 Hz, 1H), 2.56 (dd, J=16.1, 1.8 Hz, 1H), 2.78 (dd, J=16.1, 1.7 Hz, 1H), 3.10 (s, 2H), 4.73–4.82 (m, 2H), 5.47–5.51 (m, 1H), 6.00 (s, 2H), 6.82–7.44 (m, 8H). ^{13}C NMR (DMSO-d_6): δ 27.09, 69.91, 73.50, 77.74, 92.23, 94.98, 108.83, 120.69, 120.79, 123.20, 123.93, 128.00, 128.21, 129.79, 140.97, 177.50, 206.67. HRMS: 187.0633 (calcd) 187.0632 (found).

4.1.13. 1,2-Dihydro-1-hydroxy-1-(phenylmethyl)-2-oxacenaphthene 26. A solution of acenaphthenequinone (0.182 g, 1.0 mmol), benzyl bromide (0.265 g, 1.55 mmol), indium powder (0.120 g, 1.05 mmol) and sodium iodide (0.232 g, 1.55 mmol) in 3 mL DMF was ultrasonicated for 3 min. The usual work up followed by purification of the product by silica gel column using 10% ethyl acetate in hexane as eluent afforded (0.247 g, 90%) as a colorless solid; recrystallized from dichloromethane/hexane solvent system (mp: 155–157°C). IR (KBr) $\nu_{\max}$: 3454, 3056, 3029, 2921, 1721, 1613, 1506, 1438, 1344, 1276, 1074, 1013, 784, 703, 542 cm^{-1}. ^{1}H NMR: δ 2.96 (s, 1H), 3.10 (d, J=13.3 Hz, 1H), 3.35 (d, J=13.3 Hz, 1H), 6.98–8.06 (m, 11H). ^{13}C NMR: δ 44.45, 80.32, 121.21, 121.93, 125.24, 126.75, 127.71, 128.09, 128.34, 130.43, 130.61, 131.75, 134.57, 138.72, 141.33, 204.84. Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.19; H, 5.14. Found: C, 83.02; H, 5.46.

4.1.14. 9,10-Dihydro-9-hydroxy-9-(phenylmethyl)-10-oxophenanthrene 27. Yield (90%), colorless solid (mp: 149–151°C). IR (KBr) $\nu_{\max}$: 3480, 3068, 3030, 2918, 1670, 1595, 1445, 1276, 1220, 1095, 1008, 902, 758, 727, 696 cm^{-1}. ^{1}H NMR: δ 2.94 (d, J=13.3 Hz, 1H), 3.01 (d, J=13.3 Hz, 1H), 3.97 (s, 1H), 6.80–6.81 (m, 2H), 7.12–7.14 (m, 3H), 7.33–7.42 (m, 3H), 7.58–7.80 (m, 2H), 7.86–7.91 (m, 3H). ^{13}C NMR: δ 51.12, 80.13, 123.06, 123.77, 126.40, 126.89, 127.36, 127.63, 128.08, 128.32, 128.71, 129.05, 130.19, 134.55, 134.82, 137.51, 140.05, 202.26. Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.97; H, 5.36. Found: C, 84.02; H, 5.64.

4.1.15. 1,2-Dihydro-1-(phenylcarboxymethyl)-1-hydroxy-2-oxacenaphthene 28. A mixture of acenaphthenequinone (0.182 g, 1.0 mmol), phenacyl bromide (0.308 g, 1.55 mmol), indium powder (0.120 g, 1.05 mmol) and sodium iodide (0.232 g, 1.55 mmol) in 3 mL DMF was ultrasonicated for 5 min. The usual work up followed by purification of the product on silica gel column using 10% ethyl acetate in hexane as eluent afforded **28** (0.281 g, 93%) as a pale yellow semi-solid.

Spectral data for **28**: IR (KBr) $\nu_{\max}$: 3420, 3060, 2928, 1735, 1688, 1600, 1357, 1222, 1054, 1027, 791 cm^{-1}. ^{1}H NMR: δ 3.55 (d, J=17.4 Hz, 1H), 3.90 (d, J=17.4 Hz, 1H), 4.61 (s, 1H), 7.25–8.14 (m, 11H). ^{13}C NMR: δ 44.32, 78.14, 120.80, 122.50, 125.66, 128.27, 128.40, 128.70, 130.84, 130.91, 131.90, 133.79, 136.43, 139.83, 141.45, 198.84, 202.18. HRMS: 302.0943 (calcd) 302.0956 (found).

4.1.16. 9,10-Dihydro-9-hydroxy-9-(phenylcarboxymethyl)-10-oxophenanthrene 29. Yield (95%), colorless solid; recrystallized from dichloromethane/hexane solvent system (mp: 73–75°C).

Spectral data for **29**: IR (KBr) ν_{max}: 3474, 3070, 2935, 1704, 1676, 1600, 1465, 1297, 1209, 1013, 764, 697, 589 cm^{-1}. ^{1}H NMR: δ 3.17 (d, J=14.8 Hz, 1H), 3.61 (d, J=14.8 Hz, 1H), 4.48 (s, 1H), 7.24–7.91 (m, 13H). ^{13}C NMR: δ 51.26, 78.54, 123.02, 124.40, 126.27, 128.01, 128.51, 128.71, 128.78, 129.36, 129.57, 129.60, 133.31, 134.60, 136.77, 137.20, 140.12, 196.49, 202.15. HRMS: 328.1099 (calcd) 328.1093 (found).

4.1.17. 1,2-Dihydro-1-(methoxycarbonylmethyl)-1-hydroxy-2-oxacenaphthene 30. A mixture of acenaphthenequinone (0.182 g, 1.0 mmol), ethyl bromoacetate (0.259 g, 1.55 mmol), indium powder (0.120 g, 1.05 mmol) and sodium iodide (0.232 g, 1.05 mmol) in 3 mL DMF was ultrasonicated for 6 min. The usual work up followed by purification of the product on silica gel column using 10% ethyl acetate in hexane as eluent afforded **30** (0.162 g, 60%) as a colorless solid; recrystallized from dichloromethane/hexane solvent system (mp: 169–171°C).

Spectral data for **30**: IR (KBr) ν_{max}: 3440, 3056, 2982, 2928, 1737, 1714, 1607, 1202, 1027, 791 cm^{-1}. ^{1}H NMR: δ 1.03 (t, J=7.0 Hz, 3H), 3.02 (s, 2H), 4.02 (q, J=7.0 Hz, 2H), 4.51 (s, 1H), 7.62–8.12 (m, 6H). ^{13}C NMR: δ 13.88, 41.20, 61.05, 76.66, 120.63, 122.45, 125.79, 128.41, 128.76, 131.94, 138.98, 141.48, 170.67, 202.56. Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.80; H, 5.00.

4.1.18. 9,10-Dihydro-9-hydroxy-9-(3-ethoxycarbonylmethyl)-10-oxophenanthrene 31. Yield (60%), colorless solid; recrystallized from dichloromethane/hexane solvent system (mp: 175–178°C).

Spectral data for **31**: IR (KBr) ν_{max}: 3467, 3070, 2982, 1735, 1701, 1607, 1458, 1372, 1297, 1202, 1135, 1108, 1040, 946, 771 cm^{-1}. ^{1}H NMR: δ 1.16 (t, J=7.1 Hz, 3H), 2.73–2.84 (m, 2H), 3.98–4.08 (m, 3H), 7.38–7.93 (m, 8H). ^{13}C NMR: δ 14.22, 48.92, 60.97, 77.78, 123.21, 124.34, 126.33, 127.87, 128.80, 129.11, 129.52, 134.93, 137.08, 139.58, 168.75, 201.97. Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 73.02; H, 5.48.

4.1.19. 1,2-Dihydro-1-(1-ethoxycarbonyl-2-propenyl)-1-hydroxy-2-oxacenaphthene 32. Yield (87%), pale yellow semi-solid was found to be a diastereomeric mixture in the ratio 1:3 as determined by the ^{1}H NMR.

Spectral data for **32**: IR (neat) ν_{max}: 3443, 3055, 2980, 2899, 1732, 1713, 1632, 1489, 1432, 1370, 1314, 1251, 1183, 1014, 933, 833, 777, 671 cm^{-1}. ^{1}H NMR (1:3 ratio of diastereomers, * denotes minor isomer): δ 0.81* (t, J=7.0 Hz, 0.75H), 1.07 (t, J=7.0 Hz, 2.25H), 3.64 (d, J=9.5 Hz, 0.75H), 3.80–3.84* (m, 0.25H), 3.85–3.90* (m, 0.5H), 4.03–4.10 (m, 1.5H), 4.58 (s, exchangeable with D_2O), 4.63 (s, exchangeable with D_2O), 5.10–5.23 (m, 2H), 5.76–5.82 (m, 0.75H), 5.97–6.03* (m, 0.25H), 7.58–8.05 (m, 6H). ^{13}C NMR: δ 13.42, 13.78, 56.12, 56.64, 60.99, 61.14, 79.19. 79.39, 121.06, 121.49, 121.74, 121.86, 122.24, 125.51, 125.62, 128.04, 128.22, 128.44, 129.82, 130.15, 130.42, 130.75, 131.12, 131.65, 131.74, 132.42, 136.94, 137.81, 141.70, 170.62, 171.34, 202.57. HRMS: 296.1049 (calcd) 296.1051 (found).

4.1.20. 9,10-Dihydro-9-hydroxy-9-(3-ethoxycarbonyl-2-propenyl)-10-oxophenanthrene 33. Yield (68%), pale yellow semi-solid.

Spectral data for **33**: IR (neat) ν_{max}: 3475, 3071, 2983, 1722, 1695, 1595, 1452, 1365, 1272, 1197, 1041, 761, 730 cm^{-1}. ^{1}H NMR: δ 1.19 (t, J=7.0 Hz, 3H), 2.49–2.67 (m, 2H), 4.09–4.16 (m, 3H), 5.54 (d, J=15.6 Hz, 1H), 6.69–6.74 (m, 1H), 7.36–8.12 (m, 8H). ^{13}C NMR: δ 14.16, 46.88, 60.13, 78.99, 123.17, 125.23, 126.27, 127.40, 128.40, 128.51, 129.23, 130.32, 135.19, 135.75, 137.39, 139.37, 141.15, 165.46, 179.94, 202.14. HRMS: 322.1205 (calcd) 322.1220 (found).

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