

Clay-mediated reaction of indoles with cyclohexane-1,3-diones: an expedient route to indolylcyclohexenones

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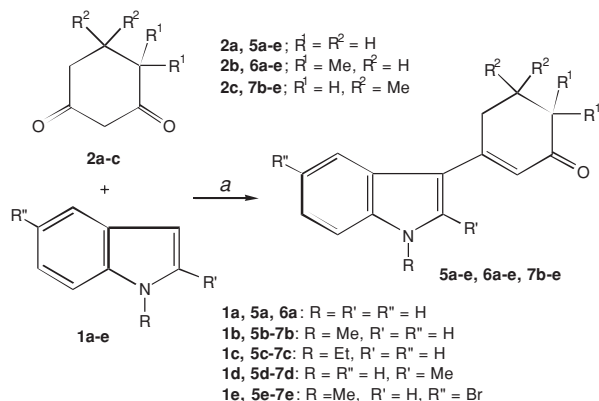
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Indoles (**1a–e**) react with cyclohexane-1,3-diones (**2a–c**) on montmorillonite K10 clay at 60–70 °C to furnish the corresponding 3-(3'-indolyl)cyclohex-2-en-1-ones (**5a–e**, **6a–e**, **7b–e**) in 27–75% yields in 2.5–4 h.

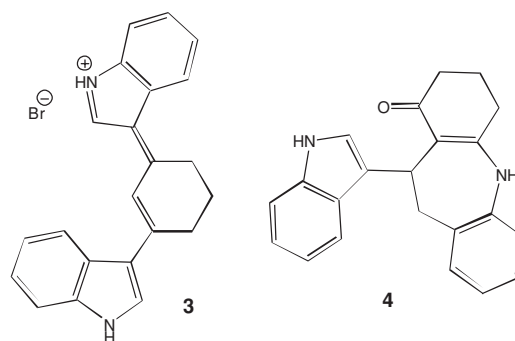
Keywords: indoles, cyclohexane-1,3-diones, clay, indolylcyclohexenones

The acid-catalysed reaction of indoles with aldehydes and ketones to form diindolylalkanes is well documented.^{1–3} In contrast, only limited studies have been carried out on the reaction of indoles with cyclic diketones. Cyclohexane-1,3-diones are conspicuous in this regard, since their reactions with indoles are reported to lead to non-uniform and even contradictory results. Thus, while indole (**1a**) was initially reported to react with cyclohexane-1,3-dione (**2a**) in refluxing aqueous hydrobromic acid to furnish a bisindolic cyclohexene hydrobromide (**3**),⁴ a subsequent reinvestigation⁵ demonstrated the sole product to be the hemihydrobromide hydrate of an indolylhexahydrodibenzazepinone (**4**). On the other hand, the reaction of indole and alkylindoles with **2a** and dimedone in dichloromethane in the cold using boron trifluoride etherate as the catalyst furnished either or both of the indolylidibenzazepinones and indolylcyclohexenones.^{6–8} The nature of the acidic catalyst thus appeared to play a significant role in determining the course of these reactions. In continuation of our interest in the use of the eco-friendly acidic clay montmorillonite K10 in the study of acid-catalyzed reactions of indoles,^{9–10} we investigated the reaction of indoles (**1a–e**) with **2a**, its 4,4-dimethyl derivative (**2b**) and the 5,5-dimethyl analogue dimedone (**2c**) on this commercially available clay. The uniform outcome of our experiments is presented in this paper.



a: Montmorillonite K10 clay, 60–70°C, 2.5–4 h, 27–75%

When an equimolar mixture of indole (**1a**) and **2a**, adsorbed on K10 clay, was heated at 60–70 °C, the indole was consumed (TLC) in 4 h. The sole reaction product, which underwent considerable decomposition, was isolated in 27% yield by leaching the clay with a suitable solvent, followed by preparative TLC. It was identified spectroscopically to be 3-(3'-indolyl)cyclohex-2-en-1-one (**5a**).⁶ Before checking the generality of the reaction, it was repeated using two and four equivalents of indole separately, which neither expedited the reaction, nor resulted in any other product. The use of



Scheme 1

equimolar proportions of the reactants was, therefore, the choice. Also, when subjected to microwave irradiation, the same product was isolated but in a considerably lower yield. This alternate source of heating was therefore not adopted.

Accordingly, the reaction was extended to 1-methyl, 1-ethyl, 2-methyl and 5-bromo-1-methylindoles (**1b–e**, respectively) with equimolar proportions of **2a–c** separately on the clay at 60–70 °C. Indole behaved somewhat differently from *N*-alkylindoles. Thus, indole reacted with **2b** to furnish the indolylcyclohexenone **6a** (27%) along with a minor product (13%) which we could not identify. With **2c**, the reaction of indole took place (TLC), but no product could be isolated on leaching the clay. In all other cases, the respective 3-(3'-indolyl)cyclohex-2-en-1-ones (**5a–e**, **6a–e**, **7b–e**) were obtained in 40–75% yields in 2.5–4 h (Scheme 1, Table 1).

All the products were characterised by thorough spectroscopic analyses (IR, ¹H and ¹³C NMR, LR EI-MS, and, for new compounds, HR FAB-MS or elemental analysis). The presence of a ¹H NMR signal at δ 5.78–6.44 (1H, s, H-2) and two non-protonated (DEPT 135) carbon signals at δ 198.6–203.6 (CO) and δ 153.2–158.9 (C-3), in addition to those expected for the 3-indolyl and the 3-substituted cyclohex-2-en-1-one rings in the spectra of all the products, documented the presence of a 3-(3'-indolyl)cyclohex-2-en-1-one skeleton in all. The products also displayed a strong IR absorption band at 1624–1646 cm^{–1}, typical of the conjugated enone chromophore common to all the products. Although **7d** showed ¹H and ¹³C spectral data similar to those reported⁸ earlier for it, its observed m.p., 194–196 °C, was widely different from the reported m.p., 40 °C. Therefore **7d** was subjected to elemental analysis, which gave satisfactory results, thereby confirming its identity.

It is noteworthy that no reaction took place between **2a** and 3-methylindole or 1,3-dimethylindole. Also, 5-bromo, 5-methoxy and 5-nitroindoles reacted separately with **2a**, but no product could be isolated from any of these reactions. These results suggest that a free 3-position of the indole ring is crucial to the success of the reaction and that 1- or 2-alkylation of the indole ring enhances the yields of the products.

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Table 1 Formation of 3-(3'-indolyl)cyclohex-2-en-1-ones^a

Dione		2a		2b			2c		
Indole	Pdt.	Yield (%) ^b ; Time (h)	M.p. (°C)	Pdt.	Yield (%) ^b ; Time (h)	M.p. (°C)	Pdt.	Yield (%) ^b ; Time (h)	M.p. (°C)
1a	5a	27; 4	176 ^d	– ^e	6a	27; 3	218–220	(Decomposition)	
1b	5b	60; 4	108–110	6b	13; 3	240–242	7b	60; 3.5	124–126
1c	5c	47; 3	182–184	6c	75; 3	148–150	7c	45; 3	120–122
1d	5d ^c	45; 3.5	200–202 ^f	6d	64; 2.5	124–126	7d ^c	40; 4	194–196 ^g
1e	5e	50; 3	168–170	6e	51; 3	200–202	7e	48; 4	180–182
					65; 4	130–132			

^aFrom 1a–e and 2a–c on montmorillonite K10 clay at 60–70 °C.^bUnoptimised yields of isolated, pure products.^cCrystallised from CH₂Cl₂.^dLit.⁶ m.p. 168–170 °C.^eUnidentified minor product.^fLit.⁷ m.p. 170 °C.^gLit.⁸ m.p. 40 °C. Product is fully characterised – see Experimental.

To conclude: we have documented the versatility of montmorillonite K10 clay in bringing about an expedient synthesis of 3-(3'-indolyl)cyclohex-2-en-1-ones, which are not in general obtainable with the use of conventional protic or Lewis acids. Recent findings^{11–14} that a number of 3-arylcyclohex- and -cyclopent-2-en-1-ones display useful liquid crystalline properties impart additional importance to the present work.

Experimental

Melting points were measured on a Toshniwal apparatus. IR spectra (nujol) were recorded on a Nicolet Impact 410 FT-IR spectrophotometer, ¹H (500 MHz) and ¹³C (125 MHz) NMR, DEPT 135 and for **6a**. HMQC and HMBC spectra (*d*₆-DMSO) on a Bruker DRX 500 NMR spectrometer. LR EI-MS on a AEI MS30 or a JEOL JMS-AX505HA mass spectrometer and HR FAB-MS (+ve mode, using *m*-nitrobenzyl alcohol as liquid matrix) on a JEOL JMS-700 MStation mass spectrometer. All new compounds showed correct results in elemental analysis / HR FAB-MS. TLCs, both analytical and preparative, were carried out on silica gel G (Merck, India) plates. Petrol refers to petroleum ether, b.p. 60–80 °C. Montmorillonite K10 clay was purchased from Fluka.

Reaction of indoles (1a–e) with 2a–c: general procedure: A solution of the indole (**1a–e**; 1 mmol) and the cyclohexane-1,3-dione (**2a–c**; 1.2 mmol) in CH₂Cl₂ (5 ml; in the case of dimedone, a few drops of methanol were also needed) was adsorbed on montmorillonite K10 clay (2 g) and the solvent was allowed to evaporate off at room temperature. The clay containing the reactants was then heated in an oven at 60–70 °C until the reaction was complete (monitored by TLC). The clay was leached with EtOAc (3 × 15 ml), the solvent was distilled off and the product(s) were separated from the resulting residue by prep. TLC and purified by crystallisation from petrol–CH₂Cl₂, unless otherwise stated. All the products were yellow crystalline compounds and identified spectroscopically, as stated in the text. Melting points are given in Table 1. The spectroscopic and analytical data of the new compounds are presented below.

3-(1'-Methyl-3'-indolyl)cyclohex-2-en-1-one (5b): IR ν_{\max} (cm⁻¹) 1639, 1586, 1527, 751; NMR: δ_{H} 7.96 (1H, s), 7.85 (1H, d, *J* = 8 Hz), 7.50 (1H, d, *J* = 8 Hz), 7.25 (1H, t, *J* = 8 Hz), 7.19 (1H, t, *J* = 7.5 Hz), 6.43 (1H, s), 3.80 (3H, s), 2.79 (2H, t, *J* = 5.5 Hz), 2.34 (2H, t, *J* = 6.5 Hz), 2.01 (2H, pentuplet, *J* = 6 Hz); δ_{C} 198.8 (CO), 156.1 (C-3), 138.8, 125.6 and 113.9 (all Ar-C), 133.8, 123.2, 122.0, 121.3, 120.6 and 111.6 (5 × Ar-CH and 1 × olefinic CH), 37.8, 28.6 and 23.1 (all CH₂); EI-MS: *m/z* 225 (M⁺; 100%), 197 (97), 184 (12), 169 (46), 168 (51), 158 (21), 145 (19), 127 (12). Found: C, 79.85; H, 6.69; N, 6.20. C₁₅H₁₅NO requires C, 80.0; H, 6.66; N, 6.22 %.

3-(1'-Ethyl-3'-indolyl)cyclohex-2-en-1-one (5c): IR ν_{\max} (cm⁻¹) 1633, 1593, 1527, 751; NMR: δ_{H} 7.855 (1H, s), 7.66 (1H, d, *J* = 8 Hz), 7.38 (1H, d, *J* = 8 Hz), 7.06 (1H, t, *J* = 7.5 Hz), 6.99 (1H, t, *J* = 7.5 Hz), 6.25 (1H, s), 4.05 (2H, q, *J* = 7 Hz), 2.63 (2H, t, *J* = 6 Hz), 2.165 (2H, t, *J* = 6 Hz), 1.83 (2H, pentuplet, *J* = 6 Hz), 1.19 (3H, t, *J* = 7 Hz); δ_{C} 198.8 (CO), 156.2 (C-3), 137.8, 125.8 and 114.2 (all Ar-C), 132.3, 123.1, 122.0, 121.4, 120.6 and 111.6 (5 × Ar-CH and 1 × olefinic CH), 41.6, 37.9, 28.7 and 23.2 (all CH₂), 16.0 (CH₃); EI-MS: *m/z* 239 (M⁺; 100%), 211 (88), 197 (10), 196 (13), 183 (27), 182 (21), 168 (18), 167 (16), 159 (14), 154 (12). Found: C, 75.65; H, 7.09; N, 5.83. C₁₆H₁₇NO requires C, 75.89; H, 7.11; N, 5.86 %.

3-(5'-Bromo-1'-methyl-3'-indolyl)cyclohex-2-en-1-one (5e): IR ν_{\max} (cm⁻¹) 1633, 1590, 1527, 802; δ_{H} 7.84 (1H, s), 7.74 (1H, s), 7.325 (1H, d, *J* = 8.5 Hz), 7.19 (1H, d, *J* = 8.5 Hz), 6.125 (1H, s), 3.625 (3H, s), 2.595 (2H, t, *J* = 5.5 Hz), 2.16 (2H, t, *J* = 6 Hz), 1.83 (2H, pentuplet, *J* = 6 Hz); δ_{C} 198.9 (CO), 155.6 (C-3), 137.5, 127.2, 114.8, 113.5 (all Ar-C), 134.9, 125.7, 123.3, 120.9 and 113.8 (4 × Ar-CH and 1 × olefinic CH), 37.8, 28.7 and 23.1 (all CH₂), 34.0 (CH₃); EI-MS: *m/z* 305 (M⁺; 100%), 303 (100), 277 (42), 275 (51), 249 (22), 248 (20), 247 (22), 246 (19), 168 (55), 153 (21). Found: C, 59.08; H, 4.55; N, 4.58. C₁₅H₁₄BrNO requires C, 59.21; H, 4.60; N, 4.60 %.

6,6-Dimethyl-3-(3'-indolyl)cyclohex-2-en-1-one (6a): IR ν_{\max} (cm⁻¹): 3208, 1624, 1614, 1590, 1583, 1567, 749 cm⁻¹; NMR: δ_{H} 11.79 (1H, s, NH), 7.95 (1H, d, *J* = 2 Hz, H-2'), 7.83 (1H, d, *J* = 8 Hz, H-4'), 7.46 (1H, d, *J* = 8 Hz, H-7'), 7.18 (1H, dt, *J*₁ = 7.5 Hz, *J*₂ = 1 Hz, H-6'), 7.13 (1H, dt, *J*₁ = 7.5 Hz, *J*₂ = 1 Hz, H-5'), 6.36 (1H, s, H-2), 2.86 (2H, t, *J* = 6 Hz, H₂-4), 1.87 (2H, t, *J* = 6 Hz, H₂-5), 1.06 (6H, s, 2 × CH₃); δ_{C} 203.6 (CO), 154.9 (C-3), 138.3 (C-7'a), 129.7 (CH-2'), 125.3 (C-3'a), 123.0 (CH-6'), 121.7 (CH-5'), 121.1 (CH-4'), 119.0 (CH-2), 114.7 (C-3'), 113.3 (CH-7'), 40.52 (C-6), 36.6 (CH₂-5), 25.9 (CH₂-4), 25.2 (2 × CH₃); EI-MS: *m/z* 239 (M⁺; 39%), 183 (100), 167 (6), 155 (22), 154 (23), 149 (13), 127 (9), 57 (10); HR FAB-MS: found *m/z* 240.1397; calcd. for C₁₆H₁₈NO [M+H]⁺: 240.1388.

6,6-Dimethyl-3-(1'-methyl-3'-indolyl)cyclohex-2-en-1-one (6b): IR ν_{\max} (cm⁻¹) 1637, 1588, 1527, 751 cm⁻¹; NMR: δ_{H} 7.955 (1H, s), δ 7.85 (1H, d, *J* = 8 Hz), 7.51 (1H, d, *J* = 8 Hz), 7.25 (1H, t, *J* = 7.5 Hz), 7.18 (1H, t, *J* = 7.5 Hz), 6.34 (1H, s), 3.81 (3H, s), 2.83 (2H, t, *J* = 5.5 Hz), 1.87 (2H, t, *J* = 6 Hz), 1.06 (6H, s); δ_{C} 203.5 (CO), 154.4 (C-3), 138.7, 125.7 and 113.7 (all Ar-C), 133.6, 123.1, 122.0, 121.3, 119.0 and 111.6 (5 × Ar-CH and 1 × olefinic CH), 40.52 (C), 36.5 and 25.9 (both CH₂), 33.7 (N-CH₃), 25.2 (2 × CH₃); EI-MS: *m/z* 253 (M⁺; 35%), 197 (100), 169 (32), 168 (30). Found: C, 80.48; H, 7.48; N, 5.56. C₁₇H₁₉NO requires C, 80.63; H, 7.51; N, 5.53 %.

6,6-Dimethyl-3-(1'-ethyl-3'-indolyl)cyclohex-2-en-1-one (6c): IR ν_{\max} (cm⁻¹) 1645, 1590, 1533, 744; NMR: δ_{H} 7.845 (1H, s), 7.67 (1H, d, *J* = 8 Hz), 7.38 (1H, d, *J* = 8 Hz), 7.05 (1H, t, *J* = 7.5 Hz), 6.99 (1H, t, *J* = 7.5 Hz), 6.16 (1H, s), 4.05 (2H, q, *J* = 7 Hz), 2.67 (2H, t, *J* = 6 Hz), 1.70 (2H, t, *J* = 6 Hz), 1.19 (3H, t, *J* = 7 Hz), 0.885 (6H, s); δ_{C} 203.5 (CO), 154.5 (C-3), 137.7, 125.8 and 113.9 (all Ar-C), 132.1, 123.1, 122.0, 121.4, 119.0 and 111.6 (5 × Ar-CH and 1 × olefinic CH), 40.52 (C), 41.6, 36.5 and 25.9 (all CH₂), 25.2 (2 × CH₃), 16.0 (CH₃); EI-MS: *m/z* 267 (M⁺; 49%), 211 (100), 196 (7), 183 (22), 182 (11), 169 (12), 168 (12), 149 (30). Found: C, 80.83; H, 7.83; N, 5.27. C₁₈H₂₁NO requires C, 80.90; H, 7.86; N, 5.24 %.

6,6-Dimethyl-3-(2'-methyl-3'-indolyl)cyclohex-2-en-1-one (6d): IR ν_{\max} (cm⁻¹) 3270, 1633, 1613, 1593, 1566, 738; NMR: δ_{H} 11.33 (1H, s), 7.45 (1H, d, *J* = 8 Hz), 7.14 (1H, d, *J* = 8 Hz), 6.89 (1H, t, *J* = 7.5 Hz), 6.85 (1H, t, *J* = 7.5 Hz), 5.78 (1H, s), 2.70 (2H, t, *J* = 6 Hz), 2.32 (3H, s), 1.715 (2H, t, *J* = 6 Hz), 0.91 (6H, s); δ_{C} 203.4 (CO), 157.1 (C-3), 137.5, 136.3, 127.1 and 112.1 (all Ar-C), 122.6, 122.0, 120.9, 120.2 and 112.0 (4 × Ar-CH and 1 × olefinic CH), 40.53 (C), 37.4 and 28.0 (both CH₂), 25.2 (2 × CH₃), 15.0 (CH₃); EI-MS: *m/z* 253 (M⁺; 90%), 238 (4), 210 (6), 197 (100), 169 (73), 168 (69), 154 (33), 127 (9). Found: C, 80.51; H, 7.53; N, 5.55. C₁₇H₁₉NO requires C, 80.63; H, 7.51; N, 5.53 %.

6,6-Dimethyl-3-(5'-bromo-1'-methyl-3'-indolyl)cyclohex-2-en-1-one (6e): IR ν_{\max} (cm⁻¹) 1636, 1590, 1522, 797; NMR: δ_{H} 7.82 (1H, s), 7.74 (1H, s), 7.32 (1H, d, *J* = 8.5 Hz), 7.19 (1H, d, *J* = 8.5 Hz), 6.03 (1H, s), 3.62 (3H, s), 2.63 (2H, t, *J* = 6 Hz), 1.69 (2H, t, *J* = 6

Hz), 0.87 (6H, s); δ_{C} 203.6 (CO), 153.9 (C-3), 137.5, 127.2, 114.7 and 113.3 (all Ar-C), 134.7, 125.6, 123.3, 119.3 and 113.8 ($4 \times$ Ar-CH and $1 \times$ olefinic CH), 40.51 (C), 36.4 and 26.0 (both CH_2), 33.9 ($N\text{-CH}_3$), 25.1 ($2 \times \text{CH}_3$); EI-MS: m/z 333 (M^+ ; 47%), 331 (47), 277 (98), 275 (100), 249 (20), 247 (21), 196 (18), 168 (46), 167 (20), 149 (34). Found: C, 61.36; H, 5.40; N, 4.20. $\text{C}_{17}\text{H}_{18}\text{BrNO}$ requires C, 61.44; H, 5.42; N, 4.22 %.

5,5-Dimethyl-3-(1'-methyl-3'-indolyl)cyclohex-2-en-1-one (7b): IR ν_{max} (cm^{-1}) 1646, 1593, 1527, 731; NMR: δ_{H} 7.99 (1H, s), 7.85 (1H, d, $J = 8$ Hz), 7.50 (1H, d, $J = 8$ Hz), 7.25 (1H, t, $J = 7.5$ Hz), 7.18 (1H, t, $J = 7.5$ Hz), 6.43 (1H, s), 3.80 (3H, s), 2.68 (2H, s), 2.215 (2H, s), 1.04 (6H, s); δ_{C} 198.8 (CO), 153.8 (C), 138.8, 125.7 and 114.2 (all Ar-C), 133.8, 123.2, 122.0, 121.4, 119.3 and 111.7 ($5 \times$ Ar-CH and $1 \times$ olefinic CH), 40.4 (C), 51.4 and 42.4 (both CH_2), 33.7 ($N\text{-CH}_3$), 28.9 ($2 \times \text{CH}_3$); EI-MS: m/z 253 (M^+ ; 100%), 238 (16), 225 (12), 210 (15), 197 (73), 169 (33), 168 (36). Found: C, 80.45; H, 7.49; N, 5.50. $\text{C}_{17}\text{H}_{19}\text{NO}$ requires C, 80.63; H, 7.51; N, 5.53 %.

5,5-Dimethyl-3-(1'-ethyl-3'-indolyl)cyclohex-2-en-1-one (7c): IR ν_{max} (cm^{-1}) 1633, 1588, 1523, 739; NMR: δ_{H} 8.06 (1H, s), 7.86 (1H, d, $J = 8$ Hz), 7.56 (1H, d, $J = 8$ Hz), 7.24 (1H, t, $J = 7.5$ Hz), 7.18 (1H, t, $J = 7.5$ Hz), 6.43 (1H, s), 4.23 (2H, q, $J = 7$ Hz), 2.72 (2H, s), 2.23 (2H, s), 1.38 (3H, t, $J = 7$ Hz), 1.06 (6H, s); δ_{C} 198.9 (CO), 153.9 (C-3), 137.8, 125.9 and 114.4 (all Ar-C), 132.3, 123.2, 122.0, 121.5, 119.3 and 111.6 ($5 \times$ Ar-CH and $1 \times$ olefinic CH), 51.4, 41.6 and 42.4 (all CH_2), 33.7 (C), 28.9 ($2 \times \text{CH}_3$), 16.0 (CH_3); EI-MS: m/z 267 (M^+ ; 100%), 252 (17), 239 (16), 224 (16), 211 (71), 196 (9), 183 (20), 182 (13), 168 (14), 167 (13), 149 (11). Found: C, 80.71; H, 7.84; N, 5.26. $\text{C}_{18}\text{H}_{21}\text{NO}$ requires C, 80.90; H, 7.86; N, 5.24 %.

5,5-Dimethyl-3-(5'-bromo-1'-methyl-3'-indolyl)cyclohex-2-en-1-one (7e): IR ν_{max} (cm^{-1}) 1631, 1589, 1526, 793; NMR: δ_{H} 7.86 (1H, s), 7.75 (1H, d, $J = 1.5$ Hz), 7.33 (1H, d, $J = 9$ Hz), 7.20 (1H, dd, $J_1 = 9$ Hz, $J_2 = 1.5$ Hz), 6.13 (1H, s), 3.62 (3H, s), 2.50 (2H, s), 2.05 (2H, s), 0.87 (6H, s); δ_{C} 198.9 (CO), 153.2 (C-3), 137.5, 127.3, 114.8 and 113.80 (all Ar-C), 134.9, 125.7, 123.3, 119.7 and 113.86 ($4 \times$ Ar-CH and $1 \times$ olefinic CH), 33.8 (C), 51.3 and 42.4 (both CH_2), 33.9 ($N\text{-CH}_3$), 28.8 ($2 \times \text{CH}_3$); EI-MS: m/z 333 (M^+ ; 99%), 331 (100), 318 (9), 316 (9), 305 (13), 303 (14), 290 (16), 288 (13), 277 (51), 275 (52), 249 (34), 247 (28), 236 (15), 224 (7), 223 (8), 209 (7), 196 (12), 168 (67), 167 (25), 153 (13), 139 (9), 129 (14), 127 (14), 105 (18); HR FAB-MS: found m/z 331.0557; calcd. for $\text{C}_{17}\text{H}_{18}^{79}\text{BrNO}$ M^+ : 331.0572.

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