

TABLE 1—DETERMINATION OF BENZYLTHIURONATES

Benzylthiuronium	Calculated	Equivalent Weight	Found*	Deviation (%)**
Chloride	202.63		202.94	+0.15
Oxalate	211.17		211.75	+0.27
Propionate	240.21		239.65	-0.23
n-Butyrate	254.23		253.13	-0.44
Monochloroacetate	260.65		261.45	+0.31
n-Valerate	268.24		268.00	-0.09
Benzoate	288.21		289.10	+0.31
p-Aminobenzoate	303.23		302.14	-0.36
Salicylate	304.21		305.54	+0.44
Cinnamate	314.23		312.75	-0.47
Benzene sulphonate	324.27		322.95	-0.33
p-Toluene sulphonate	338.29		339.42	+0.31
Sulphanilate	339.29		340.35	+0.41
p-Chloro benzene sulphonate	358.72		359.58	+0.24
Naphthalene-1-sulphonate	374.28		373.56	-0.19

\* Average of two or three determinations.

\*\* Reported by Berger.

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### Studies on Morphine and Related Compounds : Synthesis of 2,5,9-Trimethyl and 2-Ethyl-5,9-Dimethyl-3,4 : 6,7-Dibenzomorphan

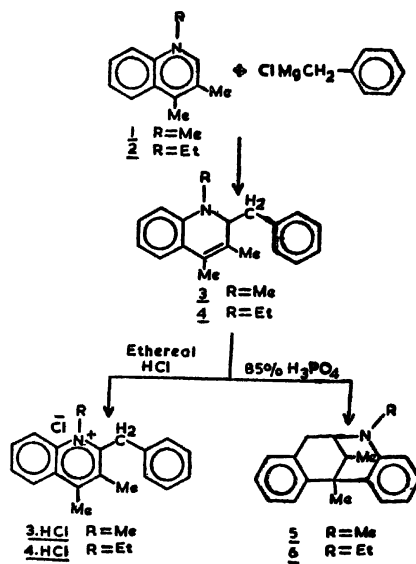
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**2,5,9**-trimethyl-3,4 : 6,7-dibenzomorphan (**5**) and 2-ethyl-5,9-dimethyl-3,4 : 6,7-dibenzomorphan (**6**) were synthesised by condensing 1,3,4-trimethyl quinolinium iodide (**1**) and 1-ethyl-3,4-dimethyl quinolinium iodide (**2**) separately with benzyl magnesium chloride under Freund's reaction conditions<sup>1</sup> followed with subsequent cyclisation of corresponding 1,2-dihydro products (**3**) and (**4**) with 85%  $H_3PO_4$ . The purity of these compounds was ascertained through

titic examination. The structures of **3** and **4** as hydrochlorides, **5** and **6** as bases were established through elemental and spectral studies.



### Experimental

Melting points are uncorrected, spectral studies were done at chemical laboratories, University of Rajasthan, Jaipur. Nmr spectra were recorded on Perkin-Elmer R12B spectrometer using TMS as internal reference standard. (Chemical shifts expressed in  $\delta$  ppm). Microanalyses were done at CDRI, Lucknow.

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2,5,9-Trimethyl-3,4 : 6,7-Dibenzomorphan (5)

To a suspension of 1,3,4-trimethyl quinolinium iodide (1) (5.98g., 0.03M) in absolutely dry ether, benzyl magnesium chloride (benzyl chloride 3.78g., 0.3M; magnesium 0.72g, 0.03M; ether 50 ml) was added within 15 min. with continuous stirring. The reaction mixture was further stirred continuously for 4 hr at 10-15° and another 4 hr at 30-40°. The reaction mixture was left overnight. This was treated in usual manner<sup>4</sup>. and was distilled at 140-50°/0.3 mm., when an oily substance 3 was obtained [Yield 2.10g., (40%)]. As the dihydro compounds are generally unstable, a small portion of it was converted to 3.HCl for identification (m.p. 125°) and rest of the oily compound was subjected to cyclization with 85% H<sub>3</sub>PO<sub>4</sub> at 140-60° for 48 hr. The reaction mixture on usual treatment<sup>4</sup> gave a crude product which was distilled under reduced pressure 160-65°/0.3 mm. to give a white solid base 5 and was crystallized with acetone-pet. ether mixture, yield, 0.672g., (32%), m.p. 135°. 5 was converted to its hydrochloride salt (m.p. 120°), foliage green picrate (m.p. 160-65°) and in small white needles of methiodide (m.p. 242-45°). The purity of 5 was ascertained through tlc by using Silica Gel-G as adsorbent and acetone-pet-ether (1 : 9) as mobile phase

Rf=0.62.

Analyses :

Found C<sub>19</sub>H<sub>21</sub>N (5)  
 C, 86.58 ; H, 7.86 ; N, 5.58%.  
 Calcd. C, 86.69 ; H, 7.98 ; N, 5.33%.

2-Ethyl-5,9-Dimethyl-3,4 : 6,7-Dibenzomorphan (6)

On similar lines as followed in the synthesis of 5, 1-ethyl-3,4-dimethyl quinolinium iodide (2)(6.26g, 0.02M) was reacted with benzyl magnesium chloride (benzyl chloride 3.795g., 0.03M; Magnesium 0.72g., 0.03M; ether 50 ml) and the dihydro compound 4 b.p. 150-155°/0.3 mm, Yield 1.98g (38%) was obtained. A small portion of 4 was converted to its hydrochloride salt 4.HCl (m.p. 120°) and the rest was cyclized with 85% H<sub>3</sub>PO<sub>4</sub> at 140-60° for 48 hr. The crude base thus obtained was distilled at 162-65°/0.3 mm to give a white solid 6. It was crystallised from acetone-pet ether mixture m.p. 140°, Yield 0.594 g (30%). 6 was converted to its hydrochloride salt (m.p. 110°), foliage green picrate (m.p. 175°) and methiodide (m.p. 270°). The purity of 6 was ascertained through tlc using the same solvent system as for 5 (Rf = 0.67).

Analysis :

Found : C<sub>20</sub>H<sub>23</sub>N (6).  
 C, 86.82 ; H, 8.42 ; N, 4.88%.  
 Calcd. C, 86.64 ; H, 8.30 ; N, 5.06%.

Discussion

The present communication deals with the synthesis of 5 and 6, compounds related to 6,7-benzomorphan with an additional fusion of benzene ring at position 3 and 4. The synthesis of these compounds was an attempt to synthesise metazocine and etazocine analogs (compounds related to 6,7-benzomorphan)<sup>3</sup> to see the pharmacological activity of these compounds. 1,3,4-

TABLE 1—NMR SPECTRAL DATA (CHEMICAL SHIFTS EXPRESSED IN δ PPM)

Compound Number	Molecular formula	Aromatic protons.	C—CH <sub>3</sub>	N—CH <sub>3</sub>	—CH	—CH <sub>2</sub>	N—CH <sub>3</sub> <sup>1</sup>
3-HCl	C <sub>19</sub> H <sub>20</sub> NCl	6-9-8.45 9H	2.72(s) 3H 2.4(s) 3H	4.25(s) 3H	—	4.6 2H	
4-HCl	C <sub>20</sub> H <sub>22</sub> NCl	6.9-8.45 9H	2.72(s) 3H 2.4(s) 3H	0.97(t) 3H		4.1-4.6 4H 2H	2H
5	C <sub>19</sub> H <sub>21</sub> N	6.4-7.7 8H	1.1(d) 3H 1.82(s) 3H	2.1-3.8 7H		1H(C <sub>7</sub> ) 1H(C <sub>9</sub> ) 2H	
6	C <sub>20</sub> H <sub>23</sub> N	6.4-7.7 8H	1.85(s) 3H 0.9-1.5 6H 3H	3H		2.9-3.8 6H 2H	2H

S=singlet, d=doublet ; t=triplet.

## NOTES

Trimethyl quinolinium iodide (1) and 1-ethyl-3, 4-dimethyl quinolinium iodide (2) were reacted with benzyl magnesium chloride separately under Freund's reaction conditions<sup>1</sup>. The unstable 1,2-dihydro products 3 and 4 (presumably formed) obtained after usual treatments<sup>4</sup> were distilled under reduced pressure. Small portions of these were converted to their hydrochloride salts, 3.HCl and 4.HCl, with ethereal-HCl. The rest were immediately kept for cyclisation with 85% H<sub>3</sub>PO<sub>4</sub><sup>3</sup> separately. 3.HCl and 4.HCl were identified as 2-benzyl-1,3,4-trimethyl quinolinium chloride and 2-benzyl-1-ethyl-3, 4-dimethyl quinolinium chloride respectively. It has also been reported earlier that 2-benzyl-1,4-dimethyl-1-2-dihydroquinoline rearranged to-benzyl-1,4-dimethyl quinolinium chloride<sup>4</sup> and such rearrangements were also observed<sup>5</sup>. The purity of 3.HCl, 4.HCl, 5 and 6 were ascertained through tlc.

Nmr spectral data of 3.HCl, 4.HCl, 5 and 6 have been given in Table No. I. The structures to these compounds were assigned as follows :-

3.HCl 2-Benzyl-1,3,4-trimethyl quinolinium chloride.

4.HCl 2-Benzyl-1-ethyl-3,4-dimethyl quinolinium chloride.  
5 2,5,9-Trimethyl-3,4 : 6,7-dibenzomorphan.  
6 2-Ethyl-5,9-dimethyl-3,4 : 6,7-dibenzomorphan.

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## On the Reported Preparation of Co(III) Nitrate in Solution.

In the June, 1977 issue of the *J. Indian Chem. Soc.*, vol. 54, p. 579, U. N. Pandey has stated to have prepared Co(III) nitrate solution by simply aerating an aqueous solution of Co(II) nitrate. This appears highly improbable since the oxidation of Co(II)aq to the Co(III)aq ion is very unfavourable, its oxidation potential being -1.84 volts. In fact, such oxidation in aqueous solution can be effected only electrolytically or by ozone in perchloric acid media. In aqueous solution the Co(III)aq species is quite unstable and it decomposes with evolution of oxygen forming Co(II)aq ion with a half-life of *ca.* 1 month at 0°C (the reaction is appreciably fast at room temperature). This makes one doubtful about the authenticity of the Co(III) complexes prepared by Pandey using his so-called Co(III) nitrate as the starting material.

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