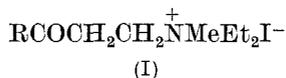


# THE USE OF MANNICH BASE METHIODIDES IN THE DIENE REACTION\*

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Mannich base methiodides (e.g. I) have been extensively used in Michael reactions as sources of vinyl ketones in order to avoid handling and keeping these usually unstable compounds (see, for example, du Feu, McQuillin, and Robinson 1937). Mannich bases themselves have been used in two instances as sources of dienophiles in Diels-Alder reactions (Jacquier and Boyer 1953) and we now report some parallel work using the methiodides (I, R=CH<sub>3</sub> or Ph) with 2,3-dimethylbutadiene. With (I, R=CH<sub>3</sub>) 4-acetyl-1,2-dimethylcyclohexene was obtained in 67 per cent. yield, compared with 75 per cent. yield from methyl vinyl ketone itself (Petrov 1941). With (I, R=Ph) 4-benzoyl-1,2-dimethylcyclohexene was obtained in 50 per cent. yield. Under somewhat different conditions Bell *et al.* (1940) obtained 35 per cent. yield based on diene from phenyl vinyl ketone. The method would appear to be generally applicable, since vinyl ketones are frequently prepared through the Mannich bases.



## Experimental

Melting points are uncorrected.

*4-Acetyl-1,2-dimethylcyclohexene.*—2,3-Dimethylbutadiene (1 mole), the methiodide from diethylaminobutan-3-one (1 mole), and a little methylene blue were heated in a sealed glass tube to 140 °C for 8 hr. The ether-soluble portion of the product was distilled to give 4-acetyl-1,2-dimethylcyclohexene, b.p. 150 °C/60 mm (yield 67%), semicarbazone, m.p. 176 °C (Found: C, 63.1; H, 9.1%. Calc. for C<sub>11</sub>H<sub>18</sub>ON<sub>3</sub>: C, 63.1; H, 9.1%). Petrov (1941) gives m.p. 181–182 °C for this derivative.

*4-Benzoyl-1,2-dimethylcyclohexene.*—3-Diethylamino-1-phenylpropanone similarly gave rise at 110 °C for 24 hr to 4-benzoyl-1,2-dimethylcyclohexene (50%), b.p. 188 °C/20 mm, 2,4-dinitrophenylhydrazone, m.p. 148–149 °C (Found: C, 63.4; H, 5.5%. Calc. for C<sub>21</sub>H<sub>22</sub>O<sub>4</sub>N<sub>4</sub>: C, 63.9; H, 5.6%). Bell *et al.* (1940) give m.p. 152 °C for this derivative.

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