

2,5-Dimethylfuran: A Remarkably Efficient Scavenger of Dibenzoyl Peroxide in Benzene

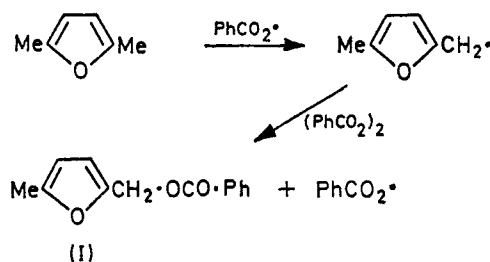
By J. I. G. CADOGAN,* J. R. MITCHELL, and J. T. SHARP

(Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ)

Summary Decomposition of dibenzoyl peroxide in a mixture of 2,5-dimethylfuran and benzene at the b.p. proceeds *via* an efficient scavenging reaction (>97%) to give, as isolated products, 2-benzoyloxymethyl-5-methylfuran (0.68 mol per mol of peroxide) and benzoic acid (1.26 mol per mol of peroxide).

WE report a second¹ unusual reaction involving 2,5-dimethylfuran which, in this case, may have some use in the removal of dibenzoyl peroxide from aromatic solvents.

Decomposition of dibenzoyl peroxide (1 mol) in a mixture of 2,5-dimethylfuran (2 mol) and benzene (12 mol) at the b.p. results in almost exclusive (>97%) reaction with the furan to give, as isolated products, benzoic acid (1.26 mol per mol of peroxide) and 2-benzoyloxymethyl-5-methylfuran (I) (0.68 mol per mol of peroxide) by comparison with an authentic sample. This remarkably efficient scavenging reaction can be rationalised in terms of an induced decomposition of the peroxide following a fast hydrogen abstraction by an initiating benzoyloxy radical (Scheme).



SCHEME

It is noteworthy that this reaction is markedly different from that in furan which gives *cis*- and *trans*-2,5-dibenzoyloxy-2,5-dihydrofuran (59%)² and, as might be expected from the foregoing, we find that 2-methylfuran exhibits intermediate behaviour in giving benzoic acid (0.99 mol per mol of peroxide), 2-benzoyloxymethylfuran (0.13), and 2-benzoyloxy-5-methylfuran (0.11), possibly *via* loss of benzoic acid from the intermediate 2,5-dibenzoyloxy-5-methyl 2,5-dihydrofuran.

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¹ J. I. G. Cadogan, M. J. P. Harger, and J. R. Mitchell, and J. T. Sharp, preceding communication.

² K. E. Kolbé and W. E. Black, *Chem. Comm.*, 1969, 1119.

The Mercuration-Demercuration of Enamines; A Tertiary Amine Synthesis

By ROBERT D. BACH* and DILIP K. MITRA

(Department of Chemistry, Wayne State University, Detroit, Michigan 48202)

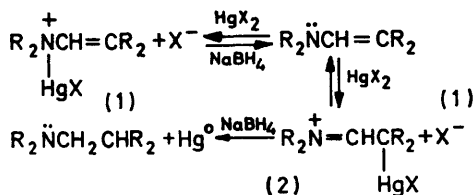
Summary The mercuration-reductive demercuration of a series of enamines is described; with ionic mercuric salts, mercuration at carbon is the dominant reaction pathway; this reaction constitutes a general synthesis of tertiary amines.

THE reversible reaction between a mercuric salt and an enamine may either result in complexation at nitrogen or in the formation of a covalent carbon-mercury bond (equation 1). It has been reported¹ that the reaction of a variety of enamines with mercuric chloride or bromide in ether resulted in the formation of *N*-mercurated $\alpha\beta$ un-

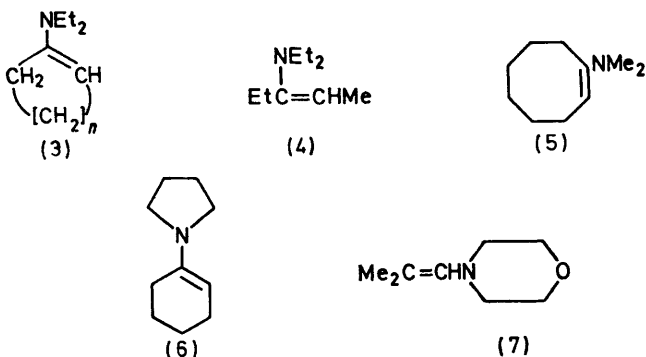
saturated ammonium salts, (1), with every enamine examined except 1-(*N*-pyrrolidinyl)cyclopentene. The latter compound afforded a *C*-mercurated iminium salt, (2), with both HgCl₂ and HgBr₂.

We report that in contrast to the above results, with the more electrophilic reagent mercuric acetate, the major pathway with enamines in the present study is attack at the β -carbon atom of the enamine affording the iminium salt (2). This *C*-mercuration reaction in aprotic solvents when followed by *in situ* demercuration and reduction of the iminium salt with sodium borohydride results in reduction of the enamine to the corresponding tertiary amine.

In a typical reaction 5.0 g (27.6 mmol) of 1-(*NN*-diethylamino)cyclo-octene in 45 ml of DMF was added to a stirred solution of 9.88 g (1.12 equiv.) of mercuric acetate in 45 ml



of DMF at -20° over 15 min. After an additional 15 min 0.72 g (19 mmol) of solid sodium borohydride was added and reduction took place immediately with the precipitation of elemental mercury. After 15 min the reaction mixture



was made basic with 100 ml of dilute NaOH solution and the tertiary amine was recovered by extraction with pentane. Isolation of the product by removal of solvent and vacuum distillation at $85-90^\circ/4$ mm gave an 81% yield of *NN*-diethylcyclo-octylamine.

¹ K. Brodersen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 70; K. Brodersen, G. Opitz, and D. Breitingen, *Chem. Ber.*, 1964, **97**, 2046; K. Brodersen, G. Opitz, D. Breitingen, and D. Menzel, *ibid.*, 1155.

² "Enamines: Synthesis, Structure and Reaction," ed. A. G. Cook, Marcel Dekker, New York, 1969.

³ K. Taguche and F. H. Westheimer, *J. Org. Chem.*, 1971, **36**, 1570; W. A. White and H. Weingarten, *ibid.*, 1967, **32**, 213.

⁴ K. Taguche and F. H. Westheimer, *J. Org. Chem.*, 1971, **36**, 1570.

⁵ R. D. Bach, *J. Org. Chem.*, 1968, **33**, 1647.

⁶ R. F. Borch, M. D. Bernstein, and H. D. Durst, *J. Amer. Chem. Soc.*, 1971, **93**, 2897.

The general availability of enamines^{2,3} and the simplicity of this procedure, which does not require isolation of the organomercury salt (2) provides a practical synthesis of a variety of tertiary amines, *e.g.*, the enamines (3)—(7) (see Table). The reaction appears to be general although in some cases *N*-mercuration competes with *C*-mercuration resulting in reduced yields. Reduction of the *N*-mercured product (1) affords the starting enamine which is hydrolysed during the isolation procedure.

TABLE

Enamine	Solvent Temp. (°C)	Amine (%)	Picrate, m.p. (°C)
(3) <i>n</i> = 2	DMF -20	78 ^a	102—103
	DMF 25	73	
	CH ₂ Cl ₂	77 ^b	
<i>n</i> = 3	DMF -20	90	89—91
	DMF 25	75	
<i>n</i> = 4	DMF -20	93	106—108
	DMF 25	89	
(4)	DMF -20	71 ^c	83—84
	DMF 25	66	
(5)	DMF 25	65 ^d	167—168
(6)	DMF 25	65 ^e	
(7)	DMF 25	51	

^a No effort has yet been made to maximize the yields. The reported yields are based on g.c. analysis. The suggested structures of the products are consistent with their i.r. and n.m.r. spectra. ^b The product was identical in every respect with an authentic sample. The yield reported in this case is an isolated yield. In general, isolated yields were 5—10% lower than g.c. yields. ^c A picrate of the product had m.p. 83—84° (lit.⁴ 84°). ^d The product was identical in every respect to a sample prepared by an independent synthesis.⁵ ^e The total reaction time for the mercuration reaction was 30 s. The picrate had m.p. 167—168° (lit.⁶ 167—169°).

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