Gas-phase Reactions on Platinum. Synthesis of Alkylpyridines and Alkylbenzenes from Acyclic Ketones

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Summary Diethyl ketone and methyl ethyl ketone combine with ammonia in the gas phase on a platinum–silica catalyst at elevated temperatures, yielding 2,6-diethyl-3-methylpyridine and a mixture of 2,3,6-trimethylpyridine and 2-methyl-6-ethylpyridine, respectively; in the absence of ammonia 1,3-dimethyl-4-ethylbenzene and a mixture of *o*- and *p*-xylene are formed.

Catalytic dehydrogenation over platinum-group metals provides a convenient, frequently used method in chemical synthesis, especially when the establishment or enlargement of an aromatic system is required.[1] In seeking to devise a new gas-phase route to pyridine we investigated the possibility of utilising diethyl ketone and ammonia along the lines suggested by equation (1). The thermodynamics of the first stage, dehydrogenation of the ethyl groups producing divinyl ketone and hydrogen, are apparently unknown, though by analogy with the dehydrogenation of an acyclic alkane, *cf.* ethane → ethylene[2] ΔG°_r (298 K) = $+24{\cdot}1$ kcal mol^{-1}, the reaction should be feasible only at elevated

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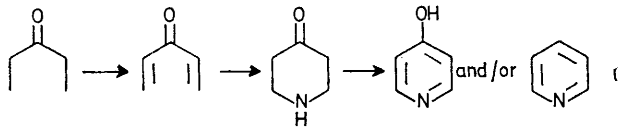

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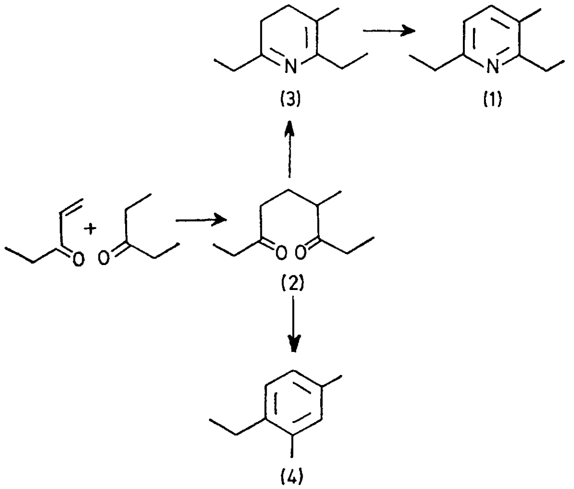

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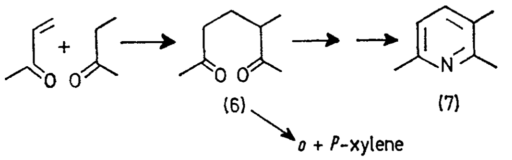

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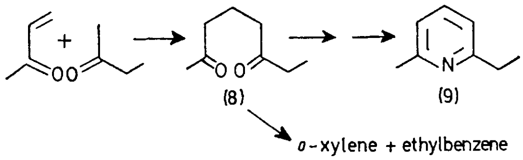

(4)

temperatures. The second stage, double conjugate addition of ammonia to the unsaturated ketone has precedent dating from Robinson's synthesis of tropinone.[3] Dehydrogenation of piperidone, the final stage, should occur readily; saturated ketones containing a potential aromatic system are dehydrogenated on platinum with or without loss of the oxygen function.[1] Whether or not dehydrogenation of an acyclic ketone could be brought about selectively on platinum in the presence of ammonia was unknown.[4]

Diethyl ketone was vaporised in a mixture of ammonia and hydrogen and passed over 2% platinum on silica at *ca.* 500 °C. The product, consisting largely (*ca.* 90%) of one component in high yield, was not pyridine but was identified by n.m.r. spectroscopy and mass spectral analysis as 2,6-diethyl-3-methylpyridine (**1**). Clearly, two molecules of diethyl ketone are involved in the reaction for which we suggest as a possible mechanism the sequence in equation (2); platinum catalyses the dehydrogenation of one ethyl group and the resulting $\alpha\beta$-unsaturated ketone combines with a second molecule of diethyl ketone, yielding the dione (**2**); condensation of the dione with ammonia should lead readily to a dihydropyridine which is dehydrogenated to (**1**) on platinum.

The following observations are in accord with this mechanism. (a) The active role of the metal: when the reaction was conducted on silica alone at 500 °C a complex mixture of products was obtained containing only small amounts of (**1**). (b) When ammonia was omitted the main product was 1,3-dimethyl-4-ethylbenzene (**4**), a structure clearly compatible with, and obtainable from, the diketone (**2**) *via* condensation and dehydrogenation. (c) The behaviour of methyl ethyl ketone under the reaction conditions: this unsymmetrical ketone should, according to the sequence in equation (2), produce a high yield of two pyridines, which indeed occurred and they were identified as 2,3,6-trimethylpyridine (**7**) and 2-methyl-6-ethylpyridine (**9**); (ratio *ca.* 1 : 1); as shown in equations (3) and (4) these two products can be obtained from the diketones (**6**) and (**8**), respectively. When ammonia was omitted, methyl ethyl ketone furnished a 1 : 1 mixture of *o*- and *p*-xylene and a trace of ethylbenzene, all three being related to the putative intermediate diones (**6**) and (**8**); *m*-xylene was not detected.

Though we have not yet succeeded in making pyridine by this method, it does open up a route to a wide variety of polyalkyl pyridines.

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[1] For a recent survey see 'Organic Synthesis with Noble Metal Catalysts,' by P. N. Rylander, Academic Press, New York, 1973, Ch. 1.

[2] J. D. Cox and G. Pilcher, 'Thermodynamics of Organic and Organometallic Compounds,' Academic Press, New York, 1970, p. 510.

[3] R. Robinson, *J. Chem. Soc.*, 1917, **111**, 762.

[4] Acetone appears to be the only simple ketone to have been used in gas-phase syntheses of alkylpyridines, though not in catalytic processes on platinum. For a comprehensive survey of synthetic pyridines see 'The Chemistry of Heterocyclic Compounds,' Vol. 14, Supplement Part I, Ed. R. A. Abramovitch, Wiley, New York, 1974, Ch. 2.