$\alpha \rightarrow \beta$ Rearrangements of Naphthyl Ketones under Friedel–Crafts Acylation Conditions

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Summary The intramolecular acylation of the acid (I) by polyphosphoric acid (PPA) affords the kinetically controlled α-naphthyl ketone (II) and/or the thermodynamically controlled β-naphthyl ketone (III); (II) rearranges quantitatively to (III) with PPA at 120°.

Friedel–Crafts acylation,[1] in contrast to the alkylation, is usually considered an irreversible process[2] free of rearrangements.[3,4] Naphthalene systems, by virtue of the dichotomy in their Friedel–Crafts acylations, *i.e.*, α *vs.* β substitution, are useful tests for evaluating the mechanisms of these reactions.[5–7] Experiments designed to detect any rearrangement of α-naphthyl ketones to β-naphthyl ketones under Friedel–Crafts conditions, have so far been mostly unsuccessful.[5,8,9] We report the quantitative rearrangement of an α-naphthyl ketone to a β-naphthyl ketone under Friedel–Crafts intramolecular acylation conditions. Our results provide experimental evidence in favour of Gore's reversibility theory which states that the Friedel–Crafts acylation reaction of reactive aromatic hydrocarbons is a reversible process.[5,10]

The model we studied was the Friedel–Crafts intramolecular acylation of (I)[11] by PPA. An attack on the α-position of the naphthalene nucleus of (I) would lead to (II) while the isomeric compound (III) would be the outcome of an attack on the respective β-position. The two ketones were synthesized independently by "unambiguous" methods. A Perkin condensation of naphthalene-2,3-dicarboxylic anhydride with phenylacetic acid gave 3-benzylidenebenzo[*f*]phthalide† which was converted into 3-(2-phenylethyl)-2-naphthoic acid† by phosphorus and HI. Cyclization of the latter acid by PPA at 100° led to (III), m.p. 92°,† 76%, δ ($CDCl_3$) 3·26 (4H, s), 7·14—7·59 (5H, m), 7·59 (1H, s), 7·66—7·94 (2H, m), 8·10—8·19 (1H, m, 4-H), and 8·47 (1H, s, 6-H). Treatment of (I) with boiling $SOCl_2$ gave the respective acyl chloride which was cyclized to (II) by $AlCl_3$ in CH_2Cl_2 at 25° in 90% yield. Recrystallization from cyclohexane afforded a pure sample of (II), free of (III), m.p. 99—100°,†‡[11] δ ($CDCl_3$) 3·20 (4H, s), 7·08—7·52 (6H, m), 7·70—7·84 (2H, m), 7·93—8·03 (1H, m, 1-H), and 8·00—8·09 (1H, m, 12-H).

The cyclization of (I) by PPA was studied at various

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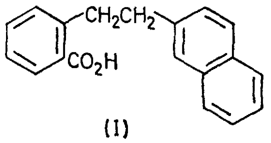
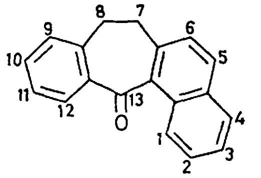
† All new compounds have been fully characterized (combustion analyses, i.r., u.v., n.m.r., mass spectra). The ^1H n.m.r. spectra were recorded at 100 MHz. ^1H Chemical shifts are reported in p.p.m. downfield from Me_4Si.

‡ The product was identical with a sample provided by Professor E. D. Bergmann and Dr. R. Ikan who established the structure of (II) by a chemical degradation.[11] These authors reported that (II) could be synthesized from (I) and PPA, at 100°.[11] In our hands, under the reported experimental conditions,[11] only (III) was obtained.

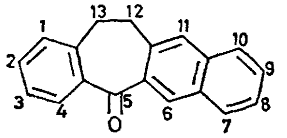
temperatures and for varying periods of time. The product distribution could be monitored by t.l.c. [alumina, 5% pyridine in hexane; R_F(II) 2·4; R_F(III) 3·1] and by the n.m.r. low-field singlet at 8·47 representing 6-H of (III).



(I)



(II)



(III)

Treatment of (I) with PPA for 6 h at 105—110° and at 80—84° gave practically pure (III) (50%) and a 2:1 mixture of (II) and (III) (80%), respectively. At 70°, the reaction afforded, after 4 and 10 h, nearly pure (II) (10% conversion) and a mixture of (II) and (III), respectively. These results indicate that in this reaction, (II) is the kinetically controlled product, while (III) is the thermo-namically controlled product. This conclusion was rified by treating (II) with PPA at 120° for 6 h: a quantitive rearrangement of (II) to (III) was achieved. The verse isomerization could not be effected over a wide nge of temperatures (20—160°). Thus, the intramolelar acylation of (I) at the α-position of the naphthalene cleus is a reversible process. The rationale for this enomenon is not inherent in the alkyl substituent *ortho* the carbonyl group, which is present in both (II) and (III). e two ketones differ, however, in the spatial relationship the carbonyl group *vis-à-vis* the naphthalene nucleus. e n.m.r. spectra indicate that a deshielding of the *peri*-phthalene proton due to the anisotropy of the carbonyl most pronounced in (III), 6-H, but hardly exists in (II), H. The carbonyl group of (II) is tilted out of the plane the naphthalene nucleus, relative to that of (III), thereby ducing the resonance stabilization in the molecule. The me arguments apply in the conjugate acids of (II) and II). Under thermodynamically controlled conditions g., in PPA at elevated temperatures), the conjugate acid (II) rearranges to that of (III) presumably through the termediate open acylium ion derived from (I).[12] The o[6,6]spirocarbonium ion, formed from the conjugate acid (II) by a 1,2-shift, may also serve as a possible interediate in the rearrangement.

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[9] See, however, R. B. Girdler, P. H. Gore, and J. A. Hoskins, *J. Chem. Soc.* (*C*), **1966**, 181, who reported a 3% slow rearrangement of 1-acetyl-2-methoxynaphthalene to 2-acetyl-6-methoxynaphthalene.

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[12] *Cf.* H. O. House, 'Modern Synthetic Reactions,' 2nd edn., W. A. Benjamin, Menlo Park, California, 1972, p. 805.