

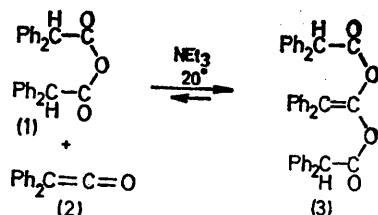
Carboxylic Anhydrides and Diphenylketen, a New Reaction Mode of Ketens

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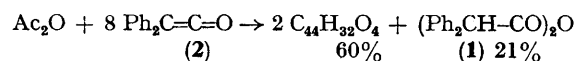
Summary Carboxylic anhydrides are converted into keten acylals or naphthalene-1,3-diol esters *via* base-catalysed *O*- or *C*-acylation by diphenylketen.

DIPHENYLACETIC ANHYDRIDE (1) combines with 1 equiv. of (2) in the presence of a trace of triethylamine (1 month, 25°) to give the keten acylal (3) (80%)† m.p. 128–129; ν (KBr) C=O 1792, 1770, C=C 1664 cm^{-1} ; τ (CDCl_3) 2.86 (s, broad, 6 Ph) and 5.07 (s, 2 benzhydryl H). On distillation at 140–160°/0.0001 Torr, (3) cleaves to give (1) and (2) and can thus be used as an *in situ* generator for diphenylketen. *E.g.*, heating of (3) in hex-1-ene (5 days, 100°) produces 3-butyl-2,2-diphenylcyclobutanone (63%)¹ and (1) (73%).

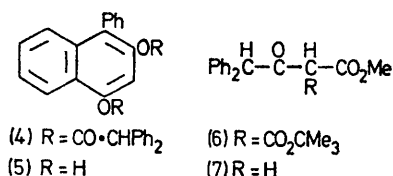


SCHEME 1

The formation of (3) is attributed to deprotonation of (1) by the tertiary amine and *O*-acylation of the enolate anion by (2). *C*-Acylation of carboxylic anhydride anions is preferred if not sterically prevented as in the enolate from (1). This is borne out by the behaviour of acetic anhydride which reacts with (2) and triethylamine (21 days, 50°, ethyl acetate) according to the stoichiometry:

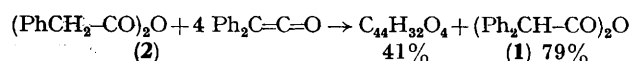


The n.m.r. spectrum of the compound $\text{C}_{44}\text{H}_{32}\text{O}_4$, m.p. 158–159°, reveals two diphenylacetyl-H as singlets at τ 4.55 and 5.02; the C=O frequency of 1758 cm^{-1} is that of a phenyl ester. Formula (4) is confirmed by degradation and independent synthesis. Methanolic potassium hydroxide converts (4) into 2 equiv. of diphenylacetic acid and 4-phenylnaphthalene-1,3-diol (5) which gives a blue FeCl_3 reaction and was synthesised *via* (6) and (7).

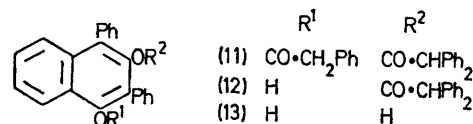


SCHEME 2

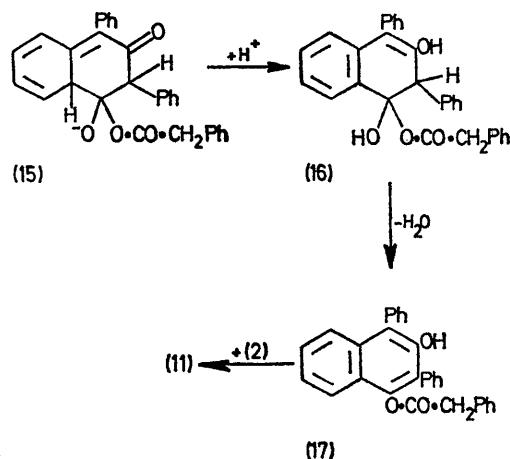
Surprisingly, the reaction of phenylacetic anhydride with (2) under triethylamine catalysis (7 days, 20°, ethyl acetate) yields an isomer of (4) in accordance with:



The n.m.r. spectrum of the new isomer (11), m.p. 156–158°, reveals 29 aromatic protons, 1 benzhydryl-H at τ 5.45 (s)



and 2 benzyl protons at δ 3.5 (s). The u.v. spectrum of (11) is similar to that of (4).



SCHEME 3

With the assumption of *C*-acylation of the acetic anhydride anion (8) by (2) as the key step, the mode of formation shown in Scheme 2 appears plausible.

Refluxing methanolic potassium hydroxide hydrolyses only the phenylacetate ester group of (11) giving the mono-ester (12), m.p. 153.5–154.5°. Hydrolysis of the second,

† All new compounds gave satisfactory CH analyses; mol.-weights with vapour pressure osmometer or mass spectrometer.

highly-screened ester group is effected by potassium hydroxide in ethylene glycol at 150° producing (13)³ and diphenylacetic acid.

Up to the cyclization product (15), the formation pathway of (11) may parallel that of the acetic anhydride reaction as far as (10). Though (10) loses the acetate anion on aromatization, the phenylacetate residue in (15) is retained and hydroxide is instead eliminated. The sequence (15) → (16)

→ (17) (Scheme 3) illustrates one of many conceivable schemes for the prototropic shifts. The reason for the mechanistic divergence starting at (10) and (15) could be, that the relative configurations at the positions 3 and 4 of (16) allow a *trans*-elimination of water only.

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