Reaction of Benzoyl Peroxide with Furan

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Summary The reaction of benzoyl peroxide with furan at temperatures between 35 and 80° was found to proceed without loss of carbon dioxide to give in good yield the *cis*- and *trans*-forms of 2,5-dibenzoyloxy-2,5-dihydrofuran.

WHILE the thermal decomposition of neat benzoyl peroxide gives nearly quantitative yields of biphenyl and carbon dioxide,[1] the presence of a solvent usually gives additional products resulting from reaction with the solvent.[2] The thermal decomposition of benzoyl peroxide can produce both benzoyloxy- and phenyl radicals:

$$PhCO_2{\cdot}O_2CPh \rightarrow PhCO_2{\bullet}$$

$$PhCO_2{\bullet} \rightarrow Ph{\bullet} + CO_2$$

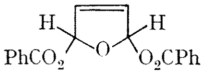
When an aromatic solvent is present, possible products include those resulting from the addition or substitution by phenyl or benzoyloxy-radicals. Reaction in benzene, which has received much attention since first reported in 1925 by Gelissen and Hermans,[3] has recently been the object of a most complete study by DeTar *et al.*[4] Their results, summarized in the Table, show that with 0·01M-benzoyl peroxide in benzene at 80° the yields were 89% CO_2, 38% biphenyl, 4% benzoic acid, 9% dihydrobiphenyl, and 25% tetrahydroquaterphenyl. These reactive products with the solvent are most probably produced by addition of the phenyl radical to benzene with the resulting biphenyl radical either abstracting a hydrogen to give the dihydrobiphenyl or dimerizing to give the tetrahydroquaterphenyl. DeTar *et al.* call this reaction a prototype for the production of aryl radicals and for arylation of aromatic rings. However, it appears that not all aromatic rings behave the same.

Reaction of benzoyl peroxide with aromatic substrates

Benzoyl peroxide in solvent	% CO_2	% Ph·Ph	% $PhCO_2H$	Other products
0·05M in benzene[4]	63	34	22	0·5% $C_{12}H_{12}$ and 1% $C_{24}H_{22}$
0·01M in benzene[4]	89	38	4	9% $C_{12}H_{12}$ and 1% $C_{24}H_{22}$
0·028M in anthracene[8] ..	12	—	45	18% 9-benzoyloxyanthracene
0·01M in thiophen[7] ..	—	—	58	3·8% 2-phenylthiophen
0·4M in furan (this work)	*ca.* 0	—	34	32% "*trans*" ester (I) 27% "*cis*" ester (II)

We report the reaction of benzoyl peroxide with furan. The reaction was run under reflux at *ca.* 35° for 2—3 weeks, and in a bomb at 50—80° for 24—42 hr. In no run was more than a trace of CO_2 detected. Thus decarboxylation of the benzoyloxy-radical is not occurring. In a typical run in furan the three major products obtained are benzoic acid and two solid esters designated as ester (I), insoluble in furan, and ester (II), soluble in furan. The structures of the insoluble ester (I) and soluble ester (II) were determined as follows: both gave satisfactory microanalyses for $C_{18}H_{14}O_5$. Molecular weights: (I) 310 (mass spec.); (II) 318 (Rast). The n.m.r. spectrum of (II) ($CDCl_3$, δ from Me_4Si) showed two singlets and two multiplets (6·41, 7·02, 7·24—7·58, 8·00—8·14) whose areas are in the ratio 1 : 1 : 2 : 3.

Both (I) and (II) yield (>75%) a *cis*-2,4-dinitrophenylhydrazone m.p. 290—295° (dec.) which is identical with that obtained from 2,5-dimethoxy-2,5-dihydrofuran as shown by mixed m.p. and i.r. (KBr). Both are isomers of 2,5-dibenzoyloxy-2,5-dihydrofuran. Ester (II), m.p. 167°, did not give n.m.r. splitting of the protons on the second and third carbons: it has been assigned the "*cis*" configuration. Ester (I), m.p. 211°, has been assigned the "*trans*" configuration.



Esters (I) and (II) "*cis*" and "*trans*"

The assignment of the "*trans*" configuration to the higher-melting isomer is in agreement with recent work in which the "*trans*" configuration for 2,5-dimethoxy-2,5-dihydrofuran was assigned the higher-boiling isomer.[5] In all runs the three products in nearly equal molar amounts accounted for over 90% of the decomposed benzoyl peroxide. Thus, with furan, the major reaction is one of addition of two benzoyl radicals. Furan has previously been found to add the acetoxy-radical ($CH_3CO_2\cdot$) to give 2,5-diacetoxy-2,5-dihydrofuran when a solution of acetic acid, sodium acetate, and furan was electrolysed.[6] That the reaction of furan with benzoyl peroxide is of a radical nature is indicated by the observation that the reaction at 35° has a considerable induction period (7—14 days) with freshly distilled furan but is initiated much sooner with furan that has been allowed to stand in contact with air and develop hydroperoxides.

This work and the results reported in the literature (in addition to the solvents cited above, thiophen[7] and anthracene[8] have also been studied) indicate that the nature of the aromatic substrate present when benzoyl peroxide decomposes determines both which radical (phenyl or benzoyloxy-) is picked up and the type of product (addition or substitution) that is obtained.

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