

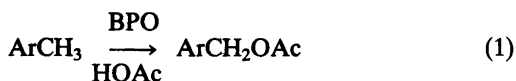
Decomposition of Benzoyl Peroxide in the Presence of Alkylaromatic Compounds. A Facile Side-Chain Substitution Reaction

LARS-GÖRAN WISTRAND

Division of Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden.

Growing interest in electron transfer reactions¹ has stimulated work on benzoyl peroxide (BPO) as a one-electron oxidant of organic compounds.² In particular, the reaction of BPO with electron-rich arenes has been studied and mechanistic evidence suggests an initial electron transfer from the aromatic substrate to BPO.³ These studies have been performed in inert solvents and under these conditions the major reaction path observed is nuclear benzyloxylation.

I here report results from the reaction of BPO with alkylaromatic compounds in the more nucleophilic medium glacial acetic acid where, in contrast to reactions in other solvents, side-chain oxidation is observed exclusively.* Decomposition of BPO in acetic acid under an argon atmosphere at 78 °C in the presence of toluene, *p*-xylene or 1,3,5-trimethylbenzene gave a complex mixture of products consisting of side-chain acetate and benzoate, aldehyde and dimers.⁵ When the alkylaromatic compound was activated by such groups as methoxy or polyalkyl, facile side-chain acetoxylation was however observed; eqn. (1).



The results are summarized in Table 1. The possibility of *trans*-esterification of a primarily formed benzyl benzoate to a benzyl acetate was excluded in a control experiment where 4-methoxybenzyl benzoate was shown to be stable under the reaction conditions.

The formation of the observed products is in agreement with an initial electron transfer from the aromatic substrate to BPO; alkylaromatic

* There is one case of a similar reaction reported in the literature where mesitol was converted into 3,5-dimethyl-4-hydroxybenzyl acetate by reaction with BPO in acetic acid.⁴

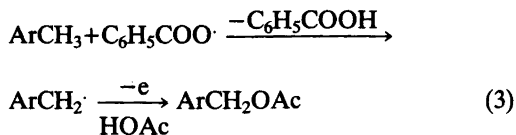
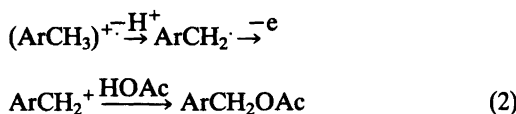
Table 1. Decomposition of BPO in HOAc in the presence of methyl benzenes at 78 °C.^a

Ar in ArCH ₃	Yield of ArCH ₂ OAc (%) ^{b,c}
2,4,5-(CH ₃) ₃	82
2,3,4,5,6-(CH ₃) ₅ ^d	93
2-OCH ₃	43 (59 ^e)
3-OCH ₃	28 (42 ^e)
4-OCH ₃	75

^a The reactions were carried out under an argon atmosphere; in the presence of oxygen the major product was the corresponding aldehyde (ArCHO).

^b Determined by GLC, based on BPO. ^c Small amounts (<5 %) of aldehydes and benzyl benzoates were formed in most reactions. ^d Substrate concentration, 0.5 M. ^e In the presence of Cu(OAc)₂ (0.1 mmol).

radical cations are known to easily lose an α -proton⁶ [eqn. (2)]. However, a hydrogen atom transfer mechanism, induced by the thermal decomposition of BPO to benzyloxy radicals would be expected to give rise to the same type of products [eqn. (3)]. The presence of benzylic radicals is indicated by the increase in the yield when the reactions were performed in the presence of Cu(II) (see Table 1), this ion is known to oxidize benzylic radicals very efficiently.⁷ In the absence of Cu(II) this oxidation is probably carried out by the weak oxidant BPO (estimated E_0 value 0.1 V vs. NHE).^{1b}



In order to distinguish between the two mechanisms, isodurene (1,2,3,5-tetramethylbenzene) was oxidized in the same medium. The selectivity of α -substitution of this compound has been used as a mechanistic tool, a high selectivity between C-2 and C-1 implying an electron transfer mechanism and a low selectivity being typical for a radical abstraction process.⁸ The results are summarized in Table 2. For comparison, reaction of isodurene with hydrogen atom abstracting (NBS)¹⁰ and hydride ion transfer (DDQ)¹¹ reagents have been included. From

Table 2. Isomer distribution in the side-chain oxidation of isodurene in acetic acid at 78 °C.

Oxidant	Isomer distribution			k_2/k_1^a	Yield (%)	Ref.
	1	2	5			
BPO	11	73	16	13	81	This work
dCBPO	11	70	19	13	83	This work
dNBPO	11	65	24	12	54	This work
Co(III)W ^{b,c}	8	79	13	20	77	This work
Co(III)W ^{b,c,d}	6	83	11	28	78	This work
Anode ^d	4	75	21	37		12
NBS ^d	27	59	15	4.4		8
Ce(IV) ^d	3	88	9	55		8
DDQ	9	42	49	9.3	21	This work

^a Correlated for a statistical factor. ^b The oxidation was performed in HOAc/H₂O (4:1, v/v). ^c K₂[Co(III)W₁₂O₄₀], 11 H₂O. ^d Reaction temperature 60 °C.

these data, it can be seen that BPO and the two substituted benzoyl peroxides 4,4'-dichloro-(dCBPO) and 4,4'-dinitrobenzoyl peroxide (dNBPO), which also initiate the same type of reaction, display similar selectivities possibly indicating similar mechanisms for the three peroxides. This selectivity is, however, lower than that observed for typical electron transfer oxidants such as the anode, Ce(IV) and potassium-12-tungstocobalt(III)ate⁹ (Co(III)W), but higher than that of hydrogen atom abstracting and hydride ion transfer reagents. Consequently, the usefulness of isodurene as a mechanistic probe in this case is doubtful, the difference in selectivities is too small for mechanistic conclusions to be drawn. Further mechanistic studies on the diaryl peroxide initiated side-chain substitution are needed and are under way in this laboratory.

Experimental. Benzoyl peroxide was recrystallized from methanol-chloroform (2:1, v/v) before use, the other peroxides were prepared from the corresponding acid chlorides and Na₂O₂, and, after recrystallization from toluene, their purity was >99 % as determined by iodometry. Aromatic substrates were of highest commercial purity. Reaction mixtures were analyzed by GLC using a Varian 1400 gas chromatograph equipped with a HP 3380 A integrator on a 2 m×0.3 cm 5 % NPGS column or a 2 m×0.3 cm 3 % OV-1701 column. Products were identified by comparison with authentic samples available from earlier work,^{9,11} and also by MS on a Finnigan 4021 mass spectrometer. Yields were determined by GLC analysis of the crude reaction mixtures to which an internal standard had been added. The standard had been calibrated against authentic samples.

A general procedure for the decomposition of

BPO is as follows: a solution of the aromatic substrate (10 mmol) in 10 ml glacial acetic acid was deaerated with argon while heated to 78 °C. BPO (1 mmol) was added, and the solution was stirred for 20 h (equivalent to ca. 10 half-lives for decomposition of BPO)¹³ under an argon atmosphere. After cooling, water was added and the mixture was extracted twice with dichloromethane. The organic phase was washed with aqueous NaHCO₃, dried and analyzed by GLC.

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1. a. Chanon, M. *Bull. Chim. Soc. France* (1982) 197; b. Ebersson, L. *Adv. Phys. Org. Chem.* 18 (1982) 79.
2. a. Pryor, W. A. and Hendrickson, W. H. *Tetrahedron Lett.* 24 (1983) 1459; b. Takeuchi, K., Murai, O., Matsui, S., Inoue, T., Kitagawa, T. and Okamoto, K. *J. Chem. Soc. Perkin Trans. 2* (1983) 1301.
3. Walling, C. and Zhao, C. *Tetrahedron* 38 (1982) 1105.
4. Wessely, F. and Schinzel, E. *Monatsh. Chem.* 84 (1953) 425.
5. Williams, G. H. *Homolytic Aromatic Substitution*, Pergamon, London 1960.
6. Ebersson, L., Jönsson, L. and Wistrand, L.-G. *Acta Chem. Scand. B* 32 (1978) 520.
7. Anderson, J. M. and Kochi, J. K. *J. Am. Chem. Soc.* 92 (1970) 1651.
8. a. Baciocchi, E., Ebersson, L. and Rol, C. *J. Org. Chem.* 47 (1982) 5106; b. Baciocchi, E., Mandolini, L. and Rol, C. *Ibid.* 45 (1980) 3906.

9. a. Ebersson, L. and Wistrand, L.-G. *Acta Chem. Scand. B* 34 (1980) 349; b. Ebersson, L. *J. Am. Chem. Soc.* 105 (1983) 3192.
10. Pearson, R. E. and Martin, J. C. *J. Am. Chem. Soc.* 85 (1963) 3142.
11. Ebersson, L., Jönsson, L. and Wistrand, L.-G. *Acta Chem. Scand. B* 33 (1979) 413.
12. Ebersson, L. and Oberrauch, E. *Acta Chem. Scand. B* 33 (1979) 343.
13. Walling, C. *Free Radicals in Solution*, Wiley, New York 1957, p. 474.

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