Preparation of liquid substituted benzoyl peroxide mixtures

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A series of alkyl substituted benzoyl peroxide mixtures were synthesised from two or three acid chloride combinations in aqueous sodium peroxide and butanone solutions to form liquid benzoyl peroxide mixtures.

Keywords: liquid benzoyl peroxide mixtures, substituted bis(benzoyl)peroxide.

In this paper we describe the synthesis of colourless, liquid alkyl-substituted benzoyl peroxide mixtures which are radical initiators. To the best of our knowledge, a liquid bis(benzoyl)peroxide is not commercially available, although one example of a liquid, namely a viscous, yellow oil of bis(*o*-[2-ethylhexyloxycarbonyl]benzoyl)peroxide, is known.[2] Bis(benzoyl)peroxide can be obtained commercially as a slurry in oil and has been used for quite some time.[2,3] We have previously found that bis(*p*-*n*-decylbenzoyl)-, bis(*p*-*n*-hexylbenzoyl)- and bis(*p*-*n*-butylbenzoyl) peroxides have low melting points of 26°, 38° and 30°C respectively.[4] A mixture of alkyl substituted bis(benzoyl)peroxides, where the individual members have a low melting point, can be expected to produce a product whose melting point is much lower than the individual compounds. By using benzoyl chlorides which are known to produce bis(benzoyl)peroxides that already have low melting points, the asymmetric peroxides are expected to have a lower melting point. To this end, two alkyl substituted benzoyl chlorides were reacted with an aqueous sodium peroxide solution in the presence of stearyltrimethylammonium chloride (STAC) as a surfactant and butanone as the organic solvent. This produced a mixture of three substituted benzoyl peroxides in a more or less 1:2:1 ratio (Scheme 1, Table 1). Some of these mixtures were easily and cheaply prepared. Unlike bis(benzoyl)peroxide which has the disadvantage that it is a solid, impact sensitive compound which dissolves with difficulty in hydrocarbon solvents, some of the mixtures of benzoyl peroxide liquids described here have a low active oxygen content and may not necessarily be impact sensitive. Some of these mixtures are also very soluble in hydrocarbon solvent. Most of the benzoylperoxide mixtures described here are liquids at room temperature and do not solidify at –10 °C (Table 1).

Table 1 Mixtures of liquid benzoylperoxides at –10 °C

R^1	R^2	Yield	Active oxygen
o-Me	*m*-Me	80%	6.0%
p-Et	*o*-Me	86%	5.7%
p-Et	*p*-*n*-Bu	98%	5.0%
o-Me	*p*-*n*-Bu	80%	5.3%
m-Me	*p*-*n*-Hex	93%	4.9%
p-*n*-Bu	*p*-*n*-Hex	95%	4.2%
p-Et	*p*-*n*-Hex	92%	4.7%
p-Et	*m*-Me	86%	5.7%
p-*n*-Bu	H	Impure	5.6%

$t_{\frac{1}{2}}$(10h) of all liquid benzoylperoxide mixtures is expected to be between 69° and 72 °C.[4]

Caution: Because of the known explosive nature of benzoyl peroxides, however, these mixtures should be handled with great caution during and after isolation and also during use.

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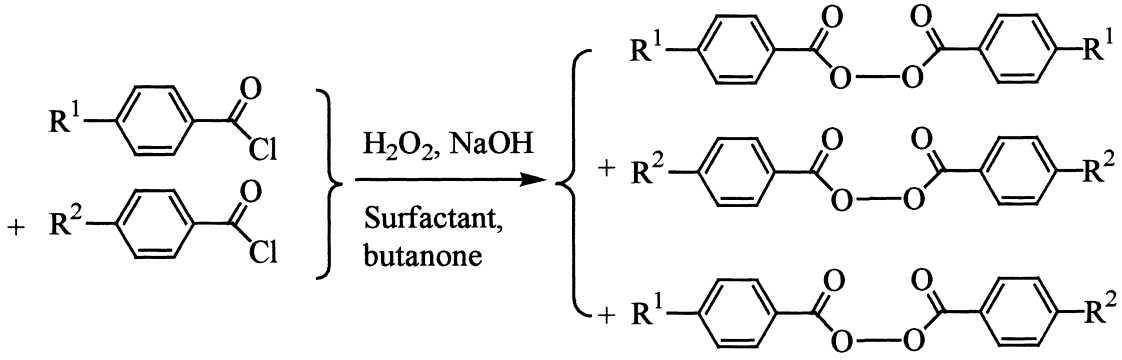

Scheme 1

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