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MECHANISM OF DECOMPOSITION FOR DIACYL PEROXIDES AND RELATED CARBOXY INVERSION COMPOUNDS IN AQUEOUS ACETONE

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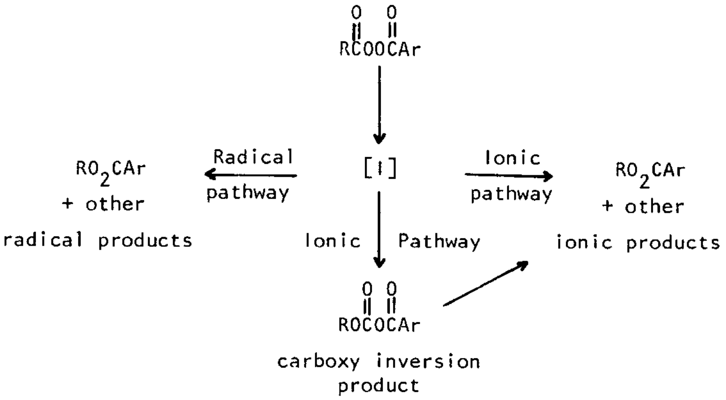
The recent report of CIDNP during the decomposition of t-butylacetyl m-chlorobenzoyl peroxide, which was interpreted as arising from polarized, rearranged ion pair intermediates,[1] prompts us to report the behavior of ion pairs derived from substituted diphenylacetyl benzoyl peroxides in aqueous acetone. This solvolytic technique allows the study of the polar pathway of peroxide decomposition by comparing product compositions with well-defined energy surfaces established by related solvolytic studies.

It has been proposed that peroxide decompositions occur by radical and ionic mechanisms.[2] Recent results have been interpreted (Scheme I) as involving a common resonance hybrid intermediate [I] leading to ion pairs and radicals.[3]

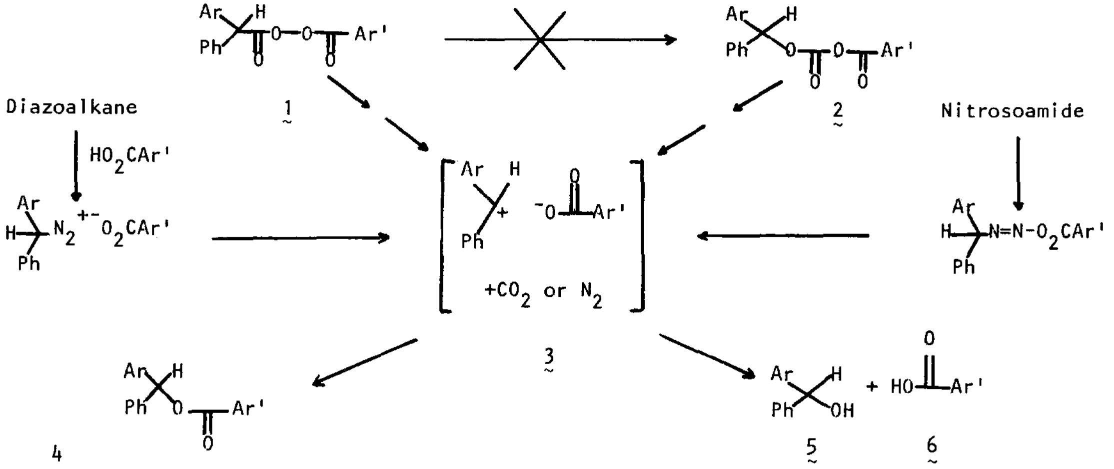
SCHEME I



Ion pairs are intermediates in the solvolysis of benzhydryl esters,[4a,b] halides,[4a] thiocyanates,[4a] diphenylmethane diazonium benzoate,[4b,c] and benzhydryl nitrosobenzamide[4d,e] in 90% aqueous acetone. We wish to examine the behavior of the ion pairs from diacyl peroxides in 90% aqueous acetone.

We report: 1) the preparation and characterization of the least stable unsymmetrical diacyl peroxide yet prepared (1, Scheme II); 2) the independent preparation of its "carboxy inversion compounds" (2); 3) the decomposition of the peroxide and inversion compound in dichloromethane with net retention of configuration; 4) the solvolysis of four diacyl peroxides and two related inversion compounds in 90% acetone. Our results provide definitive evidence for the ion pair intermediates from peroxides and inversion products that partition to ester and alcohol plus acid (the alcohol cannot arise from an immediate radical precursor) as do the ion pairs from other substrates.[4a-e] Unexpectedly, our peroxides do not undergo the carboxy inversion reaction.

SCHEME II



1a Ar = Ph, Ar' = *p*NO_2Ph
1b Ar = *p*CH_3Ph, Ar' = *p*NO_2Ph
1c Ar = Ph, Ar' = *m*ClPh
1d Ar = *p*ClPh, Ar' = *p*NO_2Ph

2a Ar = Ph, Ar' = *p*NO_2Ph
2b Ar = *p*CH_3Ph, Ar' = *p*NO_2Ph

m-Chlorobenzoyl diphenylacetyl peroxide, **1c**, was prepared in dichloromethane from *m*-chloroperbenzoic acid and diphenylacetyl chloride at -78°C by adding tri-n-butylamine[5a] (all at .047M) with stirring. After 1 hr, this solution was pumped into a low temperature infrared cell,[5b] giving the characteristic doublet at 1799 (m) and 1768 (s) corresponding to peroxide[6] **1c**. On warming to -5°C, over a period of 10 mins, the peroxide was completely converted to ester **4c**. No infrared bands associated with the inversion product **2c** were observed (vide infra[10]). Additional evidence for the presence of peroxide **1a** and **1c** has been obtained by low temperature (-55°C) nmr spectra[7] in acetone-d6 showing almost complete conversion of a mixture of peracid and diphenylacetyl chloride to diacylperoxide upon addition of tri-n-butylamine (all 0.2m) Acid chloride and peracid in acetone-d6 (-55°C) gave the simple superimposition of their nmr spectra. Upon adding amine, the acid chloride benzhydryl proton disappeared within 15 mins, giving a new signal *ca*. 0.2δ upfield, attributed to the peroxide. This new benzhydryl proton signal persisted, the solution was then warmed to 20°C, resulting in a spectrum identical to the corresponding ester; no carboxy inversion product was detected.

The inversion compound **2** was prepared by the carbonation and acylation of the sodium salt of benzhydrol in THF (-78°C).[8,9] The inversion product **2a** decomposed in chloroform with $t_{\frac{1}{2}}$ = *ca*. 16 hrs (36°C) affording ester **4** in 90% yield.

Optically active *p*-methyldiphenylacetic[10] and *p*-nitroperbenzoic acid in dichloromethane-ether (1:1) was treated with dicyclohexylcarbodiimide at 4°C, for 16 hrs.[11] Upon workup at 4°C the ester was isolated in 90% yield showing 14% net retention. The optically active *p*-methylbenzhydryl *p*-nitrobenzoyl carbonic anhydride[12] was prepared from optically active alcohol.[13]

Thermolysis in dichloromethane gave ester with net retention in >90% yield (by infrared).

TABLE I

Products of Solvolysis[*][a]

% Yield[c,e]

Compound at .04M	Ester(4) + Alcohol(5) (or Acid(6))	Temp°C	R[b,c,d]
$\underline{p}CH_3PhPhCHCO_2O_2CPh\underline{p}NO_2$ (1b)	96%	15	0.38
$Ph_2CHCO_2O_2CPh\underline{p}NO_2$ (1a)	79%	15	0.40
$\underline{p}ClPhPhCHCO_2O_2CPh\underline{p}NO_2$ (1d)	95%	15	0.46
$Ph_2CHCO_2O_2Ph\underline{m}Cl$ (1c)	75%	15	0.50
$PhCHOCOO_2CPh\underline{p}NO_2$ (2a)	>90%[f]	22	0.51
$\underline{p}CH_3PhPhCHOCOO_2CPh\underline{p}NO_2$ (2b)	>90%[f]	0	0.55

a) all compounds decomposed in 90% aqueous acetone v/v 25°C; b) R = (Ester)/(Ester + Alcohol); c) peroxides analyzed by gas chromatography; d) inversion compounds analyzed by titration; e) isolated yield; f) minimum yield by infrared; g) amine•HCl present during peroxide decomposition.

The solvolysis of the diacyl peroxide and inversion compound afforded alcohol and ester. The fraction substrate leading to ester (R) gives a measure of total ion pair return.[4b] The large fraction of alcohol requires that a correspondingly large fraction of ester arises via ionic intermediates. The solvolysis of benzhydryl benzoates and diphenylmethane diazonium benzoate both show partitioning of ca. R = 0.7.[4a] The R values in the solvolysis of N-benzhydryl-N-nitrosobenzamides (ca. R = 0.5)[4d] closely resemble those given for our compounds in Table I.

The kinetic data thus far obtained are approximate solvolysis rates, for compound 2a, $t_{\frac{1}{2}}$ = 50 mins (T = 22°C) and 2b, $t_{\frac{1}{2}}$ = 150 mins (T = 0°)C. These rates are much faster than those of the corresponding ester,[4b] but considerably slower than for the decomposition of peroxides.

No evidence for the involvement of radicals in the thermolysis of diacyl peroxides 1 or inversion compound 2 has been observed, the yields of ester are generally high and no solvent-derived products[14] have been seen. The related p-bromobenzoyl phenylacetyl peroxide[7] and p-nitrobenzoyl phenylethylacetyl peroxide[15] do not give capturable radicals in their decomposition. We have not observed CIDNP during the decomposition of our peroxides.

These studies demonstrate the involvement of ion pairs in peroxide and inversion compound decomposition that behave like ion pairs generated by other systems. Furthermore, our results suggest the usefulness of the decomposition of diacyl peroxides in aqueous media. Work is continuing on this system in a search for special salt effects[16] and to obtain detailed Hammett plots.

[*] The peroxide was prepared in 5 ml acetone at -78°C from the acid chloride, peracid and tri-n-butylamine. After stirring 1 hr, the peroxide solution was allowed to warm to -50°C and then solvolyzed with 20 ml of rapidly injected aqueous acetone (at 25°C), bringing the final temperature to 15°C and producing a 90% aqueous acetone solution where [ester] + [alcohol] = .04M.

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