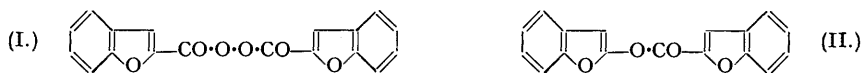# 179. *Coumariloyl Peroxide and its Decomposition in Organic Solvents.*

By M. C. FORD and WILLIAM A. WATERS.

Coumariloyl peroxide has been prepared, and its decomposition studied.
It does not appear to yield radicals capable of attacking carbon tetrachloride,
benzene, chlorobenzene, or nitrobenzene.

DURING an investigation of methods for obtaining heterocyclic free radicals attention was turned to the diacyl peroxides derived from heterocyclic carboxylic acids. Peroxides of this type, which should undergo homolytic fission in the usual manner, have been little studied; furoyl peroxide (Milas and McAlevy, *J. Amer. Chem. Soc.*, 1934, **56**, 1219) and nicotinoyl peroxide (Milas and Panagiotakos, *ibid.*, 1940, **62**, 1878) have been prepared but their decompositions have not been investigated.

In the nitrogen-ring series, the formation of dimeric and polymeric forms of acid chlorides owing to their internal-salt formation makes the preparation of the corresponding diacyl peroxides difficult. However, in the oxygen-ring series no such internal-salt formation is possible, and in the one example in the literature (Milas and McAlevy, *loc. cit.*) the peroxide was obtained in good yield.

Coumariloyl peroxide (I) has now been prepared in 49% yield by an adaptation of the methods of von Pechmann and Vanino (*Ber.*, 1894, **27**, 1510) and Gelissen and Hermans (*Ber.*, 1925, **58**, 292), and its decomposition has been studied in a number of solvents (see Table II). In each case coumarilic acid was isolated, there was no observable attack upon the solvent, and the only other major product was an amorphous polymeric substance insoluble in light petroleum, sparingly soluble in ether, and partly soluble in hot aqueous sodium hydroxide.

From the decompositions of the peroxide in benzene and in carbon tetrachloride solution, small amounts (*ca.* 2·5%) of a yellow crystalline product of m. p. 124—125° were also obtained. On the basis of its analysis, its ultra-violet absorption, and the identification of coumarilic acid as a hydrolysis product, this was considered to be 2-(coumariloyloxy)coumarone (II).

It is significant that the decomposition did not appear to generate any radicals capable of attacking the solvents which have been examined. Thus, whereas the decomposition of a diaroyl peroxide, $(Ar \cdot CO_2)_2$, in carbon tetrachloride solution (Böeseken and Gelissen, *Rec. Trav. chim.*, 1924, **43**, 869) leads to the corresponding carboxylic acid, $Ar \cdot CO_2H$, only after hydrolysis of the ω-trichloro-derivative, $Ar \cdot CCl_3$, resulting from attack of the aryl radical upon the solvent, yet in the present case the reaction mixture after boiling with water contained no chloride ion. Again, in the decompositions of the peroxide in chlorobenzene and in nitrobenzene, both the crystalline and the amorphous reaction products were shown not to contain chlorine and nitrogen, respectively.

Thus, coumariloyl peroxide does not resemble in its behaviour the diaroyl peroxides which are easily capable of arylating benzene (Gelissen and Hermans, *Ber.*, 1925, **58**, 285), chlorobenzene, and nitrobenzene (Hey, *J.*, 1934, 1966), and the closest analogy is in that of cinnamoyl peroxide, whose decomposition in benzene solution was studied by Wieland and Rasuwajew (*Annalen*, 1930, **480**, 165), who could isolate only carbon dioxide, cinnamic acid, and what they believed to be polymeric styryl cinnamate.

This lack of attack upon the solvent is perhaps caused by the dominance of a radical-catalysed polymerisation of the αβ-unsaturated system present both in the coumariloyl peroxide and in any fragments resulting from its decomposition. However, the isolation of coumarilic acid in 26% yield from the decomposition of coumariloyl peroxide in carbon tetrachloride solution shows that hydrogen transfer between solute molecules and radicals must also occur to a considerable extent.

The decomposition of many aliphatic peroxides which can only yield free radicals of low intrinsic reactivity, *e.g.*, phenylacetyl peroxide (Bartlett and Leffler, *J. Amer. Chem. Soc.*, 1950, **72**, 3030), are similar to the above in that they do not lead to substitution of aromatic solvents, and we would suggest that in spite of the aromatic nature of the benzofuran ring system, coumariloyl peroxide should be classed with aliphatic rather than with aromatic diacyl peroxides.

<div align="center">EXPERIMENTAL.</div>

(M. p.s are uncorrected. The elementary analysis is by Drs. Weiler and Strauss.)

Coumariloyl Chloride (cf. Stoermer and Calov, *Ber.*, 1901, **34**, 773).—Coumarilic acid (*Org. Synth.*, **24**, 33; 30 g.) was dried at 100°, treated with fresh phosphorus pentachloride (45 g.) (ice-cooling), and heated on the steam-bath until evolution of hydrogen chloride had ceased (1½ hours). Unless the acid was perfectly dry, an uncontrollable reaction set in at the start, with the formation of a black resin. The liquid mixture obtainable from dry materials was fractionated, coumariloyl chloride being collected at 267—269°/746 mm. as a pale yellow oil (26·2 g., 78%) which rapidly solidified (m. p. 54—55°).

Coumariloyl Peroxide.—The procedure of adding an ethereal solution of coumariloyl chloride to a stirred ice-cold partial solution of sodium peroxide in water is unsatisfactory owing to premature decomposition of the resulting alkaline hydrogen peroxide; the purity of the product thus obtained was only 81%, and the following method is preferable.
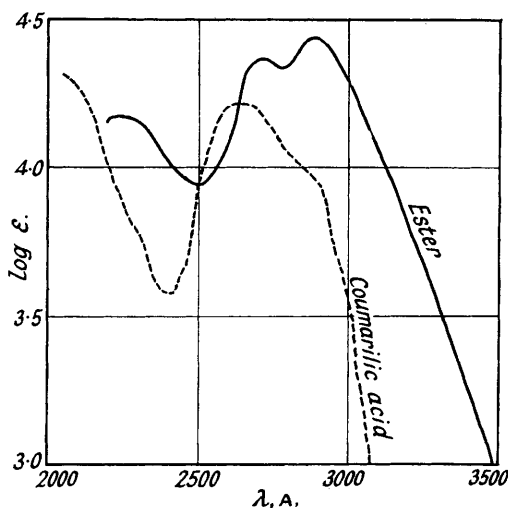
Aqueous sodium hydroxide (5N.; 30 ml.) and a solution of the acid chloride (23·6 g.) in sodium-dried ether (75 ml.) were dropped simultaneously into mechanically-stirred aqueous hydrogen peroxide (6·0%; 50 ml.) at 0° in such a way that the addition took 40 minutes and the solution was always just alkaline to phenolphthalein. After a further 1½ hours' stirring, the smell of the acid chloride had disappeared. The crude peroxide was collected (15 g.), dried in a vacuum (CaCl$_2$), and rapidly dissolved in chloroform (200 ml.) pre-heated to 50°. This solution was shaken with anhydrous magnesium sulphate and filtered, and the peroxide precipitated from the filtrate by dropwise addition of light petroleum (b. p. 60—80°; 400 ml.). The resulting *coumariloyl peroxide* (10·4 g., 49%) formed small, pale yellow needles which exploded at 117° and flashed violently in a flame (Found : equiv., 156·3. C$_{18}$H$_{10}$O$_6$ requires equiv., 161·1). The equivalent was determined by liberation of iodine in acetic anhydride solution (compare Vogel, " Practical Organic Chemistry," 1948, p. 766), and shows the purity to be 97%.

Decomposition of Coumariloyl Peroxide in Benzene Solution.—A solution of the peroxide (8·1 g.) in dry benzene (" AnalaR "; 50 ml.) was refluxed (CaCl$_2$ guard-tube) for 30 hours. Carbon dioxide was gradually evolved. On cooling, a small amount of solid separated; this was dissolved in more benzene, and the whole extracted repeatedly with aqueous sodium hydroxide (2N.). Acidification of the combined extracts gave a brown solid (2·7 g.) which when crystallised twice from toluene (charcoal) gave coumarilic acid, m. p. and mixed m. p. 187—189°.

The benzene layer was washed with water and dried (Na$_2$SO$_4$), and the benzene removed to give a brown gum (2·7 g.) of which only a trace was volatile in steam (2-phenylcoumarone is readily volatile; cf. Stoermer, *Ber.*, 1903, **36**, 3979). The residue from the steam-distillation was isolated with ether, the resulting gum dissolved in fresh ether (30 ml.), and filtered from tar, and the filtrate precipitated by an excess of light petroleum (b. p. 40—60°). A yellowish-brown amorphous solid was obtained which gave much tar in contact with solvents.

The mother-liquor on slow evaporation gave a yellow solid which, crystallised twice from methyl alcohol, gave 2-(*coumariloyloxy*)*coumarone* (0·22 g.) as yellow prisms, m. p. 124—125° (Found : C, 73·1; H, 3·62. C$_{17}$H$_{10}$O$_4$ requires C, 73·4; H, 3·62%). Its ultra-violet absorption in methyl alcohol is compared in Table I with that of coumarilic acid (both determined by Dr. F. B. Strauss). A comparison of the two curves (see figure) shows that no further conjugation is present in the ester. The structure was further confirmed by isolating coumarilic acid (0·1 g.), m. p. 192°, mixed m. p. 189—190°, as a product of the hydrolysis of this substance (0·4 g.) with aqueous alkali. The other component was phenolic (in aqueous solution it gave a clear violet colour with ferric chloride), and was probably *o*-hydroxyphenylacetic acid, but owing to its high solubility in water its isolation was impracticable with the amount of material available.

Decomposition of Coumariloyl Peroxide in Carbon Tetrachloride Solution.—A solution of the peroxide (12·5 g.) in purified carbon tetrachloride was refluxed for 20 hours. Carbon dioxide was gradually evolved and the solution slowly became dark brown. On cooling, coumarilic acid (2·8 g.) was precipitated together with a little tar. The acid immediately dissolved in cold N-sodium hydroxide, and after precipitation with dilute acid and crystallisation from aqueous alcohol and finally from toluene had m. p. and mixed m. p. 189—190°. A further quantity (2·5 g.) of this acid was obtained by extracting the carbon tetrachloride solution with 2N-sodium carbonate. After this extraction the carbon tetrachloride was evaporated and from the solid residue there were isolated, in the manner described above, 2-(coumariloyloxy)coumarone (0·3 g.; m. p. and mixed m. p. 126°) and polymeric material (3·2 g.).

In order to show that the coumarilic acid obtained in the preceding experiment did not arise from hydrolysis of chlorine-containing compounds, a separate decomposition reaction was carried out in similar circumstances, after which the whole of the initial reaction product was boiled with water for 6 hours : the resulting aqueous layer was shown not to contain chloride ions.

TABLE I.

Ultra-violet absorptions in methanol.

Ester.		Coumarilic acid.	
$\lambda_{max.}$, A.	$\log_{10} \varepsilon_{max.}$	$\lambda_{max.}$, A.	$\log_{10} \varepsilon_{max.}$
2250	4·17	2000	4·33
2650	4·36	2655	4·21
2875	4·425		

TABLE II.

Decomposition of coumariloyl peroxide in various solvents.

Solvent.	[Peroxide], moles/l.	Reflux time, hrs.	Yields (% of weight of peroxide taken).		
			Alkali-soluble.[a]	Polymer.	Ester.
C_6H_6	0·5	30	33	31	2·5
C_6H_5Cl	0·4	20	36	48 [b]	Traces
$C_6H_5 \cdot NO_2$	0·6	20	23	25 [c]	—
CCl_4	0·45	20	42	26 [b]	2·5
$n\text{-}C_6H_{14}$	0·45	60	12	28	Traces

[a] Crude coumarilic acid. [b] Product does not contain chlorine. [c] Product does not contain nitrogen.

The other decompositions were carried out similarly and the results are tabulated. In each case the alkali-soluble portion was recrystallised twice from toluene and shown to be coumarilic acid by m. p. and mixed m. p.