254. *Decomposition Reactions of Heterocyclic Diacyl Peroxides. Part III.*[1] *5-Methyl-1-phenyl-1 : 2 : 3-triazole-4-carbonyl Peroxide.*

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The triazolecarbonyloxy-radicals (II) generated by decomposition of the peroxide (I) resemble 2-thenoyloxy-radicals (Part II) in their behaviour towards aromatic solvents; in particular they attack chlorobenzene and bromobenzene, with displacement of the halogen, to give the phenyl triazolecarboxylate. They dehydrogenate toluene, and, in the presence of oxygen, benzyl hydroperoxide is formed.

THE study of decomposition reactions of representative heterocyclic diacyl peroxides has now been extended to 5-methyl-1-phenyl-1 : 2 : 3-triazole-4-carbonyl peroxide (I), reported by Cooper [2] to be a very active catalyst for vinyl polymerisation.

In aromatic solvents lacking side-chain hydrogen resins were produced, and the chief simple products were the methylphenyltriazole (TH) and the methylphenyltriazolecarboxylic acid ($T{\cdot}CO_2H$). The formation of the carboxylic acid recalls that of coumarilic acid from coumariloyl peroxide (Part I [3]) and of 2-thenoic acid from 2-thenoyl peroxide [1]

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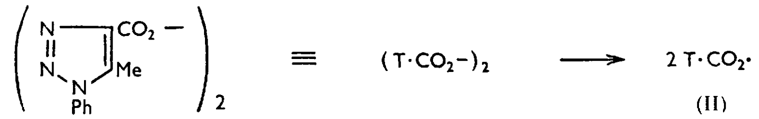
[1] Part II, *J.*, 1957, 4620.
[2] Cooper, *J.*, 1952, 2408.
[3] Ford and Waters, *J.*, 1951, 824.

in such solvents: it probably arises mainly by processes in which the triazolecarbonyloxy-radicals (II) dehydrogenate solute molecules: the 5-methyl group in the peroxide (and in any species derived from it) would be an obvious point of attack. The methylphenyltriazole, which could have arisen as the result of similar processes involving triazolyl radicals (T·), was probably, however, an artefact: the triazolecarboxylic acid was independently shown to undergo slow decarboxylation at the temperature of the experiments, and the methylphenyltriazole formed could be accounted for in this way. No other compounds for which reactions of triazolyl radicals could be considered responsible were isolated. The more interesting simple products, obtained in smaller amount, were aryl triazolecarboxylates ($T{\cdot}CO_2Ar$) derived by attack of the triazolecarbonyloxy-radicals on the solvent. They were not formed with the same regularity as were the aryl 2-thenoates from 2-thenoyl peroxide, but the reactions took parallel courses: in particular, the *phenyl* triazoloate was produced in chlorobenzene and bromobenzene, with displacement of the halogen.


(I) (II)

In benzene there was no nuclear attack, and in nitrobenzene only traces of the *p*-nitrophenyl triazolecarboxylate were formed. The phenyl ester initially isolated from the decompositions in chlorobenzene and bromobenzene was difficult to purify, and when the latter solvent was used the chief contaminant was shown to be the *p*-bromophenyl triazolecarboxylate. In neither solvent was the fate of the displaced halogen discovered. In the decomposition in bromobenzene, however, the crude carboxylic acid fraction contained a little combined bromine, and the uncrystallisable residues were slightly lachrymatory: if bromination had occurred at the 5-methyl group in the peroxide, or in species derived from it, both 5-bromomethyl-1-phenyl-1 : 2 : 3-triazole-4-carboxylic acid and 5-bromomethyl-1-phenyl-1 : 2 : 3-triazole would be expected as products. The lachrymatory bromomethylphenyltriazole was independently prepared, by the action of *N*-bromosuccinimide in the presence of benzoyl peroxide upon the methylphenyltriazole, but its occurrence in the reaction mixture could not be confirmed.

In toluene, where the decomposition was carried out under nitrogen and under oxygen, there was extensive side-chain attack (equation 1): little resin was formed, and there were increased yields of the methylphenyltriazole and of the triazolecarboxylic acid. Under nitrogen, dibenzyl was formed (cf. Part II). Under oxygen the peroxidic titre of the mixture steadily rose, and the mixture, worked up when the titre had its maximum value, gave benzyl hydroperoxide, and no dibenzyl; some benzyl alcohol (a typical breakdown product of the hydroperoxide) and a small amount of the *o*-tolyl triazolecarboxylate (nuclear attack) were also obtained. In an equimolar mixture of toluene and bromobenzene the toluene reacted preferentially: dibenzyl was formed, and no product derived from the bromobenzene was isolated.

$$T{\cdot}CO_2{\cdot} + Ph{\cdot}CH_3 \longrightarrow T{\cdot}CO_2H + Ph{\cdot}CH_2{\cdot} \quad \ldots\ldots\ldots \quad (1)$$

$$Ph{\cdot}CH_2{\cdot} + O_2 \longrightarrow Ph{\cdot}CH_2{\cdot}O_2{\cdot} \quad \ldots\ldots\ldots \quad (2)$$

$$Ph{\cdot}CH_2{\cdot}O_2{\cdot} + Ph{\cdot}CH_3 \longrightarrow Ph{\cdot}CH_2{\cdot}O_2H + Ph{\cdot}CH_2{\cdot} \quad \ldots\ldots\ldots \quad (3)$$

Walling and Buckler[4] prepared benzyl hydroperoxide, by the action of oxygen on ethereal benzylmagnesium chloride, but did not characterise it. Like these authors we were unable to obtain the hydroperoxide analytically pure, but we have made a crystalline

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[4] Walling and Buckler, *J. Amer. Chem. Soc.*, 1955, **77**, 6032.

derivative, benzyl triphenylmethyl peroxide. Toluene does not readily undergo autoxidation,[5] and in the present work the yields of hydroperoxide were found to be roughly proportional to the amount of the triazolecarbonyl peroxide used, showing that the sequence (2–3) was self-sustaining only to a negligible extent.

The dehydrogenating properties of the triazolecarbonyloxy-radicals were further exhibited in the decomposition of the peroxide in 3-methylbutan-2-one, 3 : 3 : 4 : 4-tetramethylhexa-2 : 5-dione being formed, by dimerisation of the metathetically produced 1 : 1-dimethyl-2-oxopropyl radicals [6] (reactions 4 and 5).

$$\mathrm{T{\cdot}CO_2{\cdot} + CHMe_2Ac \longrightarrow T{\cdot}CO_2H + {\cdot}CMe2Ac} \quad . \; . \; . \; . \; . \; . \quad (4)$$

$$\mathrm{2{\cdot}CMe_2Ac \longrightarrow (CMe_2Ac)_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

EXPERIMENTAL

The aromatic solvents were purified as described in Part II. Commercial 3-methylbutan-2-one was shaken repeatedly with small portions of saturated aqueous ferrous sulphate, dried ($MgSO_4$), and fractionated, then having b. p. 93°/755 mm.

5-Methyl-1-phenyl-1 : 2 : 3-triazole-4-carbonyl Peroxide.—Treatment of 5-methyl-1-phenyl-1 : 2 : 3-triazole-4-carboxylic acid [7] with a large excess of thionyl chloride gave the triazolecarbonyl chloride, which was obtained directly pure (m. p. 133°). A solution of the acid chloride (10 g.) in methylene chloride (50 ml.) was added dropwise to a vigorously stirred ice-cold mixture of 2N-sodium hydroxide and aqueous hydrogen peroxide (30-vol.; 40 ml.). Water then was added and stirring continued for a further 15 min. The methylene chloride was removed by bubbling air through the mixture, the solid being then collected, air-dried, and dissolved in methylene chloride (0·5 l.). Gradual addition, with stirring, of light petroleum (b. p. 30—40°; 1 l.) to the dried ($MgSO_4$) solution gave the peroxide (70%) as crystals, m. p. 167° (sharp, with subsequent decomp.) [Found: equiv. (iodometric) 196. Calc. for $C_{20}H_{16}O_4N_6$: equiv., 202). Cooper [2] records m. p. 166° (decomp.).

Decomposition Reactions.—The reaction mixtures were worked up as described in Part II. In all cases recrystallisation of the carboxylic acid fraction from water gave pure methylphenyltriazolecarboxylic acid.

Benzene. A solution of the peroxide (5·3 g.) in benzene (1·5 l.) was refluxed under nitrogen. After 48 hr., when 94% of the peroxide had decomposed, 1·0 mole of carbon dioxide (per mole of peroxide) had been evolved. The residual peroxide was destroyed (sodium iodide in acetic acid followed by aqueous sodium sulphite); the benzene layer then gave the triazolecarboxylic acid (2·6 g.) and non-acidic material, which was distilled: the resulting oil, b. p. 165°/0·4 mm., solidified, and was obtained as prisms (0·8 g.), m. p. 64°, from ether–light petroleum (b. p. 50—60°) (Found: C, 67·9; H, 5·7; N, 26·6. Calc. for $C_9H_9N_3$: C, 67·9; H, 5·7; N, 26·4%), identical with authentic 5-methyl-1-phenyl-1 : 2 : 3-triazole, m. p. 64°, prepared [7] by heating the triazolecarboxylic acid above its m. p.

Nitrobenzene. Decomposition of the peroxide (6·0 g.) in nitrobenzene (600 ml.) for 8 hr. at 99—106° gave the triazolecarboxylic acid and a tarry residue, which on extraction with hot alcohol yielded a solid (100 mg.): recrystallisation (alcohol) gave *p-nitrophenyl 5-methyl-1-phenyl-1 : 2 : 3-triazole-4-carboxylate* as colourless needles, m. p. 224° (Found: C, 59·1; H, 3·8. $C_{16}H_{12}O_4N_4$ requires C, 59·3; H, 3·7; N, 17·3%). The m. p. was undepressed in admixture with an authentic specimen, m. p. 224° (Found: C, 59·5; H, 3·5; N, 17·1%), prepared by refluxing the triazolecarbonyl chloride with *p*-nitrophenol in pyridine.

Chlorobenzene. Decomposition of the peroxide (6·0 g.) in chlorobenzene (600 ml.) at 85—90° for 8 hr. gave the triazolecarboxylic acid (2·3 g.) and a gum (3·6 g.), which on trituration with methanol yielded a solid (0·66 g.) containing traces of combined chlorine: repeated recrystallisation from light petroleum (b. p. 80—90°) afforded *phenyl 5-methyl-1-phenyl-1 : 2 : 3-triazole-4-carboxylate* (0·38 g.) as prisms, m. p. and mixed m. p. 146° (Found: C, 68·6; H, 4·7; N, 15·0. $C_{16}H_{13}O_2N_3$ requires C, 68·8; H, 4·7; N, 15·0%). Hydrolysis with 2N-sodium

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[5] B.P. 707,006; Hock and Lang, *Ber.*, 1943, **76**, 169; Seergeev and Fedorova, *Doklady Akad. Nauk S.S.S.R.*, 1956, **109**, 796.

[6] Kharasch, McBay, and Urry, *J. Amer. Chem. Soc.*, 1948, **70**, 1269.

[7] Dimroth, *Ber.*, 1902, **35**, 1029.

hydroxide yielded the triazolecarboxylic acid, m. p. and mixed m. p. 148—149°, together with phenol (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 145·5°). The authentic ester, m. p. 146° (Found: C, 68·9; H, 4·75; N, 15·0%), was prepared from the acid chloride and phenol in pyridine.

The methanol-soluble fraction was chromatographed on alumina from benzene solution, and yielded traces of the phenyl ester, together with an oil, which when further chromatographed, from ether–light petroleum (b. p. 40—60°) (2 : 1), gave a small quantity of the methylphenyltriazole.

Bromobenzene. A solution of the peroxide (7·5 g.) in bromobenzene (750 ml.) was heated at 80—85° for 36 hr. Recrystallisation of the acid fraction (3·2 g.) (Found: Br, 3·1%) gave the triazolecarboxylic acid. The non-acidic material (4·8 g.) was extracted with hot benzene, and the extract was passed down a short alumina column. Removal of the benzene and trituration of the resulting gum with ether–light petroleum (b. p. 30—40°) gave an ester fraction (0·52 g.) (Found: Br, 9·6%), which was chromatographed on Norit from chloroform–light petroleum (b. p. 60—70°) (1 : 8): elution, with this mixture containing an increasing proportion of chloroform, first gave some crystalline material of indefinite m. p., and then the phenyl ester, m. p. and mixed m. p. 144—144·5° (from methanol). Chromatography of the ether–petroleum-soluble material gave the methylphenyltriazole (0·47 g.).

In another experiment the ester fraction was hydrolysed with aqueous-methanolic sodium hydroxide, and gave the triazolecarboxylic acid and a phenolic fraction, which was benzoylated: recrystallisation of the product from light petroleum (b. p. 30—40°) gave prisms, m. p. 99—102°, undepressed in admixture with *p*-bromophenyl benzoate.

Toluene. (*a*) Under nitrogen. When a suspension of the peroxide (5·2 g.) in toluene (580 ml.) was heated under nitrogen at 90—95° for 3 days the triazolecarboxylic acid (1·7 g.) and a non-acidic fraction (4·7 g.) were obtained: chromatography of the latter on alumina from ether–light petroleum (b. p. 30—40°) solution yielded dibenzyl (0·82 g.), m. p. and mixed m. p. 50—51°, and the methylphenyltriazole (2·1 g.).

(*b*) Under oxygen. Dry oxygen was slowly bubbled through a suspension of the peroxide (3·0 g.) in toluene (305 ml.) at 75—85°: the iodometric titre of the mixture reached its maximum after 4½ days, having then increased by 140%. After removal of the triazolecarboxylic acid (1·0 g.) the almost colourless solution was extracted with 2N-sodium hydroxide: acidification of the extracts gave an oil (1·5 g.), which was isolated with ether. Further quantities of the peroxide (12 g. in all) were similarly decomposed, and the alkali-soluble oil, benzyl hydroperoxide (see below), was accumulated.

The non-acidic fractions from these decompositions were combined (7·2 g.) and triturated with ether–light petroleum (b. p. 30—40°): the resulting solid (0·95 g.) was recrystallised (twice) from benzene–light petroleum (b. p. 80—90°) and finally from methanol, giving o-*tolyl* 5-*methyl*-1-*phenyl*-1 : 2 : 3-*triazole*-4-*carboxylate* as prisms, m. p. 138—139° (Found: C, 69·7; H, 5·0. $C_{17}H_{15}O_2N_3$ requires C, 69·6; H, 5·1; N, 14·3%), identical with a specimen, m. p. 142° (Found: C, 69·4; H, 5·1; N, 14·3%), prepared from the acid chloride and *o*-cresol in pyridine.

Fractionation of the mother-liquor from the initial separation of the ester gave benzyl alcohol (1·9 g.) (1-naphthylcarbamate, m. p. and mixed m. p. 130—131°) and the methylphenyltriazole (2·0 g.). No dibenzyl was isolated.

Toluene–bromobenzene. A suspension of the peroxide (6·0 g.) in a mixture of toluene (305 ml.) and bromobenzene (300 ml.) heated at 85—95° for 38 hr. under nitrogen gave the triazolecarboxylic acid (1·7 g.) and an oil, which was chromatographed on alumina, first from benzene–light petroleum (b. p. 80—90°) (1 : 1) and then from light petroleum (b. p. 50—60°): dibenzyl (0·7 g.) and the methylphenyltriazole (0·9 g.) were obtained.

3-*Methylbutan*-2-*one.* A suspension of the peroxide (5·4 g.) in the ketone (270 ml.) was refluxed for 8 hr. under nitrogen. The mixture gave the triazolecarboxylic acid (3·4 g.) and an oil, which afforded 3 : 3 : 4 : 4-tetramethylhexa-2 : 5-dione (0·5 g.), b. p. 70—80°/1·0 mm., identified by conversion into its tetrabromo-derivative, obtained as rods, m. p. 117·5°, from methanol (lit.,[6] 117°) (Found: Br, 65·8. Calc. for $C_{10}H_{14}O_2Br_4$: Br, 65·8%), and a higher-boiling fraction (1·0 g.) consisting substantially of the methylphenyltriazole.

Decarboxylation of 5-*Methyl*-1-*phenyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid in Boiling Benzene.*—The concentration of a *ca.* 0·01N-solution of the acid in benzene was determined by shaking an aliquot part with an excess of 0·05N-sodium hydroxide and back-titrating it with 0·01N-hydrochloric acid. The solution was refluxed for 3 days and the determination repeated: the figures obtained showed that 45% of the acid had undergone decarboxylation. The methylphenyltriazole was isolated from the solution.

Bromination of 5-*Methyl*-1-*phenyl*-1 : 2 : 3-*triazole.*—A solution of the triazole (2·6 g.) in carbon tetrachloride (30 ml.) was refluxed with *N*-bromosuccinimide (4·0 g.) for 12 hr., a crystal of benzoyl peroxide being introduced at intervals during the first hour. The mixture was filtered and the filtrate taken to dryness: repeated extraction of the residue with hot ether–light petroleum (b. p. 50—60°) and evaporation of the extracts yielded crystals (0·5 g.) which on recrystallisation from light petroleum gave the slightly lachrymatory 5-*bromomethyl*-1-*phenyl*-1 : 2 : 3-*triazole* as prisms, m. p. 66° (Found: C, 45·7; H, 3·3; N, 17·9; Br, 33·0. $C_9H_8N_3Br$ requires C, 45·4; H, 3·4; N, 17·7; Br, 33·6%). Proof of side-chain bromination was obtained by oxidation to 1-phenyl-1 : 2 : 3-triazole-5-carboxylic acid, m. p. 172—174°, identical with an authentic specimen.[7]

Characterisation of Benzyl Hydroperoxide.—When a small quantity of the alkali-soluble oil obtained from the reactions in toluene under oxygen was heated at atmospheric pressure, decomposition set in with vigour, yielding benzaldehyde (2 : 4-dinitrophenylhydrazone, m. p. 238°), benzyl alcohol (1-naphthylcarbamate, m. p. 131°), and water. Attempted distillation at 0·01 mm. from glass wool (bath $\not>$50°) resulted in an explosion, but distillation under nitrogen gave the hydroperoxide as a colourless liquid, b. p. 50—51°/0·01 mm. (lit.,[4] 55—57°/0·1 mm.) [Found: equiv. (iodometric), 55. Calc. for $C_7H_8O_2$: equiv., 62], with a faint "metallic" odour and skin-irritant properties. Treatment of a glacial acetic acid solution with triphenylmethanol and a trace of concentrated sulphuric acid [8] gave *benzyl triphenylmethyl peroxide*, which formed large prisms, m. p. 82°, from light petroleum (b. p. 60—70°) [Found (combustion in air): C, 85·2; H, 6·0. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·05%] and appeared to be stable indefinitely.

A reference sample of the hydroperoxide was obtained, in low yield, by portion-wise addition of ethereal benzylmagnesium chloride, with stirring, to oxygen-saturated ether (cooled by solid carbon dioxide–methanol) at such a rate that the internal temperature remained between $-50°$ and $-60°$; dropwise addition [4] of the Grignard solution led to a very much poorer yield. The triphenylmethyl derivative, m. p. 82° (Found: C, 85·3; H, 6·0%), was identical with the above.

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[8] Davies, Foster, and White, *J.*, 1954, 2200.