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Anionic decomposition of an organic peroxide leading to *o*-xylene

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Reaction of 1,2-dimethyl-1,2-dihydrophthalic anhydride (8) with *t*-BuOONa at 40°C gave o-xylene as the only observed product. This reaction is proposed to occur through intermediacy of the anionic peroxide 10 whose conversion to o-xylene is calculated to be exothermic by 84 kcal/mol. Extension of this reaction to systems that do not have the possibility for gaining aromatic stabilization was unsuccessful.

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L'anhydride de l'acide diméthyl-1,2 dihydro-1,2 phtalique (8) réagit avec le *tert*-BuOONa à 40°C en donnant uniquement du o-xylène. On pense que cette réaction se produit par l'intermédiaire du peroxyde anionique 10 qui par la transformation en o-xylène libèrerait 84 kcal/mol. On a vainement tenté d'étendre cette réaction aux systèmes qui n'ont pas la possibilité d'acquérir la stabilité aromatique.

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The reactions of peroxides derived from 1,2-dicarboxylic acid systems have been the subject of continuing interest. Examples include reaction of di-*tert*-butylperoxy meso-2,3-diphenylsuccinate (1), which proceeds with rate limiting scission of one peroxide bond to give the benzylic radical 2, which gives exclusive formation of *trans*-stilbene (eq. [1]) (1). This general reaction was developed as a general synthetic method for the conversion of 1,2-dicarboxylic acid systems to alkenes (eq. [2] (2).



PhCH=CHPh



The aromatic analog di-*tert*-butylperoxy phthalate (3) was the object of careful study in our laboratory (3), and it was found that, although the free radical reactions of this substrate did not involve direct interaction between the two carboxyl groups, there was evidently a nonradical decomposition of the peroxidic intermediate 4 involved (eq. [3]) as one of the reaction paths followed.



Related studies have dealt with cyclic diacyl peroxides 5-7 derived from 1,2-dicarboxylic acids.



The study of 5 and several related systems was reported by Dervan and Jones (4), who presented evidence for their thermal decomposition according to eq. [4]. Even though these reactions were

potentially sufficiently exothermic to produce excited states of the product alkenes, the evidence indicated that this did not occur. However, in the reaction of eq. [5] the species 6 was evidently



generated and the observation of fluorescence in the reaction indicated that the product terphenyl was formed as an excited singlet (5).

The most recent of a variety of studies of the reactivity of phthalyl peroxide (7) involves electron transfer from pyrene (5b).

The goal of the present study was to search for a case of concerted reaction of a derivative of a vicinal dicarboxylic acid system. A system of the type $\mathbf{6}$ appeared to be most appropriate, as the potential for aromatization of the ring would in-

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crease the exothermicity of a bisdecarboxylation. However, the presence of reactive α -hydrogens in 6 and its immediate precursors appeared undesirable because of their potential for facile isomerization to α , β -unsaturated carbonyl derivatives.

Results and discussion

The anhydride $\mathbf{8}$, originally prepared (6*a*) in one of two classic syntheses of cantharidin (6), was selected for study. The preparation followed the established methods, but the yield of $\mathbf{8}$ from the dibromide $\mathbf{9}$ was increased to 78% from the pre-



viously reported 11% by the use of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) as base instead of the previously utilized trimethylamine (6a). The hydrolysis of 8 to the corresponding diacid was carried out by the reported procedure (6a) but all attempts to convert the diacid or 8 to a diacyl chloride led to isolation of only 8 in every case. Consequently preparation of a cyclic peroxide or bisperester from 8 could not be attempted.

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Reaction of 8 with t-BuOONa in a mixed solvent (DME-CH₂Cl₂-pentane) at 40°C followed by distillation of the solvent at 60°C and vpc separation of the volatile products led to the isolation of o-xylene as the only product derived from 8. Similarly reaction of 8 with t-BuOOK in THF-d₈ at 0°C and prompt observation of the nmr spectrum showed signals ascribable to o-xylene and t-BuOK as the only products. One possible route to these products is shown (eq. [6]). The method of group equiva-



lents (7) predicts the decomposition of the conjugate acid of 10 to $2CO_2 + t$ -BuOH to be exothermic by about 84 kcal/mol and it would appear that the reaction of eq. [6] would be equally exothermic. Other pathways for the process may be envisaged, including stepwise ionic (eq. [7]) or radical (eq. [8]) routes.

The powerful driving force for the concerted pathway suggests that this route is favored. The cyclohexadienyl anion and radical formed in eqs. [7] and [8], respectively, would not appear to be

[7] 10
$$\xrightarrow{-CO_2}$$
 $(a^+ CO_3 t - Bu) \xrightarrow{-CO_2} o$ -xylene

[8] 10
$$\xrightarrow{-CO_2}$$
 $\overbrace{CO_2Na}^{\bullet}$ $\stackrel{\circ}{\underbrace{O}-t-Bu} \xrightarrow{-CO_2}{-t-BuONa}$ o-xylene

sufficiently stabilized to form under these conditions.

Thus our goal of observing a facile bisdecarboxylation reaction has been met, although in a rather unexpected and novel fashion. The possibility of developing a preparatively useful procedure for biscarboxylation in analogous systems that do not lead to aromatic systems occurred to us, but in several experiments (e.g., eq. [9]) this goal has not



yet been realized. Variable amounts of the products 13-15 were identified by their nmr spectra, but the inconsistency of the yields suggested that radicalinduced decompositions may have been occurring. Comparable results were obtained in benzene or toluene, with or without added KH or Et₃N.

A semiquantitative kinetics determination for decomposition of E-12 gave a rate constant of $5.3 \times 10^{-5} \text{ s}^{-1}$ at 98.0°C in toluene. Comparison to the value of $6.9 \times 10^{-4} \text{ s}^{-1}$ at 110°C reported (8) for *tert*-butyl cyclohexanepercarboxylate indicates similar rate limiting steps for these two peresters. Other anionic decompositions of organic perox-



ides include the reaction of diphenic anhydride (16) with t-BuOONa yielding lactone as shown in eq. [10] (9). This reaction was proposed to involve the



intermediate 17, but it may be noted that the reaction conditions (refluxing tetrahydrofuran) would not ordinarily be sufficient to result in homolytic reaction of a model compound such as *tert*-butyl perbenzoate.

Another reported (10) case of anionic decomposition of a peroxide is shown in eq. [11] and may be seen to be closely related to the proposal of eq. [6].

[11] t-BuOOCMe₂CO₂⁻ \rightarrow t-BuO⁻ + O==CMe₂ + CO₂

Experimental

Qualitative ir spectra were measured on a Perkin-Elmer 237 instrument. The nmr spectra were recorded on a Varian T-60 spectrometer. Elemental analyses were performed by A. B. Gygli Microanalysis Ltd., Toronto. Dimethoxyethane (DME) was freshly distilled from Na.

1,2-Dimethyl-1,2-dihydrophthalic anhydride (8)

³A mixture of 1.7 g (5.0 mmol) dibromide 9 (6b) and 1.52 g (8.6 mmol) DBU (Aldrich) were heated 5 min at 150°C. Sublimation gave 0.69 g (3.9 mmol, 78%) of 8, mp 64°C (lit. (6a) mp 63–67°C); nmr (CDCl₃) δ : 1.35 (s, 6, 2Me); 5.5–6.2 (m, 4, A₂B₂ pattern of vinyl H).

Reaction of 8 with t-BuOONa

A solution of 0.078 g (0.44 mmol) 8 in 5 mL CH₂Cl₂ and 3 mL pentane was added dropwise to a mixture of 1 mmol NaH (washed free of oil) and 1 mmol *t*-BuOOH in 15 mL dry DME. The mixture was heated 4 h at 40°C, poured into ice water, and extracted twice with ether. The combined ether layers were washed twice with 10% HCl, dried, and the solvent was distilled away below 60°C. Separation of the residue by vpc using a 3 m × 10 mm OV-17 column gave 36 mg (0.34 mmol, 77%) of *o*-xylene, identified by nmr. Reaction of 8 (1.0 mmol) in 1.0 mL THF-*d*₈ with *t*-BuOOK (1.5 mmol, from *t*-BuOOH and KH) with ice cooling, followed by prompt measurement of the nmr spectrum, gave peaks ascribable to *o*-xylene and a *tert*-butyl signal as the only reactant-derived absorptions.

E-2-Carbo-tert-perbutoxy cyclohexanecarboxylic acid (E-12)

trans-1,2-Cyclohexanedicarboxylic anhydride (7.2g, 50 mmol, Fluka) was added over 0.5 h to a mixture of 50 mmol NaH (washed free of oil with pentane) and 50 mmol *t*-BuOOH in 100 mL dry ether. The solution was stirred 1 h at 25°C, poured into ice water, acidified with HCl, and extracted with ether. After drying and evaporation of solvent there was obtained 9.3g (3e mmol, 76%) of *E*-12 which was recrystallized from CHCl₁/pen tane (10:1), mp 114–116°C (resolidification and remelting at 225–229°C); ir (toluene): 1710 cm⁻¹ (C=O of CO₂H), 1775 (C=O of CO₃-t-Bu) cm⁻¹; nmr (CDCl₃) δ : 1.30 (s, 9, t-Bu), 1.4–2.2 (m, 8, (CH₂)₄), 2.7 (m, 2, 2 methine H), 10 (broad s, 1, CO₂H). Anal. calcd. for C₁₂H₂₀O₅ (244.29): C 59.00, H 8.25; found: C 58.77, H 8.18.

Z-2-Carbo-tert-perbutoxy cyclohexanecarboxylic acid (Z-12)

This isomer was prepared in the same way as the *E*-isomer from the *Z* anhydride (Aldrich) and recrystallized from CHCl₃, mp 196–198°C; ir (CHCl₃): 1710 (C=O of CO₂H), 1765 (C=O of CO₃-t-Bu) cm⁻¹. nmr (CDCl₃) & 1.30 (s, 9, t-Bu), 1.4–2.0 (m, 8, (CH₂)₄), 3.0 (m, 2, 2 methine H), 8.5 (broad s, 1, CO₂H). Anal. calcd. for C₁₂H₂₀O₅ (244.29): C 59.00, H 8.25; found: C 59.18, H 8.26.

Product studies from E-12 and Z-12

The perester (0.6 g, 2.5 mmol) was dissolved in 10 mL solvent, sealed in a glass tube, and heated at 100°C for 24 h. The product was esterified with CH₂N₂ and analyzed by vpc with a 5 m × 3 mm Carbowax column at 130°C and 60 mL/min He flow. Products were isolated and identified by their nmr spectra and mass spectral molecular weights. Authentic samples of the methyl esters of cyclohexanecarboxylic acid and the 1,2-cyclohexanedicarboxylic acids were prepared for comparison. An authentic sample of methyl 2-*tert*-butoxycyclohexanecarboxylate was not available so this identification must be regarded as tentative. The nmr spectrum (CDCl₃) of this material from either *E*- or *Z*-12 showed pairs of closely spaced sharp singlets at δ 1.15 and 3.65 attributable to the *t*-BuO and MeO groups, respectively, of an *E/Z* mixture of products from either source.

Kinetics of decomposition of E-12

Ampules of a 0.064 M solution of the perester were removed at intervals from a constant temperature bath at 98.0°C and the disappearance of the perester band at 1775 cm⁻¹ was monitored as a function of time using a Perkin–Elmer 180 spectrophotometer. A single run was performed, which gave good first order kinetics (r = 0.999).

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