Oxygen Insertion Reactions.[1] A Re-investigation of the Reaction of Chromium Pentoxide Etherate with Tetracyclone

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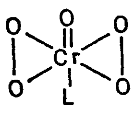
Summary In contradiction to an earlier report we have found that chromium pentoxide etherate solution oxidises tetraphenylcyclopentadienone to a known keto-lactone, which can be obtained more efficiently by chromic acid oxidation; we have been unable to prepare the earlier claimed peroxide.

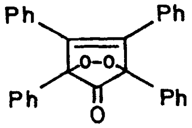
RECENTLY it was reported[2] that a remarkable and efficient oxygen transfer reaction took place between chromium pentoxide (I; L = Et_2O)[3] and tetracyclone (tetraphenylcyclopentadienone) to yield the endo-peroxide (II). Furthermore, this same substance (II) was claimed to be formed by the action of the unsaturated fatty acid oxygenating enzyme, lipoxidase, on tetracyclone in the presence of ethyl linoleate.[4] These observations were used to support the hypothesis that oxidations by chromium pentoxide and lipoxidase may involve the generation of an intermediate which is a "close analog of singlet oxygen".[4] Because of the important nature of such claims with respect to the problem of oxygenation reactions we report the results of a re-investigation of the chromium pentoxide reaction.

Reaction of tetracyclone with chromium pentoxide etherate, made from chromium trioxide or chromate solutions, in the dark at 25° in ether solution, slowly produced a new compound with an i.r. absorption at 1792 cm^{-1}, as previously recorded.[2] Chromatography of the crude product over silica gel gave a substance (A) (eluted with benzene–hexane 1 : 1) along with several minor components, none of which absorbed above 1750 cm^{-1}. Comparison of spectral data (i.r. and u.v.) showed that the crude product was largely a mixture of (A) and tetracyclone. Compound (A), initially obtained as a low-melting solid,[2] contaminated by some peroxidic material (weakly positive starch–iodide test), was recrystallized (EtOH) to m.p. 110—112°, ν_{max} 1792 and 1678 cm^{-1}, λ_{max} 261 nm (ϵ 21,000) without change in spectral properties. This substance was identical (m.p., mixed m.p., and i.r. spectrum) with compound (III), whose structure was elucidated in an elegant investigation by Yates and Stout,[5] and was identical in i.r. and u.v. absorptions with a sample of the material originally described as (II).[2]

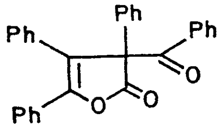
As further evidence for the original assignment (II), the thermal decomposition in refluxing benzene (48 h) to 2% yield of *cis*-dibenzoylstilbene, and at 210° conversion into diepoxide (IV),[6] m.p. 196—197°, ν_{max} 1755 cm^{-1}, was reported.[2] The pure substance (III) was quite stable to the former conditions but at 210° transformed into a mixture of products from which we isolated a compound, m.p. 183—185°, ν_{max} 1755 cm^{-1}, λ_{max} 287 nm (ϵ 19,200) (95% EtOH). This was shown to be the furan (V) by hydrolysis (3% methanolic hydrochloric acid) to the known lactone (VI), m.p. 122—125°,[7] and benzoic acid. This identification was confirmed by *O*-benzoylation of the readily enolisable lactone (VI) with benzoyl chloride in the presence of triethylamine to the same compound (V). Thus the thermal formation of (V) from (III) is formally a 1,3-acyl shift; however we have no information on the detailed mechanism of this process.



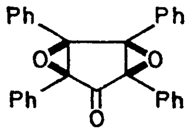
(I)



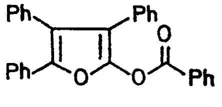
(II)



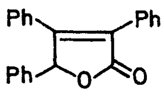
(III)



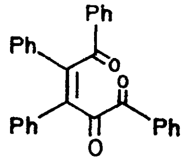
(IV)



(V)



(VI)



(VII)

With regard to the mechanism of formation of (III) we noted that washing of the blue chromium pentoxide solution with sodium hydrogen carbonate inhibited the reaction with tetracyclone (monitored by i.r.).[8] Furthermore, chromium trioxide in acetic acid (95%) rapidly and cleanly (80% overall) converted tetracyclone into (III). It is a distinct possibility, although not proven in this work that chromic acid, formed by degradation of the pentoxide, is responsible for the formation of (III). In any event the trione (VII), obtained by oxidative cleavage of tetracyclone, is a reasonable intermediate as was suggested.[5]

The structure (II)[2] is the expected adduct of singlet oxygen on tetracyclone.[9] It is known that sensitised oxygenation of tetracyclone, at ambient temperature, yields *cis*-dibenzoylstilbene (65% isolated, 72 h), the expected fragmentation product of the peroxy-ketone (II),[10] presumably the result of the extended reaction time required for oxygenation of this rather deactivated diene.

In the light of these findings the previous suggestions concerning the reactivity of chromium pentoxide[2] and the mechanism of lipoxidase action[4, 11] will require reconsideration.

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[1] Previous papers in this series are, (a) J. E. Baldwin, H. H. Basson, and H. Krauss, jun., *Chem. Comm.*, 1968, 984; (b) J. E. Baldwin and J. C. Swallow, *Angew. Chem.*, 1969, **81**, 571.

[2] H. W.-S. Chan, *Chem. Comm.*, 1970, 1550.

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[6] A compound of structure (V) is reported, m.p. 192°; *cf.* J. J. Basselier, *Compt. rend.*, 1959, **248**, 700.

[7] P. Pütter and W. Dilthey, *J. prakt. Chem.*, 1937, **149**, 183.

[8] We assayed the CrO_5 solution by *cautious* evaporation of small volumes in high vacuum and weighed as CrO_3. These approximate procedures ensured that we had at least 10 moles excess of reagent.

[9] K. Gollnick, *Adv. Photochem.*, 1968, **6**, 1.

[10] C. F. Wilcox, jun., and M. P. Stevens, *J. Amer. Chem. Soc.*, 1962, **84**, 1258.

[11] In this connection attempts to intercept singlet oxygen like activity from lipoxidase with the reactive diene laevopimaric acid were unsuccessful. (Personal communication from Dr. B. Malloy).