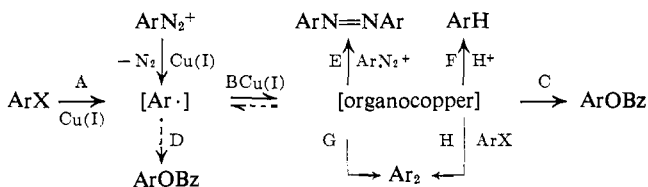


1,5-hydrogen atom transfer.<sup>10a</sup> (B) Evidence to support the novel concept that aryl radicals can react readily with cuprous benzoate to form organometallics was obtained by treating *p*-toluenediazonium fluoroborate dissolved in sulfolane with cuprous benzoate in diglyme. A rapid evolution of nitrogen occurred and the typical arylcopper coupling product, bitolyl,<sup>2a</sup> was produced along with *p*-tolylbenzoate, toluene, and *p,p'*-dimethylazobenzene. It is now well established that radicals are produced upon decomposition of diazonium ions induced by Cu(I).<sup>10a,d,11</sup> Biaryls and azoarenes are frequently observed products from the copper-promoted decomposition of diazonium ions, and their mode of formation has never been satisfactorily explained.<sup>4,12</sup> It now seems likely that they are both formed from organocopper intermediates, coupling<sup>2a,3</sup> (G) of which produces biaryl and addition (E) of which across the nitrogen–nitrogen bond of the diazonium ion leads to azoarene.<sup>13,14a</sup>

The mechanism of the formation (C) of the aryl benzoate from the organometallic intermediate remains obscure. It would be tempting to postulate that organocopper formation from the radical is reversible (see B) and that the aryl radical is capable of abstracting a benzyloxy radical from a Cu(II) salt of benzoic acid<sup>10a,d</sup> (broken arrows B and D), but we have found that cupric benzoate does not react with phenyl radicals generated by cuprous oxide catalyzed decomposition of the *p*-toluenediazonium ion.<sup>15</sup>



The results reported here and summarized in the above scheme suggest mechanistic explanations for a number of known copper-induced reactions, and this topic will be explored in subsequent papers.

(11) J. K. Kochi, *J. Am. Chem. Soc.*, **79**, 2942 (1957); S. C. Dickerman and G. B. Vermont, *ibid.*, **84**, 4150 (1962); C. S. Rondstedt, *Org. Reactions* **11**, 189 (1960).

(12) W. A. Cowdrey and D. S. Davies, *Quart. Rev. (London)*, **6**, 358 (1952); E. Pfeil, *Angew. Chem.*, **65**, 155 (1953).

(13) This explanation is in excellent accord with all of the data<sup>4,12</sup> concerning the formation of these by-products of copper-catalyzed diazonium decomposition including the rate dependence on cuprous salt concentration and substituent effects. It should be noted that Grignard and organozinc compounds have been reported to yield azo compounds on treatment with diazonium salts.<sup>14</sup>

(14) H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, 274 (1945); D. Y. Curtin and J. A. Ursprung, *J. Org. Chem.*, **21**, 1221 (1956).

(14a) NOTE ADDED IN PROOF. It has been called to our attention that a similar suggestion has been tentatively put forth by Kochi (footnote 19 of ref 11).

(15) However, the cupric benzoate was only slightly soluble in the diglyme-sulfolane reaction medium. Furthermore, a very specific form of the Cu(II) salt might be required.<sup>10c</sup>

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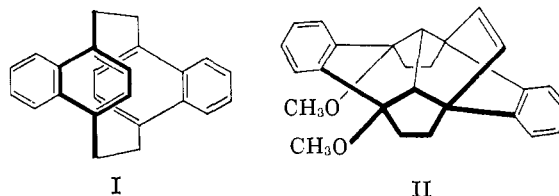
Received August 17, 1966

## The Photosensitized Autoxidation of [2.2]Paracyclonaphthane

Sir:

While aromatic systems such as anthracene and rubrene readily form transannular peroxides with air and light,<sup>1,2</sup> such sensitivity toward singlet oxygen has not been exhibited by naphthalene or benzene.<sup>3</sup>

We now wish to report that the strained naphthalene system in anti[2.2]paracyclonaphthane (I)<sup>4</sup> reacts with oxygen under the conditions of photosensitized autoxidation, leading to the novel polycyclic product, II.



Air was passed through a dilute solution of I in methanol in the presence of methylene blue during irradiation with a 275-w G.E. sunlamp.<sup>5</sup> The temperature remained at 58° throughout the reaction, which was stopped after 10 days. On concentrating and cooling the solution, polymeric material and unchanged I was collected. Complete removal of solvent left a residue which, on crystallization from ethyl acetate, yielded the oxidation product (20%) as white needles, mp 209–210°. The assignment of structure II to this product was based on the following evidence: infrared spectrum, peaks at 1080 (C–O) and 2825 cm<sup>-1</sup> (O–Me); ultraviolet spectrum, λ<sub>max</sub><sup>EtOH</sup> 265 mμ (ε 676) (two substituted benzene rings); nmr, multiplet at τ 2.73 (8 aromatic H), singlet at 4.18 (2 vinyl H), singlet at 7.08 (6 methoxyl H),<sup>6</sup> multiplet at 7.63 (10 H). *Anal.* Calcd for C<sub>26</sub>H<sub>26</sub>O<sub>2</sub>: C, 84.29; H, 7.07; mol wt, 370. Found: C, 84.57; H, 7.37; mol wt (mass spectroscopy), 370. Thermal breakdown of this product during mass spectral analysis gave rise to peaks at *m/e* 306 and 280, corresponding to loss of two molecules of methanol and an acetylene residue, respectively. On catalytic hydrogenation this product absorbed 1 mole of hydrogen, leading to a dihydro derivative in which the vinyl nmr absorption at τ 4.18 was absent.

The structure which is completely compatible with all of the above physical and chemical data is the internal Diels–Alder addition product II. This conclusion was confirmed by a single-crystal X-ray structure determination carried out by Dr. Albert Fratini of the U. S. Naval Research Laboratories, Washington, D. C.<sup>7</sup>

Formation of II appears to take place by initial reaction of I with singlet oxygen to form a transannular peroxide (III). Although naphthalene normally does not add oxygen in this manner, the strain associated with the ring deformation in the paracyclonaphthane<sup>4</sup> undoubtedly imparts greater reactivity to the dienoid

(1) C. Dufraisse and J. Houpillart, *Compt. Rend.*, **205**, 740 (1937).

(2) C. Dufraisse and A. Etienne, *ibid.*, **201**, 280 (1935).

(3) C. Dufraisse and R. Priou, *Bull. Soc. Chim. France*, [5] **5**, 611 (1938); C. Dufraisse and J. Houpillart, *ibid.*, [5] **5**, 626 (1938).

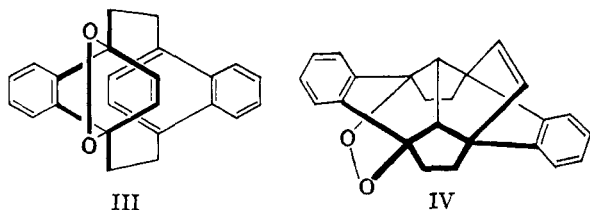
(4) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Am. Chem. Soc.*, **85**, 1088 (1963).

(5) Using visible light (150-w floodlamp) the reaction gave the same product but over a longer period of time.

(6) The abnormally high position of the methoxyl protons may be associated with the shielding effect of the proximate benzene rings.

(7) Details to be reported elsewhere.

system. A second-stage internal Diels-Alder reaction would lead to IV which is transformed by solvolysis in methanol to II.



Further investigations on the reactions of singlet oxygen with strained aromatic systems are in progress.

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### New Reactions Predicted by a [3.3.1]Bicyclic Mechanism<sup>1</sup>

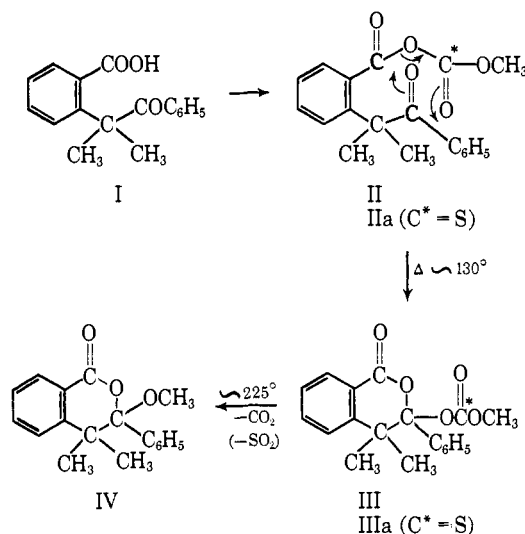
Sir:

Because certain reactions had been postulated to take place by a novel [3.2.1]bicyclic mechanism,<sup>2</sup> we were led to explore the possibility that other bicyclic paths might be discovered. Herein are described several new reactions. These reactions were discovered by predicting that they would take place by a [3.3.1]bicyclic mechanism.

On treatment of *o*-( $\alpha,\alpha$ -dimethylphenacyl)benzoic acid<sup>3</sup> (I) with methyl chlorocarbonate and Dabco,<sup>4</sup> a high yield of the mixed anhydride,<sup>5</sup> II, mp 85–88°, was obtained. The same compound was also prepared in high yield by treatment of the sodium salt of I with methyl chlorocarbonate. On heating II for a short time at 130–135° resolidification occurred. The solid isolated, mp 219° dec, was the rearranged lactonic ester,<sup>5</sup> III. On heating above the melting point III lost carbon dioxide to give the pseudo ester,<sup>3</sup> IV, mp 172–174°, in high yield. When methyl chlorosulfite<sup>6</sup> was substituted for methyl chlorocarbonate in the above reactions, we were unable to isolate compounds IIa and IIIa analogous to II and III, but they were undoubtedly present. However, on heating of the crude reaction mixture sulfur dioxide was readily lost and high yields of pseudo ester IV were obtained.

We believe that the facile rearrangement of II to III occurs by a [3.3.1]bicyclic mechanism as indicated by the arrows in formula II. The two indicated carbonyl carbons of I are the bridgehead carbons which

define the [3.3.1]bicyclic system. This rearrangement takes place with about the same ease as that of the comparable intermediate prepared from *o*-benzoylbenzoic acid and methyl chlorocarbonate,<sup>2b</sup> a reaction that involves a [3.2.1]bicyclic path.<sup>2</sup> A similar path is undoubtedly involved for the sulfur-containing intermediates IIa and IIIa.



When *o*-benzoyl- $\alpha,\alpha$ -dimethylphenylacetic acid<sup>7</sup> (V) was treated with methyl chlorocarbonate in the presence of Dabco in ether at 0–5° a compound, mp 131–132°, was obtained in 89% yield to which the lactonic ester structure VI<sup>5</sup> is assigned. The same compound was obtained in 82% yield when the sodium salt of V was allowed to react with methyl chlorocarbonate at room temperature. Undoubtedly an acyclic compound analogous to II was formed initially in both cases as shown in the illustration, but this rearranged to VI even though the temperature during work-up never exceeded 30°. Support for the argument that the initially formed compound has the acyclic mixed anhydride structure may be derived from the fact that the ultraviolet spectra of V and its sodium salt are nearly the same as that of the normal methyl ester of V ( $\lambda_{\max}^{\text{CHCl}_3}$ , 250  $\mu\mu$  ( $\epsilon$  13,720)) and quite different from that of the pseudo methyl ester of V ( $\lambda_{\max}^{\text{CHCl}_3}$ , 262  $\mu\mu$  ( $\epsilon$  533)). As in the case of the pyrolysis of III to IV, pyrolysis of VI at 160–180° resulted in loss of carbon dioxide and formation of VII, mp 119–120°, the pseudo methyl ester<sup>7</sup> of V, in almost quantitative yield. The rearrangement of the initially formed mixed anhydride (analogous to II) to the lactonic ester VI undoubtedly occurs by a [3.3.1]bicyclic path which, in this case, must provide such a favorable route that rearrangement occurs rapidly at room temperature.

When the intermediate formed by reaction of the sodium salt of V with methyl chlorosulfite was heated in benzene, sulfur dioxide was evolved and a high yield of VII was obtained. Because of the instability of the intermediates involved they were not isolated. However, we believe a [3.3.1]bicyclic reaction path similar to that involving the carbonate is involved.

If there is any generality to the [3.3.1]bicyclic path there are many new reactions, such as the ones above

(1) This research was supported by a grant from the U. S. Army Research Office, Durham, N. C.

(2) (a) M. S. Newman and C. Courduvelis, *J. Am. Chem. Soc.*, **86**, 2942 (1964); (b) *ibid.*, **88**, 781 (1966).

(3) M. Renson and L. Christiaens, *Bull. Soc. Chim. Belges*, **71**, 405 (1962).

(4) 1,4-Diaza[2.2.2]bicyclooctane. We thank the Houdry Process Co., Marcus Hook, Pa., for a generous supply of Dabco.

(5) All new compounds gave acceptable carbon and hydrogen analyses and had infrared, ultraviolet, and nmr spectra consistent with the assigned structures.

(6) M. S. Newman and W. S. Fones, *J. Am. Chem. Soc.*, **69**, 1046 (1947).

(7) M. Renson and L. Christiaens, *Bull. Soc. Chim. Belges*, **71**, 379 (1962).