

pentanoic acid, derived from decomposition of the pyridine ring of a type along with fission of the C-2 double bond in the side chain.

The presence of this novel polysubstituted pyridine ring was further confirmed by comparison of the ultraviolet spectra of HPA and acid II with that of a new model compound, 4-hydroxy-6-hydroxymethyl-2,3-dimethoxypyridine, synthesized from 2-bromo-6-hydroxymethyl-4-oxo-3-methoxy-(4H)-pyran.<sup>14</sup> Shifts of ultraviolet spectra in neutral, acidic, and basic solutions of these compounds were superimposable. Thus structures IIa and IVa are assigned to PA and HPA, respectively.

(14) (a) T. Yabuta, *J. Chem. Soc.*, 125, 575 (1924); (b) I. Ichimoto, K. Miyagawa, and C. Tatsumi, *Bull. Univ. Osaka Pref.*, B15, 61 (1964).

Nobutaka Takahashi, Akinori Suzuki, Saburo Tamura

Department of Agricultural Chemistry  
The University of Tokyo, Tokyo, Japan

Received March 8, 1965

### Photooxidative Cyclization of Quercetin Pentamethyl Ether

Sir:

Although flavone and quercetin pentamethyl ether (I) have been used as a photosensitizer<sup>1</sup> and ultraviolet absorption filter,<sup>2</sup> respectively, their irradiation products have not been reported. We have found that whereas intense, short wave length ultraviolet radiation causes extensive degradation and polymerization of I, less energetic treatment (350 m $\mu$ ) induces a novel and important type of ring closure.

A methanolic solution (2.7  $\times 10^{-3}$  M) of I, freed from oxygen and under pure dry nitrogen, was irradiated in a Pyrex flask set in a photochemical reactor<sup>3</sup> for 40 hr., using low pressure mercury lamps at 350 m $\mu$ . Light yellow crystals (II) were isolated as the major product in 31% yield.<sup>4</sup>

Compound II is a monomer, C<sub>20</sub>H<sub>18</sub>O<sub>7</sub>, m.p. 209–210°. *Anal.* Calcd. for C<sub>18</sub>H<sub>8</sub>O<sub>3</sub>(OCH<sub>3</sub>)<sub>4</sub>: C, 64.86; H, 4.90; OCH<sub>3</sub>, 33.5. Found: C, 64.6; H, 5.04; OCH<sub>3</sub>, 33.1. Ultraviolet maxima appeared at 375, 261, and 243 m $\mu$ ; infrared showed a broad peak at 1610–1640 cm<sup>-1</sup>. The parent compound, I, showed maxima at 339, 264, and 249 m $\mu$  and absorption bands in the infrared at 1610 and 1630 cm<sup>-1</sup>. The n.m.r. spectrum of II gave five singlets at  $\tau$  2.90, 3.41, 4.90, 6.03, and 6.14, integrated for 1, 1, 2, 3, and 9 protons, respectively, and two one-proton doublets ( $J = 2.5$  c.p.s.) at  $\tau$  3.55 and 3.80.

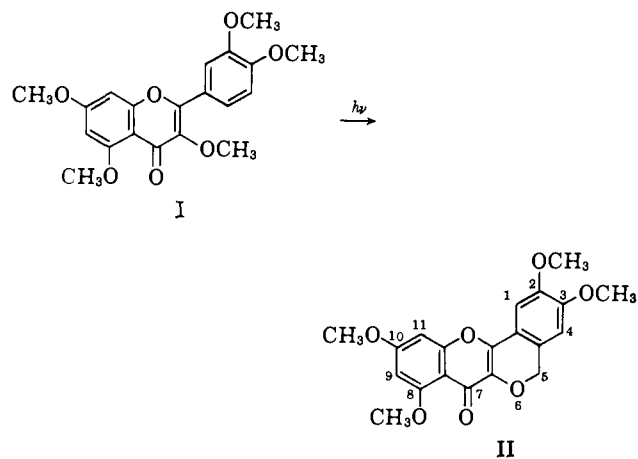
The physical data are in agreement with compound II being 2,3,8-10-tetramethoxy-7-oxo[2]benzopyrano[4,3-*b*][1]benzopyran, and the reaction occurring as shown.

(1) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Corvan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, 86, 3197 (1964).

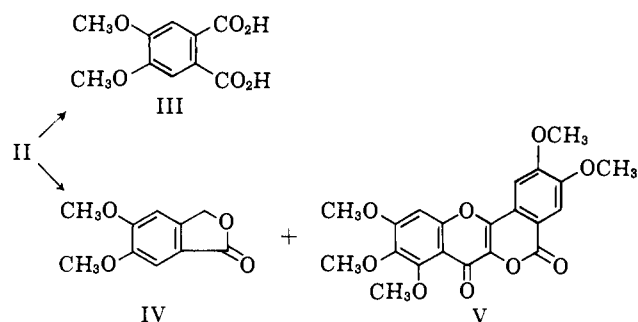
(2) H. Ikeda and K. Toba, *J. Soc. Sci. Phot. Japan*, 18, 110 (1956).

(3) Available from New England Ultraviolet Co., Middletown, Conn. Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

(4) A minor product (16% yield) isomeric with quercetin pentamethyl ether has been isolated. The structure of this compound is under investigation.



The n.m.r. absorption bands at  $\tau$  6.03 and 6.14 belong to the four methoxyl groups and the  $\tau$  3.55 and 3.80 (doublets,  $J = 2.5$  c.p.s.) peaks are attributed to the two *meta* protons at positions 9 and 11, respectively. Since the  $\tau$  2.90 and 3.41 peaks are singlets they are assigned to the *para* protons at positions 1 and 4, respectively. The proton at position 1 would be expected to absorb at lower field because of the deshielding effect of its *ortho*  $\alpha,\beta$ -unsaturated substituent. The two-proton singlet at  $\tau$  4.90 is reasonably assigned to the benzylic protons.



The structure of II was further supported by chemical evidence. Treatment with magnesium and hydrochloric acid gave a deep red solution typical of flavones.<sup>5</sup> Oxidation of photoproduct II in basic potassium permanganate solution gave *m*-hemipinic acid (III) which dehydrated during sublimation to its anhydride (m.p. 176–178°). Mild potassium permanganate oxidation of II in acetone yielded a mixture of *m*-meconin (IV, m.p. 155–157°) and the lactone V (m.p. 322–324°). The authenticity of *m*-meconin (IV) and the anhydride of III was demonstrated by comparison with synthetic samples.<sup>6</sup> The structure of lactone V was determined by elemental analysis (*Anal.* Calcd. for C<sub>20</sub>H<sub>16</sub>O<sub>8</sub>: C, 62.5; H, 4.20; OCH<sub>3</sub>, 32.6. Found: C, 62.6; H, 4.25; OCH<sub>3</sub>, 32.2) and infrared and ultraviolet spectroscopic data ( $\nu_{\text{KBr}}$  1730 cm<sup>-1</sup>;  $\lambda_{\text{max}}^{\text{MeOH}}$  362, 348, 270, and 262 m $\mu$ ). The absorption of benzylic protons originally observed at  $\tau$  4.90 in the n.m.r. spectrum of photoproduct II is absent in lactone V.

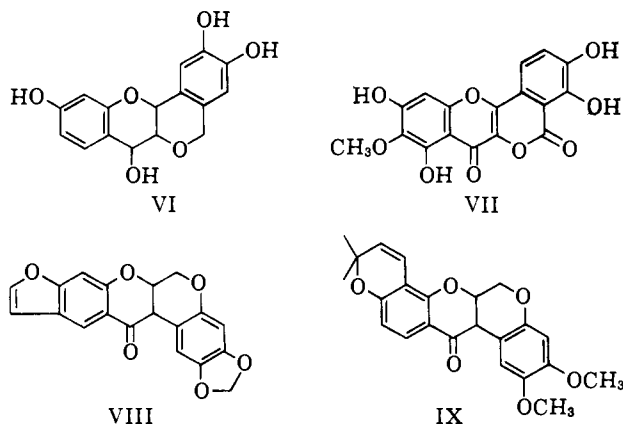
It is interesting to note that, although various photooxidative condensations between aromatic nuclei have been reported,<sup>7</sup> this is the first example of photooxidative

(5) J. Shinoda, *J. Pharm. Soc. Japan*, 48, 214 (1928).

(6) G. A. Edwards, W. H. Perkin, Jr., and F. W. Stoye, *J. Chem. Soc.*, 195 (1925).

(7) (a) P. de Mayo, R. A. Raphael, E. C. Taylor, and H. Wynberg, *Advan. Org. Chem.*, 2, 367 (1960); (b) A. Schönberg, "Präparative Or-

cyclization of an alkoxy group with an aromatic nucleus. This type of cyclization also raises some attractive speculations on the biogenetic origin of some "uncommon flavonoid compounds." In view of the present results it should not be difficult to envisage that the biosynthesis of peltogynol<sup>8</sup> (VI), a constituent of the heartwood of *Peltogyne porphyrocardia*, and distemonanthin<sup>9</sup> (VII), a pigment from *Distemonanthus benthamianus*, arise from the well-known uncyclized flavonoid leucofisetinidin and quercetagenin by an analogous process.



The co-occurrence of 2-methoxyisoflavonoids and rotenoids such as the rotenones dolichone<sup>10</sup> (VIII) and  $\alpha$ -toxicarol<sup>11</sup> (IX) is again very interesting from a biosynthetic point of view. Whether isoflavonoids are the precursors of rotenoids, *via* oxidative cyclization, or *vice versa*, is still open to further investigation. Nevertheless, oxidative cyclization presents an alternative possibility to the rotenoid biogenetic scheme offered by Grisebach and Ollis.<sup>12</sup>

**Acknowledgment.** The authors wish to thank Drs. L. Jurd and R. E. Lundin for their suggestions and Mr. L. M. White and Miss G. Secor for elemental analyses.

ganische Photochemie," Springer-Verlag, Berlin, 1958; (c) D. H. R. Barton and T. Cohn, "Festschrift A. Stoll," Birkhäuser, Basel, 1957, p. 117.

- (8) G. M. Robinson and R. Robinson, *J. Chem. Soc.*, 744 (1935).  
 (9) F. E. King, T. J. King, and P. J. Stokes, *ibid.*, 4594 (1954).  
 (10) L. Crombie and R. Peace, *ibid.*, 5445 (1961).  
 (11) S. H. Harper, *ibid.*, 1178 (1940).  
 (12) H. Grisebach and W. D. Ollis, *Experientia* 17, 4 (1961).

Anthony C. Waiss, Jr., Joseph Corse  
 Western Regional Research Laboratory  
 Western Utilization Research and Development Division  
 Agricultural Research Service, U. S. Department of Agriculture  
 Albany, California

Received February 12, 1965

## New Synthesis of Phenylcyclopropanes

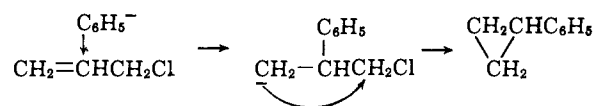
Sir:

The addition of phenyllithium to allylic chlorides in ether has been found to form phenylcyclopropanes in addition to the allylbenzenes. The ratio of the cyclopropane to the phenyl olefins varies with the structure of the allylic halide. Ratios of cyclopropane to olefins of 13:87, 19:81, and 40:60 were obtained by gas chromatography for the products from allyl chloride, crotyl chloride, and 1-chloro-5,5,7,7-tetramethyloctene-2, respectively. The cyclopropanes can be separated

from the olefins by oxidizing the latter with potassium permanganate. Phenylcyclopropane and 1-phenyl-2-methylcyclopropane were identified by comparing their migration times on a Carbowax column, and infrared and n.m.r. spectra with authentic samples. The structure assignment of 1-phenyl-2-(2,2,4,4-tetramethylpentyl)cyclopropane, which boils at 89–90° (0.29 mm.), depends on analysis (*Anal. Calcd.* for C<sub>18</sub>H<sub>28</sub>: C, 88.45; H, 11.55. Found: C, 88.29; H, 11.62), the n.m.r. spectra which showed no vinyl hydrogens, and the infrared spectrum which showed absorption for the cyclopropane ring at 9.72  $\mu$ .

This coupling reaction has been studied previously only with crotyl chloride and has been reported to give olefins.<sup>1</sup> Repetition of this work, in which the crotyl chloride was added to excess phenyllithium in ether, and examination of the products by gas chromatography indicated that 1-phenyl-2-methylcyclopropane was also formed under these conditions to the extent of 21%.

The reaction responsible for the formation of the cyclopropanes is probably similar to an S<sub>N</sub>2' reaction with attack of the phenyl carbanion occurring on the  $\beta$ -carbon atom instead of the  $\gamma$ -carbon. The resulting anion then undergoes an intramolecular reaction with displacement of the halogen. The yields obtained would indicate that steric factors are more important



than the type of carbanion formed.

The extent to which this reaction occurs with other basic reagents is being studied further.

**Acknowledgment.** This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donor of said fund.

(1) S. J. Cristol, W. C. Overhultz, and J. S. Meek, *J. Am. Chem. Soc.*, 73, 813 (1951).

S. Wawzonek, B. Studnicka  
 H. J. Bluhm, R. E. Kallio

Departments of Chemistry and Microbiology  
 University of Iowa, Iowa City, Iowa 52240

Received March 4, 1965

## Partial Head-to-Head Polymerization of Propylene Oxide by Stereospecific Catalysts

Sir:

Natta<sup>1</sup> has recently suggested the possibility that non-crystalline polymer chains may arise not only from atactic stereochemistry but from structural irregularities as well. We wish to report here that our investigation of the degradation of amorphous fractions of poly(propylene oxide) prepared by certain catalysts which simultaneously produce isotactic polymers demonstrates that the irregularities in structure preventing crystallinity are largely, if not entirely, units with head-to-head structure.

(1) G. Natta, A. Valvassori, and F. Ciampelli, *J. Polymer Sci.*, A3, 1 (1965).