

reacts very slowly and is thus a typically hindered amine. This observation, together with other evidence cited, leads to the conclusion that the "ortho" effects in quaternary salt formation are steric effects and are not secondary valence effects as has been supposed.

Rates of quaternary salt formation have also been determined for 1-dimethylamino-2,6-dimethylbenzene, 1-dimethylamino-3-methyl-4-nitrobenzene, and 1-dimethylamino-3,5-dimethyl-4-nitrobenzene.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

## The Photochemical Dimerization of *trans*-Cinnamic Acid<sup>1</sup>

BY HERBERT I. BERNSTEIN<sup>2</sup> AND WILLIAM C. QUIMBY

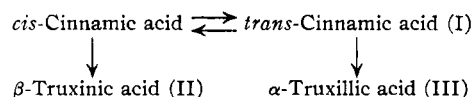
Moderately large amounts of  $\alpha$ -truxillic acid (III) were needed for studies of configurational changes during molecular rearrangements.<sup>3</sup> The simplest method of preparation according to most textbooks,<sup>4</sup> should be the irradiation of *trans*-cinnamic acid (I) with sunlight.

This unanimity, however, is lacking in the original literature. Stoermer and co-workers<sup>5</sup> and Stobbe and his co-workers<sup>6</sup> reported that the *trans*-cinnamic acid yielded principally  $\alpha$ -truxillic acid upon irradiation in the dry state, while the *cis*-acid was converted into a mixture of  $\alpha$ -truxillic (III) and  $\beta$ -truxinic acid (II). DeJong,<sup>7</sup> on the other hand, obtained  $\beta$ -truxinic acid from freshly precipitated *trans*-cinnamic acid. The longer the cinnamic acid stood before irradiation, the smaller was the yield of  $\beta$ -truxinic, while that of  $\alpha$ -truxillic acid increased.

We have found that irradiation of the commercial *trans*-cinnamic yielded only  $\beta$ -truxinic acid. The same was true of a rapidly precipitated cinnamic acid. If the commercial acid was allowed to stand for four months,  $\beta$ -truxinic acid was still the only dimerization product. However, if the *trans*-cinnamic acid were slowly recrystallized from aqueous alcohol, dried and irradiated, the

sole product was  $\alpha$ -truxillic acid. Addition of the peroxide, ascaridole, to this recrystallized cinnamic acid exerted no influence upon the reaction products. The irradiation of an aqueous suspension of freshly precipitated *trans*-cinnamic acid is the best known method for preparing  $\beta$ -truxinic acid.

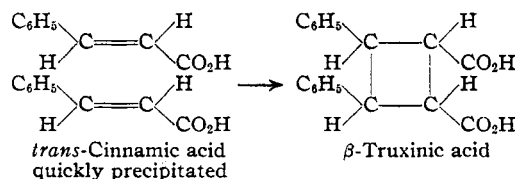
Stobbe<sup>6</sup> sought to explain his data by means of the following transitions:



The assumption that only the *cis* acid yields  $\beta$ -truxinic, while only the *trans*-cinnamic gives  $\alpha$ -truxillic acid probably accounts for the textbook over-simplification.

DeJong<sup>7</sup> made use of the reported existence of two polymorphic forms of *trans*-cinnamic acid, the metastable *beta* and the stable *alpha*.<sup>8,9</sup> Both have the same melting point. He assumed that the *beta* form isomerized to the *cis*-cinnamic acid, which then combined with a molecule of *trans*-cinnamic to yield  $\beta$ -truxinic acid. The  $\alpha$ -truxillic comes from two molecules of *trans*-cinnamic acid.

However, these assumptions seem unnecessary. It is possible that in the metastable *beta* form of *trans*-cinnamic acid resulting from rapid precipitation, the phenyl groups lie next to each other in the crystal, while they are opposite in the stable *alpha* form.



(1) Presented before the Organic Division of the American Chemical Society, Memphis, April 20-21, 1942.

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(3) Bernstein and Wallis, *J. Org. Chem.*, **7**, 261 (1942).

(4) (a) Houben-Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1925, Vol. II, p. 1309; (b) Richter, "The Chemistry of the Carbon Compounds," "Elsevier," Amsterdam, 1939, Ed. III, Vol. II, p. 40; (c) Hans Meyer, "Synthese der Kohlenstoffverbindungen," Julius Springer, Vienna, 1938, Part I, Vol. II, pp. 1173 and 1182; (d) Whitmore, "Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 634; (e) Karrer, "Organic Chemistry," "Elsevier," Amsterdam, 1938, p. 602.

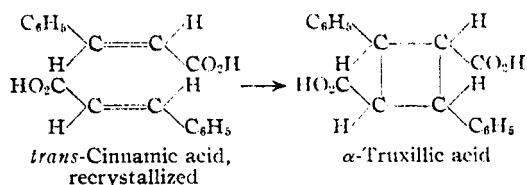
(5) (a) Stoermer and Foerster, *Ber.*, **52**, 1263 (1919); (b) Stoermer and Laage, *ibid.*, **54**, 77 (1921).

(6) (a) Stobbe, *ibid.*, **52**, 666 (1919); (b) Stobbe and Steinberger, *ibid.*, **55**, 2225 (1922); (c) Stobbe and Lehfeldt, *ibid.*, **58**, 2415 (1925).

(7) DeJong, *ibid.*, **55**, 463 (1922).

(8) Erlenmeyer, Brakow and Hery, *ibid.*, **40**, 653 (1907).

(9) Lehmann, *Z. Krist.*, **10**, 329 (1885).



An attempt to test this theory will be made when X-ray diffraction equipment becomes available.

### Experimental<sup>10</sup>

**Irradiation of *trans*-Cinnamic Acid.**—In two evaporating dishes covered by soft glass watch crystals was placed 111 g. of *trans*-cinnamic acid, m. p. 132–133° (Paragon Testing Laboratories). They were placed on the roof for two months, and stirred about twice a week. The solid at the end of this period had a m. p. of 125–182°. It was digested with 700 cc. of ether, and filtered while hot. The residue was similarly treated with 250 cc. of ether. The final residue was recrystallized from 100 cc. of 95% alcohol; wt. 5.0 g., m. p. 195–207°, m. p. 208–210° when placed in the bath at 205°. Concentration of the alcoholic mother liquor yielded an additional 3.1 g. of product, m. p. and mixed m. p. as above. This product would be contaminated with  $\alpha$ -truxillic acid, were any formed by the photochemical action.<sup>6b</sup>

Proof that the product was  $\beta$ -truxinic acid was furnished by preparation of the following derivatives: dichloride, m. p. 95–96°, known m. p. 96°<sup>11</sup>; monoethyl ester, m. p. 131–132°, known m. p. 133°<sup>10</sup>; dimethyl ester, m. p. 75–76°, known m. p. 76°.<sup>12</sup>

Another experiment using 53.5 g. of commercial cinnamic acid which had stood in the laboratory for four months was irradiated for six months, and worked up as above. There resulted 5.9 g. of  $\beta$ -truxinic acid, m. p. and mixed m. p. 206–209° (put in bath at 200°).

**Irradiation of Recrystallized *trans*-Cinnamic Acid.**—A sample of the cinnamic acid used above was recrystallized

from 50% alcohol, and the solid allowed to stand overnight in its mother liquor at 50°. This converted the white needles (*beta*)<sup>7</sup> first thrown down into plates, which were filtered and dried, m. p. 131–132°. For three weeks 43.1 g. of this material was exposed to sunlight as in the above preparation of  $\beta$ -truxinic acid. When worked up exactly as in this latter experiment, there resulted 5.8 g. of  $\alpha$ -truxillic acid, m. p. and mixed m. p. 276–280°.<sup>13</sup> From the irradiation of 9.0 g. of the recrystallized cinnamic acid mixed with 10 drops of ascaridole there was obtained 0.58 g. of  $\alpha$ -truxillic acid, m. p. and mixed m. p. 274–278°.

**Irradiation of Freshly Precipitated *trans*-Cinnamic Acid.**—A sodium carbonate solution of 100 g. of cinnamic acid (Paragon Chemical Laboratories) was acidified, and the resulting suspension diluted to 3 liters with water, and placed on the roof in a five-liter Pyrex flask. It stood for three months, and was shaken every few days. The mixture was then filtered, dried, and worked up as above to yield 41.0 g. of  $\beta$ -truxinic acid, m. p. and mixed m. p. 206–208°.

The ether and alcohol mother liquors were evaporated to dryness, and the resulting precipitate digested with 20 cc. of petroleum ether, b. p. 60–70°. The hot solution was filtered, and the filtrate evaporated to dryness. There was no residue, indicating an absence of *cis*-cinnamic acid.<sup>4b</sup>

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### Summary

Rapidly precipitated or commercial *trans*-cinnamic acid yielded only  $\beta$ -truxinic acid upon exposure to sunlight. Only  $\alpha$ -truxillic acid resulted if the *trans*-cinnamic acid was first recrystallized slowly.

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(10) Melting points uncorrected. All samples of  $\alpha$ -truxillic and  $\beta$ -truxinic acids melted with decomposition, droplets of water appearing in the capillary tubes.

(11) Stoermer and Lachman, *Ber.*, **59B**, 642 (1926).

(12) Liebermann, *ibid.*, **21**, 2348 (1888).

(13) Kohler, *Am. Chem. J.*, **26**, 233 (1902).