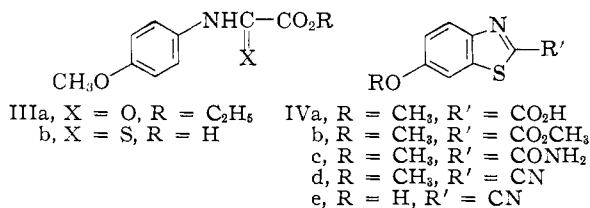


luciferin and, along with the degradative evidence, secured structure I; confirmation of this structure was achieved by a total synthesis of luciferin.

*p*-Anisidine was condensed with ethyl oxalate to give amide IIIa,<sup>5</sup> which, by reaction with phosphorus pentasulfide and then base, was converted into thioamide IIIb (m.p. 134–138° dec.); oxida-



tion of IIIb with basic ferricyanide yielded 6-methoxy-2-benzothiazolecarboxylic acid (IVa, m.p. 109–111° dec.). This acid was esterified with diazomethane and the methyl ester (IVb, m.p. 142–143°) was condensed with ammonia to give the corresponding amide (IVc, m.p. 255–257°). Dehydration of amide IVc with phosphorus oxychloride yielded nitrile IVd (m.p. 130–131°), which was demethylated with pyridine hydrochloride to give 2-cyano-6-hydroxybenzothiazole (IVe, m.p. 212–215° dec.). The reaction of this nitrile with *D*-cysteine<sup>6</sup> in aqueous methanol yielded firefly luciferin (I) in the form of pale yellow needles, m.p. 196° dec., [ $\alpha$ ]<sub>D</sub><sup>24</sup> -29° (dimethylformamide),  $\lambda_{\text{max}}$  268 and 327 m $\mu$ , log  $\epsilon$  3.88 and 4.27. Analysis gave: C, 47.11; H, 2.91; N, 9.89; S, 22.60. Calcd. for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>: C, 47.14; H, 2.85; N, 10.00; S, 22.88. Synthetic luciferin and natural luciferin gave identical infrared, ultraviolet, and fluorescence spectra and, in addition, the two luciferins exhibited identical activities in the *in vitro* enzymatic production of light.<sup>7</sup>

Satisfactory analyses and other physical data were obtained for the compounds cited in the synthesis section of this paper; the scale of operations precluded analysis of the compounds identified in the degradative work.

We thank Miss Joan Friedland for assistance, and the National Science Foundation for partial support of this work.

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### IRONTRICARBONYL-HEXATRIENE COMPLEX<sup>1</sup>

Sir:

Many iron carbonyl complexes have been prepared with cyclic unsaturated hydrocarbons, but relatively few have been reported with non-cyclic alkenes.<sup>2–10</sup>

(1) This work was supported in part by a grant from the National Science Foundation.

We wish to communicate here the synthesis and identification of a new iron carbonyl complex with *trans*-1,3,5-hexatriene as the ligand.

Iron dodecacarbonyl (3 g., 6 mmoles) and *trans*-1,3,5-hexatriene<sup>11</sup> (6 g., 75 mmoles) were refluxed on a steam-bath under dry nitrogen for about 3 hours. The color changed from green to orange-yellow during the reaction. The products were distilled in high vacuum and the unreacted hexatriene removed from the distillate. An orange-red oily material thus obtained was heated at 160–170° under dry nitrogen atmosphere and the volatile material removed. The viscous liquid remaining again was distilled in high vacuum and the portion distilling at about 100° collected; yield 1.2–1.8 g. ~30%—based on Fe<sub>3</sub>(CO)<sub>12</sub>.

The final product is an oily orange-red liquid, solidifying at about -70° and is assigned the formula Fe(CO)<sub>3</sub>(C<sub>6</sub>H<sub>8</sub>)<sub>2</sub>. *Anal.* Found: C, 60.04; H, 5.72; Fe 18.32. Calcd.: C, 60.07; H, 5.35; Fe, 18.62. The molecular weight as determined by the cryoscopic method was 303.

An infrared spectrum of the compound showed carbonyl bands at about 1970 cm.<sup>-1</sup> (very strong) and 2045 cm.<sup>-1</sup> (very strong and broad). The vinyl CH out of plane and CH<sub>2</sub> out of plane deformation frequencies of the *trans*-hexatriene<sup>12</sup> appeared in the spectrum of the complex at 998 cm.<sup>-1</sup> and at 896 cm.<sup>-1</sup>, respectively.

Obviously this was not the only complex formed during the reaction but it was the one that could be isolated in a rather pure form. An orange-yellow light material that distilled at 160–170° seemed to be another complex formed during the reaction. The molecular weight of this material determined again by the cryoscopic method was consistently in the region of 194. However, the carbon and hydrogen analyses varied significantly. Absorption from two carbonyl stretching frequencies and also vinyl groups could be identified in the infrared spectrum of this compound. It is possible that this product can be formulated as Fe(CO)<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>). More work on the structure and identification of the products of this reaction is in progress.

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