mediately was filtered and dried in a 100° oven for 2 hr. After drying, the solid was dissolved in $CHCl_3$ and chromatographed on alumina. The nitroporphin was eluted with a chloroform–benzene (50:50, v/v) mixture yielding 151 mg of product: 70% yield; extinction coefficients at maxima ϵ_{628} 6000, ϵ_{572} 6860, ϵ_{540} 8770, ϵ_{499} 13,120, ϵ_{406} 200,000.

Anal. Calcd for $C_{20}H_{13}N_5O_2$: C, 67.6; H, 3.68; N, 19.nd C, 67.44; H, 3.67; N, 19.64.

Dinitroporphin. Dinitroporphin was prepared in the same manner as mononitroporphin except that it was eluted with chloroform after a small amount of unreacted mononitroporphin was eluted with the chloroform–benzene mixture. A 56% yield of dinitroporphin was obtained (20% of the unreacted mono-nitroporphin was recovered): extinction coefficients at maxima ϵ_{632} 4820, ϵ_{578} 5400, ϵ_{543} 7000, ϵ_{504} 10,800, ϵ_{407} 145,000.

Anal. Calcd for $C_{20}H_{12}N_6O_4$: C, 60.02; H, 3.02; N, 20.99. Found: C, 59.98; H, 3.00; N, 20.89.

Oxidative Degradation of Nitro- and Dinitroporphin. The degradations were accomplished according to the method of Neuberger and Muir[17] for the degradation of mesoporphyrin. The porphin in question was dissolved in a 50% aqueous H_2SO_4 solution at 0°. To this solution was added dropwise an ice-cold 10% aqueous CrO_3 solution. The mixture was then stirred at 0° for 2 hr and an additional 2 hr at room temperature. The solution was then diluted with 50 ml of distilled water and extracted four times with anhydrous ether. The ether extracts were washed once with 50 ml of water and dried over anhydrous $CaSO_4$. The ether was evaporated leaving a white solid. In all cases, the solid melted at 90–92° and was shown to be identical with an authentic sample of maleimide. The maleimide degradation product was analyzed *via* tlc for the presence of nitromaleimide. The tlc analysis was accomplished using a developing solvent consisting of ethyl acetate–carbon tetrachloride–cyclohexane (10:5:1) with a development distance of 10 cm. The plate was removed from the chromatography chamber, dried, and exposed to Cl_2 for 5 min. It was then heated to 100° for 5 min. The locating reagent is a 0.5% benzidene solution in ethanol containing a 10% aqueous KI solution per 100 ml of the benzidene solution.[18] No evidence of the presence of nitromaleimide was ever observed.

4-Nitro-2-pyrrolecarboxaldehyde. The preparation of 4-nitro-2-pyrrolecarboxaldehyde followed the procedure of Fournari and Tirouflet[19] except that the 4-nitro isomer was extracted from a saturated aqueous $NaHCO_3$ solution containing the 4- and 5-nitro isomers with ether. Typically, 10 g of the isomer mixture is dissolved in 500 ml of a saturated aqueous $NaHCO_3$ solution. This solution is extracted six times with 100-ml portions of anhydrous ether. The extracts are dried over $CaSO_4$ and decolorized. The ether was evaporated leaving 3.5 g of a yellow solid, 4-nitro-2-pyrrolecarboxaldehyde, which was recrystallized from alcohol–water, mp 135–136° (lit.[20] 142°).

Nitromaleimide. To an ice-cooled solution containing 5 g of 4-nitro-2-pyrrolecarboxaldehyde in 20 ml of acetone was added with stirring 150 ml of a 50% aqueous H_2SO_4 solution. After the acid addition was completed, a solution containing 40 g (0.136 mol) of $K_2Cr_2O_7$ in 100 ml of H_2O was added slowly so that the reaction temperature did not exceed 10°. After the dichromate addition was finished, the reaction mixture was heated to 60° for 30 min; then it was poured into 200 ml of ice water. The aqueous solution was extracted four times with 100-ml portions of anhydrous ether. The ether extracts were dried, decolorized, and stripped leaving a white yellow solid which was recrystallized from water, mp 205° dec.

Anal. Calcd for $C_4H_2N_2O_4$: C, 42.86; H, 2.87; N, 19.99. Found: C, 42.50; H, 2.80; N, 19.85.

Registry No.—Porphin, 101-60-0; nitroporphin, 52358-25-5; dinitroporphin, 52358-26-6; maleimide, 541-59-3; 4-nitro-2-pyrrolecarboxaldehyde, 19611-63-3; nitromaleimide, 52358-27-7.

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μ-Truxinic Acid

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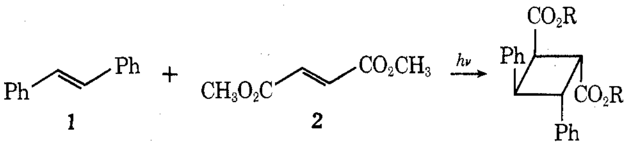
The photoaddition of *trans*-stilbene to fumaric acid would seem to be a straightforward approach to the synthesis of μ-truxinic acid since both stilbene[1] and fumaric acid derivatives[2] undergo photodimerization to cis-anti-cis configurated dimers. However, a previous approach along these lines was reported to be unsuccessful.[3]

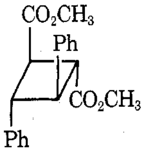
We have repeated this method, irradiating *trans*-stilbene with an excess of dimethyl fumarate in benzene solution, and find that dimethyl μ-truxinate (**3**) is formed smoothly in acceptable yields. The nmr spectrum uniquely fits that anticipated for **3**: a single carbomethoxyl signal is present at δ 3.33, shifted upfield as a result of the shielding *cis*-β-phenyl groups.[4]



3, R = CH_3
4, R = H

Although the diphenylcyclobutanedicarboxylic (truxillic and truxinic) acids are often presented as classical examples of configurational isomerism where all 11 possible isomers are known,[5] the melting point of μ-truxinic acid, **4**, obtained by acid hydrolysis of **3**, differs from that reported by Shemiakin for this material.[6] Ettlinger had earlier questioned the structure assignment to Shemiakin's μ-truxinic acid and suggested that this material was a lactonic acid.[7] Reesterification of **4** with methanol affords **3**; we thus report the first synthesis of μ-truxinic acid and its dimethyl ester.

It is noteworthy that **3** is the major isomer produced; dimethyl δ-truxinate (**5**), presumably the thermodynamically more stable isomer[8] which could *a priori* also have been produced, is formed in only trace quantities, if at all. Dimethyl *neo*-truxinate (**6**) is formed as a side product, while dimethyl ζ-truxinate (**7**) is not found in the irradiation products. These results are accommodated by a mechanism involving the addition of excited singlet state *trans*-stilbene to dimethyl fumarate *via* a nonconcerted pathway.[9]



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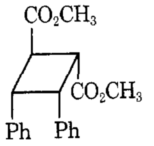

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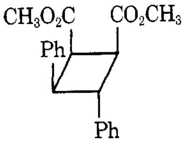

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Experimental Section

The Photoaddition of *trans*-Stilbene to Dimethyl Fumarate. A solution of **1** (2.50 g, 0.014 mol) and **2** (20 g, 0.14 mol) in 500 ml of benzene was deaerated with a stream of dry, oxygen-free nitrogen and then irradiated (450-W Hanovia immersion lamp, Pyrex) for 24 hr while passing through nitrogen. The benzene was evaporated and the residue sublimed (bulb-to-bulb, on a Büchi rotary evaporator at 2 mm pressure; heating bath at 70–80°; collecting flask cooled in Dry Ice–2-propanol bath). The sublimate consisted of dimethyl fumarate and dimethyl maleate. The residue was chromatographed on 200 g of Merck 0.05–0.20 mm silica gel. Elution with 2% ethyl acetate in *n*-hexane gave traces of stilbene and stilbene dimers. Further elution gave a total of 1.1 g of oily material. Further elution with the same mixture of solvents gave 2.0 g (46% yield) of dimethyl-μ-truxinate (**3**) which was crystallized from methanol to give 1.6 g of analytically pure material: mp 121–123°; δ ($CDCl_3$) 7.21 (10 H, s, Ph), 4.5–4.7, 3.8–4.2 (4 H, AA′BB′ multiplet, cyclobutane hydrogens), and 3.33 (6 H, s, OCH_3).

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 73.90; H, 6.11.

Elution with 3% and then 5% ethyl acetate in *n*-hexane afforded 0.20 g of oily material whose nmr spectrum and tlc chromatogram, by comparison with an authentic sample,[10] indicate the presence of a mixture containing dimethyl δ-truxinate (**5**). Elution with 10% ethyl acetate in *n*-hexane gave 0.28 g (6% yield) of dimethyl neotruxinate (**6**) which was crystallized from methanol to give 0.15 g of material with mp 131–132° (lit.[11] mp 127.5°): δ ($CDCl_3$) 6.71–7.35 (10 H, m, Ph), 3.91–4.43 (4 H, unsymmetrical m, cyclobutane hydrogens), 3.75 (3 H, s, CO_2CH_3 trans to β-Ph), and 3.28 (3 H, s, CO_2CH_3 *cis* to β-Ph). Further elution with increasing proportions of ethyl acetate afforded oily mixtures which were not investigated further.

Dimethyl μ-truxinate can also be isolated in lower yields directly after the sublimation step by several crystallizations from methanol. The first compound to crystallize is an unknown material with mp 218–220° (this substance can also be crystallized from the later chromatographic fractions) which is removed by filtration. The mother liquor then deposits dimethyl μ-truxinate.

μ-Truxinic Acid (4). A mixture of **3** (500 mg) and an aqueous HCl solution (75 ml, 1:2) was refluxed while stirring for 137 hr. The product was filtered (390 mg, 85% yield) and crystallized from aqueous acetic acid to give **4** (226 mg) with mp 252–254°: δ (DMSO) 7.20 (10 H, s, Ph), 4.58–4.26, 3.90–3.56 (4 H, AA′BB′, cyclobutane hydrogens).

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.86; H, 5.52.

A mixture of the acid **4** (50 mg) in methanol (20 ml) was treated with several drops of thionyl chloride and warmed overnight. Evaporation of solvent left **3** having an nmr spectrum identical with that of the irradiation-derived sample. Crystallization from methanol gave 34 mg of **3**, mp 118–121°.

Acknowledgment. We are grateful to Miss Edna Gati for performing some preliminary experiments.

Registry No.—**1**, 103-30-0; **2**, 624-49-7; **3**, 52306-38-1; **4**, 528-35-8; **6**, 52305-39-2.

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Facile Synthesis of *tert*-Butylacetylene

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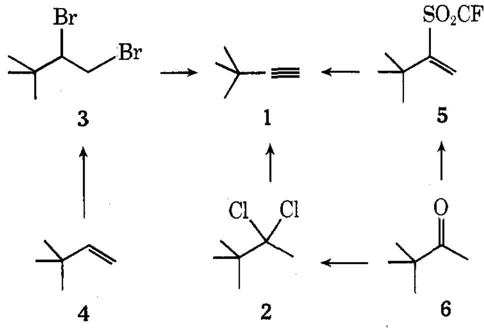
Until recently, *tert*-butylacetylene (**1**) was prepared by the method of Bartlett and Rosen[1] which entails the dehydrochlorination of pinacolone dichloride (**2**) in a sodium hydroxide melt. This reaction is difficult to control to the point of being hazardous on a large scale and affords only a moderate yield of **1**. With these limitations in mind, alternate preparations have recently appeared. Collier and Macomber[2] prepared the *vic*-dibromide **3** by the addition of Br_2 to *tert*-butylethylene (**4**) which was subsequently dehydrobrominated to **1**. However, the bromination must be carried out at −78° to avoid contamination of the product with substantial amounts of rearranged products. Hargrove and Stang[3] prepared the vinyl triflate **5** from pinacolone (**6**) and subsequently effected a base-catalyzed elimination of CF_3SO_3H to afford **1**. The latter procedure is disadvantaged by the expense of the $(CF_3SO_2)_2O$ required to prepare **5**.



With emphasis on experimental facility and economy, a modification of the Bartlett–Rosen procedure has been developed which permits the synthesis of **1** on a mole scale without recourse to low temperatures or expensive reagents. Pinacolone dichloride (**2**), readily prepared by reaction of pinacolone (**6**) with PCl_5,[1,4] was added to a mixture of *t*-BuOK in DMSO while maintaining the temperature below 40°. The product was isolated in 95% yield (from **2**) by direct distillation from the reaction mixture in ≥95% purity by vpc analysis. By this procedure, **1** has been prepared repeatedly in >90% yield in quantities ranging from 5–100 g.

Experimental Section

Boiling points are uncorrected. The nmr spectra were recorded on a Varian A-60A spectrometer using TMS as an internal standard; infrared spectra were recorded on a Perkin-Elmer 337 spectrometer in CCl_4 solution. Gas–liquid chromatographic analyses were performed on a Varian Model 90 chromatograph using ¼-in. × 12-ft columns packed with 10% SE-30 on Chrom W. Freshly opened bottles of *tert*-BuOK from MSA Corporation were employed and the DMSO, obtained from Fisher, was used without further purification.

***tert*-Butylacetylene.** A flame-dried 250-ml three-necked flask fitted with a thermometer, condenser, magnetic stirrer, and addition funnel was charged with 50 g (0.45 mol) of *t*-BuOK and 110 ml of DMSO. With magnetic stirring, pinacolone dichloride (35 g