TABLE IV

1:1 AND 2:1 ADDUCTS

Compd	Bp, °C (mm)	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
I	100–103 (0.15)[a]	$C_{10}H_{16}Cl_3N$	46.80	6.29	46.86	6.29
II	66–68 (0.1)	$C_8H_{12}Cl_3N$	42.46	5.52	42.47	5.55
III	91–93 (0.1)	$C_{10}H_8Cl_3N$	48.34	3.24	48.98	3.14
IV	61–63 (0.3)	$C_7H_8Cl_3NO_2$	34.38	3.30	34.23	3.67
V	63–65 (0.2)	$C_6H_6Cl_3NO_2$	31.26	2.63	30.73	2.68
VI	87–88 (0.2)	$C_6H_3Cl_3N_2$	30.41	1.53	30.50	1.75
VII	94–95 (0.1)	$C_9H_{10}Cl_3N$	45.31	4.23	45.71	4.41
VIII	90–93 (0.2)	$C_{10}H_{17}Cl_2N$	54.06	7.26	54.21	7.66
IX	67–70 (0.2)	$C_8H_{13}Cl_2N$	49.50	6.75	49.29	6.61
X	122–124 (0.2)	$C_{10}H_9Cl_2N$	56.10	4.24	57.08	4.29
XI	78–80 (0.2)	$C_7H_9Cl_2NO_2$	39.85	4.76	39.45	4.77
XII	68–81 (0.2)	$C_6H_7Cl_2NO_2$	36.76	3.36	36.79	3.68
XIII	83–86 (0.2)	$C_6H_4Cl_2N_2$	36.84	2.47	36.20	2.63
XIV	85–86 (0.2)	$C_9H_{11}Cl_2N$	52.96	5.43	53.13	5.29
XV	150–152 (0.4)	$C_{12}H_{16}Cl_3NO_4$	41.84	4.68	42.28	4.89
XVII	147–148 (0.2)	$C_{12}H_{17}Cl_2NO_4$	46.47	5.52	46.37	5.41
XVIII	145–150 (0.2)	$C_{10}H_{13}Cl_2NO_4$	42.57	4.56	42.44	4.41
XVI[b]	134–140 (0.2)	$C_{10}H_{12}Cl_3NO_4$	...	...	...	...

[a] Lit.[6] bp 80–98° (0.15–0.5 mm). [b] Sufficient analytical data were not obtained.

B. Reaction of Ethyl Acrylate with Trichloroacetonitrile.—When 0.05 mole of ethyl acrylate and 0.05 mole of trichloroacetonitrile were reacted in 50 ml of acetonitrile at 130° for 18 hr using cuprous chloride (0.001 mole) as a catalyst, the 1:1 adduct was obtained only in a yield of 18%. Therefore 0.1 mole of ethyl acrylate was used in the following reaction. From 10.0 g (0.1 mole) of ethyl acrylate and 7.3 g (0.05 mole) of trichloroacetonitrile reacted in the usual manner as described above, the three fractions, f_1–f_3, were obtained: f_1 (3.2 g), bp 20–68° (0.3 mm), f_2 (5.6 g), bp 68–74° (0.3 mm), and f_3 (2.7 g), bp 140–143° (0.3 mm). Redistillation of f_1 gave 0.5 g of a yellow oil, bp ~68° (0.3 mm), and 2.5 g of a almost colorless oil, bp 68–70° (0.3 mm); the infrared spectra of these two fractions, however, were essentially identical. The latter almost colorless oil was combined with f_2 and was distilled to give 8.0 g (68%) of a colorless oil boiling at 61–63° (0.3 mm). This product was identified as ethyl 2,4,4-trichloro-4-cyanobutyrate (IV) as follows: infrared spectrum, 2280 (C≡N), 1760 cm^{-1} (C=O), nmr spectrum (CCl_4), ester absorptions at τ 5.72 (quartet, 2 H) and 8.63 (triplet, 3 H), methine absorption at 5.50 (quartet, 1 H), methylene absorption at 6.75 (octet, 2 H). Analytical data agree with the formula $C_7H_8Cl_3NO_2$ as shown in Table IV.

Reduction of 3.4 g of IV by heating under reflux with 6.5 g of zinc powder in 50 ml of 95% ethanol for 15 hr gave 1.4 g of ethyl 4-cyanobutyrate boiling at 112–117° (15 mm) which was identified by gas chromatography on DC-550 silicone and polyester DA columns at 178°.

The minor product, f_3, was purified by chromatography on silica gel. (This purification was not necessary in the case with XVII or XVIII, and analytically pure samples were obtained by redistillation.) After a large volume of benzene was passed through the column, a light yellow oil was eluted with 200 ml of benzene–ether (9:1) mixture and was distilled to give a colorless oil boiling at 150–152° (0.4 mm). The infrared spectrum of this product was essentially identical with that of IV, 2280 (C≡N), 1760, shoulder at 1750 cm^{-1} (C=O); nmr spectrum (CCl_4), ester absorptions at τ 5.72 (4 H), and 8.63 (6 H), methine absorption at 5.48 (1 H), and complex absorptions at 6.70–7.60 (5 H). From these data, this product is believed to be a 2:1 adduct of ethyl acrylate and trichloroacetonitrile, diethyl 1,5,5-trichloro-5-cyanopentane-1,3-dicarboxylate (XV). Analytical data agree with the formula $C_{12}H_{16}Cl_3NO_4$ as shown in Table IV.

C. Reduction of 1:1 Adducts.—Reduction of VIII to *n*-decylamine was carried out as described in the reduction of I. Reduction of III or X to 4-phenylbutyronitrile and reduction of XI to ethyl 4-cyanobutyrate by zinc powder were carried out in the same manner as reduction of IV as described above.

Acknowledgment.—The authors are grateful to Dr. Yoshinobu Odaira and Dr. Noboru Sonoda for their helpful suggestions during this work. The authors are also indebted to Professor Clyde R. Dillard for his helpful comments on the manuscript.

Photodimerization of *trans*-3,4-Methylenedioxycinnamyl *trans*-3,4,5-Trimethoxycinnamate[1a]

L. H. KLEMM, K. W. GOPINATH,[1b] T. J. DOOLEY,[1c] AND C. E. KLOPFENSTEIN[1d]

Department of Chemistry, University of Oregon, Eugene, Oregon

Received December 21, 1965

Irradiation of *trans*-3,4-methylenedioxycinnamyl *trans*-3,4,5-trimethoxycinnamate in the solid state produced the photodimer II in 30% yield. Hydrolysis of II gave the centrosymmetric 2,4-diarylcyclobutane-1,3-dicarboxylic acid IIIa. The structure of IIIa (and thereby also of II) was established by (a) conversion to its dimethyl ester IVa and to the anhydride Va under reaction conditions analogous to those used in the α-truxillic acid series and (b) spectral investigations on the resultant derivatives. Computer analysis of the AA'BB' system for the pmr signals due to the four cyclobutane ring protons present in dimethyl α-truxillate (IVb) is presented.

In connection with studies on the cyclization of dienic, enynic, and diynic esters to lignan lactones[2,3] we have subjected *trans*-3,4-methylenedioxycinnamyl *trans*-3,4,5-trimethoxycinnamate (I) to ultraviolet irradiation in the solid state. Compound I was readily converted thereby to the crystalline photodimer II in 30% yield. The structure of II was established by its molecular weight and by spectral and chemical means (see Scheme I). Thus, the infrared spectrum of compound II indicated that during the photoreaction the *trans*-vinylene group of the alcohol moiety in I (absorption at 962 cm^{-1}) remained unchanged but that the corresponding group of the acid moiety (absorption at 980 cm^{-1}) disappeared. In addition, a low-field doublet at δ 7.68 (ascribed to the proton β to the carbonyl in the *trans*-CH=CHC=O grouping) was present in the pmr spectrum of I but absent from the spectrum of II, which contained, instead, a poorly resolved multiplet centered at about δ 4.4 and ascribed to absorption by cyclobutane ring protons in the product (see Table I). Saponification of II, moreover, led to nearly quantitative conversion to *trans*-3,4-methylenedioxycinnamyl alcohol and an acid IIIa.

The centrosymmetric structure shown for acid IIIa was tentatively assigned on the basis of the observations that physical properties and chemical transformations of this compound were closely similar to

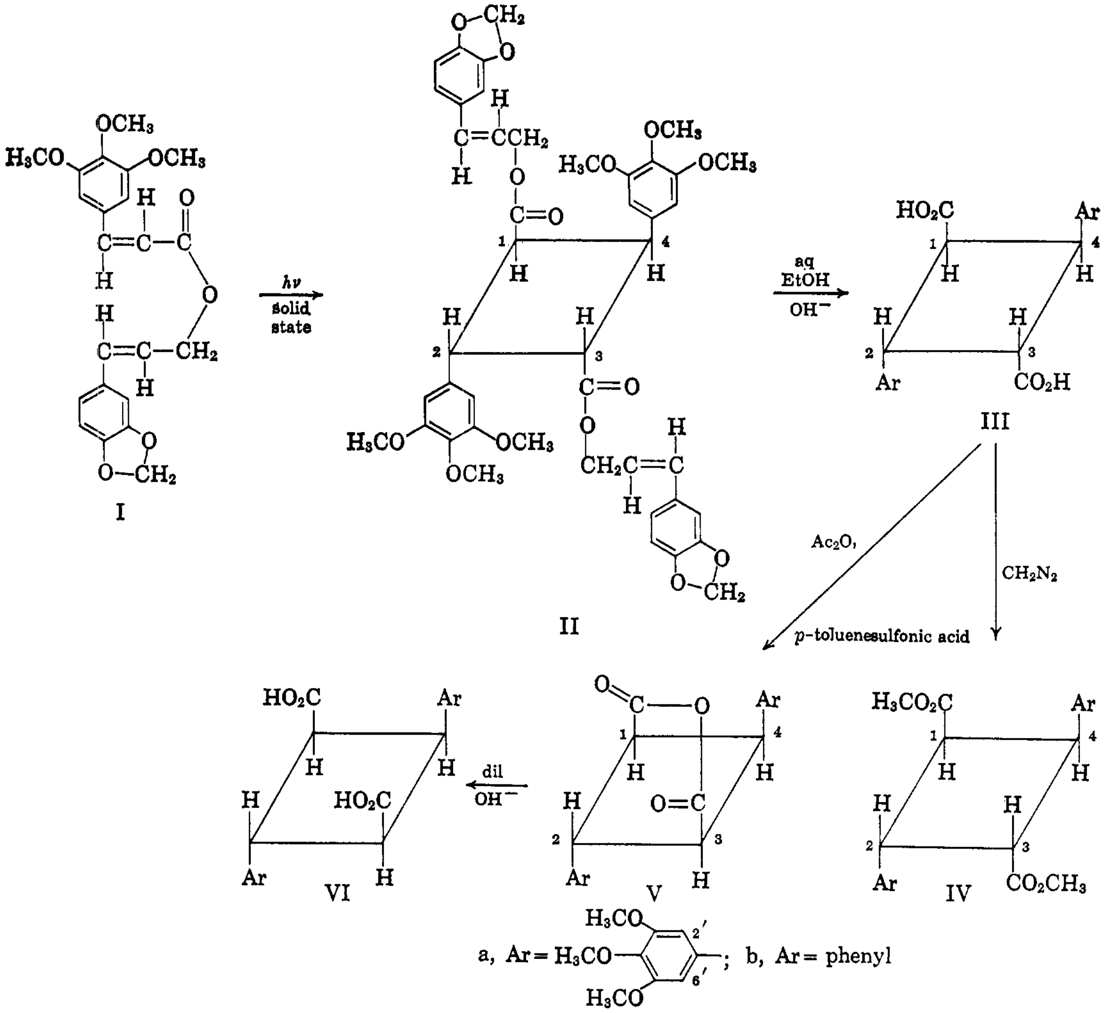
---

[1] (a) This investigation was supported by Research Grant No. CY-3097 from the National Cancer Institute and Grant No. GM 12730 from the National Institute of General Medical Sciences, U. S. Public Health Service; (b) Research Associate, 1962–1964; (c) Research Assistant, 1962–1963; (d) Research Assistant, 1963–1966.

[2] L. H. Klemm and K. W. Gopinath, *Tetrahedron Letters*, 1243 (1963).

[3] L. H. Klemm, K. W. Gopinath, D. H. Lee, F. W. Kelly, E. Trod, and T. M. McGuire, *Tetrahedron*, **22**, 1797 (1966).

SCHEME I



those of α-truxillic acid[4] (IIIb), a sample of which was readily obtained by irradiation of *trans*-cinnamic acid in our apparatus under the same conditions used for I. Thus, treatment of IIIa (mp 321°) and IIIb (mp 281°) with excess diazomethane gave the corresponding dimethyl esters IVa (mp 165°) and IVb (mp 177°),[4] while refluxing these acids with acetic anhydride containing a small amount of *p*-toluenesulfonic acid gave an anhydride (mp 204°) assigned structure Va from the former and γ-truxillic anhydride (Vb, mp 191°)[5] from the latter. Run on the same apparatus under identical conditions Va showed anhydride absorption bands for a six-membered ring (consistent with head-to-tail dimerization of the monomeric units)[6] at 1771 and 1824 cm^{-1} compared with ones at 1773 and 1827 cm^{-1} for the known Vb. Structure IIIa was then strongly corroborated by analyses of the pmr spectra of the ester IVa and the anhydride Va as well as by rationalizations of the chemistry involved in the transformations IIIa → IVa and IIIa → Va → VIa.

The presence in the pmr spectrum of IVa of a singlet for the six ester methoxy protons and of a singlet for the four aromatic protons implies that both carbomethoxy groups (at C-1 and C-3) are in magnetically equivalent environments and that both aryl groups (at C-2 and C-4) are likewise. If one assumes (as is consistent with molecular models) that the aryl groups are effectively freely rotating, then only three stereochemical arrangements for IVa are consistent with this spectral observation: (1) the centrosymmetric structure as shown, (2) an all-*cis* structure, and (3) a structure of the 1α,2β,3α,4β type.[6] It is very likely that compounds II, IIIa, and IVa are all in the same stereochemical series, inasmuch as neither the mild conditions used for hydrolysis of photodimer II nor methylation of acid IIIa by means of diazomethane should effect epimerization at one (or more) of the cyclobutane carbon atoms. As a result of their studies on the stereochemical relationships which exist between crystalline cinnamic acids and the corresponding photodimers, Schmidt and co-workers[7] have postulated that reaction in the solid state occurs with a minimum of atomic or molecular movement. Their postulation includes the special case that a *trans*-cinnamate (*e.g.*, I) in the solid state should not photodimerize to an all-*cis* product. Hence, possibility 2 that IVa is an all-*cis* isomer is considered improbable. Possibilities 1 and 3, on the other hand, remain plausible on the basis of these considerations.

In contrast to the situation for diester IVa the pmr spectrum of anhydride Va exhibits two singlets of

---

[4] E. H. White and H. C. Dunathan, *J. Am. Chem. Soc.*, **78**, 6055 (1956), and references cited therein.

[5] R. A. Raphael, "Chemistry of Carbon Compounds," Vol. IIA, E. A. Rodd, Ed., Elsevier Publishing Co., Amsterdam, 1953, pp 60–65.

[6] R. Anet, *Can. J. Chem.*, **40**, 1249 (1962).

[7] G. M. J. Schmidt, *et al.*, *J. Chem. Soc.*, 1996, 2000, 2014, 2021 (1964). See also M. J. Jorgenson, *J. Org. Chem.*, **28**, 2929 (1963), and references therein; H. I. Bernstein and W. C. Quimby, *J. Am. Chem. Soc.*, **65**, 1845 (1943).

TABLE I

PROTON MAGNETIC RESONANCE SIGNALS FOR VARIOUS COMPOUNDS[a]

Compound	Ether CH_3O	Ester CH_3O	CCH_2O	OCH_2O	Aromatic protons	Miscellaneous[b]
trans alcohol[c]			4.20 d (J = 4.5 cps) (2)	5.90 s (2)	6.0–7.0 c (5)	2.60 s (1), OH
I	3.89 s (9)		4.85 d (J = 6 cps) (2)	5.96 s (2)	6.2–7.1 c (7)[d,e]	6.39 d (J = 16 cps) (1)[d,f] 7.68 d (J = 16 cps) (1)[f]
II[d]	3.84 s (18)		3.5–4.6 c (4)[g]	5.94 s (4)	5.5–7.0 c (14)	3.5–4.6 c (4)[g]
IVa	3.87 s, 3.93 s (18 total)[d]	3.43 s (6)			6.60 s (4)	3.6–4.8 c (4)[d,h]
IVb		3.34 s (6)			7.3–7.6 m (10)	3.7–4.8 m (4)
Va	3.80 s, 3.86 s, 3.91 s (18 total)[d]				6.26 s (2), *cis* aryl[i] 6.62 s (2), *trans* aryl[i]	3.8–4.2 c (4)[d,h,j]

[a] Signals are in units of δ. Abbreviations: s, singlet; d, doublet; c, complex; m, multiplet. Numbers in parentheses refer to numbers of protons. See ref 10. [b] Signals in the region of δ 3.0–5.0 correspond to cyclobutane ring protons. [c] *trans*-3,4-Methylenedioxycinnamyl alcohol, run in carbon tetrachloride. [d] Estimated value in a system of overlapping signals. [e] Total of 8 protons in this region. [f] The doublets at 6.39 and 7.68 correspond to the respective α and β hydrogens (with respect to the carbonyl group) in the $-\overset{H}{\overset{|}{C}}=\underset{\underset{H}{|}}{C}-\underset{|}{C}=O$ system. [g] Total of 26 protons in this region. [h] Total of 22 protons in this region. [i] The *cis* and *trans* designations refer to the sides of the cyclobutane ring on which the acid anhydride function is located and not located, respectively. [j] See Figure 1.

equal intensity (two protons each) in the aromatic region. Since sterically only a *cis*-cyclobutane-1,3-dicarboxylic anhydride is possible, the appearance of two singlets for the aromatic protons in Va indicates that the trimethoxyphenyl groups at C-2 and C-4 are in magnetically distinguishable environments, *i.e.*, *trans* to one another (as shown in Scheme I). The shielding effect of an anhydride group on the aromatic protons in the *endo* ring of the maleic anhydride Diels–Alder adduct of 2-nitroanthracene has been clearly noted by Kaplan.[8] Analogously, in Va we assign the signal at δ 6.26 to the 2′ and 6′ protons of the aryl group (at C-4) which is *cis* to the anhydride function and the signal at δ 6.62 to similar protons on the aryl group (at C-2) which is *trans* to the anhydride function. If IIIa has the centrosymmetric structure shown, then anhydride formation would involve epimerization at C-3 (or C-1), *i.e.*, in a position α to a carboxylic acid group. Such epimerization occurs (under the same conditions) in the transformation α-truxillic acid → γ-truxillic anhydride.[5] On the other hand, if IIIa had the alternative 1α,2β,3α,4β stereochemistry, then formation of anhydride Va would necessitate epimerization at C-2 (or C-4), a highly unlikely process under the reaction conditions employed. That epimerization had, indeed, occurred in the reaction IIIa → Va was apparent from the fact that an acid (mp 236°) different from IIIa was obtained on hydrolysis of anhydride Va with aqueous potassium hydroxide at room temperature. The transformations IIIb → Vb → VIb in the truxillic acid series thus appear to be reproduced in a stereochemical sense in the present series of conversions IIIa → Va → VIa. Moreover, the probable stereochemical structures of II, IIIa, and IVa are those shown in Scheme I.

From a synthetic point of view the formation of acid IIIa by means of photodimerization of I is a six-step procedure from the commercially available starting materials, *trans*-3,4,5-trimethoxycinnamic acid (VII) and *trans*-3,4-methylenedioxycinnamic acid.[9] *A priori* a far simpler synthetic route to IIIa would appear to be direct photodimerization of crystalline VII itself, in a manner analogous to the formation of α-truxillic acid from *trans*-cinnamic acid. However, irradiation of either VII or crystalline *trans*-3,5-dimethoxy-4-hydroxycinnamic acid for periods of 10–12 days failed to show any reaction. Many apparent inconsistencies of the same type have been interpreted by Schmidt and co-workers[7] in terms of their aforementioned postulate.

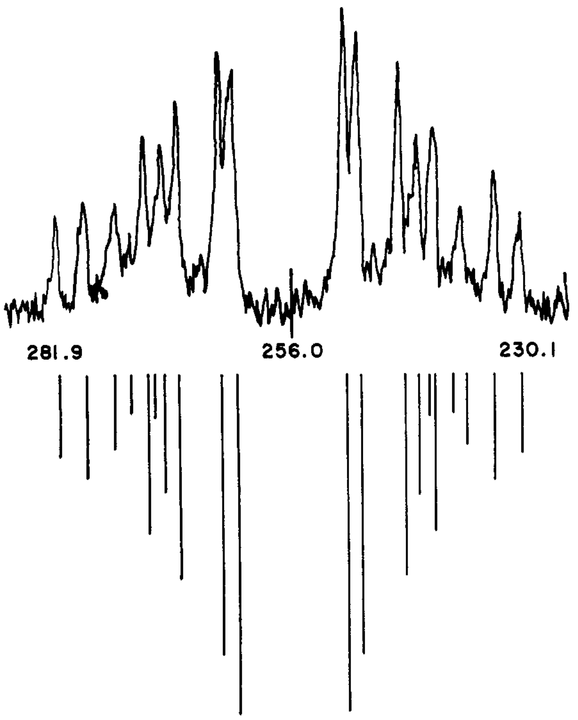


Figure 1.—A comparison of the measured pmr spectrum of dimethyl α-truxillate in the region δ 3.75–4.75 (where the multiplet due to the four protons on the cyclobutane ring occurs) with the line spectrum as calculated from a computer program. Numbers are in cycles per second and refer to the two end lines and to the center of gravity of the calculated spectrum.

For comparative purposes we obtained the pmr spectrum of dimethyl α-truxillate (IVb) which, like its hexamethoxy derivative IVa, shows a singlet for the carbomethoxy protons. However, in the spectrum of IVb one can readily see a symmetric multiplet due to

---

(8) F. Kaplan, "Electronic Effects on the Stereochemistry of the Diels-Alder Reaction," Ph.D. Dissertation, Yale University, 1959. See also F. Kaplan and H. Conroy, *J. Org. Chem.*, **28**, 1593 (1963).

(9) L. H. Klemm, K. W. Gopinath, G. C. Karaboyas, G. L. Capp, and D. H. Lee, *Tetrahedron*, **20**, 871 (1964).

the cyclobutane ring protons (AA′BB′ system, Figure 1) *sans* confusion (as occurs in the spectrum of IVa) by overlap of signals due to ether methoxy protons. We have analyzed this part of the spectrum of IVb by means of an iterative computer program. As can be seen from Figure 1, the observed spectrum is symmetrical with respect to the center of gravity at 256 cps and consists of at least 16 lines. The calculated spectrum of 20 lines has a width of 51.8 cps and is based on the parameters, $\omega_1 = \omega_3 = +14.16 \pm 0.10$ cps, $\omega_2 = \omega_4 = -14.16 \pm 0.10$ cps, $J_{1,3} = J_{2,4} = 0$, $J_{1,2} = J_{3,4} = 10.82 \pm 0.14$ cps, and $J_{2,3} = J_{1,4} = 7.32 \pm 0.16$ cps, where ω values are chemical shifts with respect to the center of gravity, the probable errors in the numerical values are indicated, and the subscripts refer to the numbering scheme in formula IVb.

Experimental Section[10]

Irradiation Experiments.—A thin layer of the finely crystalline compound was spread onto Petri dishes and irradiated in air for a period of 1–12 days by means of a 450-w Hanovia mercury lamp cooled by water running through a quartz jacket. In runs of 1 day the crystals were turned over every 5–6 hr; in longer runs, every 8–12 hr. The irradiated solid was dissolved in a suitable solvent. The solution was filtered to remove insoluble byproducts, concentrated, and cooled.

Irradiation of 13.6 g of commercial *trans*-cinnamic acid (mp 132.5–134°) for 8 days gave (from ethanol) 4.5 g (33%) of α-truxillic acid, mp 280–281.5°, lit.[4] mp 283–284°, plus some recovered cinnamic acid. Irradiation of *trans*-3,4,5-trimethoxycinnamic acid and of *trans*-3,5-dimethoxy-4-hydroxycinnamic acid for 10–12 days gave only starting materials.

Bis-*trans*-3,4-methylenedioxycinnamyl *trans*-2,4-Bis(3,4,5-trimethoxyphenyl)cyclobutane-*trans*-1,3-dicarboxylate (II).—Irradiation of 3 g of *trans*-3,4-methylenedioxycinnamyl *trans*-3,4,5-trimethoxycinnamate[9] (I, mp 119–120°) for 24 hr and extraction with ethanol gave photodimer II, recrystallized from ethyl acetate–methanol: yield 0.9 g (30%), mp 162–163°. Repeated recrystallization from ethanol containing a small amount of benzene gave fine needles: mp 169.5–171°; infrared absorptions at 1720 (saturated ester carbonyl) and 962 (*trans* CH=CH in alcohol moiety), but no absorption at 980 cm^{-1} (*trans* CH=CH in acid moiety of I).[9]

Anal. Calcd for $C_{44}H_{44}O_{14}$: C, 66.32; H, 5.57; CH_3O, 23.4; mol wt, 796. Found: C, 66.38; H, 5.90; CH_3O, 22.1; mol wt (ebullioscopic in benzene), 754.

***trans*-2,4-Bis(3,4,5-trimethoxyphenyl)cyclobutane-*trans*-1,3-dicarboxylic Acid** (IIIa).—A mixture of 0.6 g of ester II and 20 ml of 5% sodium hydroxide in 50% aqueous ethanol was refluxed for 6 hr. The cooled solution was concentrated *in vacuo* and extracted three times with 10-ml portions of chloroform. Evaporation of the organic extracts yielded 348 mg of solid neutral materials. Acidification of the aqueous alkaline phase with 10% hydrochloric acid gave a faintly colored solid which was washed with water and dried: yield 240 mg of acidic materials. Recrystallization of the acidic solid from dimethylformamide–ethanol gave fine white needles (67%) of acid IIIa, mp 320–321°.

Anal. Calcd for $C_{24}H_{28}O_{10}$: C, 60.50; H, 5.92. Found: C, 60.18; H, 5.87.

The solution from trituration of the preceding neutral fraction with boiling cyclohexane was refrigerated to yield 192 mg (75%) of lustrous, pale yellow plates of *trans*-3,4-methylenedioxycinnamyl alcohol, mp 79–80°, identified by direct comparison (mixture melting point and infrared spectrum) with an authentic sample[9] and by pmr (Table I).

Examination of the foregoing cyclohexane mother liquor showed that it contained only unreacted ester and byproducts. The molar ratio of isolated alcoholic and acidic moieties from saponification of II was thus 2.14 (theoretical value, 2).

***trans*-2,4-Bis(3,4,5-trimethoxyphenyl)cyclobutane-*cis*-1,3-dicarboxylic Anhydride** (Va).—A mixture of 123 mg of acid IIIa, 3 ml of acetic anhydride, and *ca.* 3 mg of *p*-toluenesulfonic acid monohydrate was refluxed for 4 hr. Removal of the solvent *in vacuo* left a brown residue which crystallized from benzene–petroleum ether as light tan prisms, mp 203–204°, yield 72 mg (61%). The infrared spectrum shows anhydride absorption bands[11] for a six-membered ring at 1771 and 1824 cm^{-1} compared with ones at 1773 and 1827 cm^{-1} for γ-truxillic anhydride (Vb) obtained from α-truxillic acid in the same manner (lit.[6] 1762 and 1814 cm^{-1} for γ-truxillic anhydride; 1768 and 1854 cm^{-1} for β-truxinic anhydride, five-membered ring).

Anal. Calcd for $C_{24}H_{26}O_9$: C, 62.87; H, 5.72. Found: C, 63.06; H, 5.94.

***trans*-2,4-Bis(3,4,5-trimethoxyphenyl)cyclobutane-*cis*-1,3-dicarboxylic Acid** (VIa).—A mixture of 25 mg of anhydride Va and 2 ml of 10% aqueous potassium hydroxide was allowed to stand at room temperature until a clear solution resulted. Acidification with hydrochloric acid gave a solid which was collected, washed with water, dried, and recrystallized from ethyl acetate–petroleum ether: yield 22 mg (83%) of acid VIa, obtained as faintly tan prisms; mp 235–236° dec.

Anal. Calcd for $C_{24}H_{28}O_{10}$: C, 60.50; H, 5.92. Found: C, 60.24; H, 6.03.

Dimethyl *trans*-2,4-Bis(3,4,5-trimethoxyphenyl)cyclobutane-*trans*-1,3-dicarboxylate (IVa).—The dimethyl ester of IIIa was prepared by treatment of IIIa with an ether solution of diazomethane (excess). It was recrystallized twice from methanol to give faintly cream prisms, mp 164–165°.

Anal. Calcd for $C_{26}H_{32}O_{10}$: C, 61.89; H, 6.39. Found: C, 61.78; H, 6.45.

Pmr Spectrum of Dimethyl α-Truxillate (IVb).—Dimethyl α-truxillate[4] was prepared by treatment of α-truxillic acid (IIIb) with excess diazomethane in ether solution. In the pmr spectrum of IVb (Table I) the symmetric multiplet of 16 prominent peaks centered at δ 4.27 (256 cps, designated as ν_0) and covering a range of *ca.* 60 cps for the four cyclobutane ring protons (Figure 1) was analyzed (by means of an IBM 7094 computer using a Fortran program Laocoon II,[12] adapted to the requirements of the particular computer)[13] in order to obtain numerical values for the four chemical shift parameters, ω_1, ω_2, ω_3, and ω_4 (for protons on the respective carbons C-1 to C-4 in formula IVb, taking ν_0 as the origin), and the six coupling constants, J, associated therewith. From considerations of symmetry in the molecule and in the spectrum one has the relationships, $\omega_1 = \omega_3 = -\omega_2 = -\omega_4$, $J_{1,2} = J_{3,4}$, $J_{1,4} = J_{2,3}$, $J_{1,3} = J_{2,4}$. From chemical intuition one also can write $\omega_1 > 0$ (*i.e.*, the low-field half of spectrum results from protons on C-1 and C-3; the high-field half, from protons on C-2 and C-4), $J_{1,3} = 0$, $J_{1,2} > J_{1,4}$ (*i.e.*, *trans* coupling > *cis* coupling). From the half-width of the spectrum one sees that $\omega_1 < 30$ cps. Effectively then one chooses a trial set of only three parameters. The combination, $\omega_1 = 15$ cps, $J_{1,2} = 12$ cps, $J_{1,4} = 8$ cps, gave an interpretable fit between the calculated and observed spectra with a root mean square (rms) error of 1.21 cps. Eigenstate pairs were assigned to all but the four least intense (of 20 total) transition energies and the iterative technique (of the program) for parameter correction was applied. A second iteration gave values of $\omega_1 = 14.16 \pm 0.10$ cps, $J_{1,2} = 10.82 \pm 0.14$ cps, and $J_{1,4} = 7.32 \pm 0.16$ cps with an rms error of 0.16, where the variations in ω_1 and the J values are probable errors. A third iteration gave no improvement in the rms error. A check showed that the parametric values could not be altered significantly and collaboratively without increasing the value of the rms error.

Acknowledgment.—We wish to thank Drs. A. A. Bothner-By and S. Castellano for a listing of their Fortran "Laocoon II" computer program, Mr. Charles L. Wilkins for punching the program on cards, and the Western Data Processing Center at the University of California at Los Angeles for time on their IBM 7094 computer.

---

[10] Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill., and by Clark Microanalytical Laboratories, Urbana, Ill. Infrared spectra were determined (in chloroform solution) by means of a Beckman IR-7 instrument and pmr spectra by means of a Varian A-60 spectrometer using tetramethylsilane as internal standard and (unless otherwise specified) deuteriochloroform as solvent.

[11] These wave numbers were read directly from the dial of the spectrometer during slow scan of the spectrum.

[12] A. A. Bothner-By and S. Castellano, "Laocoon II," report to Air Force Office of Scientific Research, Mellon Institute, Pittsburgh, Pa., 15213; *J. Chem. Phys.*, **41**, 3863 (1964).

[13] *Cf.* Chem 6 program, C. L. Wilkins and C. E. Klopfenstein, *J. Chem. Educ.*, **43**, 10 (1966).