TABLE III

COMPARISON OF b AND d FROM EQUATIONS 1 AND 12

Set (no.)[a]	b_{12}	b_1	d_{12}	d_1
2 (5)	0.111	0.168	−0.825	−0.847
4 (2)	0.211	0.251	0.688	0.669
5 (3)	0.194	0.257	−0.259	−0.322
18 (10)	0.250	0.274	−0.136	−0.120
20 (9)	0.193	0.227	0.475	0.481
21 (8A)	0.270	0.374	0.305	0.168
25	−0.504	−0.545	0.0854	0.0413

[a] Set numbers in parentheses refer to Table III of the first paper of this series. Subscripts of b and d refer to the equations from which they were obtained. Values of b_1 and d_1 are from Table II of this paper.

including the statistical factor for the tetraethylbenzenes, set 26C. The results for the latter set are by far the best. Furthermore, b for set 26C is essentially the same as b for set 26A which we judge from the models to be free of steric effects. We conclude that the use of the statistical factor is justified in the case of the tetraethylbenzenes. It seems reasonable to apply this argument to any polysubstituted benzene donor in which inspection of models shows one side of the ring incapable of complex formation and the other side unhindered.

TABLE IV

X^1X^2	H,H	H,F	F,F (1,3)
K_N	1.23	0.34	0.10

X^1X^2	F,Me (1,2)	F,Me (1,3)	F,Me (1,4)	H,Me
K_N	0.79	0.65	0.74	1.75

Acknowledgment.—The author acknowledges the use of the facilities of the Computer Laboratories, School of Engineering and Science, Pratt Institute.

Copper Salts Catalyzed Addition of Trichloro- and Dichloroacetonitriles to Olefins

SHINJI MURAI AND SHIGERU TSUTSUMI

Department of Chemical Technology, Faculty of Engineering, Osaka University, Miyakojima-ku, Osaka, Japan

Received October 22, 1965

The copper salts catalyzed addition of trichloro- and dichloroacetonitriles to olefins gives good yields of 1:1 adducts. From 1-octene, 1-hexene, styrene, ethyl acrylate, methyl acrylate, and acrylonitrile, 4-substituted 2,2,4-trichloro- and 2,4-dichlorobutyronitriles are prepared. From norbornene, 1:1 adducts are also obtained.

Peroxide-induced additions of alkyl polyhalides to olefins are well known.[1] Recently additions of carbon tetrachloride,[2a–f] chloroform,[2a,b,d,g] N-chloroamines,[3] and sulfonyl chlorides[4] to olefins using catalytic amounts of copper or iron salts were reported and an oxidation–reduction mechanism was suggested for these reactions. In these "oxidation–reduction additions," chain transfer occurs on the metallic ion of higher oxidation state and this suppresses the telomerization almost completely and therefore the use of a large excess of organic halide is unnecessary. Hence this oxidation–reduction addition reaction is of great importance as a synthetic tool. Moreover, it is worth noting that the adducts of chloroform and olefins are 1,1,3-trichloroalkanes, as distinguished from 1,1,1-trichloroalkanes which are the products of peroxide-catalyzed reactions as reported by Minisci and Galli[2a,b] and also by Asscher and Vofsi.[2d,g]

It has previously been shown in this laboratory that ethyl trichloroacetate can also be added to olefins in the presence of a catalytic amount of copper salts.[5] In a further effort to prepare polychloroalkanes having important substituents, the copper salts catalyzed reactions between polychloroacetonitriles and olefins were investigated. Experiments described in this paper show that, by the reaction of trichloro- and dichloroacetonitriles with various olefins, 2,2,4-trichloro- and 2,4-dichlorobutyronitriles were obtained in good yields. The results are summarized in Tables I and II. In the reactions of ethyl acrylate and methyl acrylate, small amounts of 2:1 adducts were formed as well as the 1:1 adducts.

In a typical experiment, a mixture of an olefin (0.1 mole), a polychloroacetonitrile (0.1 mole), a copper salt (0.002 mole), and acetonitrile (50 ml) was heated at 130–140° for 18 hr in a sealed-glass tube in an oil bath. Afterwards solvent and unchanged materials were removed *in vacuo* and precipitated inorganic material were removed by filtration. Then the 1:1 adduct was distilled within a very narrow boiling point range. No significant amount of polymeric residue was left.

A wide range of catalysts was employed in the reaction of 1-octene with trichloroacetonitrile. When either CuCl, CuBr, CuCN, CuSCN, Cu_2O, CuS, $CuCl_2$, or $Cu(OAc)_2H_2O$ was used, the yield of 1:1 adduct was essentially the same (73–83%). Copper powder or ferrous chloride tetrahydrate was also an effective catalyst, but gave lower yields of 1:1 adduct. When the reaction of 1-octene with trichloroacetonitrile was carried out in the presence of cuprous chloride for 24 hr in refluxing acetonitrile (*ca.* 80°), the yield of 1:1 adduct was only 16%. In the reactions with olefins

---

(1) (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 247; (b) C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 91 (1963).

(2) (a) F. Minisci and R. Galli, *Tetrahedron Letters*, 533 (1962); (b) M. De Male, F. Minisci, E. Volterra, and A. Quilico, *Chim. Ind.* (Milan), 371 (1956); (c) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 2261 (1961); (d) M. Asscher and D. Vofsi, *Chem. Ind.* (London), 209 (1963); (e) M. Asscher, E. Levy, H. Rosin, and D. Vofsi, *Ind. Eng. Chem., Prod. Res. Develop.*, **2**, 121 (1963); (f) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1887 (1963); (g) M. Asscher and D. Vofsi, *ibid.*, 3921 (1963).

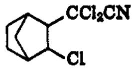
(3) F. Minisci and R. Galli, *Tetrahedron Letters*, 167 (1964); 546 (1964); 3179 (1964); *Chim. Ind.* (Milan), **45**, 1400 (1963).

(4) M. Asscher and D. Vofsi, *Chem. Ind.* (London), 32 (1964); *J. Chem. Soc.*, 4962 (1964).

(5) S. Murai, N. Sonoda, and S. Tsutsumi, *J. Org. Chem.*, **29**, 2104 (1964).

TABLE I

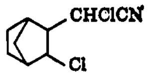
ADDITION OF TRICHLOROACETONITRILE TO OLEFINS[a]

Olefins	Olefins, mole	Trichloro-acetonitrile, mole	Catalysts	Products	Yield,[b] %
1-Octene	0.05	0.05	CuCl	$CH_3(CH_2)_5CHClCH_2CCl_2CN$ (I)	79
	0.05	0.05	CuBr	I	80
	0.05	0.05	CuCN	I	83
	0.05	0.05	CuSCN	I	74
	0.05	0.05	Cu_2O	I	76
	0.05	0.05	CuS	I	76
	0.05	0.05	$CuCl_2$	I	73
	0.05	0.05	$Cu(OAc)_2H_2O$	I	79
	0.05	0.05	Cu (powder)	I	65
	0.05	0.05	$FeCl_24H_2O$	I	43
	0.05	0.05	CuCl	I	16[c]
1-Hexene	0.05	0.05	CuCl	$CH_3(CH_2)_3CHClCH_2CCl_2CN$ (II)	68
Styrene	0.05	0.05	CuCl	$C_6H_5CHClCH_2CCl_2CN$ (III)	75
Ethyl acrylate	0.05	0.05	CuCl	$ClCH(COOC_2H_5)CH_2CCl_2CN$ (IV)	18
	0.1	0.05	CuCl	IV	68
				$Cl[CH(COOC_2H_5)CH_2]_2CCl_2CN$ (XV)	16
	0.05	0.05	CuCl	. . .	0[c]
Methyl acrylate	0.1	0.05	CuCl	$ClCH(COOCH_3)CH_2CCl_2CN$ (V)	73
				$Cl[CH(COOCH_3)CH_2]_2CCl_2CN$ (XVI)	8
Acrylonitrile	0.1	0.05	CuCl	$ClCH(CN)CH_2CCl_2CN$ (VI)	48
	0.2	0.1	CuCl[d]	VI	78
Norbornene	0.05	0.05	CuCl	 (VII[e])	72

[a] All of the reactions were carried out at 130° for 18 hr in 50 ml of acetonitrile using 0.001 mole of catalysts unless indicated otherwise. [b] Yields are based on trichloroacetonitrile used. [c] Reaction was carried out at the boiling point of acetonitrile. [d] 0.2 g (0.002 mole) of cuprous chloride was used. [e] The stereochemistry of VII was not determined.

TABLE II

ADDITION OF DICHLOROACETONITRILE TO OLEFINS[a]

Olefins	Olefins, mole	Dichloro-acetonitrile, mole	Catalysts	Products	Yield,[b] %
1-Octene	0.1	0.1	CuCl	$CH_3(CH_2)_5CHClCH_2CHClCN$ (VIII)	47
1-Hexene	0.1	0.1	CuCl	$CH_3(CH_2)_3CHClCH_2CHClCN$ (IX)	52
Styrene	0.05	0.05	CuCl[c]	$C_6H_5CHClCH_2CHClCN$ (X)	58
	0.1	0.1	CuCl	X	66
Ethyl acrylate	0.2	0.1	CuCl	$ClCH(COOC_2H_5)CH_2CHClCN$ (XI)	45
				$Cl[CH(COOC_2H_5)CH_2]_2CHClCN$ (XVII)	10
Methyl acrylate	0.2	0.1	CuCl	$ClCH(COOCH_3)CH_2CHClCN$ (XII)	62
				$Cl[CH(COOCH_3)CH_2]_2CHClCN$ (XVIII)	14
Acrylonitrile	0.2	0.1	CuCl	$ClCH(CN)CH_2CHClCN$ (XIII)	72
Norbornene	0.1	0.1	CuCl	 (XIV[d])	85

[a] All of the reactions were carried out at 140° for 18 hr in 50 ml of acetonitrile using 0.2 g (0.002 mole) of cuprous chloride as a catalyst unless indicated otherwise. [b] Yields are based on dichloroacetonitrile used. [c] 0.1 g (0.001 mole) of cuprous chloride was used. [d] The stereochemistry of XIV was not determined.

other than 1-octene, only cuprous chloride was used as a catalyst.

As shown in the reactions of trichloroacetonitrile with ethyl acrylate and acrylonitrile, higher concentration of the reactants resulted in better yields of 1:1 adduct. The use of slightly higher temperatures also gave better results; therefore, the reactions of the less reactive dichloroacetonitrile were carried out at higher concentrations and an elevated temperature (140°).

The infrared spectra of all adducts showed a weak absorption at 2280–2290 cm^{-1} (C≡N) and the characteristic absorptions corresponding to the substituents of the original olefins.

From the results of the copper salts catalyzed addition of ethyl trichloroacetate to olefins,[5] it could be predicted that the 1:1 adducts (I–VI and VIII–XIII), might have straight carbon-chain structure. This was confirmed by reducing the adducts from 1-octene, styrene, and ethyl acrylate to *n*-decylamine, 4-phenylbutyronitrile, and ethyl 4-cyanoglutarate, respectively.

The nmr absorption data of 1:1 adducts are given in Table III. The compounds I–VI showed methine absorptions at τ 4.86–5.84 (1 H) and methylene absorptions at 6.72–7.08 (2 H). Each of VIII–XIII showed two methine absorptions (a proton on a carbon substituted with the cyano group and on that substituted with R) at τ 4.96–5.90 (both 1 H) and a methylene absorption at 7.16–7.60 (2 H). Thus it is revealed from these data that compounds VIII–XIII are not 4-substituted 2,2-dichlorobutyronitriles which are the

TABLE III

NUCLEAR MAGNETIC RESONANCE ABSORPTION DATA OF 1:1 ADDUCTS[a]

A. $RCHClCH_2CCl_2CN$

Compd (R)	*R*	RC*H*Cl	C*H*₂CCl₂CN
I (C_6H_{13})	8.05–9.17 (13)	5.83 (1)	7.07 (2)
II (C_4H_9)	8.05–9.15 (9)	5.84 (1)	7.08 (2)
III (C_6H_5)	2.67 (5)	4.86 (1)	6.78 (2)
IV ($COOC_2H_5$)	5.72 (2), 8.63 (3)	5.50 (1)	6.75 (2)
V ($COOCH_3$)	6.17 (3)	5.48 (1)	6.76 (2)
VI (CN)	...	5.17 (1)	6.72 (2)

B. $RCHClCH_2CHClCN$

Compd (R)	*R*	RC*H*Cl	C*H*₂	C*H*ClCN
VIII (C_6H_{13})	8.10–9.10 (13)	5.90 (1)	7.60 (2)	5.20 (1)
IX (C_4H_9)	8.08–9.10 (9)	5.90 (1)	7.60 (2)	5.18 (1)
X (C_6H_5)	2.66 (5)	4.96 (1)	6.30 (2)	5.26–5.62 (1)
XI ($COOC_2H_5$)	5.71 (2), 8.14 (3)	5.50 (1)	7.29 (2)	5.22 (1)
XII ($COOCH_3$)	6.15 (3)	5.45 (1)	7.28 (2)	5.20 (1)
XIII (CN)	...	5.27 (1)	7.16 (2)	5.27 (1)

C. 1:1 Adducts of Norbornene

Compd	Band position
VII	5.86 (1), 7.40 (2), 7.60 (1), 7.80–8.67 (6)
XIV	5.30–6.10 (2), 7.40 (2), 7.60 (1), 7.80–8.80 (6)

[a] Reported as τ values. The figures in parentheses indicate relative intensities, determined by integration.

expected products of the usual peroxide-induced reaction, but rather these compounds are 4-substituted 2,4-dichlorobutyronitriles; hence the reaction must be according to path A in the equations given below.

$$RCH{=}CH_2 + CHCl_2CN \xrightarrow{Cu^+} RCHClCH_2CHClCN \qquad (A)$$

$$\not\longrightarrow RCH_2CH_2CCl_2CN \qquad (B)$$

These copper salts catalyzed additions may proceed *via* the following oxidation–reduction chain mechanism as suggested previously.[2–5]

$$CHCl_2CN + Cu^+ \longrightarrow \dot{C}HClCN + Cu^+Cl \qquad (1)$$

$$RCH{=}CH_2 + \dot{C}HClCN \longrightarrow R\dot{C}HCH_2CHClCN \qquad (2)$$

$$R\dot{C}HCH_2CHClCN + Cu^+Cl \longrightarrow RCHClCH_2CHClCN + Cu^+ \qquad (3)$$

By this process the formation of 4-substituted 2,4-dichlorobutyronitriles is easily understood. As mentioned above this α,γ relationship was reported previously in the reaction of chloroform with olefins.[2a,b,d,g] Step 3 suppresses the telomer formation and this enables the use of olefins in excess over the halides. On the other hand, the benzoyl peroxide induced addition of trichloroacetonitrile to 1-octene to obtain a 66% yield[6] required a threefold excess of halide.

Experimental Section

Nmr spectra were taken on a Model JNM-4H-100 from Japan Electron Optic Laboratory. All boiling point data reported below are uncorrected.

Materials.—Cuprous chloride was purified by Keller's method.[7] Other inorganic materials were obtained commercially and used without further purification. Acetonitrile was purified by the method described in the literature.[8] All olefins were freshly distilled before use. Trichloroacetonitrile was prepared according to the McBee's method.[9] Dichloroacetonitrile was prepared by the essentially same procedure used for the preparation of trichloroacetonitrile except for purification. The crude dichloroacetonitrile, distilled from phosphorus pentoxide was yellow. It was washed twice with small portions of water and dried over anhydrous potassium carbonate and magnesium sulfate. Then colorless dichloroacetonitrile was obtained by distillation, bp 113–114°. The over-all yield from dichloroacetic acid was 57%. Ethyl 4-cyanobutyrate[10] and 4-phenylbutyronitrile[11] were prepared by the reported methods. *n*-Decylamine was prepared by lithium aluminum hydride reduction of *n*-decanenitrile according to the Amundsen's method.[12]

Copper Salts Catalyzed Addition.—Examples of the experimental procedures for the copper salts catalyzed addition are described below under A–C. Results are summarized in Tables I–IV.

A. Reaction of 1-Octene with Trichloroacetonitrile.—A mixture of 5.6 g (0.05 mole) of 1-octene, 7.3 g (0.05 mole) of trichloroacetonitrile, 0.1 g (0.001 mole) of cuprous chloride, and 50 ml of acetonitrile was placed in a glass tube. The glass tube was flushed with nitrogen and sealed and heated in an oil bath at 130° for 18 hr. Solvent and unchanged materials were removed by distillation under reduced pressure and precipitated inorganic materials were removed by filtration. The residual oil was distilled to give 0.2 g of a yellow oil contaminated with a small amount of crystals as a forerun, and 10.1 g of a pale yellow oil boiling at 100–103° (0.15 mm), lit.[6] bp 80–98° (0.15–0.5 mm). This main product became colorless by repeated distillation and was identified as 2,2,4-trichlorodecanenitrile (I) as described below. The yield was 79%. This compound had infrared absorptions at 2280 (C≡N, very weak) and 2880 cm⁻¹ (CH_2); nmr spectrum (CCl_4), methine absorption at τ 5.83 (multiplet, 1 H), methylene absorption at 7.07 (multiplet, 2 H) and complex absorptions at 8.05–9.17 (13 H). Analytical data agree with the formula $C_{10}H_{16}Cl_3N$ as shown in Table IV.

Reduction of I by lithium aluminum hydride was carried out as follows. To a solution of 19 g of lithium aluminum hydride in 500 ml of dioxane was added 12.8 g of I dissolved in 50 ml of dioxane in a period of 1 hr at 80°. After the reaction mixture was refluxed for 16 hr and cooled to 0°, 100 ml of water and 15 ml of 20% NaOH were added. The organic layer was separated by centrifuging, dried over anhydrous magnesium sulfate, and distilled to give 3.5 g of a colorless oil [bp 80–90° (12 mm)], which had characteristic amine odor. This product had the identical infrared spectrum with an authentic *n*-decylamine and showed identical retention time in gas chromatographic analysis on a DC-550 silicone column at 170°.

---

(6) E. C. Ladd, U. S. Patent 2615915 (1952); *Chem. Abstr.*, **48**, 1416 (1954).

(7) R. N. Keller and H. D. Wycoff, *Inorg. Syn.*, **2**, 1 (1946).

(8) P. Walden and E. J. Birr, *Z. Phys. Chem.*, **144A**, 269 (1929).

(9) E. T. McBee, O. R. Pierce, and R. O. Bolt, *Ind. Eng. Chem.*, 391 (1947).

(10) D. J. G. Ives and K. Sames, *J. Chem. Soc.*, 513 (1943).

(11) J. K. Kochi and D. D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964).

(12) L. H. Amundsen and L. S. Nelson, *ibid.*, **73**, 242 (1951).

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)	$C_6H_5Cl_3N_2$	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)	$C_5H_4Cl_2N_2$	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$\equiv$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$\equiv$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).