the spectrum of *trans*-1,2-dicyanocyclobutane indicating that I and III were dimethyldicyanocyclobutanes. Comparison of the infrared spectra of dimer I and of a 1,2-dimethyl-1,2-dicyanocyclobutane prepared by Byrd and Overberger[5] proved that the two compounds were identical. Both dimers I and III yield diacids, m.p. 237-238° and 134-135°, respectively, on hydrolysis, but only the diacid from dimer III gave a crystalline anhydride on warming with acetyl chloride. After being crystallized from benzene-petroleum ether, the anhydride of the dimer III diacid melted at 89-90°. In view of its ability to form an anhydride, dimer III diacid was considered to be the *cis* isomer; dimer I diacid was, accordingly, considered to be *trans*.

Methacrylonitrile Trimer.—This trimer was obtained from both batch and continuous operation. Distillation of a sample from a continuous run gave a yellow oil, b.p. 194° (1 mm.), n^{25}_D 1.4720, which solidified just below room temperature. Recrystallization from methanol gave a white solid, m.p. 47-49°.

Anal. Calcd. for $C_{12}H_{15}N_3$: C, 71.6; H, 7.5; N, 20.9. Found: C, 71.4; H, 7.8; N, 21.0.

Infrared examination revealed a band at 10.60 μ characteristic of $CH_2{=}CRCN$ unsaturation as in the spectrum of methacrylonitrile.

Addition of Methacrylonitrile to Diethyl Fumarate.—From 100 g. of methacrylonitrile and 200 g. of diethyl fumarate, after heating at 300° for 15 minutes in a stainless steel autoclave at autogenous pressure, there was obtained 100 g. of recovered reactants, 35 g. of residues and 31 g., b.p. 146-148° (3.5 mm.), n^{25}_D 1.4545.

Anal. Calcd. for $C_{12}H_{17}O_4N$: N, 5.9. Found: N, 5.7.

This adduct was probably diethyl (β-cyanoallyl)-succinate. Similar treatment of diethyl fumarate with acrylonitrile gave no 1:1 adduct.

Addition of Methyl Methacrylate to Acrylonitrile.—A mixture of 106 g. of acrylonitrile, 100 g. of methyl methacrylate and 80 g. of xylene was heated at 240° for 4 hours. The crude product consisted of 113 g. of monomers and xylene and 47 g. of products which included dimethyl α-methylene-δ-methyladipate. By distillation there was obtained 8 g. of methyl α-cyano-δ-methylenevalerate, b.p. 136-137° (25 mm.), n^{25}_D 1.4511.

Anal. Calcd. for $C_8H_{11}O_2N$: N, 9.2. Found: N, 9.5.

Hydrogenation of the product followed by hydrolysis and crystallization of the diacid from hydrochloric acid gave a product melting at 56-59°. Treatment of the diacid with thionyl chloride gave an acid chloride which was treated with aniline to give a dianilide, m.p. 173-174° (lit.[11] 174-175°).

Acknowledgments.—We wish to thank Dr. J. R. Downing for the interpretation of the infrared spectrograms and Dr. W. H. Wood for the design and operation of the continuous equipment. The presence of methacrylonitrile dimer III was first noted by Dr. D. B. Pattison, Jackson Laboratory, Organic Chemicals Department, du Pont Company. Many helpful suggestions were made by Drs. J. E. Kirby and B. W. Howk.

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[11] L. Bouveault and R. Locquin, *Bull. soc. chim.*, [4], **3**, 449 (1908).

WILMINGTON, DEL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

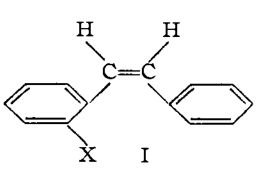
The Preparation of and the Spectral Characteristics of Some 2-Substituted *cis*- and *trans*-Stilbenes[1]

BY DELOS F. DETAR AND LOUIS A. CARPINO

RECEIVED MAY 20, 1955

The preparation of a series of *cis*- and *trans*-2-stilbene derivatives is described. The ultraviolet and the infrared absorption spectra of the stereoisomers differ sufficiently so that configurations can be assigned with considerable certainty to stilbenes of unknown configurations.

In continuation of a study concerning the mechanisms of intramolecular free-radical reactions it was desirable to prepare *cis*-stilbene-2-carboxylic acid (I, X = COOH). The decomposition of the corresponding peroxide should give rise to the *cis*-β-styrylphenyl radical (I, X = ·), and would constitute an alternative route to the radical considered to be an intermediate in reactions of diazotized *cis*-2-aminostilbene under alkaline conditions.[2] In order to be certain of the stereochemistry of the various stilbene derivatives, an examination was undertaken of the infrared and the ultraviolet spectra of a number of 2-substituted *cis*- and *trans*-stilbenes.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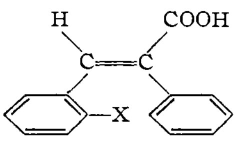
II

Several workers have examined the spectra[3,4] of *trans*-stilbene derivatives, but the corresponding *cis*-isomers have been less extensively investigated.[5] Very few 2-substituted stilbenes have been studied.

The preparation of *cis*-stilbene derivatives usually involves either decarboxylation of the corresponding cinnamic acids[6] or photochemical isomerization[7] of the *trans* compounds. The first method is more convenient for large-scale work. A previous attempt[8] to prepare *cis*-stilbene-2-carboxylic acid by treatment of *cis*-2-chlorostilbene with lithium followed by carbonation led to small amounts of the *trans*-acid together with some *trans*-stilbene.

In the present work *cis*-2-bromostilbene was prepared by condensation of 2-bromobenzaldehyde with phenylacetic acid to give *trans*-α-phenyl-2-bromocinnamic acid (II, X = Br; phenyl groups

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[1] This research was supported by National Science Foundation grant NSF G439.

[2] D. F. DeTar and Y. W. Chu, THIS JOURNAL, **76**, 1686 (1954).

[3] E. A. Braude, *J. Chem. Soc.*, 1902 (1949); R. H. Beale and E. M. F. Roe, THIS JOURNAL, **74**, 2302 (1952).

[4] H. W. Thompson, E. E. Vago, M. C. Corfield and S. F. D. Orr, *J. Chem. Soc.*, 214 (1950).

[5] M. Calvin and H. W. Alter, *J. Chem. Phys.*, **19**, 765 (1951).

[6] P. Ruggli and A. Staub, *Helv. Chim. Acta*, **20**, 37 (1937).

[7] L. Zechmeister and W. H. McNeely, THIS JOURNAL, **64**, 1919 (1942).

[8] D. F. DeTar and Y. W. Chu, *ibid.*, **77**, 4410 (1955).

are *cis*), which was decarboxylated by the quinoline–copper chromite method. Attempted conversion of the *cis*-2-bromostilbene to the Grignard reagent with one sample of magnesium turnings seemed to occur normally, but no acid could be isolated after carbonation with gaseous carbon dioxide. Instead the products were phenanthrene (45%) and *cis*-stilbene (17%). On the other hand, with a newer sample of magnesium it was possible to obtain a 60% yield of pure *cis*-2-stilbenecarboxylic acid, accompanied by lesser amounts of phenanthrene. When the Grignard reagent was decomposed with hydrochloric acid (without passing carbon dioxide into the solution), the product consisted of roughly 75% of *cis*-stilbene and 25% of phenanthrene as indicated by comparison of the infrared spectra with a known mixture. If the solution of the Grignard reagent in ether was allowed to stand for one week, before decomposition, the product consisted of approximately equal amounts of *cis*- and *trans*-stilbene along with a lesser amount of phenanthrene.

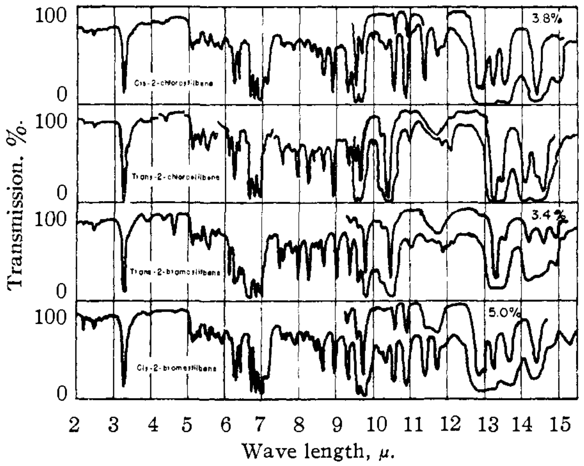

Fig. 1.—Spectra recorded on a Perkin–Elmer model 21 infrared spectrophotometer. The instrument settings were as follows: slit program 960, response 1, speed about 2 min. per micron, scale 1 cm. per micron; the two bromostilbene spectra were recorded with the scattered radiation filter out, the chlorostilbene spectra with the filter automatically inserted at 9.3 μ. The *cis*-2-bromostilbene, the *trans*-2-bromostilbenes and the *cis*-2-chlorostilbene were run as liquids (neat) in a fixed cell 0.0578 mm. thick. At the longer wave lengths they were also run as solutions in carbon disulfide in a cell 0.195 mm. thick and at the concentration indicated beside the curve (given in % by weight of total solution). The *trans*-2-bromostilbene sample contained a trace of carbon disulfide as indicated by absorption at 4.62 and at 6.6 μ; the strong 6.7-μ peak belongs to the *trans*-2-bromostilbene. All of the carbon disulfide solution spectra exhibit a broad weak peak at 11.7 μ; except for this the solvent contributes no peaks. The *trans*-2-chlorostilbene is a solid and was run using three solutions: (1) 38% solution in carbon disulfide (*i.e.*, 38% chlorostilbene and 62% solvent) in a 0.1-mm. cell 2–4.2, 4.9–5.8, 7.3–15.5; (2) 49% solution in bromoform in a 0.0578-mm. cell 4.2–4.9, 5.8–7.3; (3) 4.4% solution in carbon disulfide in a 0.195-mm. cell 9–15. The only solvent peaks present are the minute bromoform peak at 7.2 μ and the carbon disulfide peak at 11.7 μ.

Kharasch, Morrison and Urry[9] have shown that small amounts of metallic halides such as cobaltous chloride promote Grignard reactions which can most readily be represented as involving free radical intermediates. Whether such intermediates account for the above results is still an open question.

The preparation of *cis*-2-stilbenecarboxylic acid by hydrolysis of the corresponding *cis*-nitrile, obtained either from *o*-cyanobenzaldehyde or by the Rosenmund–von Braun reaction from *cis*-2-chlorostilbene, was unsuccessful. Both the *cis*-2-stilbenecarbonitrile and the *trans*-isomer were difficult to hydrolyze, although small amounts of the two acids could be obtained in this way.

Attempts to convert diazotized *cis*-2-aminostilbene to the iodo compound gave an 80% yield of phenanthrene; attempts to convert the diazonium salt to *cis*-2-cyanostilbene likewise resulted in an 80% yield of phenanthrene. Ruggli and Staub[6] have reported that the hypophosphorous acid deamination likewise gives phenanthrene rather than *cis*-stilbene. The remarkable tendency of this diazonium salt to undergo the Pschorr ring closure is probably due in large measure to the rigid ethylenic bond which holds the two *o*-positions in close proximity.

Table I lists the infrared absorption peaks which appear to be most useful in distinguishing *cis* and *trans* isomers in the 2-substituted stilbene derivatives. The strong absorption peak at about 10.38 μ in the spectra of the *trans* compounds has been noted previously[10] in the spectra of a variety of aliphatic *trans*-olefins and more recently in the spectra of a series of *trans*-stilbenes.[4] The present data show that the range of applicability of these generalizations also includes the *cis*-stilbene series. The spectra of *cis*- and *trans*-2-chlorostilbene and of *cis*- and *trans*-2-bromostilbene are given in Fig. 1.

TABLE I

DIAGNOSTIC PEAKS OF 2-SUBSTITUTED STILBENES

Substituent	Wave length, μ[a]		
	cis		*trans*
-H	10.84	12.84	10.39
-Cl	10.90	12.80	10.30
-CN	10.89	12.88	10.40
$-NO_2$	10.90	12.64	10.40
-Br	10.91	12.85	10.42
-COOH	10.90	12.89	10.34
$-NH_2$	10.88	12.76	10.25
$-NH_2\cdot HCl$	10.88	12.58	10.47
$-N_2BF_4$[b]	10.82	12.96	10.37(o) 10.40(y)
$-CONH_2$	10.89	12.88	10.43

[a] The spectra of *cis*-stilbene, of *cis*-2-aminostilbene, and of the chloro- and the bromostilbenes were carried out on liquid samples; the remainder were run on solids. [b] The *trans* isomer exists in two modifications, an orange form (o) and a yellow form (y).

On passing from the *trans*- to the *cis*-stilbenes the strong band at 10.38 μ disappears or becomes very weak while a new medium-strong peak appears at about 10.88 μ. In addition a strong band appears at 12.80 μ.

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[9] M. S. Kharasch, R. Morrison and W. H. Urry, THIS JOURNAL, **66**, 368 (1944).

[10] N. Sheppard and D. M. Simpson, *Quart. Revs.*, **6**, 1 (1952).

Though of lesser importance in distinguishing isomeric pairs, it should be noted that the *trans*-stilbenes generally exhibit greater absorption than the *cis* isomers in the 7–9 μ region whereas the situation is reversed in the 10.6–13.6 μ region.

The ultraviolet spectra are presented in Fig. 2. The observations of Calvin and Alter[5] have been confirmed: the λ_{max} values for the *trans*–compounds are shifted 15–40 mμ to the longer wave lengths and the values of the corresponding extinction coefficients are 1.5–3 times as great as those of the *cis* isomers.

The present results together with the results previously reported by other workers indicate that for a pair of *cis* and *trans* isomeric stilbenes the ultraviolet spectra or the infrared spectra will permit a definite structural assignment. Furthermore, a reasonable assignment can be made if only one of the stereoisomers is available. In addition an examination of the spectra of a large number of *cis–trans* pairs shows that it is rather easy to obtain each of the compounds with well under 1% of its stereoisomer as a contaminant.

Experimental[11]

Preparation of Compounds for Spectral Analysis.—Known compounds were prepared by methods previously described. *trans*-Stilbene from the Matheson Co., was recrystallized from ethanol (m.p. 120–121°). *cis*-Stilbene was prepared by decarboxylation of *trans*-α-phenylcinnamic acid according to the method of Taylor and Crawford.[12] The product, b.p. 90–92° (0.08 mm.), purified by chromatography on alumina[7] contained less than 3% of the *trans* isomer, possibly much less. *cis*-2-Nitrostilbene (m.p. 62.5–63.5°) was prepared by decarboxylation of the corresponding cinnamic acid.[2,6] The *trans* isomer (m.p. 70–71°) was prepared by isomerization of the *cis* compound. The *cis*-amine [b.p. 104.3–104.5° (0.2 mm.)] and the *trans*-amine (m.p. 100–101°) were prepared by ferrous sulfate reduction[2,6] of the corresponding nitro compounds. The *cis*-amine hydrochloride (m.p. 202–203°) and the *trans*-amine hydrochloride were obtained in the same process. The authors are indebted to Miss Yun Wen Chu[8] for the preparation of *cis*-2-chlorostilbene (b.p. 118–120° (1.5–2 mm.)) and *trans*-2-chlorostilbene (m.p. 39–40°).

Ultraviolet Spectra.—The ultraviolet spectra were determined on a Beckman model DU quartz spectrophotometer using 95% ethanol as solvent and concentrations of about 10^{-5} m./l. All spectra were determined in duplicate.

o-Bromobenzyl Bromide.—In a modification of the method for the dibromo compound,[13] 465 g. (2.72 moles) of *o*-bromotoluene, a few crystals of benzoyl peroxide and 448 g. (2.8 moles) of bromine (added over a period of one hour) at 100–115° with irradiation yielded 560 g. (82%) of *o*-bromobenzyl bromide, b.p. 120–130° at 13 mm.

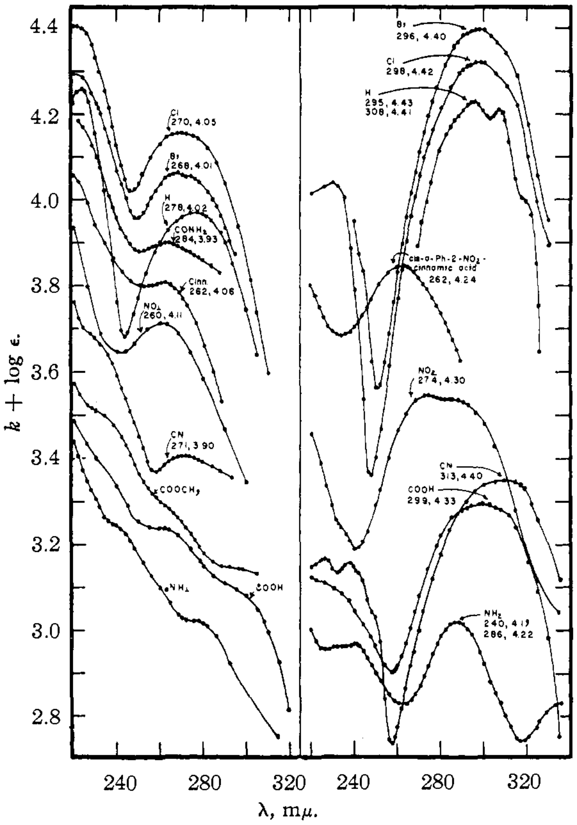
o-Bromobenzaldehyde.—The benzyl bromide was converted to the aldehyde by treatment with the sodium salt of 2-nitropropane.[14] The crude product, b.p. 63.5–77° at 0.13–0.28 mm. (65% yield) was used without further purification.

Hydrolysis of o-Bromobenzal Bromide.—The dibromide (171 g., 1 mole) was refluxed with 1800 ml. of 75% ethanol and 205 g. (2.5 moles) of sodium acetate for 12 hours.[13] Dilution with water and distillation of the precipitated oil gave 136 g. of a liquid, b.p. 94–107° at 3.5 mm., which contained active bromine. Further refluxing with 300 g. of calcium carbonate and 500 ml. of water followed by steam distillation gave 128.2 g. (70%) of the crude *o*-bromobenzaldehyde, b.p. 81.8–91.2° at 3.5 mm.

***trans*-o-Bromo-α-phenylcinnamic Acid.**—A mixture containing 65 g. (0.351 mole) of *o*-bromobenzaldehyde, 52.6 g. (0.386 mole) of phenylacetic acid, 24.2 g. of potassium carbonate and 90 g. of acetic anhydride was refluxed for 1.5 hours. The solution was cooled somewhat and diluted with water to the cloud point. Yellow crystals separated on cooling; and recrystallization from ethyl acetate gave 58 g. (54%) of colorless needles melting at 179–180°; further recrystallization from ethanol gave a sample m.p. 181–182.2°.

Anal. Calcd. for $C_{15}H_{11}O_2Br$: C, 59.42; H, 3.66; Br, 26.36. Found: C, 59.30; H, 3.62; Br, 26.23.

***cis*-2-Bromostilbene.**—Redistilled quinoline (75 ml.) was heated with stirring so that the internal temperature was 225–230°; 4.5 g. of copper-chromium oxide catalyst was added and then 30 g. of *trans*-*o*-bromo-α-phenylcinnamic acid (added during 10 minutes). After an additional 10 minutes evolution of carbon dioxide had nearly ceased. The mixture was cooled quickly by means of tap water and decanted from most of the catalyst. Material from five such runs was combined and distilled rapidly (1–2 mm.), and the clear distillate poured into a solution of 150 ml. of concd. hydrochloric acid in 1 l. of water. The undissolved oil was



cis-2-Stilbene derivatives *trans*-2-Stilbene derivatives

Fig. 2.—Ultraviolet spectra of *cis*-stilbene derivatives on the left and most of the corresponding *trans*-stilbene derivatives on the right. The spectra were measured on a Beckman model DU spectrophotometer in 95% ethanol solutions, cell length 1.005 cm., slit 0.12–0.14 mm. The samples were run in duplicate, the dots indicating observed points. $\epsilon = A/bc$, A = absorbance, b = cell length, c = molar concn. For the purpose of clarity the following additive constants K were added to log ε in order to displace the curves: *cis* curves: Cl +0.10, Br +0.05, H −0.05, $CONH_2$ −0.05, Cinn. (*trans*-α-phenyl-2-nitrocinnamic acid) −0.05, NO_2 −0.40, CN −0.50, $COOCH_3$ −0.65, COOH −0.75, NH_2 −0.90; *trans* curves: Br 0.0, Cl −0.10, H −0.20, *cis*-α-Ph-2-NO_2-cinnamic acid −0.40, NO_2 −0.75, CN −1.05, COOH −1.05, NH_2 −1.20. The numbers beside the peaks identify the 2-substituent and give wave length and log ε for the absorption peak.

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[11] All melting points are corrected.

[12] T. W. J. Taylor and C. E. J. Crawford, *J. Chem. Soc.*, 1130 (1934).

[13] R. Adams and E. H. Volwiler, THIS JOURNAL, **40**, 1732 (1918).

[14] H. B. Hass and M. L. Bender, *ibid.*, **71**, 1767 (1949).

taken up in methylene chloride and the extract washed with 10% hydrochloric acid until no quinoline separated from the extracts upon addition of dilute alkali. After drying, solvent removal and distillation there was obtained 89.4 g. (70%) of *cis*-2-bromostilbene, b.p. 122–125° at 0.8–0.9 mm.; analytical sample b.p. 121° at 0.5 mm., $n^{24.5}$D 1.6404.

Anal. Calcd. for $C_{14}H_{11}Br$: C, 64.88; H, 4.29; Br, 30.84. Found: C, 64.60; H, 4.36; Br, 30.46.

trans-2-**Bromostilbene.**—The *cis*-2-bromostilbene was isomerized by refluxing with nitrobenzene in the presence of a little iodine[6] to give *trans*-2-bromostilbene, b.p. 145° at 0.55 mm., $n^{24.5}$D 1.6822,[15] m.p. 27–28° (from pentane); dibromide m.p. 182–183° as reported.[15] Under the same conditions the *cis* compound gives the same dibromide.

cis-**Stilbene-2-carboxylic Acid.**—The Grignard reagent from 46.5 g. (0.18 mole) of *cis*-2-bromostilbene, 4.7 g. (10% excess) of fresh, clean magnesium turnings (Matheson) and 400 ml. of ether was cooled (ice-bath) while dry carbon dioxide gas was passed in. Hydrolysis and evaporation of the solvent gave a yellow-orange solid; recrystallization from 75 ml. of ethyl acetate gave 19.5 g. of small, cream-colored flaky crystals, m.p. 143–145°. An additional 5 g. (m.p. 144–146°) was obtained from the filtrate; total yield 24.5 g. (61%). A small amount of phenanthrene could be isolated from the filtrates. An analytical sample of *cis*-stilbene-2-carboxylic acid was prepared by recrystallization from *n*-heptane–benzene (1:1) and then from 85% ethanol; colorless crystals, m.p. 145–146.5°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H. 5.39. Found: C, 80.46; H, 5.26.

The preparation described above was first carried out with 5 g. of *cis*-2-bromostilbene and 0.52 g. of magnesium turnings (J. T. Baker) which were coated with a rust-like material. After carbonation and decomposition by means of dilute hydrochloric acid there was obtained from the ether layer 1.52 g. (44%) of crude phenanthrene, m.p. 84–86°, and 0.6 g. (17%) of crude *cis*-stilbene, b.p. 82.5–98° at 0.1–0.08 mm. The products were identified by comparison with the infrared spectra of the authentic compounds. A second recrystallization of the crude phenanthrene gave 0.66 g. (22%) of white crystals, m.p. 91–94°. None of the *cis*-acid was found.

trans-α-**Phenyl-2-cyanocinnamic Acid.**—*o*-Cyanobenzaldehyde was prepared by oxidation of *o*-tolunitrile with chromium(VI) oxide.[16] The aldehyde, m.p. 102–103°, was condensed with phenylacetic acid as described for *o*-bromobenzaldehyde except that triethylamine was used in place of potassium carbonate. The pure acid (m.p. 188.2–190.2°) was obtained in a yield of 44%. An analytical sample, after three recrystallizations from ethanol, melted at 191.5–192.5°, and had a slight greenish-yellow color.

Anal. Calcd. for $C_{16}H_{11}O_2N$: C, 77.09; H, 4.45; N, 5.62. Found: C, 76.78; H, 4.54; N, 5.56.

cis-2-**Cyanostilbene.**—*trans*-α-Phenyl-2-cyanocinnamic acid was decarboxylated as described above for the bromo compound to give crude liquid nitrile, b.p. 147–151° at 3.5 mm. (75% yield); redistillation and recrystallization from pentane gave large colorless crystals, m.p. 39.5–40°.

Anal. Calcd. for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.83. Found: C, 87.97; H, 5.56; N, 6.63.

cis- **and** *trans*-2-**Cyanostilbene.**—A mixture of 39.0 g. (0.181 mole) of *cis*-2-chlorostilbene, b.p. 118–120° (1.5–2 mm.), 18.2 g. (0.101 mole) of cuprous cyanide and 16.0 g. (0.202 mole) of redistilled pyridine was refluxed under a drying tube for 24 hours. All volatile material was distilled rapidly under reduced pressure, and the distillate poured into an excess of dilute hydrochloric acid. The crude nitrile was isolated by ether extraction and distilled to give two fractions, (I) b.p. 106–111.8° at 0.2 mm., and (II) m.p. 112–115° at 0.2 mm., and a residue.

Both fractions solidified on standing and proved to be mainly *cis*-2-cyanostilbene (infrared spectra).

The residue amounting to 9.5 g. solidified. Recrystallization from cyclohexane gave 4.8 g. of slightly brownish crystals, m.p. 64–66°. Recrystallization from *n*-heptane gave *trans*-2-cyanostilbene as colorless needles, m.p. 65–66°.

Anal. Calcd. for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.83. Found: C, 87.96; H, 5.62; N, 6.71.

The dibromide of *trans*-2-cyanostilbene was prepared by means of bromine in carbon tetrachloride. The product crystallized from ethanol as short colorless needles, m.p. 144–145°.

Anal. Calcd. for $C_{15}H_{11}Br_2N$: C, 49.34; H, 3.04; N, 3.84; Br, 43.78. Found: C, 49.58; H, 3.05; N, 3.44; Br, 43.18.

Attempted Hydrolysis of *cis*-2-**Cyanostilbene.**—Refluxing a mixture of 1.5 g. of *cis*-2-cyanostilbene, 1.5 g. of potassium hydroxide and 30 ml. of 50% ethanol for three days led to formation of a neutral white solid, m.p. 132–133° (from nitromethane).

Anal. Found: C, 80.78; H, 5.74.

Hydrolysis of the *cis*-nitrile in the presence of both potassium and barium hydroxides in refluxing ethanol gave a trace of the *cis*-acid, m.p. 143–146°, with an infrared curve identical with that of acid prepared by carbonation of the Grignard reagent of the *cis*-bromide.

Hydrolysis of the *trans*-nitrile was also very difficult to effect although a small amount of the *trans*-acid was obtained as well as some of the same neutral compound formed in the hydrolysis of the *cis*-nitrile.

cis-**Stilbene-2-carboxylic Acid Chloride.**—A mixture of 12 g. of *cis*-stilbene-2-carboxylic acid and 12 g. of purified thionyl chloride was heated 8 hours at 50°, the excess thionyl chloride removed (water aspirator) and the solidified residue recrystallized from cyclohexane to give 11.6 g. (89%) of large cream-colored crystals, m.p. 75–77°; after two further recrystallizations from cyclohexane the m.p. was 76–77°.

Anal. Calcd. for $C_{15}H_{11}OCl$: C, 74.23; H, 4.57. Found: C, 74.55; H, 4.65.

The amide, recrystallized three times from 85% methanol, had a m.p. of 93–94°.

Anal. Calcd. for $C_{15}H_{13}ON$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.31; H, 5.54; N, 6.30.

The methyl ester (from the acid chloride and methanol in the presence of pyridine) upon three recrystallizations from methanol was obtained in the form of colorless needles, m.p. 74–75°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 80.64; H, 5.92. Found: C, 80.50; H, 5.70.

trans-**Stilbene-2-carboxylic Acid.**—Benzal phthalide (m.p. 97–99°) from phthalic anhydride and phenylacetic acid[17] was reduced by means of zinc dust and refluxing potassium hydroxide solution.[18] Because of difficulties experienced in the conversion of benzyl phthalide to the *trans*-acid the following procedure was developed.

A mixture of 120 g. of potassium hydroxide (85%), 190 g. of benzal phthalide, 600 ml. of water and 72 g. of zinc dust was stirred and refluxed for four hours. The mixture was filtered, the filtrate acidified with dil. hydrochloric acid and the crude lactone obtained as an oil after ether extraction.

A mixture of 140 g. of potassium hydroxide (85%) in 300 ml. of diethylene glycol was heated to an internal temperature of about 150° and then a solution of the crude lactone in 100 ml. of warm diethylene glycol was added at such a rate that slow distillation of water occurred (one-half hour). The temperature was then raised gradually to 200–210° (1–2 hours). The solution was cooled, poured onto 1.5 kg. of crushed ice and then warmed on a hot-plate to dissolve the oil. The aqueous solution was treated with Norit and acidified with dil. hydrochloric acid after addition of 1.5 kg. of crushed ice. Recrystallization from acetic acid (125 g., 65%) and then from 80% ethanol gave 102 g. of *trans*-2-stilbenecarboxylic acid, small white needles, m.p. 158–160°.

trans-**Stilbene-2-carboxylic Acid Chloride and Amide.**—A mixture of 22.5 g. of *trans*-stilbene-2-carboxylic acid and 14 ml. of thionyl chloride was treated as described for the *cis* compound. After two recrystallizations from cyclohexane the acid chloride melted at 56–57°. It was converted to the amide which after three recrystallizations from ethanol melted at 191–192°.

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Anal. Calcd. for $C_{15}H_{13}ON$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.59; H, 5.79; N, 6.27.

Attempted Preparation of *cis*-2-Iodostilbene.—A solution of the diazonium salt prepared from 1.25 g. (5.4 mmoles) of *cis*-2-aminostilbene hydrochloride, 30 ml. of water, 1.3 ml. of concd. hydrochloric acid and 0.4 g. of sodium nitrite was cooled in an ice-bath and added to a solution of 0.83 g. of potassium iodide in 10 ml. of ice-cold water covered by a layer of 15 ml. of ether. After the reaction mixture had been stirred in the ice-bath for 5 hours the ether layer was washed twice with sodium thiosulfate and allowed to evaporate spontaneously. The orange solid residue (0.97 g.) upon steam distillation gave a white solid, m.p. 81–87°, which was shown by the infrared curve to be mainly phenanthrene contaminated by an unknown substance. The yield was 0.75 g. (78%). Further recrystallization from hexane raised the melting point to 97–98°.

Attempted Preparation of *cis*-2-Cyanostilbene from Diazotized *cis*-2-Aminostilbene.—A diazotized solution of 2.32 g. (10 mm.) of *cis*-2-aminostilbene hydrochloride was cautiously neutralized (litmus) by means of approximately 1.3 g. of sodium carbonate dissolved in a small amount of water. This solution was then added slowly with shaking to a cold (5°) mixture of 20 ml. of benzene and a solution of sodium cuprocyanide prepared from 3.12 g. of copper sulfate pentahydrate.[19] The benzene layer after drying (magnesium sulfate) and evaporation yielded a brown solid residue, shown by the infrared curve to be mainly phenanthrene; yield 1.47 g. (82.5%), m.p. 80–90°. Recrystallization from ethanol gave 0.91 g. (51%) of brownish flakes, m.p. 95–96°.

When the *trans*-amine was treated similarly the only products obtained were traces of *trans*-stilbene, m.p. 121–122°, and *trans*-2-cyanostilbene, m.p. 65–66.5°, isolated by chromatography on an alumina column using carbon tetrachloride as solvent. The compounds were identified by means of their infrared spectra.

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[19] H. T. Clarke and R. R. Read, "Organic Syntheses," Coll. Vol. I John Wiley and Sons, Inc., New York, N. Y., 1941, p. 514.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

Carbon Dihalides as Intermediates in the Basic Hydrolysis of Haloforms. IV. Relative Reactivities of Haloforms[1]

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The kinetics of the basic hydrolysis of six haloforms have been studied in 66⅔% dioxane–water solution. All reactions were second order and the following order of reactivity was found: $CHBrClF \gg CHBrCl_2 > CHBr_2Cl \sim CHCl_2I > CHBr_3 > CHCl_3$. The reaction of fluoroform was too slow to measure. The reactions of all six are believed to involve the intermediate formation of a reactive *carbon dihalide*. As evidence for this, all are much more reactive toward alkali than would be expected from the S_N2 mechanism. Furthermore, the reactions of $CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$ and $CHCl_3$ with sodium *p*-thiocresolate are found to be strongly catalyzed by sodium hydroxide. While most of the heats and entropies of activation are within experimental error of each other, the great reactivity of CHBrClF is at least partly an entropy effect.

In earlier articles of this series[2,3] evidence has been presented that the alkaline hydrolysis of chloroform proceeds by the mechanism

$$\text{I}\qquad \begin{aligned} CHX_3 + OH^- &\rightleftharpoons CX_3^- + H_2O \\ CX_3^- &\longrightarrow CX_2 + X^- \\ CX_2 &\xrightarrow[\text{fast}]{OH^-,\ H_2O} CO \text{ and } HCO_2^- \end{aligned}$$

In order to investigate the possibility that other haloforms react by this mechanism and to study the effect of structure on reactivity we have obtained data on some other haloforms.

Reaction Mechanism.—Each of the six haloforms studied underwent kinetically second-order alkaline hydrolysis in aqueous dioxane as required by mechanism I.[4] There are, of course, two other reasonable mechanisms that yield second-order kinetics.[2]

$$\text{II}\qquad \begin{aligned} CHX_3 + OH^- &\rightleftharpoons CX_3^- + H_2O \\ H_2O + CX_3^- &\longrightarrow H_2\overset{+}{O}\text{–}\overset{-}{C}X_2 + X^- \\ H_2\overset{+}{O}\text{–}\overset{-}{C}X_2 &\xrightarrow[\text{fast}]{OH^-,\ H_2O} CO \text{ and } HCO_2^- \end{aligned}$$

$$\text{III}\qquad \begin{aligned} CHX_3 + OH^- &\longrightarrow CHX_2OH + X^- \\ CHX_2OH &\xrightarrow[\text{fast}]{OH^-,\ H_2O} CO \text{ and } HCO_2^- \end{aligned}$$

Since III is simply an example of the S_N2 mechanism[5] which has been rather well established for the reactions of many organic halides, and no such precedent exists for II, most of our attention has been directed at distinguishing between mechanisms I and III. Our arguments are of the same type already used in the case of chloroform.[2]

Doering and Hoffmann have used olefins as nucleophilic reagents in reaction with chloroform and bromoform.[6] They find the reaction to be accelerated by the base potassium *t*-butoxide. This rules out the S_N2 mechanism (III) but does not distinguish between mechanisms I and II.

Bromoform, bromodichloromethane and dichlorofluoromethane, the only other haloforms which appear to have been studied, all undergo base-catalyzed deuterium exchange.[7] Apparently then, trihalomethylcarbanions are formed rather generally from haloforms and alkali.

Toward weakly basic nucleophilic reagents haloforms have been found to be less reactive than the analogous methylene halides in all of the cases studied. Examples of this may be seen in the

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[1] From the Ph.D. thesis submitted by Arthur M. Dowell, Jr., in 1954, and the M.S. thesis submitted by John E. Singley, Jr., in 1952, to the Graduate School of the Georgia Institute of Technology. Presented in part before the Organic Section at the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., Sept. 13, 1951. For part III see ref. 3.

[2] J. Hine, THIS JOURNAL, **72**, 2438 (1950).

[3] J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

[4] The mass law effect,[3] by which halide ions slow the reaction by combining with carbon dihalide to regenerate trihalomethyl anions, was negligible under the conditions used.

[5] For the significance of the terms S_N1 and S_N2 see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, chap. VII.

[6] W. von E. Doering and A. K. Hoffmann, THIS JOURNAL, **76**, 6162 (1954).

[7] J. Hine, N. W. Burske and R. C. Peek, Jr., unpublished work from this Laboratory.