EXPERIMENTAL[20]

General procedure for the Dieckmann cyclizations. The Dieckmann cyclizations were all run using the special apparatus previously described.[3–6,9] A 2-l. Morton flask was equipped with a Morton high speed stirrer[21] and a cyclic high dilution apparatus[3,22,23] which carried a dropping funnel and a reflux condenser with stopcock attached.[3] Nitrogen was admitted through the lower end of the stirrer shaft and passed out through a drying tube which protected the top of the reflux condenser. A third joint of the flask was used for the admission of reactants to the flask. The dry apparatus was flushed with nitrogen, and 1.2 l. of dry xylene was added to the flask. Two hundred milliliters of xylene were distilled from the flask at the stopcock on the reflux condenser. This insured removal of any moisture which might have resisted preliminary drying. Refluxing was discontinued and nitrogen passage was accelerated. Twelve molar equivalents of distilled *t*-butyl alcohol and 4.8 atomic equivalents of potassium were added to the flask. After the potassium *t*-butoxide had been formed, the excess *t*-butyl alcohol and about 100 ml. of xylene were distilled from the flask. One molar equivalent of diethyl ester (I) dissolved in 250 ml. of xylene was then introduced dropwise over a period of approximately 24 hr. During this period a nitrogen atmosphere was retained, stirring and refluxing were continued, and an ethanol-xylene mixture was removed by distillation at approximately the same rate as liquid was being added. After all of the ester had been added stirring and refluxing were continued for an hour; then the reaction mixture was allowed to cool to room temperature.

The reaction mixture was made acidic by adding glacial acetic acid in excess. The reaction mixture was washed three times with 50 ml. of water. The xylene solution was filtered to remove insoluble polymeric ketones, and the filtrate was concentrated to a small volume by distillation at reduced pressure. To the residue was added a dilute solution of hydrochloric acid (*ca.* 3*N*); hydrolysis and decarboxylation were effected by refluxing overnight. In several cases ethanol was added to the decarboxylation medium to promote solubility of the ketoesters. In these cases the unreacted starting material was recovered as diester instead of as acid. The reaction mixture was extracted with ether, and the combined ether extracts were extracted with a 10% aqueous solution of sodium bicarbonate. The bicarbonate extracts, when acidified, yielded unreacted starting material as dicarboxylic acid.

The ethereal solution was distilled and the ketones and ester were collected. The ketones were characterized by the close similarity of their physical properties with those previously reported: boiling point or melting point, n_D, and melting point of a suitable derivative. The infrared carbonyl maxima (5% solutions in carbon tetrachloride) for the diketones are given for the first time. The yields appear in Table I.

Cycloheptanone.[24]

Cycloöctanone,[24] and 1,9-cyclohexadecanedione, m.p. 83–85°,[25] ν_{max} 1713 cm.$^{-1}$

1,10-Cycloöctadecanedione, m.p. 95–97°,[25] ν_{max} 1716 cm.$^{-1}$

1,11-Cycloeicosanedione, m.p. 49–51°,[25] ν_{max} 1715 cm.$^{-1}$

Cyclohendecanone; semicarbazone, m.p. 202–204°,[26] and 1,12-cyclodocosanedione, m.p. 54–55.5°,[25] ν_{max} 1715 cm.$^{-1}$

Cyclododecanone, m.p. 58–61°,[25] and 1,13-cyclotetracosanedione, m.p. 62–63.5°,[25] ν_{max} 1716 cm.$^{-1}$

Cyclotridecanone, m.p. 26–29°;[25] semicarbazone, m.p. 205–206° (dec.),[26] and 1,14-cyclohexacosanedione, m.p. 65–68°,[25] ν_{max} 1715 cm.$^{-1}$

Cyclotetradecanone, m.p. 55.5–56°,[25] and 1,15-cyclooctacosanedione, m.p. 72–73.5°,[25] ν_{max} 1716 cm.$^{-1}$

Cyclopentadecanone, m.p. 64–66°,[25] and 1,16-cyclotriacontanedione, m.p. 76–78°,[15] ν_{max} 1716 cm.$^{-1}$

URBANA, ILL.

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(20) Melting points are corrected. Infrared spectra were recorded by Mr. James Brader and his associates in this laboratory.

(21) A. A. Morton, B. Darling, and J. Davidson, *Ind. Eng. Chem., Anal. Ed.*, **14**, 734 (1942).

(22) A. C. Cope and E. C. Herrick, *J. Am. Chem. Soc.*, **72**, 983 (1950).

(23) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Am. Chem. Soc.*, **74**, 5884 (1952).

(24) Compared with commercially available material.

(25) L. Ruzicka, M. Stoll, H. W. Huyser, and H. A. Boekenoogen, *Helv. Chim. Acta*, **13**, 1152 (1930). Reported melting points are close or identical.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD RESEARCH INSTITUTE, AND THE ETHYL CORP.]

Uncatalyzed Addition of Bromotrichloromethane to Ethylene and Substituted Ethylenes. I. Nature and Scope of the Reaction[1]

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The uncatalyzed addition of bromotrichloromethane to ethylene and various substituted ethylenes has been found to give good yields of the 1:1 adducts. The adducts are the same as those obtained from the peroxide-, light-, or gamma radiation-induced additions. The reaction is believed to be a thermally initiated free radical chain reaction.

Numerous workers[3–15] have studied the catalytic addition of bromotrichloromethane to ethylene and substituted ethylenes. These reactions have been initiated by the use of peroxides, gamma radiation,

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(1) The work reported herein was supported in part by the Ethyl Corp., Baton Rouge, La., and by Stanford Research Institute, Menlo Park, Calif.

(2) Stanford Research Institute, Menlo Park, Calif.

(3) R. L. Huang, *J. Chem. Soc.*, 1749 (1956).

(4) M. S Kharasch, U. S. Patent **2,464,869** (March 22, 1949).

(5) M. S. Kharasch, U. S. Patent **2,525,912** (Oct. 17, 1950).

(6) M. S. Kharasch, U. S. Patent **2,485,099** (Oct. 18, 1949).

(7) M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947).

or actinic light. We have now found that none of the previously used initiators is necessary. This paper reports some results of this uncatalyzed addition.

Bromotrichloromethane was found to add to ethylene at 120° in the absence of any catalyst or light to yield 1,1,1-trichloro-3-bromopropane.

This uncatalyzed addition of bromotrichloromethane to ethylene was extended to substituted ethylenes. Octene-1 and bromotrichloromethane were found to react in the dark and in the absence of air or peroxides to yield the 1:1 adduct (3-bromo-1,1,1-trichlorononane).

The free radical nature of the reaction was shown by its inhibition by Ionol (2,6-di-*t*-butyl-4-methylphenol), air, and nitromethane. Freshly distilled bromotrichloromethane and octene-1 were used to avoid traces of peroxides. Attempts to form peroxides by bubbling air through the bromotrichloromethane prior to its use resulted in a slight decrease in product yield rather than an increase. Indications are that the initiation of the addition reaction is the easy thermal dissociation of bromotrichloromethane into bromine atoms and trichloromethyl radicals.

The uncatalyzed addition of bromotrichloromethane to vinyl acetate yielded 1-bromo-3,3,3-trichloropropylacetate; to styrene, 1-bromo-3,3,3-trichloropropyl benzene; to 3,9-divinylspirobimetadioxane (3,9-divinyl-2,4,8,10-tetroxaspiro[5.5]undecane), the adduct formed by the addition of two moles of bromotrichloromethane to one of the divinyl compound; to butene-1, 3-bromo-1,1,1-trichlorobutane, to butene-2, 2-bromo-3-methyl-4,4,4-trichlorobutane; to allyl chloride, 2-bromo-1,4,-4,4-tetrachlorobutane; and to butadiene, 1-bromo-5,5,5-trichloropentene-2 and 3-bromo-5,5,5-trichloropentene-1.

In the butadiene addition, the major product was identified as the 1,4-adduct by infrared and halide analyses. A low yield of this butadiene adduct was obtained when butadiene was passed through refluxing bromotrichloromethane for 24 hr.

In all cases, the yields were not as high as those previously reported by Kharasch[7] when acetyl peroxide was used as initiator. With styrene, a 78% yield of the 1:1 adduct was obtained in 4 hr. at 70° using 2.3 wt. % of diacetyl peroxide as initiator. The same proportions of reagents in an uncatalyzed reaction gave a 40% yield in 5.5 hr. at 100°. With octene-1, a 71% yield of the 1:1 adduct was obtained in 4 hr. at 70° using 1.4 wt. % of diacetyl peroxide as initiator. Using comparable amounts of starting materials, a 50 % yield was obtained at 100° in 3 hr. without catalyst. With vinyl acetate, Kharasch[7] reports an 89% yield of the adduct in 3 hr. at 60° with 1.5 g. of acetyl peroxide. The uncatalyzed addition to vinyl acetate gave a 63% yield in 5.5 hr. at 100°.

The uncatalyzed addition of bromotrichloromethane to diethylmaleate, maleic anhydride, allylidene diacetate, isopropenyl acetate, 1-methoxy-1,3-butadiene, methyl methacrylate, divinylcarbitol, and ethyl crotonate failed to yield any appreciable amounts of the 1:1 adducts at 100°.

Polymers were obtained when the uncatalyzed addition of bromotrichloromethane to methyl isopropenyl ketone, bischloroethylvinylphosphonate, vinyl crotonate, diallyl cyanamide, diethylaminoethylacrylate, or diallylphthalate was attempted.

EXPERIMENTAL

Uncatalyzed addition of bromotrichloromethane to ethylene. Bromotrichloromethane (780 g., 3.9 moles, freshly distilled) was added to a 1.4-liter stainless steel rocking bomb, purged with ethylene to remove air, pressurized with ethylene to 700 p.s.i.g., and heated at 120° for 4 hr. The products were removed from the bomb and distilled. The 1:1 adduct, 1,1,1-trichloro-3-bromopropane (174 g., b.p. 82° at 34 mm.), was isolated by distillation (weight of silver halide from 0.3358 g. sample: calcd., 0.9060; found, 0.9056). In addition to the 1:1 adduct, 11.2 g. of 1,1,1-trichloro-5-bromopentane was formed (b.p. 110° at 2 mm., weight of silver halide from 0.2476 g. sample: calcd. 0.4830; found, 0.4881).

When bromotrichloromethane (200 ml.) was dissolved in heptane (200 ml.), pressured to 1200 p.s.i.g. with ethylene, and heated at 120° for 4 hr., 129 g. of 1,1,1-trichloro-3-bromopropane and 24 g. of 1,1,1-trichloro-5-bromopentane were produced.

Uncatalyzed addition of bromotrichloromethane to vinyl acetate. Bromotrichloromethane (198 g., 1.0 mole, freshly distilled) was refluxed under nitrogen and vinyl acetate (25 ml., 0.25 mole) was added over a 4.5-hr. period and heated 1 hr. longer under reflux. 1-Bromo-3,3,3-trichloropropylacetate (45 g., 63% yield, n_D^{24} 1.4920, b.p. 65° at 0.5 mm., weight of silver halide for 0.2348 g. sample: calcd., 0.5060; found, 0.5033) was produced. When 2,4-dinitrophenylhydrazine in alcohol was added to the adduct and the solution acidified with sulfuric acid, the orange-red hydrazone of 3,3-dichloroacrolein precipitated (m.p. 162–164°). Kharasch[7] reported m.p. 164–165° for this hydrazone formed from the peroxide-catalyzed reaction.

Uncatalyzed addition of bromotrichloromethane to styrene. Bromotrichloromethane (136 g., 0.69 mole, freshly distilled) was refluxed under nitrogen, and styrene (20.7 g., 0.19 mole, freshly distilled) was added over a 2.5-hr. period and heated 0.5 hr. longer. The major product was 1-bromo-2,2,2-trichloropropyl-benzene (4.8 g., b.p. 98°, m.p. 53–55°, weight of silver halide for 0.1519 g. sample: calcd. 0.3096; found, 0.2854). Kharasch[15] reports a melting point of 54–55°. When styrene (13 g., 0.12 mole) and bromotrichloromethane (100 g., 0.50 mole) were heated under nitrogen on a steam bath for 5.5 hr., 14.5 g., 40% yield, of the 1:1 adduct was

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[13] H. W. Melville, J. C. Robb, R. C. Tutton, *Discussions Faraday Soc.*, **19**, 150 (1953).

[14] A. M. Lovelace and D. A. Rausch, W.A.D.C. Tech. Report No. 55461, April (1956).

[15] M. S. Kharasch, U. S. Patent **2,468,208** (April 26, 1949).

formed. Kharasch[15] reported a yield of 18.6 g. of crude addition product under identical conditions when magnesium and iodine was used as a "catalyst".

Study of the effect of Ionol, nitromethane, air, and light on the uncatalyzed addition of bromotrichloromethane to octene-1. Bromotrichloromethane (98 g., 0.44 mole, freshly distilled) and octene-1 (24 g., 0.22 mole, Phillips, 99 mole %, freshly distilled) were refluxed under nitrogen for 3 hr. The major product was 3-bromo-1,1,1-trichlorononane (31.5 g., 50% yield, b.p. 85° at 0.6 mm.).

When the above reaction was repeated with 10 g. of Ionol (2,6-di-*t*-butyl-4-methylphenol) added, only 11.0 g. of 3-bromo-1,1,1-trichlorononane was produced.

When the reaction was repeated without Ionol but with air bubbling through the solution for the 3-hr. period, only 18.5 g. of 3-bromo-1,1,1-trichlorononane was produced.

Blowing air through the bromotrichloromethane for 4 hr. prior to use resulted in a lower yield of adduct.

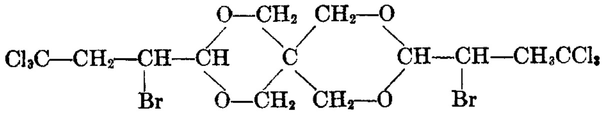
No change in the yield of 3-bromo-1,1,1-trichlorononane was obtained when the bromotrichloromethane used was refluxed under nitrogen for 17 hr. to destroy any peroxides present prior to reacting with octene-1. Kharasch[15] claimed that peroxides build up in bromotrichloromethane.

When the uncatalyzed reaction between bromotrichloromethane and octene-1 was carried out in the dark, no change in the product yield from that obtained under normal laboratory lighting conditions was noticed.

The use of nitromethane (125 ml.) as a solvent for the uncatalyzed addition of bromotrichloromethane (146 g., 0.74 mole) to octene-1 (32 g., 0.28 mole) resulted in only 16.8 g. of 3-bromo-1,1,1-trichlorononane after 5 hr. of refluxing.

When bromotrichloromethane (146 g., 0.74 mole), *n*-heptane (125 ml., Phillips 95 mole %, freshly distilled), and octene-1 (28 g., 0.25 mole) was refluxed under nitrogen for 5 hr., 73 g., 94% yield, of 3-bromo-1,1,1-trichlorononane was produced.

Uncatalyzed addition of bromotrichloromethane to 3,9-divinylspirobimetadioxane. 3,9-Divinylspirobimetadioxane (15 g., 0.07 mole, m.p. 42°, Union Carbide Chemicals Co.) was slowly added to refluxing bromotrichloromethane (97.5 g., 0.49 mole) under nitrogen. The solution was refluxed for 6 hr., and upon cooling a crystalline solid crystallized was obtained. The yield of solid product was 25.6 g. (0.04 mole, 57% yield). Unlike 3,9-divinylspirobimetadioxane, the product was very insoluble in water and melted at 184–186°. The product was identified as having the following formula by halide analysis.



Weight of silver halide for 0.2500 g. sample: calcd., 0.5140; found, 0.4926.

Uncatalyzed addition of bromotrichloromethane to butene-1 and butene-2. Bromotrichloromethane (390 g., 1.97 moles, freshly distilled) and butene-1 (21 g., 0.38 mole, freshly distilled, Phillips 95 mole %) were added to a 1.4-liter rocking bomb and heated at 100° for 4 hr. in the absence of air. The product was 3-bromo-1,1,1-trichloropentane (41.2 g., 0.163 mole, 43% yield, b.p. 66–68° at 3 mm., weight of silver halide for 0.1765 g. sample: calcd., 0.427; found, 0.422).

Bromotrichloromethane (390 g., 1.97 moles, freshly distilled) and butene-2 (36 g., 0.64 mole, freshly distilled, Phillips 95 mole %) were heated in a 1.4-liter rocking bomb in the absence of air for 4 hr. at 100°. The product formed was 2-bromo-4,4,4-trichloro-3-methylbutane (18.5 g., 0.079 mole, 13% yield, b.p. 95° at 10 mm., weight of silver halide for 0.1546 g. sample: calcd., 0.3711; found, 0.3760).

Uncatalyzed addition of bromotrichloromethane to allyl chloride. When allyl chloride (23 g., 0.302 mole) was added slowly over a period of an hour to refluxing bromotrichloromethane (97.5 g., 0.49 mole) and the solution refluxed for 20 hr., only 6.3 g. of a product, b.p. 60° at 0.5 mm., was obtained.

When allyl chloride (46.8 g., 0.61 mole, freshly distilled) was heated with bromotrichloromethane (390 g., 1.97 moles) at 110° for 4 hr. and in a stainless steel rocking bomb, 2-bromo-1,4,4,4-tetrachlorobutane (63 g., 0.23 mole, 38% yield, b.p. 86–89° at 2.8 mm., weight of silver halide for 0.2144 g. sample: calcd., 0.5910; found, 0.5903) was formed.

Uncatalyzed addition of bromotrichloromethane to butadiene. Butadiene (130 g., 2.4 moles, Phillips 99 mole %) was distilled into an evacuated 1.4-liter stainless steel bomb containing bromotrichloromethane (390 g., 1.97 moles, freshly distilled). The bomb was heated and rocked at 100° for 4 hr. The major product was 1-bromo-5,5,5-trichloropentene-2 (62 g., 0.25 mole, 10% yield, b.p. 69° at 1.6 mm., n_D^{20} 1.5328, weight of silver halide for 0.2113 g. sample: calcd., 0.5170; found, 0.5120 for 1:1 adduct). A small amount of higher boiling material was also produced. Two possible 1:1 adducts exist: 1-bromo-5,5,5-trichloropentene-2 and 4-bromo-3-trichloromethylbutene-1. The infrared spectra of the product shows the presence of trans internal double bonds, but no terminal double bonds are present. The product is 1-bromo-5,5,5-trichloropentene-2 formed by 1,4-addition of bromotrichloromethane to butadiene.

When butadiene was bubbled through refluxing bromotrichloromethane (458 g., 2.3 moles) for 24 hr., 3-bromo-5,5,5-trichloropentene-1 (6.2 g., n_D^{20} = 0.5350) was formed.

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