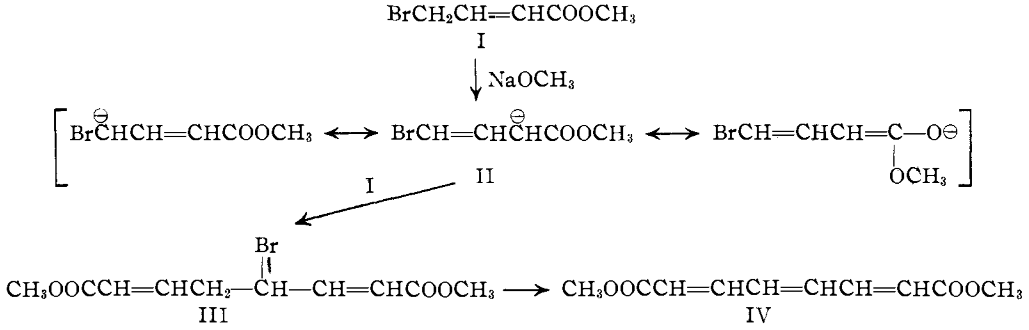


formation of the anion II. The cyclopropene ring would have to be formed by an intramolecular nucleophilic displacement of a vinyl type bromine atom. An alternative (and perhaps more likely) reaction is the displacement by II of an allyl type bromine atom in another molecule of methyl γ-bromocrotonate with the formation of III. Further elimination of the elements of hydrobromic acid gives dimethyl 2,4,6-octatrienedioate (IV) with an empirical formula of $C_5H_6O_2$. This type of reaction with a base has been described for 9-fluorenyl bromide,[4] for diethyl bromo- and chloromalonate,[5] and for allyl chloride.[6]

The properties of Owen and Sultanbawa's product coincided closely with those reported for dimethyl 2,4,6-octatrienedioate (IV, m.p. 172°,[7a] $\lambda_{\max}^{\text{methanol}}$ 303 mμ[7b]). That this is indeed its structure has now been shown by hydrogenation and saponification which afforded an 83% yield of suberic acid.

Several attempts to improve the yield of IV in the self-condensation of I by the use of inverse addition, different bases and different solvents were without success. The consistently low yield may be due to the large number of structural and geometrical isomers which could conceivably be formed in this reaction.

Experimental[8]

Dimethyl 2,4,6-Octatrienedioate (IV).—To a stirred and cooled suspension of dry sodium methoxide (prepared from 1.4 g. (0.06 mole) of sodium and 20 cc. of dry methanol followed by distillation of the methanol) in 80 cc. of dry benzene was added slowly 10 g. (0.056 mole) of methyl γ-bromocrotonate. The ice-bath was allowed to warm to room temperature and the dark mixture was stirred for a total of 45 hours. After the addition of 80 cc. of water, the benzene layer was separated and the aqueous layer was extracted with ether. The organic solution was washed with 10% hydrochloric acid and water, dried (magnesium sulfate) and concentrated. A solution of the dark residue in 10 cc. of carbon tetrachloride deposited on chilling 0.072 g. (1.3%) of dimethyl 2,4,6-octatrienedioate (IV), m.p. 164–167°. Recrystallization from methanol afforded colorless needles, m.p. 169.5–170° (reported[7a] 172°); $\lambda_{\max}^{\text{alc}}$ 301 mμ (ε 51,000), $\lambda_{\text{inflection}}^{\text{alc}}$ 290 and 314 mμ (ε 37,400 and 43,100), $\lambda_{\min}^{\text{alc}}$ 238 mμ (ε 1,170) (reported[7b] $\lambda_{\max}^{\text{methanol}}$ 303 mμ).

The mother liquor was concentrated to a dark brown heavy oil, which weighed 3.1 g., $\lambda_{\max}^{\text{alc}}$ 248 and 303 mμ (ε 2,290 and 1,270). While no further crystalline material was obtained from this oil, the spectrum suggests the possible presence of IV or a compound with a similar chromophore (possibly a geometrical isomer of IV) to an approximate extent of 2.5%.

The yield in this reaction was not improved when the sodium methoxide was added to a benzene solution of methyl γ-bromocrotonate, when sodium hydride, sodamide or potassium *t*-butoxide was used instead of sodium methoxide or when the benzene was replaced with ether or with collidine.

Suberic Acid.—A solution of 30 mg. (0.153 mmole) of dimethyl 2,4,6-octatrienedioate (IV, prepared as described in the preceding experiment) in 5 cc. of ethanol was shaken under an atmosphere of hydrogen with 5 mg. of prereduced Adams catalyst. Ten and five-tenths milliliters (0.470 mmole) of hydrogen was absorbed. The residue after filtration and concentration was heated with 3 cc. of 35% aqueous potassium hydroxide to give, after acidification and crystallization from ether–petroleum ether, 22 mg. (83%) of suberic acid, m.p. 139–141°. There was no depression in m.p. when mixed with an authentic sample.

ROLLIN H. STEVENS MEMORIAL LABORATORY
DETROIT INSTITUTE OF CANCER RESEARCH, AND
DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY
DETROIT, MICHIGAN

---

[4] J. Thiele and A. Wanschedt, *Ann.*, **376**, 278 (1910).

[5] For reference see A. H. Blatt, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 275.

[6] M. S. Kharasch and E. Sternfeld, THIS JOURNAL, **61**, 2318 (1939).

[7] (a) R. Kuhn and Ch. Grundmann, *Ber.*, **69**, 1757 (1936); (b) *ibid.*, **69**, 1979 (1936).

[8] The melting points are uncorrected. We are indebted to Dr. J. M. Vandenbelt of Parke, Davis and Co. for the ultraviolet absorption spectrum of IV.

The Preparation of 4-Bromo- and 4-Iodo-ω-nitrostyrene

BY XORGE ALEJANDRO DOMINGUEZ, JORGE SLIM S. AND ARTURO ELIZONDO

RECEIVED MARCH 30, 1953

In the course of our research work it was necessary to prepare 4-bromo- and 4-iodo-ω-nitrostyrene. It has recently been reported by Schales and Graefe[1] that several substituted ω-nitrostyrenes showed antibacterial activity and it seemed of interest to test 4-bromo-ω-nitrostyrene and 4-iodo-ω-nitrostyrene against *Staphylococcus aureus* and report their syntheses. The former was prepared but not characterized by Worrall.[2] Their antibacterial activity was determined according to the procedure of Schales and Graefe.[1] The concentrations of the test compounds needed to inhibit bacterial growth by 50% after an incubation time of 18 hours were: 0.73 mg./100 ml. for the 4-bromo-ω-nitrostyrene and 1.06 mg./100 ml. for the 4-iodo-ω-nitrostyrene.

The necessary 4-bromo- and 4-iodobenzaldehydes were prepared from the corresponding nitriles employing Stephen's reaction[3] as modified by Sah[4] in yields of 65 and 68%, respectively. The 4-halo-arylnitroalkenes were easily obtained by condensation of the corresponding 4-halobenzaldehydes with nitromethane using ammonium

---

[1] O. Schales and H. A. Graefe, THIS JOURNAL, **74**, 4486 (1952).

[2] D. E. Worrall, *ibid.*, **56**, 1556 (1934).

[3] H. Stephen, *J. Chem. Soc.*, **127**, 1874 (1925).

[4] P. P. T. Sah, THIS JOURNAL, **64**, 1487 (1942).

acetate in acetic acid as condensing agent[5]; none of the condensation procedures catalyzed by alcoholic potassium hydroxide[6] and alcoholic methylamine,[7] were found suitable.

Experimental

4-Bromo-ω-nitrostyrene.—A mixture of 1 g. of 4-bromobenzaldehyde (m.p. 56°), 2 ml. of nitromethane and 0.2 g. of ammonium acetate in 20 ml. of glacial acetic acid was refluxed for 2 hours. The hot dark mixture was poured into 200 ml. of ice-cold water and allowed to stand 4 hours. The crude yellow product was collected, rinsed thoroughly with water and recrystallized from hot ethanol. Yellow small prisms, melting at 156–158°, were obtained, yield 700 mg. (56%).

Anal. Calcd. for $C_8H_6O_2NBr$ (228.04): N, 6.13. Found: N, 6.01.

4-Iodo-ω-nitrostyrene.—Using the same procedure as described above, 1 g. of 4-iodobenzaldehyde gave 916 mg. (75%) of small yellow needles of 4-iodo-ω-nitrostyrene, melting at 183–184°.

Anal. Calcd. for $C_8H_6O_2NI$ (275.04): N, 5.09. Found: N, 5.14.

Acknowledgment.—The authors express their thanks to Miss Beatriz Gomez for the microanalytical data, to Ing. Carlos Duhne for his encouragement and to Avelino Guerra for preparing the 4-iodobenzonitrile.

---

[5] (a) M. G. S. Rao, C. Strikantia and M. S. Iyengar, *Helv. Chim. Acta*, **12**, 581 (1924); (b) L. C. Raiford and D. E. Fox, *J. Org. Chem.* **9**, 170 (1944); (c) F. A. Ramirez and A. Burger, THIS JOURNAL, **72**, 2781 (1950); (d) C. B. Gairaud and G. R. Lapping, *J. Org. Chem.*, **18**, 1 (1953); (e) J. H. Mason, *J. Chem. Soc.*, 200 (1953).

[6] J. Thiele, *Ber.*, **32**, 1293 (1899); (b) D. E. Worrall, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 413.

[7] E. Knoevenagel and L. Walter, *Ber.*, **37**, 4502 (1904).

INSTITUTO TECNOLOGICO Y DE ESTUDIO SUPERIORES DE MONTERREY
LABORATORIO DE QUIMICA ORGANICA
MONTERREY, N. L. MEXICO

The Anhydrous Chlorination of Thioesters and Related Compounds[1,2]

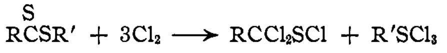
BY IRWIN B. DOUGLASS AND CHARLES E. OSBORNE

RECEIVED APRIL 27, 1953

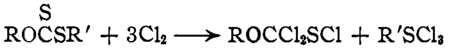
In continuing the study of the action of anhydrous chlorine on different types of organic sulfur compounds,[3] various thioesters and closely related compounds have been treated with anhydrous chlorine in liquid butane near the temperature of solid carbon dioxide. Compounds containing the thiol group are split between the acyl group and sulfur with the formation of an alkylsulfur trichloride from the thiol portion and an acyl chloride or some related compound from the other part of the molecule. When the compound chlorinated is a dithioester, in addition to the removal of the the thiol group as alkylsulfur trichloride, chlorine appears to add to the carbon–sulfur double bond of the thiocarbonyl portion to form a 1,1-dichloroalkanesulfenyl chloride. Alkoxy groups in xanthate esters, which may also be considered as being dithioesters, are not disturbed by the chlorination reaction under the conditions employed.

The following equations illustrate reaction types which have been found to occur and at least one example of each is described in the Experimental part.

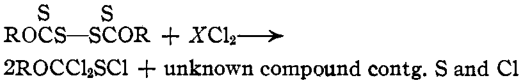
$$\mathrm{RCOSR' + 2Cl_2 \longrightarrow RCOCl + R'SCl_3} \qquad (1)$$



$$\mathrm{R\overset{S}{C}SR' + 3Cl_2 \longrightarrow RCCl_2SCl + R'SCl_3} \qquad (2)$$



$$\mathrm{RO\overset{S}{C}SR' + 3Cl_2 \longrightarrow ROCCl_2SCl + R'SCl_3} \qquad (3)$$

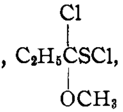


$$\mathrm{RO\overset{S}{C}S{-}S\overset{S}{C}OR + \mathit{X}Cl_2 \longrightarrow}$$
$$\mathrm{2ROCCl_2SCl + unknown\ compound\ contg.\ S\ and\ Cl} \qquad (4)$$

$$\mathrm{RSO_2SR' + 2Cl_2 \longrightarrow RSO_2Cl + R'SCl_3} \qquad (5)$$

In equation 1 shown above, the immediate formation of solid $R'SCl_3$ after beginning the passage of chlorine indicates that reaction 1 takes place rapidly. If chlorination is interrupted, however, the solid alkylsulfur trichloride gradually disappears, presumably because a slower reaction takes place between the solid sulfur trichloride and the original thiol ester.

$$\mathrm{RCOSR' + R'SCl_3 \longrightarrow RCOCl + 2R'SCl} \qquad (6)$$

An effort was made to study the action of chlorine on methyl thionpropionate, $C_2H_5CSOCH_3$. Reaction occurred and a white solid product with a chlorine content corresponding to $(C_2H_5CSOCH_3)Cl_2$ was formed, but the solid decomposed at 8° and the evolved gas appeared to consist more of chlorine than hydrogen chloride. One does not seem justified in concluding that the chlorination reaction produced 1-chloro-1-methoxypropane-1-sulfenyl chloride,  $\mathrm{C_2H_5\overset{Cl}{\underset{OCH_3}{C}}SCl}$, since the properties of analogous compounds described in this paper lead one to believe that such a compound would be a yellow liquid rather than the white solid obtained.

The formation of an alkylsulfur trichloride precipitate in a chlorination reaction affords a ready means for separating this product of the reaction provided the other product is soluble in liquid butane at the temperature employed.

Experimental Part

Preparation of Intermediates.—The thiol, xanthate and dithio esters, methyl methanethiolsulfonate and the bis-[alkoxythiocarbonyl] disulfides were prepared by standard methods.

Methyl thionpropionate was prepared by a modification of the method of Sakurada.[4] Absolute methyl alcohol, propionitrile and dry hydrogen chloride reacted to form methyl propionimidate hydrochloride. Dry pyridine was added to neutralize the hydrochloride, and hydrogen sulfide was passed into an ether solution of the free imino ether to form the thion ester. Difficulty was encountered in this preparation due to the tendency of the ester to hydrolyze and oxidize. In numerous attempts only a 10% yield was obtained.

Chlorination Procedure.—Ten grams of the ester was dissolved in approximately 50 ml. of liquid C.P. butane in a 30 × 200 mm. culture tube which was cooled in a bath containing solid carbon dioxide and acetone. A gentle stream of chlorine was led into the space above the liquid and was continued until, after alternately shaking and settling, no more solid appeared to form. The mixture was centri-

---

[1] This represents a portion of the work done on Project NR-356-165 under Contract N8 onr 647(00) with the Office of Naval Research, United States Navy.

[2] Taken from the master's thesis of Charles E. Osborne.

[3] See I. B. Douglass, K. R. Brower and F. T. Martin, THIS JOURNAL, **74**, 5770 (1952), and preceding papers.

[4] Sakurada, *Mem. Coll. Sci. Kyoto*, **9**, 237 (1926); **10**, 79 (1926); *C. A.*, **21**, 2458, 3609 (1927).