If aluminum chloride was not added to the reaction mixture, the acetylene pressure remained constant during eight days and I was recovered in high yield.

3-Chloro-2-(2',4'-dinitrophenylthio)-2-butene.—To a solution of 1.60 g. (0.007 mole) of I in 15 ml. of ethylene chloride at 0°, was added 3 ml. of ice-cold 2-butyne. The mixture was kept at 0° for two hours, the solvent removed by aspiration and the clear yellow oil refrigerated for two days. The crude crystals were dissolved in 25 ml. of absolute ethanol, and the solution was decolorized by charcoal and filtered. The filtrate yielded plate-like crystals (1.35 g., 69%), m.p. 68–70°; and, from the mother liquor, 0.33 g. more of product, m.p. 67–70°, was obtained; total yield 85%. Three recrystallizations raised the melting point to 75–76°.

Anal. Calcd. for $C_{10}H_9O_4N_2SCl$: C, 41.60; H, 3.14; N, 9.71. Found: C, 41.89; H, 3.36; N, 9.49.

4-Chloro-3-(2',4'-dinitrophenylthio)-3-hexene.—3-Hexyne (2.0 g., 0.025 mole) was added to 4.7 g. (0.02 mole) of I in a mixture of 40 ml. ethylene chloride and 10 ml. of glacial acetic acid, and the mixture let stand two hours at room temperature. The solvents were removed by aspiration and the residual oil crystallized from absolute alcohol, giving 5.12 g. of product, m.p. 65–66°, and a second crop, 0.77 g., m.p. 62–65°; total yield 93%. The analytical sample, m.p. 65–66°, was prepared by three recrystallizations from absolute alcohol.

Anal. Calcd. for $C_{12}H_{13}O_4N_2SCl$: C, 45.50; H, 4.14; S, 10.12. Found: C, 45.73; H, 4.30; S, 10.38.

2-Chloro-1-(2',4'-dinitrophenylthio)-1,2-diphenylethene.—Diphenylacetylene (2.13 g., 0.12 mole) was refluxed with 2.35 g. (0.01 mole) of I, in 25 ml. of glacial acetic acid for 8 hours. On cooling to room temperature, 3.82 g. (92.5%) of yellow prisms, m.p. 196–201°, was obtained. Three recrystallizations from glacial acetic acid gave cubic crystals, m.p. 205.5–207°, raised to 206–207° by recrystallizing from nitromethane.

Anal. Calcd. for $C_{20}H_{13}O_4N_2SCl$: C, 58.18; H, 3.17. Found: C, 58.29; H, 3.14.

When the reaction of I and diphenylacetylene was conducted as above, but at room temperature, reaction was incomplete even after several weeks—as indicated by a positive starch–iodide test for unreacted I. The major product which first precipitated from the reaction mixture was identical with the one recorded above; but from the remaining reaction mixture (after two weeks) there was isolated a lesser quantity of perfectly-formed, clear orange, diamond crystals, m.p. 167–192°. Recrystallization of the diamonds from hot glacial acetic acid, however, partially converted them to the yellow cubes melting at 206–207°. The diamond shaped crystals were not encountered at all when the reaction was carried out at reflux, as above. This alternate material was not further investigated.

Attempted Additions of I to Butynedioic Acid and to Diethyl Butynedioate.—Attempts to add I to this acid or the diethyl ester included variations, such as: refluxing equimolar quantities of the reactants in ethylene chloride solutions for periods up to 95 hours; attempted reactions in concentrated acetic acid solutions at room temperature for 4 months; attempted additions at room temperature, with aluminum chloride, in catalytic quantities (up to 0.1 mole $AlCl_3$/mole I) for extended periods; and refluxing in ethylene chloride, with 0.1 mole $AlCl_3$/mole I for 22 hours. In all of the non-catalyzed reactions with the ester, I was recovered in good yields; while with the acid some I could be recovered, but other complex products were indicated. With the catalyst present, dark colored, possibly polymeric products resulted. In no cases were any products encountered which could be identified as the desired adducts.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DEPAUW UNIVERSITY]

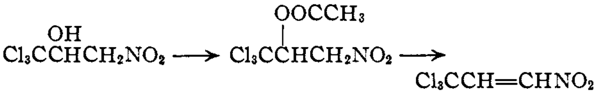
1,1,1-Trichloro-2-arylamino-3-nitropropanes

BY FRANK BROWER AND HOWARD BURKETT

RECEIVED SEPTEMBER 29, 1952

Evidence is presented which indicates that the previously reported 1,1,1,2-tetrachloro-3-nitropropane was probably 1,1,1-trichloro-3-nitropropene. Thirteen 1,1,1-trichloro-2-arylamino-3-nitropropanes have been prepared. Reduction of the nitro group of the 1,1,1-trichloro-2-arylamino-3-nitropropane to the corresponding amine was successful in only one case.

The preparation of 1,1,1,2-tetrachloro-3-nitropropane (I) by the reaction of phosphorus pentachloride with 1,1,1-trichloro-3-nitropropanol-2[1] was reported in 1897 by Henry[2] and in 1936 by Irving.[3] Upon repeating this preparation the authors obtained a product (II) which had physical properties nearly identical with those reported previously but which did not react as had been anticipated. Analyses and molecular refractivity of II correspond more nearly to *1,1,1-trichloro-3-nitropropene* (III) than to I. Moreover, the physical and chemical properties of II are the same as for III prepared by the treatment of 1,1,1-trichloro-2-acetoxy-3-nitropropane[4] (IV) with sodium carbonate



$$\overset{\text{OH}}{Cl_3CCHCH_2NO_2} \longrightarrow \overset{\text{OOCCH}_3}{Cl_3C\overset{|}{C}HCH_2NO_2} \longrightarrow Cl_3CCH{=}CHNO_2$$

The use of this procedure for the preparation of nitroölefins has been reported[5,6] but has not been used for this compound. From the above data it is doubtful that earlier workers actually prepared 1,1,1,2-tetrachloro-3-nitropropane.

The authors had planned to synthesize 1,1,1-trichloro-2-arylamino-3-nitropropanes by the reaction of I with various amines. Since the latter could not be prepared, it became necessary to seek other methods. Chattaway and co-workers[7,8] reported the replacement of the acetoxyl group of IV with certain basic groups and Irving[9] described the addition of amines to III. We have prepared twelve 1,1,1-trichloro-2-arylamino-3-nitropropanes by the reaction of IV with two equivalents of amine in alcoholic solution. Three of the above nitroamines and an additional one were prepared by the addition of amines to III. The ease of this latter reaction

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[1] M. Compton, H. Higgins, L. MacBeth, J. Osborn and H. Burkett, THIS JOURNAL, **71**, 3229 (1949).

[2] L. Henry, *Bull. acad. roy. med. Belg.*, **34**, 568 (1897).

[3] H. Irving, *J. Chem. Soc.*, **138**, 797 (1936).

[4] F. D. Chattaway and P. Wirtherington, *ibid.*, **137**, 1178 (1935).

[5] H. B. Hass, A. G. Susie and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

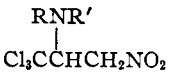
[6] E. Schmidt and G. Rutz, *Ber.*, **61**, 2142 (1928).

[7] F. D. Chattaway, *J. Chem. Soc.*, **138**, 355 (1936).

[8] F. D. Chattaway, J. G. N. Drewitt and G. D. Parks, *ibid.*, **138**, 1530 (1936).

[9] H. Irving, *ibid.*, **150**, 1989 (1948).

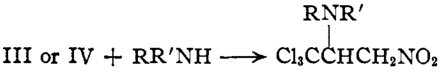
TABLE I



$$\overset{RNR'}{Cl_3C\overset{|}{C}HCH_2NO_2}$$

R	R′	Yield,[a] %	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
p-Chlorophenyl	H	82.9A	90–91	8.81	8.86
p-Bromophenyl	H	65.7A	85–86	7.73	7.94
p-Biphenyl	H	60.0A	129–131	8.35	8.10
p-Nitrophenyl	H	49.3A	155–156	12.79	12.94
p-Carboxyphenyl	H	41.1A	202–205 d.	8.55	8.62
2,5-Dimethoxyphenyl	H	66.1A	90–91.5	8.14	8.22
2,5-Dimethoxyphenyl	H	53.5B	90–91.5		
2,5-Diethoxyphenyl	H	58.5B	85–87	7.72	7.54
Phenyl	CH_3	96.5A	115–117	9.41	9.53
Phenyl	CH_3	80.7B	115–117		
Phenyl	$HOCH_2CH_2$	36.9A	116–118	8.55	8.69
Phenyl	$(CH_3)_2CHCH_2CH_2$	29.0A	54–56	7.92	8.12
Phenyl[b]	$C_6H_5CH_2$	35.2A	127–129	7.49	7.40
Phenyl[b]	$C_6H_5CH_2$	56.0B	127–129		
m-Tolyl	CH_3	81.6A	110–111	8.99	9.12
p-Tolyl	CH_3	86.2A	83–84.5	8.99	9.20

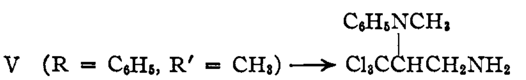
[a] The letter following the percentage yield represents the procedure used. [b] Recrystallized from 60–75° petroleum ether.



$$\text{III or IV} + RR'NH \longrightarrow \overset{RNR'}{Cl_3C\overset{|}{C}HCH_2NO_2}$$

along with the fact that a strong odor of III was always noted during the treatment of IV with amines indicate that III is an intermediate in that reaction.

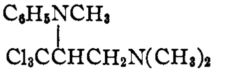
It had been hoped that the nitro group in V could be reduced readily to the amine group. Many methods were tried. Only the use of stannous chloride and hydrochloric acid was successful and this worked for only one compound, VI.



$$V\ \ (R = C_6H_5,\ R' = CH_3) \longrightarrow \overset{C_6H_5NCH_3}{Cl_3C\overset{|}{C}HCH_2NH_2}$$

VI

Attempts to methylate the primary amine group of VI using Clarke's procedure[10] to obtain VII were unsuccessful.



$$\overset{C_6H_5NCH_3}{Cl_3C\overset{|}{C}HCH_2N(CH_3)_2}$$

VII

Pharmacology.—Tests performed by Eli Lilly and Company indicate that these compounds have no significant physiological activity.

Acknowledgment.—The authors thank Research Corporation for a grant which made this investigation possible and Eli Lilly and Company for the pharmacological testing.

Experimental

Attempted **Preparation** of **1,1,1,2-Tetrachloro-3-nitropropane.**—With vigorous stirring 100 g. (0.48 mole) of 1,1,1-trichloro-3-nitropropanol-2 was added portionwise to a solution of 200 g. (0.96 mole) of phosphorus pentachloride in 500 ml. of chloroform contained in a three-necked flask so that the mixture refluxed gently. After addition was complete, the mixture was refluxed for one hour. Water was then added with vigorous stirring until all of the chlorides of phosphorus were destroyed. The layers were separated and the organic layer washed with water. The solvent was evaporated and the residue steam distilled. The organic layer was separated, dried over calcium chloride and distilled, yielding 76.4 g. of oily, yellow, lachrymatory liquid, b.p. 76–78° (12 mm.), 194–195° (740 mm.), n^{25}_D 1.5141, d^{11}_4 1.5801, d^{20}_4 1.5689. If the steam distillation was omitted the product boiled over a slightly wider range.

Henry reported the following properties: d_4^{11} 1.58, b.p. 108–109° (28 mm.), 199–200° (767 mm.).

Anal. Calcd. for $C_3H_3Cl_4NO_2$: N, 6.16; mol. ref., 41.42. Calcd. for $C_3H_2Cl_3NO_2$: C, 18.94; H, 1.06; Cl, 55.89; mol. ref., 35.82; N, 7.36. Found: C, 19.15; H, 1.02; Cl, 56.17; N, 7.56; mol. ref., 36.57.

1,1,1-Trichloro-2-acetoxy-3-nitropropane.—The following procedure was found to be more convenient and gave better yields than previously reported.

A solution of 315 g. of 1,1,1-trichloro-3-nitropropanol-2 in 220 ml. of acetyl chloride was allowed to stand at room temperature in a loosely covered container overnight. Most of the excess acetyl chloride was distilled off. Approximately an equal volume of 60–75° petroleum ether was added and a portion distilled to remove the remainder of the acetyl chloride. Petroleum ether was added to restore the original volume. Upon cooling for several hours 351 g. (93% yield) of large colorless crystals, m.p. 59–60°, were obtained.

1,1,1-Trichloro-3-nitropropene.—To 350 g. of 1,1,1-trichloro-2-acetoxy-3-nitropropane dissolved in 2400 ml. of benzene was added 150 g. of powdered sodium carbonate monohydrate. After refluxing vigorously for 0.5 hour and allowing to cool, the mixture was filtered and the solvent distilled. Distillation of the residue under reduced pressure afforded 244 g. (90.5%) of yellow, oily, lachrymatory liquid, b.p. 88–89° (16 mm.), n^{21}_D 1.5162, d^{20}_4 1.5695.

1,1,1-Trichloro-2-arylamino-3-nitropropane. **General Procedure A.**—To a solution of 40 g. (0.16 mole) of 1,1,1-trichloro-2-acetoxy-3-nitropropane in 100 ml. of ethanol was added 0.32 mole of the amine. The mixture was refluxed for 30 minutes, after which sufficient water was added to cloud the solution. The solid which separated upon chilling was filtered and recrystallized from ethanol–water. Data for these compounds are given in Table I.

General Procedure B.—A solution of 0.053 mole of the amine and 10 g. (0.053 mole) of 1,1,1-trichloro-3-nitropropene in 40 ml. of ethanol was refluxed for 30 minutes and worked up as described in the preceding paragraph. Data for these compounds are given in Table I.

1,1,1-Trichloro-2-methylanilino-3-aminopropane.—To a solution of 60 g. (0.2 mole) of 1,1,1-trichloro-2-methylanilino-3-nitropropane in 300 ml. of ethanol preheated to 75° was added 293 g. (1.3 moles) of hydrated stannous chloride in 204 ml. of concd. hydrochloric acid in portions with good stirring. The temperature was kept at 75–80° and maintained at that temperature for 30 minutes after the stannous chloride had been added. After chilling in an ice-bath, 48.8 g. of purple crystals was filtered and air-dried overnight. This tin-containing solid was placed in two

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(10) H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, THIS JOURNAL, 55, 4571 (1933).

liters of water. The partial solution was saturated with hydrogen sulfide with frequent vigorous shaking. Filtering gave a colorless solution. Addition of concd. ammonium hydroxide yielded a white solid, which was purified by dissolving in the minimum amount of ethanol at room temperature and adding water to reprecipitate the product, m.p. 64–66°. There was obtained 14.4 g. (26.6% yield). This compound gradually decomposed in boiling ethanol.

Anal. Calcd. for $C_{10}H_{13}Cl_3N_2$: N, 10.47. Found: N, 10.68.

1,1,1-Trichloro-2-methylanilino-3-acetaminopropane.— A solution of 2.0 g. (0.0075 mole) of 1,1,1-trichloro-2-methylanilino-3-aminopropane in 10 g. (0.1 mole) of acetic anhydride was heated on the steam-bath for a few minutes. Chilling overnight in the refrigerator, followed by recrystallizing from ethanol–water, yielded 2.0 g. (83.3% yield) of product, m.p. 118–119°.

Anal. Calcd. for $C_{12}H_{15}Cl_3N_2O$: N, 9.05. Found: N, 9.07.

GREENCASTLE, INDIANA

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, TENNESSEE A & I STATE UNIVERSITY]

The Synthesis, Properties and Catalytic Hydrogenation of Several Aryloxy Substituted Ketene Monomers and Dimers

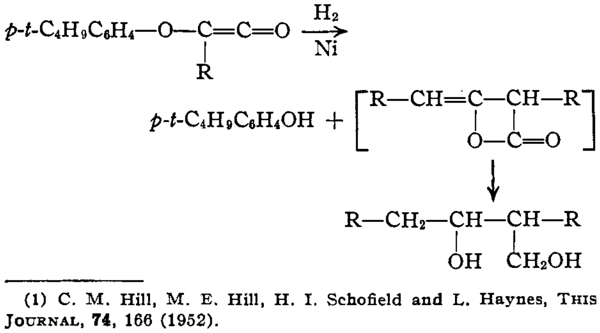
BY CARL M. HILL, MARY E. HILL, ALBERT O. WILLIAMS AND ESSIE M. SHELTON

RECEIVED OCTOBER 23, 1952

Three monomeric and two dimeric aryloxy ketenes of the type [p-t-C_4H_9-$C_6H_4OC(R)CO$], where R = H, CH_3, C_2H_5, n-C_4H_9 and n-C_5H_{11}, have been prepared by dehydrohalogenation of the corresponding acid chlorides. Properties of the acids and acid chlorides have been studied. Catalytic reduction of the p-t-butylphenoxyketenes and the isomers of three 2,4-dichlorophenoxyketene dimers of the type $[Cl_2C_6H_3OC(R)CO]_2$, where R = C_2H_5, n-C_3H_7 and n-C_4H_9, gave glycols and the corresponding phenol. p-t-Butylphenoxyketene dimer formed the glycol only.

In earlier papers[1,2] it was demonstrated that catalytic hydrogenation of alkyl and (ω-cyclohexylalkyl) ketene dimers led to the formation of aliphatic glycols only. It was of special interest, therefore, to synthesize and to investigate the behavior of aryloxyalkyl ketene monomers and dimers toward hydrogen at high pressures and temperatures, and in the presence of Raney nickel catalyst. It was postulated that the introduction of an oxygen atom between the β-olefinic carbon of the ketene functional group and the side chain would have a pronounced effect upon the reactivity of the ketene molecule during catalytic reduction. Also, it was believed that catalytic reduction of the two forms of each of three 2,4-dichlorophenoxyketene dimers[3] would give further experimental evidence of the existence of isomers.

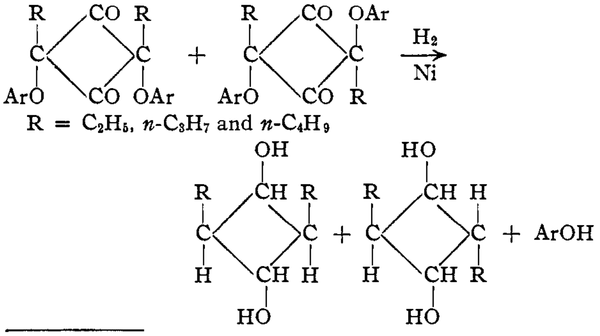
The results of this investigation indicate that, when the p-t-butylphenoxyketene monomers and one dimer are treated with hydrogen under pressures of 1500–3500 p.s.i., at temperatures of 200–350° and over Raney nickel, hydrogenation of the olefinic bond and cleavage of the ether bond take place. Such an attack of hydrogen upon the ketene molecule would lead to the formation of p-t-butylphenol and an alkyl ketene monomer.



However, the reduction products isolated from experiments using p-t-butylphenoxymethylketene dimer and p-t-butylphenoxyethyl-, p-t-butylphenoxy-n-butyl- and p-t-butylphenoxy-n-pentylketene monomers were p-t-butylphenol and glycols of the corresponding alkyl ketene dimers. This suggests dimerization of the transitory alkyl ketene monomers, followed by reduction of the dimers to glycols. Catalytic hydrogenolysis of ethers has been observed by Van Duzee and Adkins,[4] and Emerson and Heider.[5]

From p-t-butylphenoxyketene dimer, only one reduction product, 2,4-di-(p-t-butylphenoxy)-1,3-butanediol, was obtained. This is in agreement with our previous studies of cyclohexyl substituted alkyl[1] and alkyl ketene dimers.[2]

It has been observed in this Laboratory that dehydrohalogenation of 2,4-dichlorophenoxybutyryl, -valeryl and -caproyl chlorides produced, in each case, two forms of the ketene dimer.[3] It was tacitly assumed on basis of their solubility and boiling point differences that the two forms represented the *cis* and *trans* isomers. In the present study, it was observed that catalytic hydrogenation of each pair of dimers gave two different hydroxy compounds and 2,4-dichlorophenol.



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[1] C. M. Hill, M. E. Hill, H. I. Schofield and L. Haynes, THIS JOURNAL, **74**, 166 (1952).

[2] C. M. Hill, L. Haynes and M. E. Hill, *ibid.*, **74**, 3423 (1952).

[3] C. M. Hill, H. I. Schofield, A. A. Spriggs and M. E. Hill, *ibid.*, **73**, 1660 (1951).

[4] E. M. Van Duzee and H. Adkins, *ibid.*, **57**, 147 (1935).

[5] W. S. Emerson, R. L. Heider, R. I. Longley, Jr., and T. C. Shafer, *ibid.*, **72**, 5314 (1950).