

ported:^{14b} for the α,β -unsaturated ester, b.p. 60° (13 mm.), n_D^{25} 1.4341; for the β,γ -unsaturated ester, b.p. 58° (11 mm.), n_D^{25} 1.4329).

Reaction of ethyl 4-methyl-2-pentenoate with NBS. Ethyl 4-methyl-2-pentenoate (7.1 g., 0.05 mole; contained peroxides (ammonium thiocyanate-ferrous ammonium sulfate color test) formed by autoxidation on standing in a glass-stoppered bottle), NBS (7.3 g., 0.04 mole; purified by method Aa⁶) and carbon tetrachloride (30 ml.) were refluxed until a test with starch-iodide paper showed the absence of positive bromine; time for complete reaction, <20 min. The reaction mixture was cooled in an ice bath, filtered, and the succinimide (4.1 g., 100%) washed twice with 5-ml. portions of carbon tetrachloride. The washings and filtrate were combined and concentrated under reduced pressure (water aspirator). Distillation of the residue gave ethyl 4-bromo-4-methyl-2-pentenoate [7.1 g., 81%, b.p. 108–111° (18 mm.), n_D^{25} 1.4848]; reported⁴ (same general procedure except benzoyl peroxide initiator present), 67%, b.p. 105–110° (13 mm.); the bromo product is unstable, slowly evolving hydrogen bromide and becoming dark colored.

Runs in which preformed peroxides, light, and oxygen were singly or collectively excluded were performed by essentially the same technique as employed earlier in the study of effects of these environmental factors on the reaction of cyclohexene with NBS.⁶ Freshly distilled ester gave a negative test for peroxides and was used in Runs 2, 4 and 5; addition of any material to decompose peroxides was omitted to avoid possible isomerization of the β,γ -isomer during the distillation. In Runs 4 and 5 oxygen was excluded by flushing the apparatus with deoxygenated nitrogen before distillation of the ester into it and a slight positive pressure of nitrogen was maintained in the system throughout the run. Results of these runs are summarized in Table I.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASH.

Preparation of Propene-d-1

WILLIAM P. NORRIS

Received April 10, 1959

Propene-d-1 has been prepared previously in poor yield and of undisclosed deuterium content by reduction of propyne-d-1.¹

In the present work propene-d-1 was prepared by treating propenyl-1-magnesium bromide with deuterium oxide. The yield of product was 70% based on 1-bromo-1-propene and, according to parent peak analysis on the mass spectrometer, was at least 99% mono-deuterated propylene. The infrared spectrum of this propene-d-1 exhibited absorption peaks at 10.26 μ (*trans* isomer) and 12.52 μ (*cis* isomer).² By comparing the relative intensities of the two peaks, the propene-d-1 prepared is judged to be 60% *cis* and 40% *trans* isomer. Very small peaks appeared at 10.09 μ and 11.00 μ which

are probably due to undeuterated propene.³ From the work of Normant,⁴ it may be assumed that position isomerization did not occur either in the preparation of the Grignard or in the reaction of the Grignard reagent with deuterium oxide. Geometric isomerization did occur in the reaction sequence, as the Grignard reagent was prepared from 1-bromopropene which was 98% *cis* isomer.

The 1-bromo-1-propene used in the preparation of the propenylmagnesium bromide was prepared by a modification of an existing method.⁵ Instead of treating *trans*-crotonic acid dibromide with sodium carbonate in hot water or with refluxing pyridine, both of which reportedly gave yields of *cis*-1-bromo-1-propene in the range of 16–20%, the acid was treated with an excess of sodium bicarbonate in dimethylformamide at 70°. A 38% yield of 1-bromo-1-propene was obtained which was at least 99% *cis*-1-bromo-1-propene as determined by vapor phase chromatography and infrared analysis. By raising the temperature to 90° and distilling under reduced pressure, it is possible to obtain another 38% yield of 1-bromo-1-propene which analyzes for 96% *cis* and 4% *trans*-1-bromo-1-propene. This gives a total yield of 76% of 1-bromo-1-propene.

The infrared spectrum of the first fraction was identical with the spectrum of *cis*-1-bromo-1-propene prepared by Skell and Allen⁶ by the *trans* radical addition of hydrogen bromide to propyne.

The *cis*-1-bromo-1-propene is the isomer expected from this series of reactions because of the stereochemistry involved.^{7,8} *Cis*-1-bromo-1-propene is easily isomerized to the *trans* isomer. When a portion of the first fraction was redistilled, b.p. 55–55.2°, without protection from light, analysis by vapor phase chromatography showed the composition to be 90% *cis* and 10% *trans* isomer.

EXPERIMENTAL

Preparation of 1-bromo-1-propene. Three hundred and seventeen g. (1.20 mole) of *trans*-crotonic acid dibromide, m.p. 85–87°, was dissolved in the minimum amount of dimethylformamide. This solution was added, over a 20 minute period, to a reaction vessel which contained 163 g. (1.29 mole) sodium bicarbonate suspended in 500 ml. of dimethylformamide and which was connected to a Dry Ice trap. The reaction mixture was held at 70° during the addition. When

(1) B. S. Rabinovitch and F. S. Looney, *J. Am. Chem. Soc.*, **75**, 2652 (1953).

(2) Infrared spectra of essentially pure *cis*- and *trans*-propene-d-1 were provided by B. S. Rabinovitch of the University of Washington, Seattle, Washington.

(3) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1947). R. H. Pierson, A. N. Fletcher and E. Gantz, *Anal. Chem.*, **28**, 1218 (1956).

(4) H. Normant, *Compt. rend.*, **239**, 1510, 1811 (1954); **240**, 314, 440, (1955).

(5) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951). J. Wislicenus, *Ann.*, **248**, 281 (1888).

(6) P. S. Skell and R. G. Allen, Abstracts of Papers Presented at Chicago, Illinois, September 7–12, 1958, p. 27P. The infrared spectra of *trans* and *cis*-1-bromo-1-propene were kindly provided by Skell and Allen.

(7) A. McKenzie, *J. Chem. Soc.*, 101, 1196 (1912).

(8) S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **75**, 2645 (1953). E. Grovenstein, Jr., and D. E. Lee, *J. Am. Chem. Soc.*, **75**, 2639 (1953).

the addition was completed, the Dry Ice trap was replaced with another and the system was evacuated at 100 mm. pressure while the reaction vessel was heated to 90°.

The first fraction was washed with 3 portions of cold water, dried over Drierite and then filtered to give 60 g. (38% yield) of 1-bromo-1-propene, b.p. 55–55.2°/708 mm., which was 99% *cis* isomer, before distillation, according to vapor phase chromatographic analysis.⁹

The second fraction was treated in the same manner to give an additional 60 g. (38% yield) of 1-bromo-1-propene. The product consisted of 96% *cis*- and 4% *trans*-1-bromo-1-propene as determined by vapor phase chromatographic analysis.⁹ The total yield of 1-bromo-1-propene was 76%.

Preparation of Propene-d-1. Fifty g. (0.41 mole) of 1-bromo-1-propene (98% *cis* isomer) was added to 10 g. (0.41 mole) of magnesium in 250 ml. of dry tetrahydrofuran in a flask protected from atmospheric moisture and provided with means for distillation. When all the magnesium had reacted, 25 ml. of tetrahydrofuran was distilled out to remove any propene which might have been present. Receivers were changed and 17 ml. of 99.8% deuterium oxide was added dropwise to the stirred Grignard solution. The evolved gas was trapped in a Dry Ice-acetone trap to give 12 g. (70% yield) of propene-d-1. The propene-d-1 contained a small amount of tetrahydrofuran. A sample was purified by gas chromatography⁹ and parent peak analysis on the mass spectrometer indicated that it was at least 99% mono-deuterated propene.

CHEMISTRY DIVISION
U. S. NAVAL ORDNANCE TEST STATION
CHINA LAKE, CALIF.

(9) The analysis was performed by Charles M. Drew of this laboratory.

The Reaction of Oxalyl Chloride with Amine Hydrochlorides

RICHARD N. McDONALD

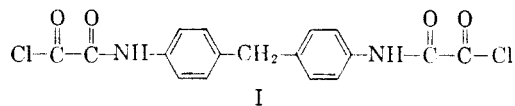
Received April 10, 1959

Stolle¹ successfully prepared oxamic acid chlorides from *N*-substituted anilines by reaction with oxalyl chloride. However, primary aromatic amines and oxalyl chloride gave only oxamides under similar conditions. Several patents² show that the oxamic acid chlorides of certain primary aromatic amines could be prepared by treating the amine hydrochlorides with oxalyl chloride, either in excess oxalyl chloride, or in an inert diluent.

This latter method has now been found applicable to the synthesis of 4,4'-(diphenylmethane)-bis-oxamic acid chloride (I). Good yields of I could be obtained when the dihydrochloride of 4,4'-diaminodiphenylmethane was heated under reflux with excess oxalyl chloride for 12 hours. Poorer yields were obtained when shorter reflux times were used.

(1) R. Stolle, *Ber.*, **46**, 3915 (1913); R. Stolle, R. Bergdoll, M. Luther, A. Auerhahn, and W. Wacker, *J. prakt. Chem.*, **128**, 1 (1930).

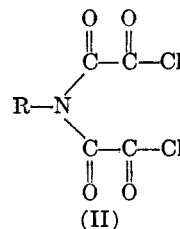
(2) I. G. Farben A-G., Brit. Patent 282,891, Sept. 30, 1926; I. G. Farben A-G., Ger. Patent 463,140, July 5, 1928; J. Haller, U. S. Patent 1,685,698, Nov. 26, 1926.



It was found that I reacted readily with ethanol to give the diester. This was shown to be identical to the diester obtained by reaction of 4,4'-diaminodiphenylmethane with diethyl oxalate by comparison of their infrared spectra and melting points, and no depression in the mixture melting point.

Surprisingly, the dihydrochlorides of *m*-phenylenediamine, piperazine, and *trans*-2,5-dimethylpiperazine were found to be unreactive towards oxalyl chloride. It is felt that this is probably due to the insolubility of these hydrochlorides as opposed to that of 4,4'-diaminodiphenylmethane, which appears to dissolve to some extent at the beginning of the reaction.

In looking for a possible extension of this reaction it was noted that Bornwater³ had reacted methylamine hydrochloride with oxalyl chloride and obtained *N,N'*-dimethyltetraketopiperazine. It appeared likely from our experience that an intermediate in this synthesis might be II (R = CH₃). This could then react with another molecule of amine hydrochloride to form the tetraketopiperazine.



This work indicates that this is indeed the case. A substantial yield of a hygroscopic, hexane soluble diacid chloride was obtained when a mixture of ethylamine hydrochloride and a large excess of oxalyl chloride was heated at reflux for 50 hr. Though the elemental analysis of the product, *N*-ethylloximidic acid chloride⁴ (II; R = C₂H₅), did not agree with the theoretical, that of its di-*N*-methylanilide derivative did. The infrared spectrum of the acid chloride was consistent with what would be expected of a compound having the structure of II.

EXPERIMENTAL⁵

4,4'-Diaminodiphenylmethane dihydrochloride. Fifteen g. of 4,4'-diaminodiphenylmethane dissolved in 350 ml. of anhydrous ether was treated with dry hydrogen chloride for 5 hr. whereupon the colorless, solid product precipitated. This was filtered, washed twice with 300-ml. portions of ether, and dried in a desiccator under vacuum. The dry weight was 19.7 g. (96%), m.p. 282° (dec.) [reported,⁶ m.p. 285° (dec.)].

(3) J. Th. Bornwater, *Rec. trav. chim.*, **31**, 105 (1912).

(4) We are assigning the name oximidic acid to the structure HO₂CCONHCOCO₂H.

(5) All melting points are uncorrected.