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THE PREPARATION AND CHEMICAL  
PROPERTIES  
OF  
THE PROPENYL HALIDES.

by  
GAYLORD JOHNSON  
A.M. The Rice Institute 1923

THESIS

Submitted in Partial Fulfillment of the Requirements

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DOCTOR OF PHILOSOPHY

In Chemistry

In

The Graduate School

of

THE RICE INSTITUTE

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## INTRODUCTION AND THEORETICAL

Several investigators within the last century have studied the compounds of the general type  $-C\equiv C-X$ , but have left the field with a wealth of unexplained data concerning methods of preparation and peculiar chemical properties.

The halogen here is not comparable to that in the alkyl and acyl halides in many ways. The  $\equiv CX$  shows less reactivity in the ordinary condensations and metatheses, the methods of preparation are widely different, and it is possible to show, at least in the case of some compounds of this type, that the halogen atom exerts actual oxidizing power. In the present investigation propynyl iodide has been found to oxidize ferrous salts, to be converted into allylene in malonic ester condensation and to yield an iodo chloride just as does iodo benzene. These are some of the outstanding examples of the unusual properties of the  $\alpha$ -halogenated alkyynes. An explanation of these unusual properties is that the halogen here is positively charged and this theory is supported by the synthesis of di-iodo acetylene using sodium hypo halides.

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 Dehn, J.A.C.S., 33, 1598 (1911)

Noyes and Howell, J.A.C.S., 42, 991, (1920)  
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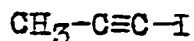
It was hoped that this same method would be applicable to the preparation of propinyl compounds but all trials were negative in so far as the production of an oil was concerned. A more significant fact was that the one apparent product of the reaction was a solid. This was secured in amounts too small for analysis though the physical constants were in agreement with those of iodoform.

The chief critic of this positive halogen theory is Nef who accounts for the unusual character  
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 Nef, Ann. 308, 509 (1899)  
 -----

of these compounds by postulating a divalent carbon atom. He maintains that this type of unsaturation  

$$\begin{array}{l} \text{H} \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \\ \text{H} \end{array}$$
 instead of the usual  $\text{HC} \equiv \text{CH}$  is more general, except for propinyl iodide and phenyl-iodo-acetylene. His conclusions are based largely upon the analogy in odor, toxicity, etc. of these compounds to hydrocyanic acid, the iso nitrils, and carbon monoxide. Since in his findings he reports propinyl iodide as a sweet smelling non-poisonous oil he infers that it has the

the true acetylene structure:-



instead of the acetylidene structure which according to his theory would be  $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{I} \end{array}$ . Foul odor and toxic properties in this series were claimed by this investigator to indicate an "acetylidene" linkage.

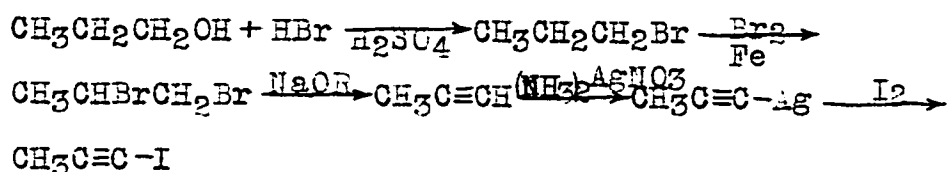
According to Nef  $\alpha$ iodo allylene ("stark süß reichendes nicht giftiges") has a boiling point of 109-110° Centigrade and a specific gravity of 2.08, yet Liebermann had reported the compound thirty four years  
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Ann. 135, 270 (1865)

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earlier as a foul smelling oil of boiling point 97-98° Centigrade and specific gravity of 1.7. Nef discounted the results obtained by Liebermann and claimed, that through faulty methods of synthesis the product of the earlier worker must have been contaminated with diiodo acetylene. Therefore, in the present work every precaution was taken to exclude all two carbon compounds and all reagents containing them were rejected. The variations in properties reported by Nef and Liebermann are so marked that the object of the present investigation is to undertake the harmonizing of the data on propynyl iodide, to develop a method for the



preparation of the two unknown propinyl halides, the chloride and bromide, and to examine the possibility of the existence of distinct isomeric forms of these compounds.

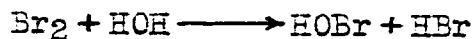
The complete synthesis employed for one member, propinyl iodide may be outlined as follows:-



A similar synthesis of the Bromo and Chloro compounds is limited by:-

(1) The more rapid addition of halogen to the triple bond.

(2) The formation of acid addenda by these halogens and water, e.g.,



(These acids may not only add but also oxidize the unsaturated compound giving many combinations.)

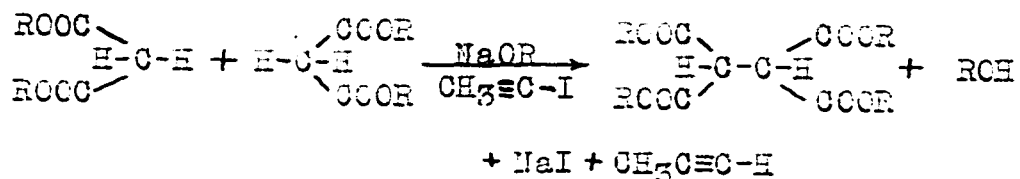
(3) The compound may polymerize as claimed by Pinner probably to yield aryl compounds as does  $\text{CH}\equiv\text{CI}$   
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 Ber. 14, 1082 (1881)

Meyer u Jacobson, Lehrbuch der Organischer  
 Chemie Bd 1, Tl 1, S 899  
 -----

It is obvious then that the isolation and purification of a pure Bromo or Chloro compound analogous to propinyl iodide is to be a difficult undertaking and these factors forced us to develop a new method of preparation in which all moisture was excluded. Several inert media were tried but all interfered with purification except heavy paraffin oil. Dry silver allylide was suspended in the cold dried oil and to this slowly added, with cooling a like amount of the paraffin oil to which had been added half the required molecular amount of bromine or chlorine. This was to prevent addition to the bonds. The whole was then subjected to steam distillation, and because of the highly inflammable character of Propinyl Bromide and Chloride the manipulations were, as far as possible, carried out in an atmosphere of carbon dioxide.

In order to study the chemical reactivity of the halogens in these propinyl halides, one member, viz, propinyl iodide, was condensed with malonic esters. It was questionable whether it would react to give alkylation similar to all normal aliphatic halides or give no condensation as is the case with the aryl halides. The evolution of allylene and the inter conden-

sation of two malonic ester residues which resulted certainly abnormal. A suggested representation of the reaction is as follows:-



A similar condensation results upon treating esters of malonic acid with iodine or bromine and sodium alkoxide as shown by Walker and Appleyard. This is  
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 J. Chem. Soc. (T) 67, 768 (1895)  
 -----  
 strong evidence that the halogen in propinyl iodide is unusual in activity.

To study further the reactivity of the halogen in the propinyl halides many attempts were made to prepare the corresponding propinyl amine and the propinyl magnesium iodide. All these efforts were without success. No traces of Grignard reagent were ever secured even under most ideal conditions.

AS to the preparation of propinyl amine, all possible methods usually productive of yields were tried to no avail. Potassium phthalimide, Sodamide, Ammonia, etc. were tried in solvents and dry, under reduced, normal and high pressures, at medium temperatures and in bombs but no traces of any amine was

found. Sodamide always yielded ammonia and allylene. The gases or liquids escaping from the bomb were passed into alkaline suspensions of Benzenesulphonyl Chloride always yielded the amide of the sulphonic acid, but no other nitrogen compound. Likewise, potassium phthalimide yielded no condensation under any condition tried; thus attesting to the unusual character of the halogen.

### EXPERIMENTAL PART

Preparation of Constant Boiling Hydro-bromic acid. This was prepared by the method of Scott as modified by Mann and Marvel. Twelve hundred grams of  
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J. Chem. Soc. 77, 646 (1900)

J. A. C. S. 42, 303 (1920)  
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bromine, fifteen hundred grams of ice and five hundred grams of water were placed in a three litre flask, suspended in an ice bath, and sulphur dioxide from a ten pound tank was rapidly passed in until the mixture was almost colorless. Excess of sulphur dioxide was avoided. Hydrobromic acid of almost constant boiling point was thus prepared as shown by the reaction:-



Air was then passed through the mixture for a half hour and the temperature raised to drive out excess sulphur dioxide. The mixed acids were then fractionated and the portion boiling 125-126° C., having a specific gravity of 1.49 was used.

2. Preparation of n-Propyl Bromide. A detailed study was made of this preparation in order to gain the maximum yields. Mann and Marvel have devised  
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J. A. C. S. 42, 303 (1920)  
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good methods for preparing ethyl, allyl, butyl, iso-amyl, cetyl, lauryl and trimethylene bromides, but did not report any work on the n-propyl compound. Their method was applied to this case. Care was taken to have the hydrobromic acid free from sulphur dioxide as preliminary experiments showed that the evolution of this dissolved gas had a marked effect upon the yield.

In this preparation n-propyl alcohol of constant boiling point  $97^{\circ}$  Centigrade was cooled to  $0^{\circ}$  Centigrade as was also the concentrated sulphuric (98%) acid and the constant boiling hydrobromic acid (48%). The sulphuric was added slowly with cooling to the n-propyl alcohol, the charring being thus only great enough to color the mixture a light red. To this was added the hydrobromic acid, the whole placed under a gentle reflux, thus heating is more comparable to a digestion than to a refluxing period and was continued for ten to fifteen hours when the heating was interrupted, the layer of propyl bromide removed and the mixture again placed under reflux. Equilibrium is seemingly hastened by this removal. Three separations of the alkyl halide from the mother liquor was always sufficient in the light of economy-likewise it was

found (1) that addition of propyl alcohol, hydrobromic acid or sulphuric acid separately to the spent mother liquor was not economical, (2) that rapid mixing of the sulphuric acid and alcohol seemed to increase excessively the percentage of allyl bromide, a side product of this reaction, (3) that when the alcohol and halogen acid were mixed and the sulphuric acid added afterward the yields were not so good as is evidenced by Run #IV (see below).

The following is typical of the quantities prepared, all chemicals stated in moles:

Run	n-Propyl Alcohol	Hydrobromic Acid	Sulphuric Acid	n-Propyl Bromide	Percent Yield
I.	14.67	15.0	10.5	12.07	82.3
II.	15.00	15.0	10.5	10.40	69.3
III.	15.00	15.0 (Not SO <sub>2</sub> free)	10.5	5.50	42.3
IV.	10.00	12.5	20.0	5.70	57.0

The alkyl halide was separated from the mother liquor, washed with concentrated sulphuric acid to remove any dipropyl ether formed until charring ceased (usually four to five times). It was then washed with water, a solution of sodium carbonate, and water again. When dried over anhydrous calcium chloride and distilled it showed a boiling point of 71° Centigrade and  $n_D^{20}$  1.4540.

The method of Morris was tried but yields  
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 Am. Chem. J. 38, 527 (1907)

J. A. C. S. 38, 1071 (1916)

-----  
 were 60-70%. By this method of purification and pre-  
 preparation no traces of ethyl bromide were found in the  
 final product.

5. Bromination of n-Propyl Bromide--Propylene  
 Dibromide. For this only the method of V. Meyer  
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 Ber. 24, 4250 (1891)

Jr. Pr. Ch. (2) 48, 171-2.

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 and Müller was used, the procedure being slightly  
 altered. By their method propyl bromide is convert-  
 ed to propylene dibromide at 30° Centigrade using  
 bromine, and iron filings as a catalyst. The early  
 yields were low because of excessive formation of  
 trimethylene bromide and higher bromination products.  
 To cut down their formation only two-thirds of the  
 calculated weight of bromine was added. The mixed  
 propylene and propyl bromides were washed with sod-  
 ium carbonate solution, then water and finally  
 dried over fused calcium chloride and fractionally  
 distilled. The monohalogened compound was then re-  
 turned to the apparatus for further bromination. The  
 hydrogen bromide evolved carries out much alkyl hal-  
 ide which is condensed when the hydrobromic acid is



absorbed in ice water.

This hydrobromic acid was fractionated and used for preparing the n-propyl bromide, it being of course entirely free from sulphur dioxide.

Yields of product averaged 75%, boiling point  $141.5^{\circ}$  Centigrade,  $n_D^{20}$  1.5168.

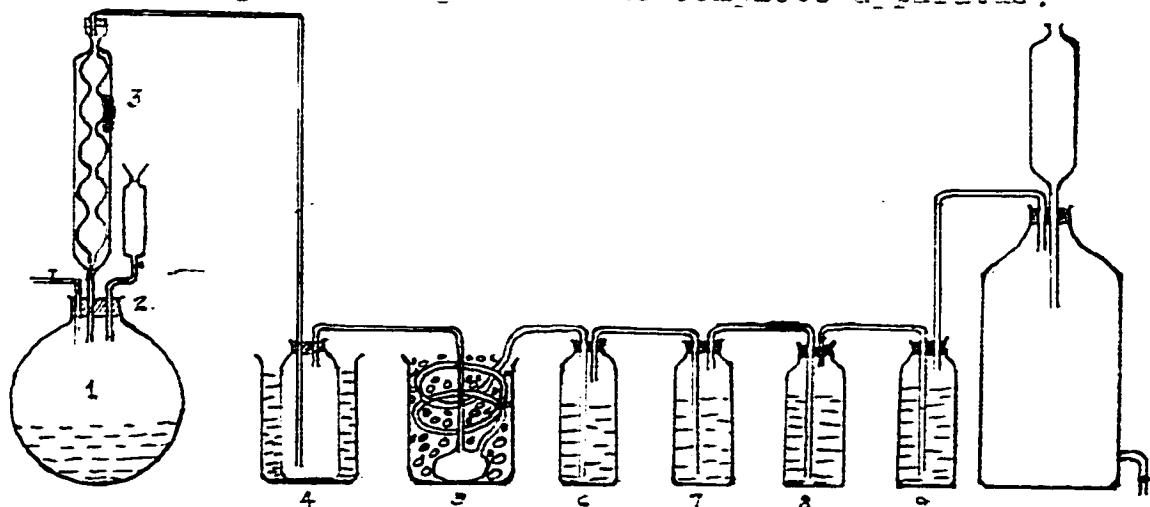
#### 4. Preparation of Allylene and Silver Allylide.

For the preparation of allylene no continuously rapid method is known. Treatment of propylene dibromide with alcoholic potash or sodium alcoholate in various concentrations constitute the chief procedures. In this work sodium methylate was used instead of sodium ethylate in order not to introduce any possibility of acetylene being produced. Propylene dibromide upon heating with alcoholic potash gives poorer yields in all concentrations than when heated with sodium methylate. The latter in very concentrated solutions gives the best results. It was used in semi-solid condition.

The gas was generated in a one litre flask (1) fitted with a three hole stopper (2) and was drawn out under reduced pressure by a falling head of water in the gasometer (G) through a 27" bulb condenser (3) and an empty gas bottle (4) to a series of coils (5) to condense the methyl alcohol, ethers etc., carried

out by the allylene through entrainment. From the coils it entered a flask (6) then aspirating bottles (7,8,9) containing ammoniacal silver nitrate, precipitated as silver allylene, the excess going to the gasometer. Beside the condenser, the stopper of the generator flask was fitted with a cylindrical dropping funnel for introducing the propylene dicromide and an air vent closed by a stop cock. The latter was provided for sweeping out the allylene gas and adjusting the pressure within the generator. All coils were submerged in freezing mixtures and the water in the bulb condenser was at 0° Centigrade.

The following is a diagram of the complete apparatus:



The ammoniacal silver nitrate was prepared by adding a ten percent solution of silver nitrate to 6 normal ammonium hydroxide, just short of the point where the precipitate failed to dissolve. This

seems to be the optimum concentration to use.

Silver allylide is a white flocculent compound, quite stable to light in contrast to most silver salts. It has been kept for several days without appreciable hardening after being washed and dried. If left exposed to light in the ammoniacal mother liquor it is not greatly affected. The solid was washed free from ammonia and silver compounds, sucked dry in a Büchner funnel and weighed. The average amount prepared by this method was 0.2 mole in eight to ten hours from 0.5 mole of propylene dibromide and two moles of sodium methylate.

5. Preparation of Propinyl Iodide (Iodo Allylene). This was prepared according to the method of Liebermann and of Nef. Iodine solution (17.2 grams  
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 Ber. 14, 1082 (1881)  
 Ann. 155, 270 (1865)

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 of iodine, 11 grams of potassium iodide, 25 grams of water) was slowly added with shaking and cooling to a cool thick suspension of silver allylide in water until the silver compound no longer removed the last traces of halogen color. Excess iodine was avoided to reduce formation of iodine addition products. It was then distilled.

Propinyl iodide is a colorless oil of nau-



at 64-65° Centigrade  $n_D$  1.4619 Sp. Gr. 1.343  $\frac{25^\circ}{25^\circ}$ .

Analysis:

Substance 0.1355 grams gave 0.2140 grams AgBr  
Calculated for Propinyl Bromide-Bromine 67.22%  
Found Bromine 67.25%

The molecular weight determinations showed no polymerization and gave values of 120, 121.

7. Preparation of the iodine addition product of Propinyl Bromide. This derivative was made for two purposes:-

- (a) To determine the amount of the addition taking place.
- (b) To check the analysis on the original compound.

Excess iodine in glacial acetic acid was added to propinyl bromide and placed in direct sunlight for two days. Thiosulfate treatment removed the excess iodine and the whole extracted with ether. The ether extract was washed, dried, and evaporated in a desiccator. Colorless crystals melting point 49-50° Centigrade were secured and analysed as mixed silver halides. These mixed halides were then converted to the chlorides and the loss in weight compared with the theoretical loss.

The results under the conditions indicated

conclusively that addition to saturation did not take place, and that a good analytical check on the original compound was easily possible.

Analysis for:-  $\text{CH}_2 = \underset{\text{I}}{\text{C}} = \underset{\text{I}}{\text{C}} \text{Br}$

Substance 0.5310 grams gave 0.5851 grams of mixed silver halides.

Theory 0.5838 grams. On conversion to silver chloride the loss was 0.2013 grams.

Theory loss 0.2019.

8. Preparation of Propinyl Chloride. This was prepared by the same method as Propinyl Bromide. The volatile oil from the steam distillation was washed, dried fractionated and the low boiling fraction ( $< 50^\circ$  Centigrade) refractionated. The product Propinyl Chloride is a colorless oil of Propinyl Bromide odor, boiling point  $54-55^\circ$  Centigrade  $n_D^{28}$  1.4097 and appears more stable than the bromine member of the series. Molecular weight determinations indicate no polymerization, gave values of 74.6, 75.

Analysis for:-

Substance 0.1462 grams gave 0.2813 grams AgCl

Calculated for Propinyl Chloride: Chlorine 47.65%

Found 47.61%

9. Preparation of the iodine addition product of Propinyl Chloride. This preparation was made by exactly analogous methods as was the Propinyl Bromide

addition product. It is not as stable as the latter and though a colorless oil it darkens rapidly in the light, decomposes on heating, and has a refractive index off the scale 1.7 at 27° Centigrade.

Analysis for  $\text{CH}_3-\underset{\text{I}}{\text{C}}=\underset{\text{I}}{\text{C}}-\text{Cl}$

Substance 0.2525 grams gave 0.4712 grams

mixed silver halides

Theory 0.4714 grams.

Conversion to Silver Chloride gave a loss  
of .1405 grams

Theory loss of 0.1707 grams.

10. Action of Sodium Hypiodite upon Allylene.

Allylene was run into a ten percent solution of potassium iodide and sodium hypochlorite added. The whole system was suspended in a freezing mixture and a stirrer was used to insure complete mixing. Concentrations of alkali in the reaction mixture were varied from a starting normality of 0.05 normal to 2 normal, the normality being increased 0.005 by each addition of alkali. No oil was obtained as might have been expected from analogous work by Dehn, Howell and W.A. Hoyes.

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W.A. Hoyes and Howell. J.A.C.S. 42, No. 5 (1920)

J.A.C.S. 53, 1598 (1911)  
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Instead of an oil a solid in small amounts

were secured, but always in insufficient amounts for analysis. This had the physical constants of Iodoform.

The hypochlorite used was prepared by adding the theoretical weight of chlorine to a ten percent solution of sodium hydroxide at less than 10° centigrade.

11. Action of Sodium Hypobromite on Allylene.

The results here obtained were equally as negative as in the hypiodite. Many attempts were made but no trace of an oil was ever secured, always traces of solids were evidenced. The solutions have an odor not accounted for.

12. Condensation of Propinyl Iodide with Malonic Esters. (a) With dimethyl malonate. 2.5 grams of sodium carefully freed from xylene by drying on filter paper and washing rapidly with cold absolute alcohol was added to 65 cubic centimeters of cold absolute ethyl alcohol. To this, when  $\text{CoCl}_2$  was added with agitation 15.8 grams of dimethyl malonate. The addition required forty five minutes. It then stood for thirty minutes more after which 16.6 grams of propinyl iodide were added over a period of forty five minutes. Allylene was immediately evolved with darkening of the solution. The gas was absorbed in ammoniacal silver nitrate, the precipitate dried and propinyl iodide



prepared from it by the usual method, refractive index and boiling point being in agreement.

Reaction mixture under gentle heat becomes neutral to litmus in about twenty four hours. The alcohol was distilled off and 11 cc. of a dark green viscous oil slightly heavier than water was secured. This was extracted with ether, dried with fused calcium chloride, the ether evaporated and the oil distilled under reduced pressure. The boiling point was 170 at 8 mm. After repeated distillations a boiling point of 158-165 at 1-2 mm. was obtained and the product was a colorless solid, needles, melting point  $26^{\circ}$  Centigrade  $n_D^{30}$  1.44725. Molecular weight determination gave 250, 250. This melting point does not correspond to that ( $76^{\circ}$  Centigrade) given for

$(COOC_2H_5)_2 CH-CH-(COOC_2H_5)_2$  by Walker and Appleyard  
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 J. Chem. Soc. 67, 768 (1895)  
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Evidently alcoholysis took place during the reaction giving a mixed methyl-ethyl ester of unknown composition. The ester on hydrolysis with potassium hydroxide and evaporated to dryness with subsequent heating with concentrated hydrochloric acid gives off carbon dioxide voluminously at  $110^{\circ}$  Centigrade.

(b) With diethyl malonate. This was carried out in exactly the same way as for the previous condensation. The allylene evolved was precipitated and

weighed 5.7 grams where 13 grams would be expected from the 14 grams of propinyl iodide and proportional amounts of sodium, diethyl malonate and absolute alcohol were used as under 10 part (a). The isolation of the product was exactly as before stated.

The oil was similar to that obtained from dimethyl malonate in appearance. Boiling point 145-150° at 1-2 mm. It is a solid of melting point 55-56°. Molecular weight 244,245 on two trials and

Analysis: 0.1985 grams gave CO<sub>2</sub> .3841 grams  
 H<sub>2</sub>O .1216 grams

Calculated for		found
$  \begin{array}{c}  \text{C}_2\text{H}_5\text{COC} \diagdown \\  \text{H}-\text{C}-\text{C}-\text{H} \\  \text{C}_2\text{H}_5\text{COC} \diagup  \end{array}  \begin{array}{c}  \diagup \\  \text{COCOC}_2\text{H}_5 \\  \diagdown \\  \text{COCOC}_2\text{H}_5  \end{array}  $	C = 52.85 H = 6.9	C = 52.89 H = 6.8

Walker and Appleyard reported the melting point of this compound to be 135° Centigrade, and due to the fact that our analysis checked so well with the theoretical it is evident there is some mistake in his melting point determination. The melting point of our compound was taken by complete immersion of the bulb of an Anshütz Thermometer in the molten solid.

13. Oxidation of Ferrous to Ferric Salts. In this experiment a small globule of propinyl iodide was suspended in water after having been carefully washed with alkali and water. A solution of ferrous sulphate

neutralized with sodium carbonate was then added and almost immediate oxidation to the ferric state was noted. Care was taken to exclude all air from the reagents and the oxidation was so complete as to render the test unquestionable.

Blanks at the same time were run on all reagents as well as on a pure sample of ethyl iodide with negative results.

On warming, the yellow precipitated ferric compound is oxidized further to a black compound seemingly an oxide.

## SUMMARY

1. Controversy between Nef and Liebermann over physical constants of Propinyl Iodide settled.

2. Two new propinyl halides, the bromo and chloro have been prepared together with their iodine addition products.

3. Propinyl iodide responds to none of the usual alkyl halide condensations, phthalimide, ammonia, sodamide, Grignard, etc.

4. Propinyl iodide has remarkable oxidizing properties, e.g.,  $Fe^{++}$  to  $Fe^{+++}$ , etc.

5. Other methods of preparing propinyl halides by  $NaOBr$  and  $NaOI$  from  $CH_2C \equiv CH$  were tried with negative results.

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- Jr. Pr. Ch.        (2) 42, 171-2