gave 10.2 g. (40%) of ethyl α-isopropylacetoacetate, b.p. 42–43° (0.2 mm.), $n^{20}\mathrm{D}$ 1.4240.[12]

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 62.60; H, 9.67.

This ester was characterized by the formation of a pyrazolone and hydrolysis to methyl isobutyl ketone. Thus from 5.0 g. (0.028 mole) of ethyl α-isopropylacetoacetate was prepared 5.5 g. (88%) of 1-phenyl-3-methyl-4-isopropylpyrazolone, m.p. 115–117°,[13] using the method of Pauly.[4a] A mixed melting point of this material and the corresponding pyrazolone obtained from ethyl α-isopropylacetoacetate prepared through the alkylation of ethyl acetoacetate with isopropyl iodide,[14] showed no depression.

Similarly the hydrolysis of 10.0 g. (0.056 mole) of ethyl α-isopropylacetoacetate by the method of Hauser and Breslow[15] gave 3.8 g. (66%) of methyl isobutyl ketone, b.p. 110–120°. This material was identified by conversion to a semicarbazone, m.p. 133–135°. The melting point of a mixture of this semicarbazone with that prepared from authentic methyl isobutyl ketone was 132–134°.

Preferred Preparation of Ethyl 2,4-Dimethyl-3-furoate (VI).—A mixture of ethyl acetoacetate (195 g., 1.5 moles) and chloroacetone (277 g., 3.0 moles) was treated with dry hydrogen chloride in the manner already described for the preparation of ethyl α-(1,2-dichloroisopropyl)-acetoacetate. As before, the reaction mixture was poured onto ice, treated with sodium carbonate, extracted with ether and washed with 10% sodium carbonate solution. Since excess chloroacetone was employed, these operations were carried out in a good hood. The ether solution was then transferred to a one liter three-necked flask equipped with a dropping funnel, a reflux condenser and a mechanically driven paddle stirrer. The flask was then immersed in an ice-bath and 600 ml. (437 g., 4.32 moles) of triethylamine was added as rapidly as possible. Almost immediately heat was evolved and triethylamine hydrochloride separated from solution. After addition was complete, the reaction mixture was stirred 8 hours at 0° and 35 hours longer at room temperature.

Enough water was then added to dissolve the amine salt which formed, the organic layer separated and the aqueous portion extracted with ether. The ether extracts and the organic layer were combined and washed cautiously with dilute hydrochloric acid until the washings were acid to congo red paper, then with water and finally dried by adding about 15 ml. of benzene and evaporating the excess solvents *in vacuo*. Distillation through an electrically heated 33 × 2.4 cm. column packed with glass helices gave 135.5 g. (54%) of ethyl 2,4-dimethyl-3-furoate, b.p. 52° (0.8 mm.), $n^{20}\mathrm{D}$ 1.4681. The infrared absorption curve of this product was identical to that prepared from the reaction of chloroacetone, ethyl acetoacetate and ammonia.

Several other bases were investigated for the dehydrohalogenation step, but none gave as good results as triethylamine. Ammonia led to a mixture of the ester and the amide in 49% yield based on the molecular weight of the ester. Aqueous and anhydrous pyridine gave the ester in yields of 2.5 and 4.3%, respectively. Direct treatment of the crude ethyl α-(1,2-dichloroisopropyl)-acetoacetate with 10% sodium hydroxide gave only traces of 2,4-dimethyl-3-furoic acid.

Summary

The *substance* obtained in the reaction of chloroacetone, ethyl acetoacetate and ammonia from which it is possible to prepare 2,4-dimethyl-3-furoic acid by alkaline hydrolysis has been found to be a mixture of ethyl 2,4-dimethyl-3-furoate and 2,4-dimethyl-3-furoamide. An improved synthesis for ethyl 2,4-dimethyl-3-furoate has been developed based upon a hydrochloric acid-catalyzed aldol-type condensation of chloroacetone and ethyl acetoacetate followed by cyclization with triethylamine.

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[12] Ethyl α-isopropylacetoacetate is known [see Adams, Levine and Hauser, *Org. Syntheses*, **27**, 35 (1947)] but apparently no refractive index has been reported.

[13] v. Auwers and Dersch, *Ann.*, **462**, 116 (1928).

[14] We are indebted to Roger Adams and Kenneth Schowalter for this sample.

[15] Hauser and Breslow, THIS JOURNAL, **62**, 2392 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XIII. Relative Reactivities of *cis*- and *trans*-Crotyl Chloride[1,2]

BY LEWIS F. HATCH AND STUART S. NESBITT

Both isomers of crotyl chloride have been studied in respect to their relative reactivities toward potassium iodide in acetone, sodium ethoxide in ethanol and in their cuprous chloride catalyzed acid hydrolysis. This investigation was made to extend our knowledge of the influence of various groups and atoms on the number one carbon atom of allyl chloride and also to learn more about the effect of geometrical configuration on these reactions. The rates of reaction of both isomers with these three reagents are greater than for allyl chloride. This general increase in reactivity is not surprising in view of the greatly increased reactivity of 1-chloro-3-methyl-2-butene over allyl chloride.[3]

In the reaction with potassium iodide the rate of *cis*-crotyl chloride was more than five times that for the *trans* isomer. The *cis* isomer, however, shows a definite drift in the specific reaction rate constant after 70 per cent. reaction while the *trans* isomer shows only a slight drift. A possible explanation for this drift is the slow rearrangement of some of the crotyl chloride to 3-chloro-1-butene which reacts very slowly with potassium iodide under these conditions. It is also quite possible that there is a slow rearrangement of the *cis* isomer to the slower reacting *trans* isomer. A similar drift in specific reaction rate constant was not noted for the reaction with sodium ethoxide.

The difference in the reactivity of the two isomers was much less pronounced for the reaction with sodium ethoxide with the rate of reaction of the *cis* isomer being only 1.16 times that for the *trans* isomer. Young and Andrews[4] have noted that crotyl chloride obtained by chlorination of a butene mixture had a rate of reaction with sodium ethoxide which was higher than for crotyl chloride obtained by other methods. This was interpreted

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[1] For number XII of this series see Hatch and Alexander, THIS JOURNAL, **72**, 5643 (1950).

[2] Presented in part at the Southwest Regional Meeting of the American Chemical Society, Oklahoma City, Okla., December 9, 1949.

[3] Hatch and Gerhardt, THIS JOURNAL, **71**, 1679 (1949).

[4] Young and Andrews, *ibid.*, **66**, 421 (1944).

as evidence for the presence of some of the *cis* isomer. The present data confirm this assumption.

The rate of cuprous chloride catalyzed acid hydrolysis of the crotyl chlorides was very fast for both isomers. The *cis* isomer hydrolyzed too fast at 40° to permit a direct comparison of its reactivity with the *trans* isomer run at that temperature but the faster rate of hydrolysis for the *cis* isomer was evident.

Table I contains comparative data for the reaction of the crotyl chlorides, 1,3-dichloropropenes and cinnamyl chlorides with potassium iodide and of the crotyl chlorides and 1,3-dichloropropenes with sodium ethoxide. These data indicate that for these reactions there is no apparent correlation between relative reactivity and electron releasing or attracting ability of the group or atom on the number one carbon atom of allyl chloride. The *cis* isomers of crotyl chloride and 1,3-dichloropropene have remarkably similar relative reactivities with potassium iodide while *cis*-cinnamyl chloride reacts about twice as fast.

TABLE I

RELATIVE REACTIVITIES OF SEVERAL ALLYLIC CHLORIDES

	Potassium iodide[a] 20°	Sodium ethoxide[b] 50°
cis-Crotyl chloride	8.35	5.14
trans-Crotyl chloride	1.56	4.43
cis-1,3-Dichloropropene[c]	8.58	2.78
trans-1,3-Dichloropropene[c]	2.90	3.47
cis-Cinnamyl chloride[d]	17.3	. .
trans-Cinnamyl chloride[d]	11.4	. .

[a] Allyl chloride as 1.00 with k 0.218. [b] Allyl chloride as 1.00 with k 1.18. [c] Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1093 (1948). [d] Hatch and Alexander, ref. 1.

The cuprous chloride catalyzed acid hydrolysis, on the other hand, shows a direct relationship between electron release and reactivity, with the crotyl chlorides being appreciably more reactive than the 1,3-dichloropropenes.[5] This dependency would be expected on the basis of the cuprous chloride–carbon–carbon double bond complex formation postulated by Keefer and Andrews[6] involving a positive addendum to the double bond.

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Experimental

***cis*-Crotyl Chloride.**—*cis*-Crotyl chloride was prepared from *cis*-crotyl alcohol by the use of phosphorus trichloride in pyridine. The *cis*-crotyl alcohol was obtained by the hydrogenation of 2-butyn-1-ol using palladium on barium sulfate and the 2-butyn-1-ol was prepared by the dehydrochlorination of 3-chloro-2-buten-1-ol. The chloroalcohol is readily available by the hydrolysis of 1,3-dichloro-2-butene (D.C.B.).[7] A detailed description of the preparation of *cis*-crotyl alcohol has been given in the literature.[8] *cis*-Crotyl chloride: b.p. 84.1° (758 mm.); $n^{20}\text{D}$ 1.4390; d^{20}_4 0.9426.

***trans*-Crotyl Chloride.**—*trans*-Crotyl chloride was prepared from *trans*-crotyl alcohol with phosphorus trichloride in pyridine. The alcohol was obtained by lithium aluminum hydride reduction of *trans*-crotonaldehyde.[9] For details of this preparation see Hatch and Nesbitt.[8] *trans*-Crotyl chloride: b.p. 84.8° (752 mm.); $n^{20}\text{D}$ 1.4350; d^{20}_4 0.9295.

3-Chloro-1-butene.—Two and one-tenth moles (152 g.) of 3-buten-2-ol[10] (boiling range 96.5 to 97°) was added to 400 ml. of concentrated hydrochloric acid in a one-liter round-bottom flask. The mixture was frequently shaken at room temperature over a period of 4.5 hours. The mixture was allowed to stand an additional 8.5 hours before the organic layer was separated and dried over calcium chloride. The yield of chlorides was 1.93 moles (175 g., 92%). The chlorides were distilled through a three-foot glass helix-packed column to give a 35% yield of material distilling between 63 and 65° (3-chloro-1-butene) with the remaining material boiling between 82 and 85° (crotyl chloride). 3-Chloro-1-butene: b.p. 63.7° (748 mm.); $n^{20}\text{D}$ 1.4151 (lit.[5] b.p. 63.5°; $n^{20}\text{D}$ 1.4151).

Reaction with Potassium Iodide in Acetone.—The same procedure was used as described previously.[11] The usual modified second order equation, $k = {}^1/_4bt \log (5 - z)/5(1 - z)$, was used and a plot of $\log (5 - z)/5(1 - z)$ *vs.* time gave a straight line between 20 and 70% reaction. The pertinent data up to 70% reaction are given in Table II. Above 70% reaction the following data were obtained:

TABLE II

cis AND *trans* CROTYL CHLORIDE

Reaction with Potassium Iodide in Acetone at 20°

cis

Time, hours	0.25	0.50	0.75	1.00	1.50
Reacted, %	19.7	33.5	44.5	52.9	67.9
k, hr. mole l.	1.95	1.84	1.79	1.74	1.79
Av. k			1.82		

trans

Time, hours	2.00	3.00	4.00	5.00	6.00
Reacted, %	26.4	37.2	46.8	51.1	55.8
k, hr. mole l.	0.342	0.351	0.361	0.330	0.316
Av. k			0.340		

Reaction with Sodium Ethoxide in Ethanol at 50°

cis

Time, hours	3	5	7	9
Reacted, %	52.8	65.4	71.4	77.8
k, hr. mole l.	6.33	6.21	5.71	6.00
Av. k		6.06		

trans

Time, hours	3	5	7	9
Reacted, %	41.4	54.3	59.3	65.7
k, hr. mole l.	5.33	5.52	4.91	5.17
Av. k		5.23		

Cuprous Chloride Catalyzed Acid Hydrolysis

cis

Time, hours	0.25	1.00	0.25	0.25
Temp., °C.	40.0	40.0	20.0	0.0
Reacted, %	92.7	93.2	85.3	63.9

trans

Time, hours	0.25	0.50	0.75	1.00	2.00
Temp., °C.	40.0	40.0	40.0	40.0	40.0
Reacted, %	74.0	81.7	87.0	88.3	90.0

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(5) Hatch, Brown and Bailey, THIS JOURNAL, **72**, 3198 (1950).

(6) Keefer and Andrews, *ibid.*, **71**, 1723 (1949).

(7) Furnished for this investigation by E. I. du Pont de Nemours & Co., Wilmington, Delaware.

(8) Hatch and Nesbitt, THIS JOURNAL, **72**, 727 (1950).

(9) Furnished for this investigation by the Tennessee Eastman Corporation, Kingsport, Tennessee.

(10) Furnished for this investigation by the Northern Regional Research Laboratories, Peoria, Illinois.

(11) Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1093 (1948).

cis-crotyl chloride, 2.00 hours, 74.0%, $k = 1.61$; 2.50 hours, 78.2%, $k = 1.67$; 3.50 hours, 79.0%, $k = 1.08$.

The last two values for the specific reaction rate constant are definitely in variance with those obtained for shorter periods of time. The deviation for the *trans* isomer was not appreciable.

For the purpose of comparison with the crotyl chlorides, the specific reaction rate constant of 3-chloro-1-butene was determined. The rate of this reaction was very slow at 20° so the measurements were made at 60° in order that better values could be obtained. The average value for the specific velocity constant for 3-chloro-1-butene was 0.044 at 60°.

Reaction with Sodium Ethoxide in Ethanol.—These rates were also determined using a previously described procedure.[12] The usual equation for a bimolecular reaction was used and a straight line was obtained when $\log b(a - x)/a\cdot(b - x)$ was plotted against time. The molar concentration of the *cis*-crotyl chloride was 0.05075 and the sodium ethoxide in ethanol was 0.05605. The molar concentration of the *trans* isomer was 0.05065 and the sodium ethoxide in ethanol was 0.04594. Table II contains the rate constants and other data.

Cuprous Chloride Catalyzed Acid Hydrolysis.—The same procedure and apparatus was used as that described in a previous paper of this series.[13] Thirty-nine-thousandth (0.039) of a mole of the chloride and 0.0035 mole of cuprous chloride (added as cuprous oxide) were used in 100 ml. of 1.5% hydrochloric acid. Because of the high rate of hydrolysis of the *cis*-crotyl chloride, the data for this isomer are not considered too accurate. It is clearly shown, however, that the *cis* isomer is appreciably more reactive than the *trans* isomer. The data are given in Table II.

Summary

The relative reactivities of *cis*- and *trans*-crotyl chloride have been determined for their reaction with potassium iodide in acetone, sodium ethoxide in ethanol and cuprous chloride catalyzed acid hydrolysis.

The replacement of a hydrogen atom on the number one carbon atom of allyl chloride by a methyl group increases the reactivity of the allylic chloride toward all three of these reagents.

With each reagent the *cis* isomer of crotyl chloride was more reactive than the *trans* isomer.

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(12) Hatch and Alexander, THIS JOURNAL, **71**, 1037 (1949).

(13) Hatch and Ballin, *ibid.*, **71**, 1041 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

The Preparation and Properties of 3-Chloro-1-propyne and 1-Chloro-2-butyne

BY LEWIS F. HATCH AND VINCENT CHIOLA

Occasional reference has been made in the literature to 3-chloro-2-propyne (propargyl chloride) and 1-chloro-2-butyne (methylpropargyl chloride) but no investigation has been reported on the influence of the carbon–carbon triple bond on the reactivity of these chlorides, especially in comparison with their olefinic and saturated counterparts. The present study was made both to clarify some apparent discrepancies in the literature of these compounds and to investigate their relative reactivities.

3-Chloro-1-propyne was first prepared by Henry[1] in 1875 by the reaction between phosphorus trichloride and 2-propyn-1-ol (propargyl alcohol). The same method was used in this investigation with the exception that pyridine was used as a solvent. We were not, however, able to obtain a material which boiled at the reported boiling point (65°) of 3-chloro-1-propyne. Three different preparations gave a chloride boiling consistently between 56 and 57°. Considering the source of the starting material, the method of synthesis and the results of the chlorine analysis, it is concluded that the boiling point reported by Henry for 3-chloro-1-propyne is incorrect.

In 1939 Hurd and Cohen[2] reported the synthesis of 1-chloro-2-butyne from 2-butyn-1-ol using phosphorus trichloride. The 2-butyn-1-ol was prepared from methylethynylmagnesium bromide and formaldehyde (from trioxymethylene). A boiling range (81–84°) and chlorine analysis were given to characterize their compound. The following series of reactions represent the method of preparation used in the present investigation to give a product which boiled approximately 20° higher (102°) than the boiling range reported by Hurd and Cohen.

$$\mathrm{CH_3CCl{=}CHCH_2Cl} \xrightarrow{\mathrm{Na_2CO_3}} \mathrm{CH_3CCl{=}CHCH_2OH} \qquad \mathrm{(I)}$$

$$\mathrm{CH_3CCl{=}CHCH_2OH} \xrightarrow{\mathrm{Alc.\ KOH}} \mathrm{CH_3C{\equiv}CCH_2OH} \qquad \mathrm{(II)}$$

$$\mathrm{CH_3C{\equiv}CCH_2OH} \xrightarrow[\mathrm{C_5H_5N}]{\mathrm{PCl_3}} \mathrm{CH_3C{\equiv}CCH_2Cl} \qquad \mathrm{(III)}$$

The identity of our compound was checked by chlorine analysis and by the preparation of the 3,5-dinitrobenzoate of both the chloride and the alcohol from which it was made. Mixture melting points of these two derivatives showed no depression. It is of interest to note that the water azeotrope of 1-chloro-2-butyne boils at 81.5° and it is suggested that the boiling point of this azeotrope was reported by Hurd and Cohen instead of the boiling point of the pure compound. The various physical data obtained for both 3-chloro-1-propyne and 1-chloro-2-butyne are given in Table I.

TABLE I

	3-Chloro-1-propyne	1-Chloro-2-butyne
B. p., °C.	56-57	102
n^{20}_D	1.4329	1.4581
n^{25}_D	1.4298	1.4552
n^{30}_D		1.4529
d^{20}_4	1.0297	1.0152
d^{25}_4	1.0239	1.0100
d^{30}_4		1.0063
Molecular (calcd.)	18.92	23.54
refract. (obs.)	18.78	23.74
Chlorine, % (calcd.)	47.58	40.05
(found)	47.78 47.83	39.86 39.96

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(1) Henry, *Ber.*, **8**, 398 (1875).

(2) Hurd and Cohen, THIS JOURNAL, **53**, 1074 (1931).