hydroanthracene-1,4-dione (XII)[6] in 10 ml. of toluene was allowed to stand at room temperature for 24 hours and was heated under reflux for an additional 48 hours. The hot toluene solution was filtered to yield 0.24 g. (25%) of white crystalline $\Delta^{4a(20a),8(8a),11a(15a)}$-octacosahydroöctaphene-6,10,17,19-tetraone (XIII), m.p. 291–293°.

Anal. Calcd. for $C_{34}H_{32}O_4$: C, 79.69; H, 7.81. Found: C, 79.77; H, 7.73.

COLLEGE PARK, MARYLAND

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

Allylic Chlorides. XXII. The 1,3-Dichloro-2-butenes[1]

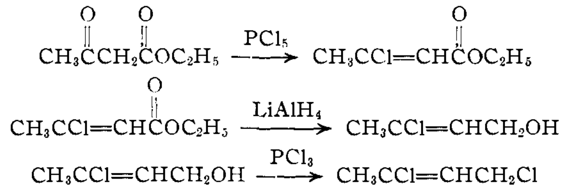
BY LEWIS F. HATCH AND ROBERT H. PERRY, JR.[2]

RECEIVED AUGUST 23, 1954

Pure α- and β-1,3-dichloro-2-butene have been prepared by unambiguous syntheses. The geometrical configurations of the various compounds involved in this synthesis were determined by the method of synthesis, the relative ease of dehydrochlorination and their infrared spectra. The configuration of α- and β-1,3-dichloro-2-butene was established by conversion to the corresponding *cis*- and *trans*-2-chloro-2-butene by means of lithium aluminum hydride and by their infrared spectra. The reactivity of α- and β-1,3-dichloro-2-butene was determined with potassium iodide in acetone and sodium ethoxide in ethanol.

The two isomers of 1,3-dichloro-2-butene have been the subject of several investigations with the object of assigning configuration[3] and relating geometrical configuration to relative reactivity.[4] The two isomers were prepared by the addition of hydrogen chloride to chloroprene,[5] a process which produced essentially pure α-1,3-dichloro-2-butene and only relatively impure β-1,3-dichloro-2-butene.

The two isomers have now been prepared from ethyl acetoacetate as represented by the equations



$$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow{PCl_5} CH_3CCl{=}CH\overset{O}{\overset{\|}{C}}OC_2H_5$$

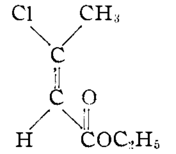
$$CH_3CCl{=}CH\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow{LiAlH_4} CH_3CCl{=}CHCH_2OH$$

$$CH_3CCl{=}CHCH_2OH \xrightarrow{PCl_3} CH_3CCl{=}CHCH_2Cl$$

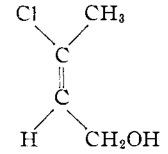
The treatment of ethyl acetoacetate with phosphorus pentachloride gave a mixture of ethyl β-chloroisocrotonate and ethyl β-chlorocrotonate.[6] This mixture was separated, by distillation, into ethyl β-chloroisocrotonate and a mixture of ethyl β-chlorocrotonate and ethyl acetoacetate.

The ethyl β-chlorocrotonate thus produced could not be separated from the ethyl acetoacetate. It was purified by conversion to β-chlorocrotonic acid, which was then esterified to obtain pure ethyl β-chlorocrotonate. In this respect it is of interest to note that Errera and Lepingle[7] determined the dielectric constant for a material they assumed to be pure ethyl β-chlorocrotonate but which, from the index of refraction they reported, must have contained a considerable amount of ethyl acetoacetate.

The configuration of ethyl β-chloroisocrotonate and ethyl β-chlorocrotonate have been established,[8] and reduction of these esters with lithium aluminum hydride produced β- and α-3-chloro-2-buten-1-ol, respectively.



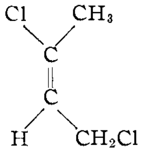
ethyl β-chloroisocrotonate



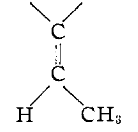
β-3-chloro-2-buten-1-ol

Geometrical configuration was retained in each case, since in neither reduction was a mixture of the two chloroalcohols produced. The configurations thus established were the same as those previously assigned from data obtained by the dehydrochlorination of the less pure chloroalcohols.[3] The physical data for the α-3-chloro-2-buten-1-ol were essentially the same as those previously reported[3,4] but the data for the β-3-chloro-2-buten-1-ol were somewhat different. The infrared spectra and the dehydrochlorination of these chloroalcohols (Table I) confirmed the assignment of configuration.

The chloroalcohols were converted to the corresponding dichlorides by phosphorus trichloride in pyridine. The α-1,3-dichloro-2-butene had essentially the same physical properties as those previously reported[5] but the physical properties of the β-isomer were appreciably different. The configuration of these dichlorides was confirmed by transforming the dichlorides to the corresponding 2-chloro-2-butene using lithium aluminum hydride.[9]



β-1,3-dichloro-2-butene



cis-2-chloro-2-butene

The infrared spectra also agree with the assigned configurations. Of particular interest is the presence of a band at 8.01 μ which is indicative of the $RR'C{=}CHCH_2Cl$ structure.[10] The configurations

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[1] Presented in part at the Northwest Regional Meeting of the American Chemical Society, Pullman, Washington and Moscow, Idaho, June 11 and 12, 1953.

[2] Eastman Kodak Company Fellow, 1951–1952.

[3] L. F. Hatch and P. S. Hudson, THIS JOURNAL, **72**, 2505 (1950).

[4] L. F. Hatch and S. G. Ballin, *ibid.*, **71**, 1041 (1949).

[5] L. F. Hatch and S. G. Ballin, *ibid.*, **71**, 1039 (1949).

[6] Thomas-Mamert, *Bull. soc. chim.*, [3] **13**, 70 (1895).

[7] J. Errera and M. Lepingle, *Bull. sci. acad. roy. Belg.*, [5] **11**, 153 (1925).

[8] A. Michael, *J. prakt. Chem.*, [2] **38**, 6 (1888); *ibid.*, [2] **40**, 29 (1899).

[9] L. F. Hatch and R. H. Perry, THIS JOURNAL, **71**, 3262 (1949).

[10] R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953).

are the same as those previously assigned from work with less pure material.[3]

The preparation of pure α- and β-1,3-dichloro-2-butene made possible the determination of more accurate values for the relative reactivities of these compounds with potassium iodide in acetone and sodium ethoxide in ethanol. The reactivities of the α-isomer in these reactions were about the same as those previously reported,[4] since the material used in that work was essentially pure. The reactivities of the β-isomer, however, were considerably greater than those previously reported. These data (Table II) confirm previous observations that the relative reactivities of compounds of this type increases when one or two hydrogen atoms on the number 1 carbon atom of allyl chloride are replaced by either electron-attracting or electron-releasing groups. The geometrical configuration of the compound also has a pronounced effect on the reactivity of the compound, especially in respect to the potassium iodide reaction.

Acknowledgment.—This investigation was supported in part by Task 2 Funds of the Defense Research Laboratory, The University of Texas, operating under Contract NOrd-9195, Bureau of Ordnance, Department of the Navy. The authors are also grateful for the financial assistance given to one of them (R. H. P.) by the Eastman Kodak Company.

Experimental

Ethyl β-Chloroisocrotonate and Ethyl β-Chlorocrotonate.—A mixture of ethyl β-chloroisocrotonate and ethyl β-chlorocrotonate was prepared from ethyl acetoacetate and phosphorus pentachloride.

Phosphorus pentachloride (700 g.) was added in small portions over a period of 2.5 hours to 500 g. (3.84 moles) of ethyl acetoacetate in 500 g. of benzene. The reaction flask was cooled by an ice-bath. Five hundred milliliters of water was added after completion of the reaction and the resulting two layers were separated. The aqueous layer was made basic with sodium carbonate, extracted with benzene and the organic solution and extracts washed several times with dilute sodium hydroxide solution. Distillation under reduced pressure gave a 40% yield of crude product. Approximately 23% of this material was ethyl β-chloroisocrotonate which had the following physical constants: b.p. 48° (10 mm.), $n^{17.9}_{\mathrm{D}}$ 1.4548, d^{20}_{4} 1.0885 (lit. b.p. 50° (10 mm.)[11]; $n^{17.7}_{\mathrm{D}}$ 1.45467,[12] d^{20}_{4} 1.088[12]).

The remaining material apparently was a mixture of ethyl β-chlorocrotonate and ethyl acetoacetate. Ethyl β-chlorocrotonate was obtained from this mixture by hydrolysis of the ester, separating the β-chlorocrotonic acid then re-esterifying the acid. Two hundred grams of crude ethyl β-chlorocrotonate and one liter of 50% hydrochloric acid were refluxed for eight hours. A 40% yield of β-chlorocrotonic acid was obtained (m.p. 94–95°; lit.[13] m.p. 94–95°). The β-chlorocrotonic acid was esterified using hydrogen chloride in ethanol. An 80% yield of ethyl β-chlorocrotonate was obtained. The ester had the following physical constants: b.p. 179–180° (745 mm.), n^{20}_{D} 1.4587, d^{20}_{4} 1.1060 (lit. b.p. 179–180°,[14] n^{20}_{D} 1.4587,[15] d^{20}_{4} 1.106[15]). Errera and Lepingle[7] give the following physical constants: $n^{17.9}_{\mathrm{D}}$ 1.4509, $d^{17.9}_{4}$ 1.1526. These constants check with those obtained for the mixture of ethyl β-chlorocrotonate and ethyl acetoacetate obtained in this work (b.p. 67.5° (10 mm.), $n^{17.9}_{\mathrm{D}}$ 1.4509, $d^{17.9}_{4}$ 1.1504). Apparently they worked with this mixture.

α-3-Chloro-2-buten-1-ol.—α-3-Chloro-2-buten-1-ol was obtained by the reduction of ethyl β-chlorocrotonate using $LiAlH_4$ and the procedure of Nystrom and Brown.[16] Twenty eight grams (0.187 mole) of ethyl β-chlorocrotonate was treated with 4.2 g. of $LiAlH_4$ in anhydrous ether. There was obtained 16.7 g. (85% yield) of α-3-chloro-2-buten-1-ol having the following physical constants: b.p. 62.5° (10 mm.), n^{25}_{D} 1.4653; d^{25}_{4} 1.0940 (lit.[5] n^{25}_{D} 1.4630, d^{25}_{4} 1.1058).

β-3-Chloro-2-buten-1-ol.—β-3-Chloro-2-buten-1-ol was obtained by the $LiAlH_4$ reduction of ethyl β-chloroisocrotonate. Eighty-four grams (0.57 mole) of ethyl β-chloroisocrotonate was treated with 13 g. of $LiAlH_4$ in anhydrous ether. There was obtained 55 g. (90% yield) of β-3-chloro-2-buten-1-ol which had the following physical constants: b.p. 67.5° (10 mm.), 77–78° (20 mm.), n^{25}_{D} 1.4712, d^{25}_{4} 1.1122 (lit.[5] 75° (20 mm.), n^{25}_{D} 1.4653, d^{25}_{4} 1.1085).

Anal. Calcd.: Cl, 33.3. Found: Cl, 33.0, 33.1.

Dehydrochlorination of the 3-Chloro-2-buten-1-ols.—The 3-chloro-2-buten-1-ols were dehydrochlorinated using a 30% solution of sodium hydroxide at 112° for three different periods of time. The results are compared in Table I with those previously reported.[3]

TABLE I

DEHYDROCHLORINATION OF THE 3-CHLORO-2-BUTEN-1-OLS USING 30% AQUEOUS NaOH AT 112°

	α		β	
Time, hr.	This work	Lit.[3]	This work	Lit.[3]
2	54	51	18	46
4	59	59	25	50
6	61	60	25	51

α-1,3-Dichloro-2-butene.—α-1,3-Dichloro-2-butene was prepared by the reaction between α-3-chloro-2-buten-1-ol and phosphorus trichloride in pyridine. Fifty grams (0.47 mole) of α-3-chloro-2-buten-1-ol and 9 g. (0.11 mole) of pyridine were treated, dropwise, with 27 g. (0.20 mole) of phosphorus trichloride at 5°. The addition took 1.5 hours after which the reaction mixture was stirred for an additional two hours at room temperature. A yield of 44 g. (75%) was obtained and the α-1,3-dichloro-2-butene had the following physical constants: b.p. 35° (20 mm.), 127.6° (749 mm.), n^{25}_{D} 1.4695, d^{25}_{4} 1.1530 (lit.[5] b.p. 34.3° (20 mm.), 127.9° (745 mm.), n^{25}_{D} 1.4695, d^{25}_{4} 1.1528).

3,5-Dinitrobenzoate: m.p. 75°; lit.[5] 75–76°.

The configuration of the α-1,3-dichloro-2-butene was further established by the conversion of the dichloride to *trans*-2-chloro-2-butene using lithium aluminum hydride.[9] One hundred twenty-five grams (1.00 mole) of the dichloride was added dropwise to 11.2 g. (0.25 mole) of $LiAlH_4$ in anhydrous ether over a period of three hours. After addition the reaction mixture was refluxed for an additional three hours. A 98% yield of *trans*-2-chloro-2-butene was obtained. The *trans*-2-chloro-2-butene had the following physical constants: b.p. 61° (744 mm.), n^{20}_{D} 1.4190; d^{20}_{4} 0.9139 (lit.[17] b.p. 62.4° (760 mm.), n^{20}_{D} 1.4190, d^{20}_{4} 0.9137).

β-1,3-Dichloro-2-butene.—The β-1,3-dichloro-2-butene was prepared from β-3-chloro-2-buten-1-ol in a manner analogous to that used for the preparation of the α-isomer. An 89% yield was obtained. The β-1,3-dichloro-2-butene had the following physical constants: b.p. 40° (20 mm.), 133° (747 mm.), n^{20}_{D} 1.4791, n^{25}_{D} 1.4470; d^{25}_{4} 1.1620 (lit.[5] b.p. 129.9° (745 mm.), n^{25}_{D} 1.4711, d^{25}_{4} 1.1542).

Anal. Calcd.: Cl, 56.7. Found: Cl, 56.8, 56.7.

3,5-Dinitrobenzoate: m.p. 60–61°, lit.[5] m.p. 58–59°.

The configuration of the β-1,3-dichloro-2-butene was established by conversion to *cis*-2-chloro-2-butene by use of $LiAlH_4$ in a manner similar to that used for α-1,3-dichloro-2-butene. A 72% yield was obtained with none of the *trans*-isomer being formed.

Infrared Spectra.—The infrared spectra of all of the compounds prepared during this investigation were obtained through the courtesy of Robert E. Kitson and E. I. du Pont de Nemours & Co., Kinston, North Carolina. A Perkin–Elmer Model C21 spectrophotometer was used with sodium chloride optics and a cell thickness of 0.030 mm. except with ethyl β-chloroisocrotonate and β-3-chloro-2-buten-1-ol with which a 0.037 mm. cell was used.

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(12) K. von Auwers, *Ber.*, **45**, 2807 (1912).

(13) A. Michael and O. Schultess, *J. prakt. Chem.*, [2] **46**, 236 (1892).

(14) W. Autenrieth, *Ber.*, **29**, 1655 (1896).

(15) K. von Auwers and H. Wissenbach, *ibid.*, **56**, 724 (1923).

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(17) A. L. Henne and J. B. Hinkamp, *ibid.*, **67**, 1194 (1945).

Following are the principal wave lengths in microns (w = weak, m = medium, s = strong).

Ethyl β-chloroisocrotonate: 3.35s, 4.2w, 4.8w, 5.2w, 5.79s, 6.08s, 7.00m, 7.25m, 7.31m, 7.50s, 7.89m, 8.38s, 9.18s, 9.60s, 10.9w, 11.6m, 12.3w, 14.6m.

Ethyl β-chlorocrotonate: 3.34s, 4.7w, 4.9w, 5.2w, 5.80s, 6.06s, 6.92m, 7.24m, 7.31m, 7.67m, 7.78m, 8.46s, 9.04m, 9.54s, 10.6w, 10.8m, 12.3w, 13.1w, 14.6w, 15.1m.

α-3-Chloro-2-buten-1-ol: 3.0s, 3.40s, 5.97s, 6.95s, 7.24m, 7.80m, 8.15m, 8.95s, 9.20s, 9.85s, 10.7w, 12.2m, 12.7m.

β-3-Chloro-2-buten-1-ol: 3.0s, 3.42s, 5.02w, 6.02s, 6.65w, 7.00s, 7.24m, 7.75w, 8.18m, 9.00s, 9.35m, 9.97s, 10.8w, 12.0m, 14.7m.

α-1,3-Dichloro-2-butene: 3.35m, 5.99s, 6.91s, 7.22m, 7.66m, 7.98s, 8.39s, 9.10s, 9.61w, 10.0m, 11.2m, 12.1s, 14.4s.

β-1,3-Dichloro-2-butene: 3.35m, 5.76w, 6.02s, 6.96s, 7.71s, 7.51m, 7.96s, 8.45s, 9.12s, 9.30m, 10.4m, 11.0w, 11.7s, 14.9m, 15.1s.

Relative Reactivities of α- and β-1,3-Dichloro-2-butenes. With Potassium Iodide in Acetone at 20°.—The usual procedure was used[18] with $k = 2.303/4bt \log_{10}(5 - z)/5(1 - z)$. The data obtained for α-1,3-dichloro-2-butene gave a relative reactivity of 20.6 compared to the value of 23.3 previously reported.[4] Data for β-1,3-dichloro-2-butene were appreciably different from those previously reported and they are in Table II. A plot of log $(5 - z)/5(1 - z)$ *vs.* time gave a straight line between 35 and 75% reacted.

TABLE II

RELATIVE REACTIVITY OF β-1,3-DICHLORO-2-BUTENE

Reaction with potassium iodide in acetone at 20°

Time, hr.	0.084	0.117	0.167	0.217	0.250
Reacted, %	38.5	50.3	61.7	70.6	84.8
k, hr.$^{-1}$ (mole/l.)$^{-1}$	30.0	31.4	32.5	30.5	30.0
Av. k			30.9 ± 0.9		
Relative reactivity[a]			60.6		

Reaction with sodium ethoxide in ethanol at 50°

Time, hr.	1.00	2.00	3.00	4.00	5.00
Reacted, %	46.3	64.0	73.5	79.8	84.4
k, hr.$^{-1}$ (mole/l.)$^{-1}$	16.0	15.6	15.1	15.5	15.4
Av. k			15.5 ± 0.2		
Relative reactivity[b]			13.0		

[a] Allyl chloride as 1.00 with k 0.502. [b] Allyl chloride as 1.00 with k 1.19.

With Sodium Ethoxide in Ethanol at 50°.—A previously described procedure[19] was also used with this reaction and the data were calculated using the rate expression for a second order reaction. The data for α-1,3-dichloro-2-butene were similar to those previously reported[4] and gave a relative reactivity of 4.08 compared to the literature value of 4.77. The data for β-1,3-dichloro-2-butane are given in Table II. The sodium ethoxide solution was 0.04256 *M* and the β-1,3-dichloro-2-butene was 0.05064 *M*. A plot of $\log b(a - x)/a(b - x)$ *vs.* time gave a straight line between 45 and 85% reacted. No correction was made for reaction of the vinyl chloride in calculating the reaction rate of the allylic chlorine. The extent of reaction would be very small under the conditions used.

AUSTIN, TEXAS

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Action of Grignard Reagents on β-Benzopinacolones

BY REYNOLD C. FUSON AND PHILIP E. WIEGERT

RECEIVED OCTOBER 15, 1954

β-Benzopinacolone and certain of its derivatives have been found to undergo nucleophilic substitution in the *para* position of the benzoyl group when treated with suitable Grignard reagents. *p*-Alkylation has been effected with the *t*-butyl, *t*-amyl and benzyl reagents. Displacement of the methoxyl group from *o*-methoxyphenyl trityl ketone has been achieved with methylmagnesium iodide and phenylmagnesium bromide. Methoxyl and acetoxyl groups have been displaced in the *p*-position by the *t*-butyl Grignard reagent. Displacement of the acetoxyl group has been realized also with the *t*-amyl reagent. Condensation of triphenylmethylsodium with substituted benzoyl chlorides has been found to be a useful method of synthesis for substituted β-benzopinacolones and has served to establish the structures of a number of the compounds isolated in this work. Unlike the mesityl ketones, β-benzopinacolone is reduced by certain alkylmagnesium halides. Cleavage has been observed also. Anisyl trityl ketone has been found to react with benzylmagnesium chloride to give 1,1,1,2-tetraphenylethane.

The condensation of phenylmagnesium bromide with β-benzopinacolone, originally carried out by Schmidlin and Wohl[1] and only recently correctly interpreted by Mosher and Huber,[2] takes a course that has been observed with a number of ketones and anils. Among these are benzophenone anil[3] and β-naphthil,[4] α,β,β-triphenylacrylophenone,[5] benzanthrone,[6] bz-1-phenylbenzanthrone,[7] napthacenequinone,[8] 6,13-pentacenequinone,[9] 1-benzonaphthen-1-one,[10] 3-methoxy-2-phenyl-1-benzonaphthen-1-one,[11] 2,2-dimethyl-1-benzonaphthene-1,2-dione[12] and mesityl phenyl ketone.[13]

Conjugate addition reactions of this type have been accomplished also with reagents other than phenylmagnesium bromide. In particular it was shown that *t*-butylmagnesium chloride and certain other Grignard reagents react more readily than the phenyl reagent and attack the *p*-position preferentially.[14] Moreover, indirect nucleophilic substitution had been realized with variously substituted hindered ketones.[15]

The present work was undertaken in the hope of effecting similar reactions with β-benzopinacolones. Experiments with *t*-butylmagnesium chloride and

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[15] See R. C. Fuson and W. S. Friedlander, *ibid.*, **76**, 5782 (1954).