solution of 10 g. of potassium iodide in 15 cc. of water was added, and the product precipitated as a heavy oil by addition of water. The supernatant solution was decanted and the product dissolved in chloroform, washed with water and isolated again by evaporation of the solvent. The residue was dissolved in ethyl acetate, on standing, crystals deposited, which were filtered off and recrystallized from methanol, yield 3.5 g., m.p. 150–154°. Further recrystallization raised the melting point of the tetraacetate to 156–160°.

Anal. Calcd. for $C_{17}H_{25}HgIO_{10}$: Hg, 28.0; I, 17.7; acetyl, 24.0. Found: Hg, 27.6; I, 17.6; acetyl, 24.0; $[\alpha]^{25}D$ +27.4° (1% in chloroform).

Tetrol (XIX), 2-Iodomethyl-*p*-dioxane-5,6-bis-ethanediol.—Demercuration: 3.6 g. of iodomercuri derivative XIV was dissolved in 20 cc. of chloroform. A solution of 1.27 g. of iodine in 30 cc. of chloroform was added and the mixture warmed to 60° for 5 min., then allowed to stand at room temperature for 16 hr. The mercuric iodide was filtered off and excess iodine removed from the filtrate by washing with sodium thiosulfate solution. Evaporation of the chloroform gave 2.80 g. of residue.

Hydrolysis.—The residue (2.80 g.) was refluxed with 100 cc. of methanol containing 1% anhydrous hydrogen chloride for 45 min., the solution was then evaporated to dryness leaving a residue of 1.73 g. which crystallized partly on standing. Recrystallization from ethyl acetate–hexane gave crystals of the tetrol (XIX) melting at 99–100°.

Anal. Calcd. for $C_9H_{17}IO_6$: C, 31.1; H, 4.9. Found: C, 31.4; H, 5.0; $[\alpha]^{26}D$ +10.8° (2% in ethanol).

Periodate oxidation: 87.7 mg. of tetrol (XIX) was dissolved in 10 cc. of methanol and 4 cc. of 0.1580 molar sodium periodate, water to 25 cc. was added.

Consumption after min.	Moles $NaIO_4$/mole
15	1.57
50	1.86

Formation of formaldehyde[14]: 36.0 mg. of tetrol (XIX) gave 49.3 mg. of dimedon derivative (oxidation time 30 min.) and 53.9 mg. of dimedon derivative (oxidation time 60 min.) corresponding to 1.63 and 1.79 moles HCHO/mole tetrol, respectively.

Hydrolysis and Acetylation of Iodomercuri Compound XIIIb. 2-Iodomercurimethyl-*p*-dioxane-5,6-bis-ethanediol Tetraacetate (XX).—A solution of 5.54 g. of the diisopropylidene–iodomercuri compound XIIIb in 70 cc. of 50% aqueous acetic acid was warmed 1.5 hr. to 60–70°, then concentrated *in vacuo*. A thick sirup remained which contained a small amount of mercuric iodide. The product was extracted with warm ethyl acetate and after concentrating the solution, acetylated with 12 cc. of acetic anhydride and 25 cc. of pyridine. The acetylation mixture was allowed to stand for 16 hours at room temperature and then worked up as usual. By cooling and stirring with isopropyl ether the acetylated product could be crystallized. The tetraacetate XX was recrystallized from ethyl acetate–hexane and melted at 84–85°.

Anal. Calcd. for $C_{17}H_{25}HgIO_{10}$: Hg, 28.0; acetyl, 24.0; Found: Hg, 27.9; acetyl, 24.5; $[\alpha]D$ +33.5° (1% in chloroform).

Acknowledgment.—We wish to thank Mr. M. E. Walsh and Mr. N. P. Loire for technical assistance and Mr. Louis Dorfman and his associates for the analytical data.

SUMMIT, NEW JERSEY

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

Allylic Chlorides. XXI. 3-Chloro-2-phenyl-1-propene[1]

BY LEWIS F. HATCH AND TAD L. PATTON

RECEIVED DECEMBER 22, 1953

3-Chloro-2-phenyl-1-propene has been prepared by the reaction between 2-phenyl-2-propen-1-ol and thionyl chloride. The allylic alcohol was prepared by the hydrolysis of the corresponding acetate made by selenium dioxide oxidation of 2-phenyl-1-propene and by the hydrolysis of the corresponding bromide (3-bromo-2-phenyl-1-propene) made by the reaction between 2-phenyl-1-propene and N-bromosuccinimide. The relative reactivities of 3-chloro-2-phenyl-1-propene with potassium iodide in acetone and sodium ethoxide in ethanol have been determined.

The study of the influence of various groups and atoms on the reactivity of the allylic chlorine atom of various substituted allylic chlorides has been extended to include 3-chloro-2-phenyl-1-propene (β-phenylallyl chloride). This chloride belongs to the type $CH_2{=}CYCH_2Cl$. Previously reported compounds of this type have had Y as H, Br, Cl and CH_3.[2,3]

The 3-chloro-2-phenyl-1-propene was prepared by two different routes from 2-phenyl-1-propene (α-methylstyrene) as indicated in Fig. 1.

The oxidation of 2-phenyl-1-propene by selenium dioxide in the presence of an acetic anhydride–acetic acid mixture to give 3-acetoxy-2-phenyl-1-propene has been reported by Butler.[4] Recovery of the product by steam distillation as prescribed by Butler led to extremely low yields. Much higher yields were obtained by low pressure distillation of the product. The ester was saponified to 2-phenyl-2-propen-1-ol (β-phenylallyl alcohol) which was characterized by its 3,5-dinitrobenzoate, α-naphthylurethan, infrared spectrum and by reduction of 2-phenylpropan-1-ol.

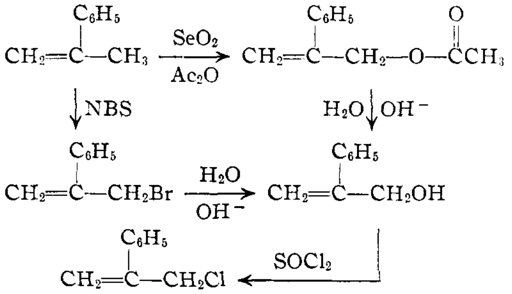

Fig. 1.—Preparation of 3-chloro-2-phenyl-1-propene from 2-phenyl-1-propene.

The same alcohol was obtained by the N-bromosuccinimide bromination of 2-phenyl-1-propene followed by hydrolysis of the 3-bromo-2-phenyl-1-propene. The fact that the bromination proceeded

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[1] For number XX of this series see L. F. Hatch and K. E. Harwell, THIS JOURNAL, **75**, 6002 (1953).

[2] L. F. Hatch, L. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948).

[3] L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1037 (1949).

[4] J. M. Butler, U. S. Patent, 2,537,622 (Jan. 9, 1951); *C. A.*, **45**, 5723 (1951).

slowly was not unexpected because Ziegler, *et al.*,[5] have previously reported that the NBS bromination of 2-phenyl-1-propene goes with great difficulty although they neither gave experimental details nor identified the product of the reaction. A similar lack of reactivity has been observed in these laboratories for 2-bromo-1-propene and 2-nitro-1-propene and seems to be general for compounds containing an electron attracting group on the carbon atom attached to the methyl group being brominated.

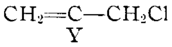
The 3-bromo-2-phenyl-1-propene was readily hydrolyzed to 2-phenyl-2-propen-1-ol. This alcohol gave a 3,5-dinitrobenzoate which was identical to that obtained from the selenium dioxide oxidation product of 2-phenyl-1-propene. The alcohol was converted to 3-chloro-2-phenyl-1-propene by treatment with thionyl chloride. The 3,5-dinitrobenzoate of both the bromide and chloride were identical with the 3,5-dinitrobenzoate of the corresponding alcohol.

The infrared spectra of the allylic compounds are in agreement with their assigned structures. The 3-bromo-2-phenyl-1-propene has the absorption at 8.20 μ which is characteristic of the $CR_2{=}CR'CH_2Br$ structure when R′ is other than hydrogen.[6] The 7.91 μ absorption of 3-chloro-2-phenyl-1-propene is characteristic of the corresponding allylic chloride structure (7.94[6]).

The relative reactivities of 3-chloro-2-phenyl-1-propene with potassium iodide in acetone at 20° and with sodium ethoxide in ethanol at 50° are given in Table I.

TABLE I

RELATIVE REACTIVITIES OF ALLYLIC CHLORIDES OF THE TYPE



$CH_2{=}\underset{Y}{C}{-}CH_2Cl$

Y	KI in acetone at 20°	C_2H_5ONa in ethanol at 50°
H	1.00[a]	1.00[b]
Br	0.87[a]	0.82[b]
Cl	0.72[a]	0.47[b]
CH_3	1.58[a]	1.03[b]
C_6H_5	2.27	1.12

[a] L. F. Hatch, L. B. Gordon and J. J. Russ, THIS JOURNAL, **70**, 1093 (1948). [b] L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1037 (1949).

The data obtained for 3-chloro-2-phenyl-1-propene correlate with those previously obtained for compounds of the same type, at least with respect to the lack of a pronounced influence upon the reactivity of the allylic chlorine atom by the Y substituent. This is in contrast to the influence of the same groups in compounds of the type $CHY{=}CHCH_2Cl$, all of which showed a marked increase in reactivity for both the *cis* and *trans* isomers regardless of electron attracting or releasing tendencies of the substituent groups. There also seems to be no relationship between the electron attracting or releasing tendencies of these groups and their influence on the reactivity of the allylic chlorine atom in compounds of the type $CH_2{=}CYCH_2Cl$. The difference in the reactivities of the $CH_2{=}CYCH_2Cl$ compounds, however, are too small to be of much significance.

It is difficult to correlate the observed influence of various groups and atoms on the reactivity of the allylic chlorine atom using the generally accepted S_N2 type reaction mechanism.

Experimental

3-Acetoxy-2-phenyl-1-propene.—This compound was prepared by the selenium dioxide oxidation of 2-phenyl-1-propene. Eighty grams (0.70 mole) of selenium dioxide was added in small portions to a vigorously stirred mixture of 236 g. (2.00 moles) of 2-phenyl-1-propene, 158 g. (1.55 moles) of acetic anhydride and 108 g. (1.80 moles) of acetic acid. The mixture had an initial temperature of 50° which increased to 70° during the addition of the selenium dioxide. After addition of the dioxide the temperature was maintained at 75° for one hour, then at 125° for 2.5 hours. Filtration removed the selenium metal and distillation at reduced pressure removed the acetic acid and acetic anhydride. Distillation at 5 mm. (110–115°) gave 150 g. of crude 3-acetoxy-2-phenyl-1-propene. Redistillation gave a 44% yield of material having the following properties: b.p. 112–113° (5 mm.), $n^{20}D$ 1.5281, $n^{25}D$ 1.5261, $n^{30}D$ 1.5248, d^{20}_4 1.0571, d^{25}_4 1.0543.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.01; H, 6.83. Found: C, 75.04; H, 7.09.

3-Bromo-2-phenyl-1-propene.—A mixture of 236 g. (2.00 moles) of 2-phenyl-1-propene, 178 g. (1.00 mole) of N-bromosuccinimide, 450 ml. of dry carbon tetrachloride and 6.0 g. of benzoyl peroxide was heated on a steam-bath for 54 hours. The solid succinimide and unreacted NBS were removed by filtration and the carbon tetrachloride was removed by distillation at 40° under reduced pressure. Distillation of the residue gave 78 g. of unreacted 2-phenyl-1-propene and 102 g. (0.52 mole) of 3-bromo-2-phenyl-1-propene. The yield on the basis of the NBS was 52%. The 3-bromo-2-phenyl-1-propene had the following physical properties: b.p. 90° (5 mm.); $n^{20}D$ 1.5869, $n^{25}D$ 1.5840, $n^{30}D$ 1.5818, d^{20}_4 1.3700, d^{25}_4 1.3653, d^{30}_4 1.3602.

Anal. Calcd. for C_9H_9Br: Br, 40.55. Found: Br, 40.49, 40.43.

3,5-Dinitrobenzoate (from silver 3,5-dinitrobenzoate): m.p. 116.5–117.5°.

There was no depression of the melting point when this derivative was mixed with the 3,5-dinitrobenzoate of 2-phenyl-2-propen-1-ol.

3-Bromo-2-phenyl-1-propene is a painful lachrymator and vesicant.

2-Phenyl-2-propen-1-ol.—This compound was prepared by the hydrolysis of 3-acetoxy-2-phenyl-1-propene and by the hydrolysis of 3-bromo-2-phenyl-1-propene.

Hydrolysis of 3-Acetoxy-2-phenyl-1-propene.—A solution of 42 g. (1.05 moles) of sodium hydroxide in 368 ml. of water was added to 176 g. (1.00 mole) of 3-acetoxy-2-phenyl-1-propene and 0.1 g. of hydroquinone, and the mixture was refluxed with vigorous stirring for seven hours. The reaction mixture was worked up in the usual manner and the ether solution of the product was dried over anhydrous potassium carbonate. Distillation at low pressure gave 105 g. (0.79 mole, 79% yield) of 2-phenyl-2-propen-1-ol which had the following physical properties: b.p. 116–118° (11 mm.), 95–96° (1.5 mm.), m.p. 19°, $n^{20}D$ 1.5675, $n^{25}D$ 1.5662, $n^{30}D$ 1.5648, d^{20}_4 1.0509, d^{25}_4 1.0470, d^{30}_4 1.0438.

Anal. Calcd. for $C_9H_{10}O$: C, 80.59; H, 7.50. Found: C, 80.41; H, 7.45.

3,5-Dinitrobenzoate: m.p. 116–117°.

Anal. Calcd. for $C_{16}H_{12}N_2O_6$: N, 8.54. Found: N, 8.76.

α-Naphthylurethan: m.p. 98.5–99.0°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: C, 79.18; H, 5.61; N, 4.62. Found: C, 78.90; H, 5.64; N, 4.58.

The 2-phenyl-2-propen-1-ol was hydrogenated in the presence of palladium to yield 2-phenylpropan-1-ol. Three and one-half grams (0.026 mole) of 2-phenyl-2-propen-1-ol took up 590 cc. of hydrogen (calcd. for one double bond of $C_9H_{10}O$: 582 cc.). The product boiled between 110–112° (15 mm.) and had an index of refraction $n^{25}D$ 1.5225. The **α-naphthylurethan** had m.p. 100°. Golumbic and Cottle[7] report for

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(5) K. Ziegler, A. Spaeth, E. Schaaf, A. Schumann and E. Winkelmann, *Ann.*, **551**, 80 (1942).

(6) R. E. Kitson, *Anal. Chem.* **25**, 1470 (1953).

(7) C. Golumbic and D. L. Cottle, THIS JOURNAL, **61**, 1000 (1939).

2-phenylpropan-1-ol: b.p. 108–109° (14 mm.), n^{25}_{D} 1.5221; **naphthylurethan**, m.p. 100–101°.

Hydrolysis of 3-bromo-2-phenyl-1-propene.—A mixture of 154 g. (0.78 mole) of 3-bromo-2-phenyl-1-propene and 350 ml. of a 10% aqueous sodium hydroxide solution was refluxed eight hours with vigorous stirring. The reaction mixture was worked up in the usual manner to give 82 g. (0.61 mole) of 2-phenyl-2-propen-1-ol (79% yield); b.p. 106–107° (7 mm.), n^{25}_{D} 1.5655; **3,5-dinitrobenzoate**, m.p. 116°.

3-Chloro-2-phenyl-1-propene.—This compound was prepared by treating 2-phenyl-2-propen-1-ol with thionyl chloride in the presence of pyridine. Fifty-one grams of pyridine and 50 ml. of dry chloroform were placed in a 250-ml. erlenmeyer flask and cooled to 0–10°, and 71 g. (0.60 mole) of thionyl chloride was added over a period of ten minutes while the temperature was kept below 10°. This solution was then added over a period of two hours to a solution of 62 g. (0.46 mole) of 2-phenyl-2-propen-1-ol dissolved in 100 ml. of dry chloroform. The temperature was kept below 10°. When all of the thionyl chloride had been added, the mixture was refluxed for one hour. The reaction mixture was worked up in the usual manner and distilled to yield 35 g. (0.23 mole) of 3-chloro-2-phenyl-1-propene (50% yield): b.p. 87–88° (5 mm.), n^{20}_{D} 1.5550, n^{25}_{D} 1.5538, n^{30}_{D} 1.5525, d^{20}_{4} 1.0820, d^{25}_{4} 1.0790; **3,5-dinitrobenzoate** (from silver 3,5-dinitrobenzoate), m.p. 116–117°.

There was no depression of melting point when the 3,5-dinitrobenzoate was mixed with the 3,5-dinitrobenzoate from 2-phenyl-2-propen-1-ol.

Anal. Calcd. for C_9H_9Cl: Cl, 23.30. Found: Cl, 23.41, 23.37.

3-Chloro-2-phenyl-1-propene is a painful lachrymator and vesicant.

Reaction with Potassium Iodide in Acetone at 20°.—The usual procedure was followed.[2] With the modified second-order equation $k = 2.303\ ^1/_4\ bt \log (5 - z)/5(1 - z)$, a plot of $\log (5 - z)/5(1 - z)$ *vs.* time gave a straight line between 16 and 61% reacted. Representative data are given in Table II.

Reaction with Sodium Ethoxide in Ethanol at 50°.—The procedure was the same as that previously described and the data were calculated using the rate expression for a second-order reaction. The sodium ethoxide solution was 0.04975 M and the 3-chloro-2-phenyl-1-propene was 0.05000 M. A plot of $\log b(a - x)/a(b - x)$ *vs.* time gave a straight line between 29 and 77% reacted. Representative data are given in Table II.

TABLE II

RELATIVE REACTIVITY OF 3-CHLORO-2-PHENYL-1-PROPENE

Potassium iodide in acetone at 20°					
Time, hr.	0.75	2.00	3.00	3.50	4.50
Reacted, %	15.8	34.8	47.0	53.4	60.8
k, hr.$^{-1}$ mole^{-1}-l.	1.17	1.12	1.12	1.17	1.12
	0.509	0.484	0.488	0.507	0.489
Av. k			1.14 ± 0.02		
Relative reactivity[a]			2.27		
Sodium ethoxide in ethanol at 50°					
Time, hr.	6.25	11.5	14.0	41.0	52.0
Reacted, %	29.4	42.6	47.7	73.2	76.8
k, hr.$^{-1}$ mole^{-1}-l.	1.34	1.30	1.32	1.34	1.29
Av. k			1.32 ± 0.02		
Relative reactivity[b]			1.12		

[a] Allyl chloride as 1.00 with $k = 0.502$. [b] Allyl chloride as 1.00 with $k = 1.18$.

Infrared Spectra.—The infrared spectra data were obtained through the courtesy of R. K. Kitson and the Chemical Division, Polychemicals Department, E. I. du Pont de Nemours and Company, Inc. The spectra were made in the liquid phases using a Perkin–Elmer Model 21 double-beam spectrophotometer. Sodium chloride optics were used with a cell thickness of 0.037 mm. The following are the principal wave lengths in microns (w = weak, vw = very weak, m = medium, s = strong, vs = very strong).

3-Bromo-2-phenyl-1-propene (β-Phenylallyl Bromide).—3.25 s, 5.11 w, 5.30 w, 5.55 m, 5.85 m, 6.20 s, 6.33 m, 6.67 s, 6.92 s, 7.19 m, 7.63 m, 8.20 s, 9.30–9.37 m, 9.56 w, 9.72 m, 10.25 m, 10.99 s, 11.90 w, 12.54 m, 12.88 s, 13.2 s, 13.3 vs, 13.9 s, 14.4 s.

2-Phenyl-2-propen-1-ol (β-Phenylallyl Alcohol).—2.95 vs, 3.26 s, 3.47 s, 5.10 w, 5.29 w, 5.50 w, 6.10 s, 6.22 m, 6.32 m, 6.67 s, 6.91 s, 7.1 s, 7.66 m, 8.15 m, 8.99 s, 9.31 m, 9.56 vs, 9.75 vs, 11.08 vs, 12.8 vs., 14.20 vs.

3-Chloro-2-phenyl-1-propene (β-Phenylallyl Chloride).—3.25 m, 3.51 w, 3.65 w, 5.08 w, 5.28 w, 5.49 w, 6.10 m, 6.20 m, 6.31 m, 6.66 s, 6.86 s, 7.13 m, 7.64 m, 7.91 s, 8.59 w, 9.03 w, 9.32 w, 9.70 m, 10.56 m, 11.01 s, 12.87 vs, 13.31 s, 14.35 vs.

AUSTIN, TEXAS

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Separation of Alkylated Ketones

BY WILLIAM J. BAILEY[1] AND MILTON MADOFF[2]

RECEIVED DECEMBER 1, 1953

A method for the separation of the mixture of tetraalkylated ketones obtained in the Haller–Bauer alkylation was developed. Using this procedure, 2,2-dimethylcyclohexanone was synthesized in an over-all yield of 59% and 2-methyldecalone in an over-all yield of 77%.

The Haller–Bauer method of alkylating ketones,[3] using sodamide and alkyl halides, has been widely used but very often leads to a mixture of products that is very difficult to separate. Thus, Haller[4] methylated 2-methylcyclohexanone (I) to produce a mixture of 85% of 2,2-dimethylcyclohexanone (II) and 15% of 2,6-dimethylcyclohexanone (III), determined by conversion to their benzylidene derivatives. Separation of II and III by distillation was difficult and the pure ketones were obtained in very low yield by fractional crystallization of their semicarbazones and subsequent hydrolysis. Johnson and Posvic[5] were able to synthesize II in an over-all yield of 32% in four steps, using their very elegant isopropoxymethylene blocking group to direct the methyl group into the 2-position of the cyclic ketone. Using this enol ether method, Horning, Horning and Platt[6] alkylated 2,3-dimethylcyclohexanone to obtain 2,2,3-trimethylcyclohexanone in a 32% yield.

Although the method of Johnson and Posvic[5]

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[1] Department of Chemistry, University of Maryland, College Park, Md.

[2] Office of Naval Research Fellow, 1949–1950.

[3] A. Haller, *Bull. soc. chim.*, [4] **31**, 1073 (1922).

[4] A. Haller, *ibid.*, [4] **39**, 1724 (1926); [4] **41**, 367 (1927).

[5] W. S. Johnson and H. Posvic, THIS JOURNAL, **69**, 1361 (1947).

[6] E. C. Horning, M. G. Horning and E. J. Platt, *ibid.*, **71**, 1771 (1949).