(s, $C_{arom}CH_3$, 3 H), 4.46 (d, J = 6 Hz, $-CH_2-$, 2 H), 7.0 (d, J = 8 Hz, $C_{arom}H$, 2 H), 7.16 (s, $C_{arom}H$, 4 H), 8.1 (d, J = 8 Hz, $C_{arom}H$, 2 H), 8.82 (m, NH, 1 H).

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.29; H, 7.16. Found: C, 80.35; H, 7.07.

Hydrolysis of *cis*-*N*-(2-*p*-Toluamido-1,2-di-*p*-tolylethenyl)toluamide.—Amide **7b** (54 mg, 1.1 mmol) was hydrolyzed, in an identical manner with amide **7a**, affording *p*-toluic acid, mp 177–180°, and 24 mg (91%) of 2,4,5-tris-*p*-tolyloxazole, which was recrystallized from absolute ethanol, mp 143–145° (lit.[24] mp 145°).

Pyrolysis of *cis*-*N*-(2-*p*-Toluamido-1,2-di-*p*-tolylethenyl)toluamide.—Amide **7a** (200 mg, 0.43 mmol) was pyrolyzed, in an identical manner with amide **7a**, affording a distillate (*p*-tolunitrile, *p*-toluic acid, and *p*-toluic acid anhydride) and a residue, which was recrystallized from ethanol giving 130 mg (90%) of 2,4,5-tris-*p*-tolylimidazole, mp 232–233°. Each compound was substantiated by spectral comparisons with authentic samples.

Registry No.—**7a,** 33511-25-0; **7b,** 33511-26-1; **9a,** 33511-27-2; lithium nitride, 26134-62-3; benzaldehyde, 100-52-7; *threo*-2-amino-1,2-diphenylethanol, 13286-63-0; *cis*-*N*-(2-benzamidoethenyl)benzamide, 33511-28-3; *trans*-*N*-(2-benzamidoethenyl)benzamide, 33511-29-4; *p*-tolualdehyde, 104-87-0; *p*-xylyl *p*-toluate, 21086-87-3; 2,4,5-*tris*-*p*-tolylimidazole, 33515-43-4; *p*-methylbenzyl alcohol, 589-18-4; *N*-*p*-xylyl-*p*-toluamide, 33515-44-5.

The Preparation and Oxidation of α-Hydroxyaldehydes[1]

P. BLUMBERGS* AND M. P. LAMONTAGNE

Ash Stevens Inc., Detroit, Michigan 48202

J. I. STEVENS

Chemical Process Laboratory, Edgewood Arsenal, Maryland 21010

Received May 17, 1971

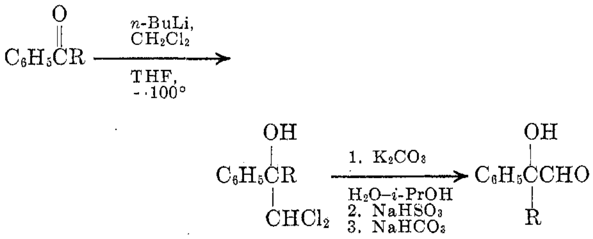
A series of α-hydroxyaldehydes have been prepared in 33–62% yield *via* the hydrolysis of the corresponding dichloromethylcarbinols. The latter compounds were conveniently prepared by the addition of dichloromethyllithium to the appropriate ketone at −100° in tetrahydrofuran. The glycolic aldehydes were oxidized to the corresponding glycolic acids by cold, neutral potassium permanganate in yields of 40–55%. Hydrolysis of trichloromethylcarbinols, obtained by the addition of trichloromethyllithium and the appropriate ketone, resulted in the elimination of chloroform to regenerate the parent ketone.

The syntheses of α-hydroxyaldehydes have been severely limited in the past. Freon[2] has added Grignard reagents to the oximes of difficultly accessible α-keto aldehydes to yield α-hydroxyaldoximes which could then be hydrolyzed by acid to the corresponding α-hydroxyaldehyde in low yields. Also, the hydrolysis of α-haloaldehydes[3,4] affords α-hydroxyaldehydes in low yields.

The purpose of this work, in part, was to investigate the synthesis of α-hydroxyaldehydes by the reaction of dichloromethyllithium with an alkyl aryl ketone followed by hydrolysis of the resulting dichloromethylcarbinols. Avy[5] reported the synthesis of dimethyldichloromethylcarbinol, but no aldehyde was isolated upon hydrolysis of this compound with calcium carbonate. Avy noted that hydrolysis of diethyldichloromethylcarbinol with boiling aqueous calcium carbonate did afford diethyl glycolic aldehyde, isolated as the semicarbazide derivative.

In our work, we found that dichloromethyllithium adds readily to alkyl aryl ketones at −100° in tetrahydrofuran to yield the corresponding dichloromethylcarbinols in yields of 75–85% (eq 1).[6] One example of this reaction was reported in 1964 by Kobrich and coworkers[6b] who treated benzophenone with the same reagent to obtain the corresponding dichloromethylcarbinol.

Hydrolysis of the dichloromethylcarbinols with potassium carbonate in aqueous isopropyl alcohol afforded a mixture of products which was shown by ir spectroscopy to contain the desired glycolic aldehyde. Distillation of the mixture resulted in extensive decomposition. However, the desired aldehydes could be isolated as the bisulfite adducts from which the free aldehydes could be readily regenerated.[7] The overall equations are shown in eq 1.



$$C_6H_5\overset{\overset{O}{\|}}{C}R \xrightarrow[\text{THF, }-100^\circ]{n\text{-BuLi, }CH_2Cl_2} C_6H_5\underset{\underset{CHCl_2}{|}}{\overset{\overset{OH}{|}}{C}}R \xrightarrow[\substack{H_2O-i\text{-PrOH}\\ 2.\ NaHSO_3\\ 3.\ NaHCO_3}]{1.\ K_2CO_3} C_6H_5\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}CHO \quad (1)$$

1, R = $CH(CH_2)_3$ **5**, R = $CH(CH_2)_3$
2, R = $CH(CH_2)_2$ **6**, R = $CH(CH_2)_2$
3, R = $CH(CH_2)_4$ **7**, R = $CH(CH_2)_4$
4, R = $CH(CH_3)_2$ **8**, R = $CH(CH_3)_2$

Investigation of the hydrolysis of compound **2** led also to the isolation of a solid α-hydroxyaldehyde dimer. The structure was assigned on the basis of ir and nmr spectral data and an acceptable elemental analysis. Treatment of the dimer with 4% meth-

---

[1] (a) This work was conducted at Ash Stevens Inc. under Edgewood Arsenal Contract No. DAAA15-67-C-0519. (b) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

[2] P. Freon, *Ann. Chim. (Paris)*, **11**, 480 (1939).

[3] A. Kirrmann and J. Druesne, *C. R. Acad. Sci.*, **259**, 3285 (1964).

[4] A. Kirrmann, P. Chancel, M. Vignalou, and P. Federling, *Bull. Soc. Chim. Fr.*, 707 (1950).

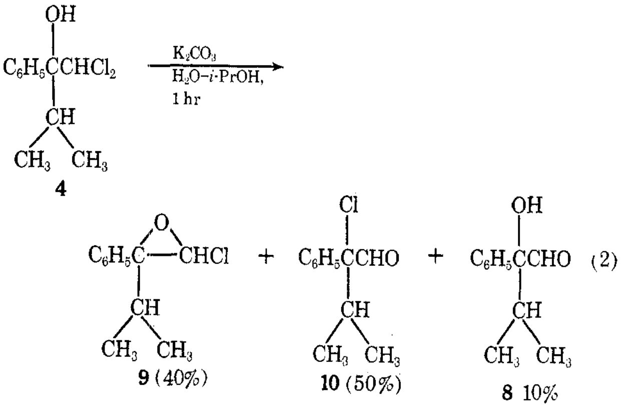
[5] M. A. Avy, *ibid.*, **49**, 12 (1931).

[6] Recent literature has described the preparation of α-chloroalkyllithium compounds by the reaction of polyhalomethanes with *n*-butyllithium in tetrahydrofuran or tetrahydrofuran–ether mixtures at −100°. These salts were reported to be stable indefinitely at −100° but decomposed spontaneously above −65°. Tetrahydrofuran was observed to have a great stabilizing influence on α-chloroalkyllithium structures. (a) D. Hoeg, D. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, **87**, 4147 (1965); (b) G. Kobrich, K. Flory, and W. Drischel, *Angew. Chem.*, **76**, 536 (1964); (c) G. Kobrich, H. R. Merkle, and H. Trapp, *Tetrahedron Lett.*, 969 (1965).

[7] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1962, p 149.

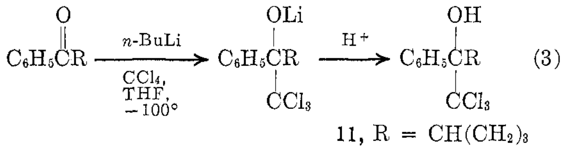
anolic potassium hydroxide solution led to a partial regeneration of the monomeric aldehyde, evidenced by the appearance of a carbonyl group in the ir spectrum. The regenerated aldehyde was isolated as its bisulfite adduct, subsequently reconverted to pure monomeric glycolic aldehyde. When this procedure was applied to the crude hydrolysis mother liquor of compound **2**, the yield of aldehyde **6** was raised from 31 to 54%. By a similar procedure, aldehyde **5** was obtained in 62% yield.

Kobrich and Weiner reported recently[8] the conversion of an α-dichloromethylcarbinol to an α-chloro epoxide by treatment with *n*-butyllithium in tetrahydrofuran solvent. Upon heating, the epoxide rearranged to an α-chloroaldehyde. The hydrolysis conditions, employed in the present work, consist of potassium carbonate in a 2-propanol–water solvent mixture at room temperature for 17 hr. In an effort to determine if, under these mild reaction conditions, the α-chloro epoxide rearranged to an α-chloroaldehyde prior to hydrolysis, the hydrolysis reaction of compound **4** was quenched after 1 hr. Examination of the reaction mixture by ir and nmr spectroscopy showed the epoxide **9** and chloroaldehyde **10** to be the major components (eq 2). Based on these data, at least 80% of the α-chloro epoxide rearranges to an α-chloroaldehyde prior to hydrolysis.



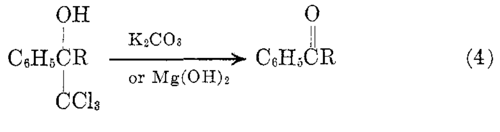
Pure samples of **9** were prepared by treating **4** with either potassium hydroxide or potassium carbonate in dry methanol. Ir and nmr spectral analyses of the crude reaction product showed no α-chloroaldehyde or α-hydroxyaldehyde to be present. Distillation of **9** under reduced pressure at 50° caused a partial rearrangement to yield a mixture of **9** and α-chloroaldehyde **10**. The rearrangement proceeded readily at 80° to yield pure 2-chloro-2-phenyl-3-methylbutyraldehyde. Pure **10** could also be prepared by a reaction of dichloromethylcarbinol **4** with 1 equiv of butyllithium in THF. Upon warming the cold (−30°) reaction solution to room temperature, α-chloro epoxide **9** was formed, as evidenced by the formation of lithium chloride. Heating this solution at reflux for 1 hr produced pure **10**. In this case, the presence of lithium chloride hastens the rearrangement. These results are in agreement with those reported by Kobrich and Weiner.[8] The rearrangement of the epoxide is also catalyzed by silica gel. When pure **9** was placed on a silica gel column and eluted with petroleum ether, a mixture of **9** and **10** was obtained.

Trichloromethylcarbinols **11** and **12** were prepared in 44 and 54% yield, respectively, *via* addition of trichloromethyllithium to the appropriate ketones (eq 3). However, it was found that these compounds were stable to dilute acid and attempted hydrolysis under a variety of basic conditions resulted in the elimination of chloroform to regenerate the parent ketone (eq 4).



$$C_6H_5\overset{O}{\overset{\|}{C}}R \xrightarrow[\text{CCl}_4,\ \text{THF},\ -100^\circ]{n\text{-BuLi}} C_6H_5\underset{CCl_3}{\overset{OLi}{C}}R \xrightarrow{H^+} C_6H_5\underset{CCl_3}{\overset{OH}{C}}R \quad (3)$$

11, R = $CH(CH_2)_3$
12, R = $CH(CH_3)_2$

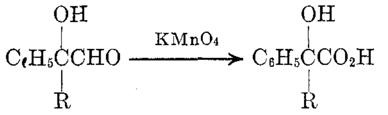


$$C_6H_5\underset{CCl_3}{\overset{OH}{C}}R \xrightarrow[\text{or } Mg(OH)_2]{K_2CO_3} C_6H_5\overset{O}{\overset{\|}{C}}R \quad (4)$$

Next, the oxidation of α-hydroxyaldehydes **5**–**8** was investigated as a possible synthetic route for α-hydroxy acids. Oxidizing agent studies included silver oxide as a suspended solid or dissolved in ammonium hydroxide, chromium trioxide in aqueous acetone and in pyridine, bromine, nitric acid, peracetic acid, Caro's acid, potassium permanganate and air oxidation with a cobalt catalyst. With the exception of potassium permanganate, the parent alkyl aryl ketone was the sole oxidation product. Potassium permanganate oxidation gave a moderate yield of the glycolic acid although the alkyl aryl ketone still was a major side product. Several solvent systems were evaluated with dioxane–water (1:1) being the preferred solvent. The results are shown in Table I.

TABLE I

PERMANGANATE OXIDATION OF α-HYDROXYALDEHYDES



$$C_6H_5\underset{R}{\overset{OH}{C}}CHO \xrightarrow{KMnO_4} C_6H_5\underset{R}{\overset{OH}{C}}CO_2H$$

Hydroxy acid	R	Yield, %	Mp, °C
13	$CH(CH_2)_3$	43	138–139
14	$CH(CH_2)_2$	37	88.5–89.5
15	$CH(CH_2)_4$	48	146.5–147.5
16	$CH(CH_3)_2$	40	148–149

The stability of an α-hydroxy acid toward two of the oxidizing agents was established. Thus, 2-hydroxy-2-cyclobutylphenylacetic acid was stable to silver oxide under the reaction conditions employed for the oxidation of the corresponding α-hydroxyaldehyde. Chromium trioxide, however, converted the acid to cyclobutyl phenyl ketone and potassium permanganate gave partial conversion to ketone.

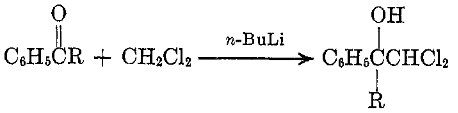
Another possible route to α-hydroxy acids would be the oxidation of α-chloroaldehyde **10** to the α-chloro acid which, if it did not hydrolyze under the reaction conditions, could be converted readily to α-hydroxy acid. It was found that the oxidation of **10** with potassium permanganate in acid media afforded the desired α-hydroxy acid in 61% yield (eq 5). Apparently, the chloro acid hydrolyzed as it was formed. The nonacidic material was found to be starting material which could be recycled. For synthetic purposes, this route appears to be preferred over the oxidation of the α-hydroxyaldehydes.

---

[8] G. Kobrich and W. Weiner, *Tetrahedron Lett.*, 2181 (1969).

TABLE II

PREPARATION OF DICHLOROMETHYLCARBINOLS

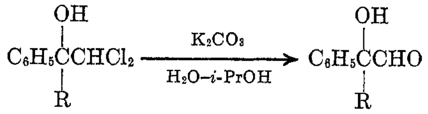


$$C_6H_5C(=O)R + CH_2Cl_2 \xrightarrow{n\text{-BuLi}} C_6H_5C(OH)(R)CHCl_2$$

Carbinol	R	Yield, %	Bp, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H
1	$CH(CH_2)_3$	84	98 (0.22)	58.79	5.76	58.88	5.76
2	$CH(CH_2)_2$	82	83 (0.15)	57.17	5.23	57.44	5.35
3	$CH(CH_2)_4$	75	108 (0.30)	60.26	6.22	60.51	6.24
4	$CH(CH_3)_2$	73	83–84 (0.15)	56.67	6.05	56.58	5.98

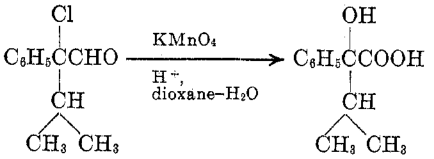
TABLE III

HYDROLYSIS OF DICHLOROMETHYLCARBINOLS



$$C_6H_5C(OH)(R)CHCl_2 \xrightarrow[H_2O\text{-}i\text{-PrOH}]{K_2CO_3} C_6H_5C(OH)(R)CHO$$

Aldehyde	R	Yield, %	Mp, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H
5	$CH(CH_2)_3$	62	35.5–36.5	75.76	7.42	75.98	7.34
6	$CH(CH_2)_2$	54	51.5–52.5	74.98	6.86	74.73	6.92
7	$CH(CH_2)_4$	44	75–76.5	76.44	7.90	76.70	7.80
8	$CH(CH_3)_2$	33	37–38.5	74.13	7.92	74.31	7.84



$$C_6H_5C(Cl)(CH(CH_3)_2)CHO \xrightarrow[H^+,\ dioxane\text{-}H_2O]{KMnO_4} C_6H_5C(OH)(CH(CH_3)_2)COOH \quad (5)$$

Experimental Section

Boiling points and melting points are uncorrected. Microanalyses were performed by Midwest Microlab, Ltd., Indianapolis, Ind. The ir spectra were measured on a Perkin-Elmer Model 237B spectrophotometer. The nmr spectra were measured on a Varian Model T-60 nmr spectrometer.

Preparation of Dichloromethylcarbinols. General Procedure. Cyclobutyl dichloromethylphenylcarbinol (1).—A solution of methylene chloride (10 ml) in dry tetrahydrofuran (225 ml) was cooled to −100° with a liquid nitrogen bath. To this cooled solution was added dropwise a hexane solution of *n*-butyllithium (88 ml, 0.14 mol) over approximately 45 min. After the addition was complete, the mixture was stirred at −100° for 45 min. Cyclobutyl phenyl ketone (20.8 g, 0.13 mol) was added slowly over *ca.* 30 min. After an additional 30 min at −100°, the mixture was allowed to warm to −20° and poured onto an ice–water mixture (400 ml) containing concentrated sulfuric acid (10 ml). Ether was added and the layers were separated. The aqueous layer was extracted once more with ether. The combined organic phase was dried (sodium sulfate) and the solvent was removed. The residue was distilled under reduced pressure. The results are shown in Table II.

Hydrolysis of Dichloromethylcarbinols. General Procedure. 2-Hydroxy-2-cyclobutylphenylacetaldehyde (5). **A.**—Potassium carbonate (10 g) was added to a solution of cyclobutyldichloromethylphenylcarbinol (10 g, 41 mmol) in 1:1 2-propanol–water (400 ml). The mixture was stirred at room temperature for 19 hr and extracted with ether (200 ml). The ether extract was dried (Na_2SO_4) and the ether was removed under reduced pressure. The residue was treated with standard[7] sodium bisulfite solution, the mixture filtered, and the solid washed with ether to yield 5 g of the bisulfite adduct. The filtrate and ether washings were saved (see B). The bisulfite adduct was added to a saturated aqueous sodium bicarbonate solution (100 ml) and ether (100 ml) and the two-phase system was stirred at room temperature for 4 hr. The layers were separated and the ether layer was concentrated under reduced pressure to yield 3.2 g of the glycolic aldehyde as an oil which solidified on standing.

B.—For the title aldehyde 5 and 2-hydroxy-2-cyclopropylphenylacetaldehyde (6), the yields were improved by the following procedure. The aqueous filtrate and ether washings from the bisulfite adduct formation were combined and shaken and the layers separated. The ether was removed and the residual oil was stirred with 4% methanolic potassium hydroxide (50 ml) for 1 hr at room temperature. The solution was diluted with water (100 ml) and extracted with ether (two 60-ml portions). The ether was removed and the residue treated with sodium bisulfite solution followed by aqueous sodium bicarbonate, as in A, to yield additional glycolic aldehyde. The combined crude product was purified by sublimation at room temperature (0.1 mm). The hydrolysis results are summarized in Table III.

α-Isospropyl-β-chlorostyrene Oxide (9).—To a solution of potassium hydroxide (1.1 g) in anhydrous methanol (35 ml) at 10° was added dichloromethylisopropylphenylcarbinol (2.15 g, 9.3 mmol). The solution was allowed to warm to room temperature and stirred for 1 hr. The solution was then poured into water (150 ml) and extracted twice with petroleum ether (bp 30–60°). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure at 0–5°. Examination of the reaction mixture by nmr showed it to contain *ca.* 50% of chloroaldehyde **10**, 40% of epoxide 9, and about 10% of α-hydroxyaldehyde **8**.

Preparation of Trichloromethylcarbinols. General Procedure. Cyclobutylphenyltrichloromethylcarbinol (11).—To a solution of carbon tetrachloride (10.05 g, 65 mmol) in tetrahydrofuran (150 ml) cooled to −105° was added dropwise a hexane solution of *n*-butyllithium (44 ml, 70 mmol). After the addition was complete, the solution was stirred at −100° for 1 hr and cyclobutyl phenyl ketone (10.4 g, 65 mmol) was added. The reaction mixture was stirred an additional 40 min at −100°, then allowed to warm to −20°, and poured into ice water (500 ml) containing 5 ml of concentrated sulfuric acid. The mixture was extracted with ether. The ether extract was washed with water, followed by saturated sodium chloride solution, and dried over sodium sulfate. Removal of the ether gave a viscous oil which was distilled *in vacuo*. The first fraction, bp to 90° (0.07 mm), consisted of a mixture of cyclobutyl phenyl ketone and the product. The subsequent fractions, bp 85–95° (0.04 mm), consisted of nearly pure product. The material was purified by recrystallization from petroleum ether and amounted to 7.93 g (44%), mp 59–61°.

Anal. Calcd for $C_{12}H_{13}Cl_3O$: C, 51.55; H, 4.69; Cl, 38.04. Found: C, 51.78; H, 4.73; Cl, 38.02.

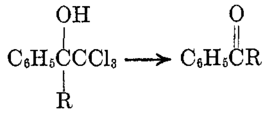
Isopropylphenyltrichloromethylcarbinol (12).—Isobutyrophenone (10.4 g, 0.07 mol) was allowed to react with trichloromethyllithium by the general procedure and gave 9.9 g (53%) of the carbinol 12, mp 37–38.5° (petroleum ether).

Anal. Calcd for $C_{11}H_{13}Cl_3O$: C, 49.38; H, 4.90; Cl, 39.75. Found: C, 49.59; H, 4.97; Cl, 39.49.

Studies of the Hydrolysis of Alkylphenyltrichloromethylcarbinols.—A number of attempts were made to hydrolyze alkyl-

TABLE IV

HYDROLYSIS OF ALKYLPHENYLTRICHLOROMETHYLCARBINOLS



$$C_6H_5\underset{R}{\overset{OH}{C}}CCl_3 \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}R$$

R	Reagent	Product	Yield, %
Cyclobutyl	H_2SO_4	Starting material	71
Cyclobutyl	K_2CO_3	Ketone	94
Cyclobutyl	ZnO	Starting material	98
Cyclobutyl	MgO	Starting material	98
Cyclobutyl	Pyridine	Starting material	95
Cyclobutyl	$AgNO_3$	Starting material + ketone	
Isopropyl	K_2CO_3	Ketone	83

phenyltrichloromethylcarbinols to the respective α-hydroxy acids. The results are shown in Table IV. In all cases studied, the only product formed was the parent ketone, arising from the elimination of chloroform. In the cases in which no ketone was formed, starting carbinol was nearly quantitatively recovered.

Oxidation of Glycolic Aldehydes. General Procedure. 2-Hydroxy-2-cyclobutylphenylacetic Acid (13).—To 2-hydroxy-2-cyclobutylphenylacetaldehyde (300 mg, 1.58 mmol) in dioxane (10 ml) at 10–15° was added potassium permanganate (250 mg) in water (10 ml). The solution was filtered to remove manganese dioxide and 5% sodium hydroxide was added to pH 10. The solution was extracted with ether (two 10-ml portions) to afford an oil (110 mg). The ir spectrum indicated the oil contained about 65% of cyclobutyl phenyl ketone and 35% of unreacted aldehyde. The aqueous basic solution was acidified with hydrochloric acid and extracted with ether (two 10-ml portions) to afford crude acid **13** which was recrystallized from chloroform to yield 140 mg (43%) of pure acid, mp 138–139° (lit.[9] mp 143–143.5°).

2-Hydroxy-2-cyclopropylphenylacetic Acid (14).—2-Hydroxy-2-cyclopropylphenylacetaldehyde (300 mg, 1.7 mmol) was oxidized with permanganate by the general procedure. The crude material was recrystallized from benzene–petroleum ether to yield 122 mg (37%) of pure product, mp 88.5–89.5° (lit.[9] mp 91–92°).

2-Hydroxy-2-cyclopentylphenylacetic Acid (15).—The glycolaldehyde **7** (300 mg, 1.47 mmol) was converted to the acid by the general procedure. The crude product was recrystallized from chloroform and gave 155 mg (48%) of pure acid, mp 146.5–147.5° (lit.[10] mp 147–148°).

2-Hydroxy-2-phenyl-3-methylbutanoic Acid (16). A.—2-Hydroxy-2-phenyl-3-methylbutyraldehyde (300 mg, 1.7 mmol) was oxidized with permanganate by the general procedure. The product was recrystallized from chloroform and amounted to 130 mg (40%), mp 148–149°.

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.22; H, 7.55.

B.—To a cooled solution of 2-chloro-2-phenyl-3-methylbutyraldehyde (1.4 g, 71 mmol) in dioxane (110 ml) and concentrated HCl (6 ml) was added potassium permanganate (4.5 g, 28.5 mol) in water (55 ml). The solution was stirred in an ice bath for 45 min, at which time all potassium permanganate was consumed. The solution was filtered and extracted with chloroform (three 30-ml portions). The organic layer was dried ($MgSO_4$) and concentrated. The residue was dissolved in chloroform (5 ml) and petroleum ether (60 ml) and the solution was washed with saturated sodium bicarbonate solution (two 20-ml portions). The bicarbonate solution was acidified with HCl and filtered to yield 0.85 g (61%) of crude hydroxy acid **16**, mp 144–145°. A sample was recrystallized from chloroform and melted at 148–149°; the ir spectrum ($CHCl_3$) was identical with that of the material prepared above. The petroleum ether solution was dried and concentrated to yield 0.35 g of an oil which was shown by ir analysis to be predominantly unreacted α-chloroaldehyde.

Registry No.—**1**, 33483-07-7; **2**, 33483-08-8; **3**, 33483-09-9; **4**, 33483-10-2; **5**, 33483-11-3; **6**, 33483-12-4; **7**, 31142-50-4; **8**, 33483-14-6; **11**, 33487-50-2; **12**, 33487-51-3; **13**, 1460-47-5; **14**, 1460-46-4; **15**, 427-49-6; **16**, 15879-60-4.

Acknowledgment.—The authors wish to acknowledge Mr. James P. Lockhard for his valuable technical assistance.

---

[9] S. B. Kadin and J. G. Cannon, *J. Org. Chem.*, **27**, 240 (1962).

[10] J. H. Biel, H. L. Friedman, H. A. Leiser, and E. P. Sprengler, *J. Amer. Chem. Soc.*, **74**, 1485 (1952).

Notes

Charge Distribution in the Addition of Dichlorocarbene to Olefins

ELLIS V. COUCH[1] AND JOHN A. LANDGREBE*

Department of Chemistry, University of Kansas, Lawrence, Kansas 66044

Received September 30, 1971

Although numerous qualitative observations have demonstrated the electrophilic nature of dichlorocarbene in its addition to carbon–carbon double bonds,[2,3] quantitative measurements of the extent of charge development have been meager and are summarized in Table I. The addition of the carbene to styrenes[4] and α-methylstyrenes[5] was best correlated by σ^+, with the more reactive (more nucleophilic) α-methylstyrene system yielding the smaller ρ value. The order of magnitude of these ρ values reflects only modest charge development at the benzylic position in the transition state relative to the ground state in accord with expectations for a concerted but unsymmetrical addition passing through a transition state with unequal bond formation to the two carbon atoms of the double bond.[5-7]

In contrast to the above studies was a report by

---

[1] Taken from the Ph.D. dissertation of E. V. Couch. Partial support from the Petroleum Research Fund is hereby acknowledged.

[2] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 163.

[3] D. Bethell, *Advan. Phys. Org. Chem.*, **7**, 153 (1969).

[4] D. Seyferth, J. Y-P. Mui, and R. Damrauer, *J. Amer. Chem. Soc.*, **90**, 6182 (1968).

[5] I. H. Sadler, *J. Chem. Soc. B*, 1024 (1969).

[6] R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

[7] Such results do not clearly distinguish between the unsymmetrical concerted reaction or a two-step process involving a zwitterionic intermediate with a transition state which occurs early along the reaction coordinate.