which 0.10 g. of hydroquinone had been added, was heated under reflux for 15 hr. The reaction mixture was poured into 100 ml. of water and allowed to stand overnight. The precipitate was separated by filtration, washed with several portions of hot water, and discarded. The filtrate and washings were extracted with ether, and the ether was in turn extracted with 5% sodium bicarbonate solution. Removal of the ether resulted in a residue of 1.23 g. (65% yield) of crude product VII. Recrystallization from benzene accompanied by charcoal treatment yielded 0.34 g. (20%) of colorless crystals, m.p. 136–137°.

The identity of VII, as obtained by these three different methods, was established by the identity of the infrared spectra and mixed melting point determinations.

When I was treated under acidic conditions for short periods of time, only starting material was obtained from the reaction mixture. A sample of 1.00 g. (4.2 mmoles) of I with a trace of hydroquinone was dissolved in a mixture of 10 ml. of glacial acetic acid, 2 ml. of concentrated hydrochloric acid, and 5 ml. of water. The solution was heated under reflux for 1.5 hr. and then was cooled in an ice bath. There was obtained 0.65 g. (65%) of I (Identity with the starting material was established by a mixed melting point determination). None of the expected product VII could be isolated from the reaction mixture.

Longer heating (12 hr.) in the absence of hydroquinone resulted in intractable reaction mixtures from which only traces of product and no starting material could be isolated. The necessity of having hydroquinone present to prevent resinification of some of the substances involved was clearly demonstrated.

p-Nitrobenzoate of VII. In a procedure similar to those previously described,[3] 1.00 g. (5.4 mmoles) of *p*-nitrobenzoyl chloride and 0.42 g. (2.5 mmoles) of VII in 10 ml. of pyridine reacted to yield 0.90 g. of crude enol ester. Recrystallization from a benzene-ligroin mixture accompanied by charcoal treatment gave 0.39 g. (39% yield). An analytical sample was prepared by recrystallizing twice from benzene to give clear, colorless platelets, m.p. 174–176°.

Anal. Calcd. for $C_{16}H_{15}NO_6$: C, 60.57; H, 4.77; N, 4.41. Found: C, 60.60; H, 4.98; N, 4.46.

The infrared absorption spectrum revealed bands that were assignable to enol ester (1760 cm.$^{-1}$, s), conjugated γ-lactone (1737 cm.$^{-1}$, s), and C=C (1646 cm.$^{-1}$, m; 1607 cm.$^{-1}$, m).

Acknowledgments. This investigation was supported by a Frederick Gardner Cottrel grant from the Research Corporation and in part by research funds of the State College of Washington. We are indebted to Mr. George D. Wagner of the Division of Industrial Research of the State College of Washington for determination of infrared absorption spectra and aid in their interpretation.

PULLMAN, WASH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF RHODE ISLAND]

Hunsdiecker Reaction of Silver Salts of *Cis*- and *Trans*-1,2-Cyclohexanedicarboxylic Acid[1]

PAUL I. ABELL

Received January 2, 1957

The Hunsdiecker reaction was carried out on the silver salts of *cis*- and *trans*-1,2-cyclohexanedicarboxylic acid. The same product, *trans*-1,2-dibromocyclohexane, was obtained from both salts. The isomerization appears to take place at an intermediate stage in the reaction. The mechanistic implications are discussed briefly.

The Hunsdiecker reaction, by which metal salts of carboxylic acids, usually the silver salts, are decarboxylated to the organic halide by the action of halogen, has attracted considerable attention in the past few years both as a method of synthesis of halogen compounds and mechanistically.[2] The present study was initiated from the former point of view in connection with a study of routes to the synthesis of alicyclic vicinal dihalides. The synthesis of the *cis* isomers of 1,2-dihalocycloalkanes was the principal interest, and accordingly it was decided to determine whether the Hunsdiecker reaction was capable of yielding *cis* dibromides from *cis* dicarboxylic acids.

The problem of isomerization was immediately apparent. A review of the literature disclosed that isomerization is not uncommon in the Hunsdiecker reaction. It was obvious from an examination of the literature that racemization of optically active compounds is to be expected when the carboxylic acid salt group is attached to the asymmetric carbon.[3] Little or no optical activity is preserved in the alkyl halides resulting from Hunsdiecker reactions of this type. However, the work in this laboratory was to be undertaken using geometrical isomers rather than optical isomers, the materials chosen being the silver salts of *cis*- and *trans*-1,2-cyclohexanedicarboxylic acid. It was not so evident from the literature that isomerization would take

---

[1] This work was performed under Contract No. DA-19-020-ORD-3171, OOR Project 1037, of the Office of Ordnance Research, U. S. Army. Support for this work is gratefully acknowledged.

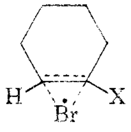
[2] For an extensive review see: R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956).

[3] (a) C. L. Arcus, A. Campbell, and J. Kenyon, *J. Chem. Soc.*, 1510 (1949). (b) R. T. Arnold and R. Morgan, *J. Am. Chem. Soc.*, **70**, 4248 (1948). (c) J. Cason, M. J. Kalm, and R. H. Mills, *J. Org. Chem.*, **18**, 1670 (1953). (d) Heintzeler, *Ann.*, **569**, 102 (1950). (e) R. G. Johnson and R. K. Ingham, Ref. (2), cite also: C. E. Berr, Doctoral Dissertation, University of California, Los Angeles (1952).

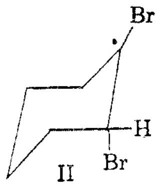
place with geometric isomers. Prelog and Zalan[4] obtained an optically active bromide by the bromine decarboxylation of the silver salt of *cis*-1,2-diethyl-4-cyclohexanecarboxylic acid, but the configuration at carbon atom number four was not investigated in either starting acid or subsequent bromide.

Similarly Hunsdiecker, Hunsdiecker, and Vogt[5] prepared ethyl 1-bromo-2-cyclohexanecarboxylate from the silver salt of the monoethyl ester of 1,2-cyclohexanedicarboxylic acid, but apparently without establishing configurations. A more careful examination of the steric nature of some Hunsdiecker reaction products was made in a study by Price and Berman[6] on the bromine decarboxylation of both the *cis* and *trans* isomers of silver cinnamate. Both isomers produced *trans*-β-bromostyrene. Wieland and Fischer[7] actually decarboxylated the silver salts of both *cis*- and *trans*-1,2-cyclohexanedicarboxylic acid using iodine, but failed to recover anything except small amounts of the starting acids.

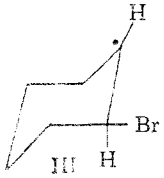
It thus appeared likely, but not certain, that both the *cis* and *trans* isomers of silver 1,2-cyclohexanedicarboxylate would yield the more stable *trans*-dibromide. It was of interest to compare the latter reaction to a reaction involving a rather similar free radical intermediate: the addition of hydrogen bromide to 1-bromocyclohexene under the influence of ultraviolet light. It has already been established that this reaction produces almost exclusively *cis*-1,2-dibromocyclohexane.[8] The presumed free radical intermediates in the two reactions are not the same, but have interesting points of similarity. The intermediate in the hydrogen bromide reaction has been described as either a bridged free radical of structure Ia[8], or of conformation II.[9]



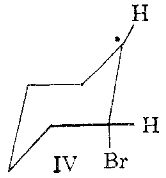
Ia X = Br
Ib X = H



II



III



IV

If the bridged free radical, Ia, is the intermediate, then the approach of the hydrogen atom donor must be from the side opposite the bromine bridge and *cis*-1,2-dibromocyclohexane is produced. If the more classical structure, II, is the intermediate, then the approach of the hydrogen bromide to give up its hydrogen atom is to be expected from the side opposite the axial bromine to yield, again, *cis*-dibromide. The latter explanation assumes that II is either a preferred conformation of the intermediate free radical or that isomerization to the alternate conformation with equatorial halogen is much slower than attack by hydrogen bromide. In either case the product, *cis*-1,2-dibromocyclohexane, is the result of the geometry or conformation of the intermediate free radical. In the case of the Hunsdiecker reaction the intermediate after one silver carboxylate group has been converted to bromide would presumably have structure Ib, III, or IV. *Trans*-1,2-dibromocyclohexane would result from the reaction of Ib with bromine. Probably a mixture of *cis* and *trans* isomeric dibromides would be produced from III since both sides of the ring at the free radical carbon are about equally accessible. Finally, the *trans* isomer would arise from IV, the bromine molecule being less hindered in its approach to the ring from the side away from the axial bromine.

In order to test the hypothesis on the stereochemistry of the Hunsdiecker reaction as outlined in the preceeding paragraph, both the *cis* and *trans* isomers of the silver salts of 1,2-cyclohexanedicarboxylic acid were treated with bromine under anhydrous conditions in carbon tetrachloride. Two different temperatures were employed to determine effect on yield and to find the most satisfactory reaction time. The temperatures chosen were room temperature or below and reflux temperature. The reactions at reflux temperature were very fast whereas the reactions run at room temperature were very slow, but the yields were independent of temperature. In all reactions the only saturated dibromide obtained was *trans*-1,2-dibromocyclohexane. The *trans* configuration was established by comparison of the infrared spectrum with the spectra of known *cis*- and *trans*-dibromides. While the spectra of the two isomers are quite similar, there are sufficient differences to detect any appreciable contamination of one isomer with the other. (The *cis* isomer has a moderately strong absorption band at 7.75 μ which is absent in the *trans* isomer.) No evidence of the *cis*-1,2-dibromocyclohexane was found in any of the decarboxylations.

The observation that anhydrous silver bromide and bromine in carbon tetrachloride can cause isomerization of initial products[10] was also considered, inasmuch as it might be possible that *cis*-dibromide had been formed which was then re-

---

(4) V. Prelog and E. Zalán, *Helv. Chim. Acta* **27**, 535 (1944).

(5) C. Hunsdiecker, H. Hundsdiecker, and E. Vogt, German Patent 730,410 [*Chem. Abstr.*, **38**, 374 (1944)].

(6) C. C. Price and J. D. Berman, Unpublished work. Cited by Johnson and Ingham, ref. (2).

(7) H. Wieland and F. G. Fischer, *Ann.*, **446**, 49 (1926).

(8) H. L. Goering, P. I. Abell, and B. F. Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952).

(9) H. L. Goering and L. L. Sims, *J. Am. Chem. Soc.*, **77**, 3465 (1955).

(10) D. C. Abbott and C. L. Arcus, *J. Chem. Soc.*, 3195 (1952).

arranged to the more stable *trans* isomer. Neither *cis*- nor *trans*-1,2-dibromocyclohexane was altered in configuration by such isomerization conditions, even after much more prolonged treatment than the Hunsdiecker reactions received. Also, addition of *cis*-1,2-dibromocyclohexane to a typical Hunsdiecker reaction of the *cis*-dicarboxylic acid gave a product containing about the expected percentage of *cis*-dibromide. Again, the lack of isomerization was established by examination of the infrared spectra of the recovered dibromides.

Although there was no reason to suspect that isomerization had taken place in the formation of the silver salts from the acids, or that they were unstable on standing, they were checked by conversion back to the free acids. The configurations were unchanged. Likewise, the action of silver bromide and bromine in carbon tetrachloride under anhydrous conditions was without effect on configuration of the free acids.

The conclusion was reached that the isomerization of the *cis*-1,2-cyclohexanedicarboxylic acid to the *trans*-dibromide was taking place in the course of the reaction and was not a prior isomerization of the acid or a postreaction isomerization of the dibromide. As a consequence of these findings the assumption must be made that either Ib or IV represents the structure of the intermediate radical if kinetic and steric control of the reaction prevails. Structure III is plausible only if complete thermodynamic control of the reaction is assumed.

EXPERIMENTAL

All melting points are uncorrected.

The *cis*-1,2-cyclohexanedicarboxylic anhydride was furnished through the courtesy of the National Aniline Division of Allied Chemical and Dye Corp.

The bromine used was analytical reagent grade, dried just before use by shaking with concentrated sulfuric acid. The carbon tetrachloride was analytical reagent grade, dried and stored over phosphorus pentoxide.

cis-1,2-Cyclohexanedicarboxylic acid. Hydrolysis of *cis*-1,2-cyclohexanedicarboxylic anhydride in boiling water gave the acid, m.p. 191–194° (lit.[11] m.p. 191°).

trans-1,2-Cyclohexanedicarboxylic acid. Isomerization of *cis*-1,2-cyclohexanedicarboxylic acid in a sealed tube with a small amount of aqueous hydrochloric acid at 170–180° for 8 hours gave a 61.5% yield of *trans*-1,2-cyclohexanedicarboxylic acid after recrystallization from ethyl alcohol. M.p. 228.5–230.5° (lit.[12] m.p. 227–229°).

Silver salts of cis- and trans-1,2-cyclohexanedicarboxylic acids. The silver salts were prepared by adding an exactly equivalent quantity of aqueous silver nitrate solution to a carefully neutralized solution of the sodium salt of the acid. Filtration of the white precipitate followed by careful washing with water, alcohol, and ether gave a quantitative yield of the silver salt. Drying for several days under vacuum over phosphorus pentoxide, followed by screening to 100 mesh gave the salts in a form suitable for the reaction with bromine. The salts were white and remained white even after storage for several months in brown bottles.

Reactions of the silver salts with bromine. The method selected was the inverse addition procedure described by Conly[13] in which the dry silver salt is added to the carbon tetrachloride solution of bromine. All runs were made and worked up in exactly the same manner with the exception of the temperature at which the reaction was run. The procedure is described as follows.

All apparatus was oven-dried at 110° just before assembly A 300 ml. three necked flask was fitted with a condenser, a pressure equalized addition funnel and a bent-tube adapter which could be rotated to allow the dry silver salt to drop into the reaction flask from a small auxiliary flask. Stirring was performed by a magnetic stirrer. A heating mantle was employed for those reactions carried out a reflux temperature, while a cooling bath was provided for the reactions carried out at 0–25°. The top of the condenser was connected *via* a drying tube to a gas collecting system in order to follow the speed and extent of the reaction by observation of the carbon dioxide evolved. The small auxiliary flask was filled with 38.6 g. (0.10 mole) of the silver salt of the dicarboxylic acid and connected to the reaction flask. A slight excess of dry bromine (11.0 ml., 0.215 mole) was mixed with 200 ml. of anhydrous carbon tetrachloride and placed in the addition funnel over a layer of phosphorus pentoxide on a bed of glass wool. The bromine–carbon tetrachloride mixture was allowed to pass slowly through the drying bed into the flask. This mixture was brought to reflux or cooled to 0° depending on the conditions selected, and then the silver salt was added in small portions. At the lower temperature the reaction started slowly and proceeded very slowly for about 8 hr. as evidenced by the evolution of carbon dioxide. At reflux temperatures the reaction started immediately, was very exothermic, and proceeded as rapidly as the silver salt could be added safely, being complete in less than an hour. As soon as the carbon dioxide evolution was complete the reaction was discontinued. The silver bromide was removed by filtration and the carbon tetrachloride and excess bromine removed by distillation at atmospheric pressure through a short packed column. The residue was fractionated through a short all-glass semimicro column at water pump vacuum. Only one low boiling fraction was found. A residue remained which could not be distilled without decomposition. The distillate was washed several times with cold concentrated sulfuric acid. The acid-insoluble material was separated, treated with dry sodium carbonate, filtered, and refractionated. The products are described in Table I.

TABLE I

PRODUCTS OF THE HUNSDIECKER REACTION WITH THE SILVER SALTS OF *cis*- AND *trans*-1,2-CYCLOHEXANEDICARBOXYLIC ACIDS

Silver Salt	Temp., °C.	% Yield	M.P. °C.	n_{D}^{25}	I.R. Spectrum
cis	0–25	43	−4.8	1.5503	All *trans*
cis	Reflux	47	−4.7	1.5505	All *trans*
trans	0–25	48	−4.5	1.5507	All *trans*
trans	Reflux	37	−2.5	1.5510	All *trans*

Establishment of absence of isomerization. In order to establish whether isomerization of products was taking place, the known *cis*- and *trans*-1,2-dibromocyclohexanes, prepared according to previously described methods[8], were each subjected to treatment with bromine and silver bromide in anhydrous carbon tetrachloride at reflux for 12 hr. The results are presented in Table II.

That the reaction intermediates did not isomerize product was also established by carrying out a completely typical Hunsdiecker reaction on the silver salt of *cis*-1,2-cyclohexane-

---

(11) E. F. Jenkins and E. J. Costello, *J. Am. Chem. Soc.*, **68**, 2733 (1946).

(12) R. P. Linstead, S. B. Davis, and R. R. Whetstone, *J. Am. Chem. Soc.*, **64**, 2009 (1942).

(13) J. C. Conly, *J. Am. Chem. Soc.*, **75**, 1148 (1953).

TABLE II

Attempted Isomerization of the Isomeric 1,2-Dibromocyclohexanes with Silver Bromide and Bromine

	Before Treatment		After Treatment			
Dibromide	M.p., °C.	n_D^{25}	% Recovery	M.p., °C.	n_D^{25}	I.R. spectrum
cis	10.0	1.5512	60	6.5	1.5511	All *cis*
trans	−4.5	1.5505	94	−4.5	1.5505	All *trans*

dicarboxylic acid (using reflux temperature) to which was added a sample of known *cis*-1,2-dibromocyclohexane. The product, worked up in the usual fashion, showed a melting point depression of about 30° and gave an infrared spectrum completely identical with that of a synthetic mixture made up of authentic *cis*- and *trans*-dibromides. The data could not distinguish partial isomerization from complete retention of configuration, but there could be no doubt that a very large portion of the *cis*-1,2-dibromocyclohexane survived the reaction.

cis-1,2-Cyclohexanedicarboxylic acid was also subjected to the treatment with bromine and silver bromide in anhydrous carbon tetrachloride at reflux for 12 hr. The acid was recovered quantitatively with no change in melting point indicating that no isomerization had taken place.

All infrared spectra were obtained using a Baird Associates recording spectrophotometer with a sodium chloride prism. The samples were run as pure liquid films.

Kingston, R. I.

[Communication No. 1875 from the Eastman Kodak Research Laboratories]

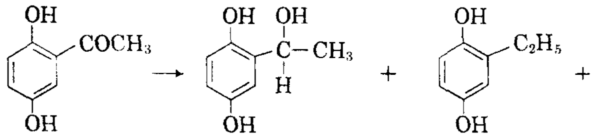
Hydrogenolysis of Acylhydroquinones

J. L. R. WILLIAMS

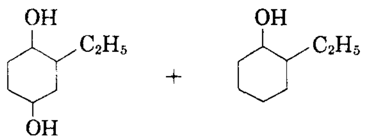
Received January 7, 1957

Four acylhydroquinones have been hydrogenated to the corresponding dialkylhydroquinones at 140–150° and 3000–4000 p.s.i. In the case of 2,5-dihydroxycaprylophenone, the hydrogenation either was stopped at the intermediate carbinol stage or was carried to completion, yielding *n*-octylhydroquinone, by the use of suitable operating conditions.

In an earlier work[1] when acetylhydroquinone (I) was hydrogenated using Adams' catalyst, W-6 Raney nickel, or W-7 Raney nickel catalysts at room temperature and 25–50 p.s.i., the products included 2,5-dihydroxyphenylmethylcarbinol (II), ethylhydroquinone (III), ring hydrogenated products, and possibly some of the corresponding hydrogenolysis products, such as IV and V.



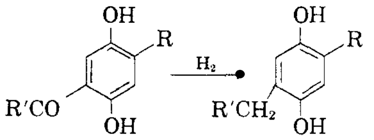
I II III



IV V

The use of copper chromite-type catalysts, such as HJS-2 and Harshaw Cu-X, with proper temperature control made possible the stepwise hydrogenation at about 2000–4000 p.s.i. of acetylhydroquinone (I) to 2,5-dihydroxyphenylmethylcarbinol (II) and ethylhydroquinone (III) in excellent yields.[2]

Since the above work was completed, further examples of the hydrogenolysis reaction have been carried out, using other acylhydroquinones.



R = alkyl or H

Table I summarizes the results obtained when four acylhydroquinones underwent hydrogenolysis at 140–150° and 3000 − 4000 p.s.i.

TABLE I

Hydrogenolysis of Alkylacylhydroquinones

Ketone	Product
2,5-Dihydroxy-4-methylacetophenone	2-Methyl-5-ethylhydroquinone
2,5-Dihydroxy-4-methylpalmitophenone	2-Methyl-5-hexadecylhydroquinone
2,5-Dihydroxy-4-*n*-octylcaprylophenone	2,5-Di-*n*-octylhydroquinone
2,5-Dihydroxycaprylophenone	*n*-Octylhydroquinone

2,5-Dihydroxycaprylophenone can also be hydrogenated under milder conditions to 2,5-dihydroxyphenylheptylcarbinol in low yield. While these hydrogenations require the use of medium-pressure equipment (2000–4000 p.s.i.), the reaction times are convenient, being of the order of 1–2.5 hours.

---

(1) D. D. Reynolds, J. A. Cathcart, and J. L. R. Williams, *J. Org. Chem.*, **18**, 1709 (1953).

(2) J. L. R. Williams, *J. Org. Chem.*, **19**, 1205 (1954).