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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PA.]

Stereochemical Evidence for Bridged Radicals. Photobromination of *cis*- and *trans*-4-Bromo-*t*-butylcyclohexane

BY P. S. SKELL AND P. D. READIO

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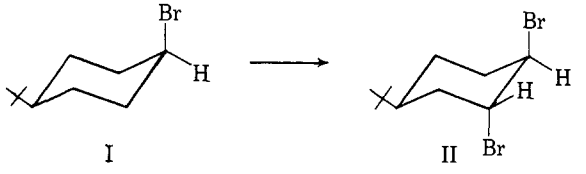
Photobromination of *cis*-4-bromo-*t*-butylcyclohexane (I) is a highly selective reaction, yielding *trans*-3-*cis*-4-dibromo-*t*-butylcyclohexane (II). By contrast, *trans*-4-bromo-*t*-butylcyclohexane is considerably less reactive and less selective to attack by bromine atoms. These results are interpreted in terms of bromine assistance in the transition state and a bridged radical intermediate which opens in accord with the "diaxial rule." This neighboring group effect is operative only with a neighboring axial bromine.

We previously demonstrated that bridged bromine radicals play an important role in photobrominations of alkyl bromides.[1] This paper is concerned with the steric requirements for bromine bridging in a cyclohexane system fixed by the presence of a *t*-butyl group.

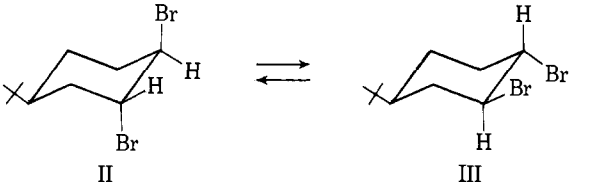
Thaler has reported[2] that the hydrogen abstraction process occurring in the radical–chain photobromination of bromocyclohexane was highly selective, resulting in almost exclusive formation (94%) of *trans*-1,2-dibromocyclohexane. This result, when contrasted with the less selective bromination of chlorocyclohexane,[2] strongly suggested bromine atom assistance in the hydrogen abstraction step.

Results

Photobromination of *cis*-4-Bromo-*t*-butylcyclohexane (I).—Photobromination of *cis*-4-bromo-*t*-butylcyclohexane (I) yielded *trans*-3-*cis*-4-dibromo-*t*-butylcyclohexane (II) as the predominant product (>90%). The



bromination reaction proceeded quickly and gave crude product mixtures, the infrared spectra of which were composites of the spectra of the starting material and the diaxial dibromide II. Vapor phase chromatography (v.p.c.) revealed two peaks in the dibromide region with relative areas of 86:14. A third peak with an area approximately 1% that of the larger peak was also detected. The major peak resulted from the diaxial isomer II while the secondary peak was attributable to *cis*-3-*trans*-4-dibromo-*t*-butylcyclohexane (III). Peak assignments were made by comparing the v.p.c. trace of the crude product with that of a sample containing both isomers II and III. The diaxial dibromide II was prepared by the addition of bromine to 4-*t*-butylcyclohexene, while the mixture of isomers II and III was obtained by heating a sample of II in a sealed ampoule at 135° for 6 hr.[3] Since the infrared spectrum of the crude product contained no positive evidence for the dibromide III (characteristic absorptions, particularly at 14.24 and 14.7 μ, were not observed), it was assumed that this isomer resulted in great part from thermal isomerization[3] of the diaxial isomer II in the heated injection block of the gas



chromatography apparatus. This was supported by the observation that the ratio III:II in a sample as determined by v.p.c. analysis increased as the injection temperature increased. Several small peaks (5%) were also observed with retention times similar to that of the monobromide. One of these was possibly 1-bromo-4-*t*-butylcyclohexene since it appeared before the peak of the saturated monobromide. Heating a sample of the crude product for 25 hr. at 100° in 80% ethanol[4] did not produce 4-*t*-butylcyclohexanone in amounts sufficient for detection by gas chromatographic methods, indicating less than 3% 4,4-dibromo-*t*-butylcyclohexane in the sample.

Additional evidence which supports the above conclusions comes from examination of the n.m.r. spectrum of the crude product (70% dibromide) which showed a characteristic narrow equatorial proton absorption at 283 c.p.s. (base 272–300 c.p.s.) attributable to II and unreacted I. There was only a small nondiscernible broad absorption in the region 220–250 c.p.s. which might be attributed to axial *H*–C–Br protons, in area less than 6% of the total absorptions in the 220–300 c.p.s. region. Since the starting material contained 3% *trans*-4-bromo-*t*-butylcyclohexane (v.p.c.), very little, if any, axial *H*–C–Br is derived from I.[5]

Photobromination of *trans*-4-Bromo-*t*-butylcyclohexane (IV) and *cis*-3-Bromo-*t*-butylcyclohexane (V).—An equimolar mixture of *trans*-4-bromo-*t*-butylcyclohexane

(1) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2849 (1963).

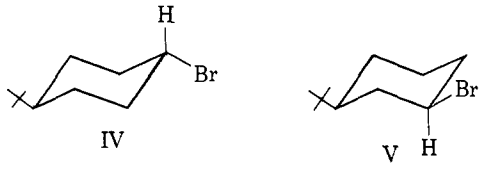
(2) W. Thaler, *ibid.*, **85**, 2607 (1963).

(3) E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **24**, 143 (1959).

(4) The first-order rate constant for solvolysis of 1,1-dibromocyclohexane in 80% ethanol is 75.9×10^{-5} sec.$^{-1}$ at 99.8°: H. L. Goering and H. H. Espy, *J. Am. Chem. Soc.*, **78**, 1454 (1956).

(5) Equatorial proton absorptions occur at lower fields, in narrow, relatively unsplit peaks, than similarly substituted axial protons: L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 115; N. O. Brace, *J. Am. Chem. Soc.*, **84**, 3020 (1962).

(IV) and *cis*-4-bromo-*t*-butylcyclohexane (V) was photobrominated using essentially the same conditions



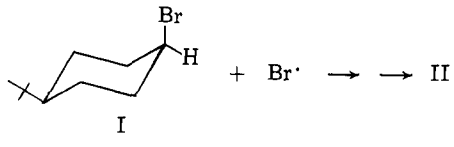
as in the bromination of *cis*-4-bromo-*t*-butylcyclohexane (I). The time of irradiation necessary for complete reaction of bromine (0.8 equiv.) was considerably greater than required for the bromination of I. A v.p.c. analysis of the crude product was obtained, but definitive identification of the products was not attempted. The ratio of unreacted starting materials was essentially unchanged. Two peaks (estimated 53% of product area) came before the starting monobromide peaks and were possibly due to the bromo-*t*-butylcyclohexenes resulting from decomposition of the 4,4- and 3,3-dibromo products. Ten additional peaks (47% product area) were observed in the dibromide region of the gas chromatographic trace.

Competitive Bromination of *cis*- and *trans*-4-Bromo-*t*-butylcyclohexane.—A mixture[6] of *cis*-4-bromo-*t*-butylcyclohexane (I) and *trans*-4-bromo-*t*-butylcyclohexane (IV) in CCl_4, *cis*:*trans* = 1.0:0.15, was photobrominated using 0.8 equiv. of bromine. Analysis employing v.p.c. indicated no detectable loss of the *trans*-bromide IV, whereas 79% of the *cis*-bromide I had reacted (Table I). If one assumes that a 10% loss of the

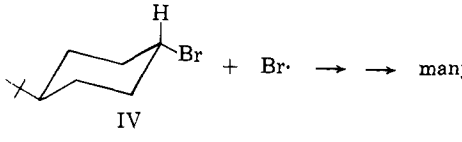
TABLE I
COMPETITIVE BROMINATION

t-Butylcyclohexane	Initial wt., g.	Final wt., g.
cis-4-Bromo- (I)	0.95	0.20
trans-4-Bromo- (IV)	0.14	0.15

trans isomer might not have been detected, then a value of the ratio of rate constants for the brominations of the bromides may be calculated, $k_{cis}:k_{trans} \geqslant 15$.



(1)



(2)

(6) This mixture was prepared from a mixed bromide product (brominative decarboxylation) by dilution with relatively pure *cis* isomer. Brominative decarboxylation of a 4-*t*-butylcyclohexanecarboxylic acid mixture employing mercuric oxide, bromine, and bromotrichloromethane yielded a monobromide product, *cis*:*trans* = 1.8. This result contrasts with that obtained by Eliel and Acharya.[7] They found that the silver salt of either 4-*t*-butylcyclohexanecarboxylic acid gave the same ratio of monobromides (*cis*:*trans* = 0.45) when heated with bromine in CCl_4. On the other hand, Greene, Chu, and Walia[8] showed that the decompositions of both *cis*- and *trans*-dimethyl(4-*t*-butylcyclohexyl)carbinyl hypochlorite in CCl_4 afforded the same isomer distribution of *cis*- and *trans*-4-*t*-butylcyclohexyl chloride (*cis*:*trans* = 2.0).

(7) E. L. Eliel and R. V. Acharya, *J. Org. Chem.*, **24**, 151 (1959).

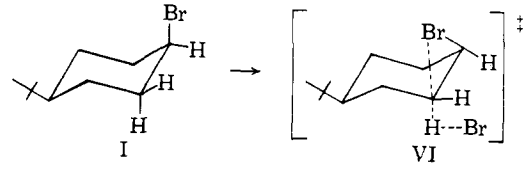
(8) F. D. Greene, C. Chu, and J. Walia, *J. Am. Chem. Soc.*, **84**, 2463 (1962).

Discussion

It is well accepted that the conformational preference which a *t*-butyl group has for the equatorial position is sufficient to preclude chair–chair interconversion of cyclohexyl rings to which it is attached.[9] Thus the *cis* and *trans* configurations of 4-bromo-*t*-butylcyclohexane are conformationally pure, having the bromine substituent fixed in axial and equatorial positions, respectively.

The difference in behavior in radical substitution resulting from a β-bromine fixed in an axial or equatorial position is striking. Reactivities generally observed in radical–chain halogenations are at variance with the observed behavior in two respects. First, tertiary C–H is more reactive than secondary C–H in photobrominations.[10] Second, a halogen deactivates the β-C–H linkages, so that substitution occurs preferentially at the γ-position or beyond, and at the α-position.[11,12] These generalizations apply to an equatorial bromine in the 4-*t*-butylcyclohexane system, but fail to correlate with the observations for an axial bromine substituent.

A high degree of selectivity of bromine atom attack is evident in the photobromination of *cis*-4-bromo-*t*-butylcyclohexane, the product being mainly *trans*-3-*cis*-4-dibromo-*t*-butylcyclohexane (II). The apparent activation of the β-hydrogen is striking in light of the availability of a tertiary hydrogen for abstraction. On the other hand, the brominations of *trans*-4-*t*-butylcyclohexane (IV) and *cis*-3-bromo-*t*-butylcyclohexane (V) are much slower processes and produce a complex mixture of dibromides. These results clearly indicate bromine participation is involved in the abstraction step if the bromine is axial, in a manner analogous to anchimerically assisted solvolyses and *trans* E2 eliminations. The enhanced reactivity of hydrogen β to an axial bromine in photobromination implies bromine assistance in the transition state (VI) for hydrogen abstraction, and little if any assistance with an equatorial bromine.



The nature of the intermediate radical resulting on hydrogen abstraction is also evident in the above results. It has been demonstrated[6–8] that the 4-*t*-butylcyclohexyl radical yields significant amount of *cis* and *trans* isomers on reaction with ROCl and bromine. This implies that both *cis*-3-*cis*-4-dibromo-*t*-butylcyclohexane (VII) and *trans*-3-*cis*-4-dibromo-*t*-butylcyclohexane (II) would likely result from the classical radical VIII.[13] On the other hand, if the

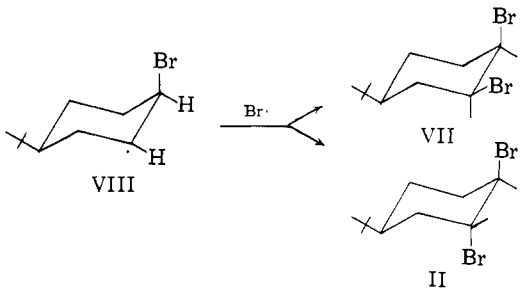
(9) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

(10) M. S. Kharasch, W. Hered, and F. R. Mayo, *J. Org. Chem.*, **6**, 818 (1941); G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4025 (1955); P. C. Anson, P. S. Fredricks, and J. M. Tedder, *J. Chem. Soc.*, 918 (1959).

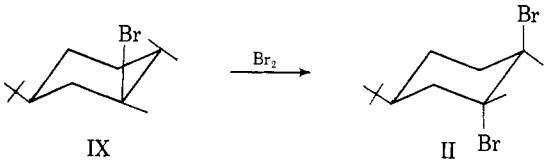
(11) H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, **77**, 4019 (1955); P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960).

(12) M. S. Kharasch, W. S. Zimmt, and W. Nudenberg, *J. Org. Chem.*, **20**, (1955); P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 3530 (1961).

(13) This conclusion is subject to the reservation that the steric effect exerted by the β-bromine atom cannot be estimated. The possibility of equatorial approach being hindered by an adjacent axial substituent is not ruled out, but is unlikely.

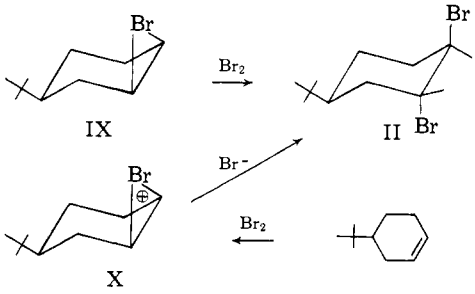


assisting bromine were to remain bridged in the intermediate radical, then reaction of this bridged form would of necessity give a *trans*-dibromide. The maintenance of stereochemistry at C-3 as indicated by nearly exclusive formation of *trans*-3-*cis*-4-dibromo-*t*-butylcyclohexane (II) strongly suggests the intervention of the bridged bromoalkyl intermediate IX with a lifetime sufficiently long to react with bromine before isomerizing to the classical radical VIII.

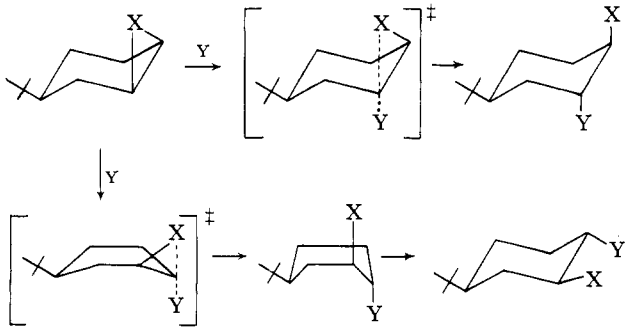


Ring opening of the bridged intermediate on reaction with bromine to give the diaxial dibromide II conforms to the "diaxial rule"[14] for ring openings of epoxides. Attack of bromine at C-4 of the intermediate radical would afford the diequatorial dibromide III, a substance not observed as a primary product in photobromination of I.

It is significant that the diaxial rule applies equally well to the opening of the bridged radical and the corresponding cation X.



The rationale for diaxial opening is derived from consideration of results of the two alternative ring openings. The transition states leading to diaxial products have chair configurations, whereas the diequatorial products are formed *via* boat-like, higher energy, transition states.



(14) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

Experimental

Vapor Phase Chromatography.—All v.p.c. analyses referenced in this paper were accomplished using a 100 ft. × 0.01 in. (i.d.) stainless steel Golay column coated with dioctyl phthalate. A column temperature of 132–135° was used.

cis-**4-Bromo-*t*-butylcyclohexane** (I).—Commercial 4-*t*-butylcyclohexanol was treated with PBr_5 according to the procedure of Eliel and Haber.[3] Several recrystallizations of the monobromide product mixture (v.p.c. indicated *cis*- and *trans*-3- and 4-bromo-*t*-butylcyclohexanes) from pentane at −78° and distillation through a 24 in. spinning band column yielded *cis*-4-bromo-*t*-butylcyclohexane (I), b.p. 80° (4.25 mm.), $n^{25}D$ 1.4888. Analysis by v.p.c. indicated a maximum of 3% *trans*-4-bromo-*t*-butylcyclohexane (IV) and 1% of the presumed *trans*-3-bromo-*t*-butylcyclohexane. The infrared absorptions agreed with those reported[3] and the n.m.r. spectrum (neat sample, Varian A-60) was consistent with a *cis* configuration of the bromide, showing a characteristic equatorial proton absorption at 5.40 τ (275 c.p.s. *vs.* TMS; base width of 15 c.p.s.).

trans-**3-*cis*-4-Dibromo-*t*-butylcyclohexane** (II).—Addition of bromine to 4-*t*-butylcyclohexene[3] gave *trans*-3-*cis*-4-dibromo-*t*-butylcyclohexane (II), b.p. 68° (0.3 mm.), $n^{25}D$ 1.5247. The infrared absorptions agreed with those reported[3]; additional absorptions at 12.32 and 14.24 μ indicated a small amount of the diequatorial dibromide III. The n.m.r. spectrum of II (neat sample, Varian A-60 spectrometer) was consistent with the diaxial relationship of the bromine atoms since it reflected a characteristic equatorial proton absorption at 5.33 τ (280 c.p.s. *vs.* TMS; base width of 23 c.p.s.). The dibromide II was partially isomerized to the diequatorial isomer III (sealed ampoule at 135° for 6 hr.). The infrared absorptions of this latter substance could be assigned; they were consistent with those reported by Eliel and Haber.[3] The n.m.r. spectrum of the isomerized sample indicated approximately 40% isomer III. The axial *H*–C–Br proton absorptions of III appeared at 6.0 τ (240 c.p.s. *vs.* TMS; base width of 40 c.p.s.).

trans-**4-Bromo-*t*-butylcyclohexane** (IV) **and** *cis*-**3-Bromo-*t*-butylcyclohexane** (V).—The filtrate obtained from the recrystallization of the monobromide product mixture (4-*t*-butylcyclohexanol and PBr_5) was treated with sodium ethoxide in refluxing ethanol. The product in petroleum ether was washed several times with concentrated sulfuric acid and distilled to yield a mixture of the bromides, b.p. 80–81° (3.5 mm.), $n^{25}D$ 1.4868. The infrared absorptions were those reported by Eliel and Haber[3] for IV and for the presumed *cis*-3-bromo-*t*-butylcyclohexane (V). Analysis by v.p.c. showed these bromides to be present in nearly equal amounts.

cis- **and** *trans*-**4-Bromo-*t*-butylcyclohexane.**—A mixture of 4-*t*-butylcyclohexanecarboxylic acids was obtained by low pressure hydrogenation of *p*-*t*-butylbenzoic acid according to the procedure of Stolow.[15] Brominative decarboxylation of this acid mixture was accomplished by adding it and mercuric oxide in bromotrichloromethane to a solution of bromine and bromotrichloromethane (75–90°) in a manner similar to that reported by Baker, Holtz, and Stock.[16] A mixture of *cis*- and *trans*-4-bromo-*t*-butylcyclohexane (v.p.c. indicated approximately a 1.8:1 ratio of *cis* to *trans*) was obtained, b.p. 62–63° (1.8 mm.), $n^{25}D$ 1.4911. The infrared spectrum of this product contained absorptions characteristic of I and IV as well as several extraneous absorptions. Analysis by v.p.c. revealed no more than 3% impurity.

Bromination Procedure. *cis*-**4-Bromo-*t*-butylcyclohexane** (I).—The majority of the photobrominations of *cis*-4-bromo-*t*-butylcyclohexane were conducted with carbon tetrachloride as a solvent. The initial quantity of bromine was varied from 0.4 to 2 equiv. The following will indicate the general procedure utilized. *cis*-4-Bromo-*t*-butylcyclohexane (1.0 g., 0.0045 mole) was sealed in an ampoule (helium atmosphere) with bromine 0.3 g., 0.002 mole) and carbon tetrachloride (5 ml.). The ampoule was placed in a water bath (31–40°) and the solution irradiated with a 50-watt frosted bulb. After 1-hr. irradiation, only a very light yellow color remained. The ampoule was opened, the hydrogen bromide and carbon tetrachloride re-

(15) R. D. Stolow, *J. Am. Chem. Soc.*, **81**, 5806 (1959).

(16) F. H. Baker, H. D. Holtz, and L. M. Stock, *J. Org. Chem.*, **28**, 514 (1963).

moved under reduced pressure, and the crude product analyzed by infrared and v.p.c.

The procedure using 2 equiv. of bromine was essentially the same except that after 20 min. irradiation the ampoule was opened and the excess bromine neutralized by addition of the carbon tetrachloride solution to aqueous sodium sulfite.

Experiments employing 0.4, 0.7, 0.75, and 2.0 equiv. of bromine all proceeded readily to give crude products with infrared spectra which were composites of the spectra of I and II. Two small unassigned peaks at 12.31 and 14.43 μ were observed in each case. None of the spectra revealed absorptions characteristic of the diequatorial dibromide III. Analysis by v.p.c. indicated the same relative areas for the diaxial and diequatorial isomers in the chromatograms of each product from the above experiments. That the diequatorial dibromide likely resulted from thermal isomerization in the injection block is suggested by the following evidence. Analysis of a product by v.p.c. with the injection block at 156° indicated II:III = 93:7; with the same sample and the injection block at 218°, II:III = 82:18.

One bromination was run without the use of solvent. *cis*-4-Bromo-*t*-butylcyclohexane (7.0 g., 0.032 mole) and bromine (2.5 g., 0.016 mole) were placed in a small flask equipped with a reflux condenser and magnetic stirring bar. The system was swept out with helium and maintained under positive helium pressure. The flask was immersed in a water bath (10–44°) and the stirred solution was irradiated with a 50-watt frosted bulb until the reaction mixture became colorless (1 hr.). Potassium carbonate was added. Infrared analysis of the product (8.8% in carbon disulfide, 0.33-mm. liquid cells) indicated 52 ± 3% *cis*-4-bromo-*t*-butylcyclohexane (I) and 45 ± 5% *trans*-3-*cis*-4-dibromo-*t*-butylcyclohexane (II). Distillation of the product yielded a fraction with b.p. 64° (0.5 mm.), $n^{25.2}D$ 1.5229, and an infrared spectrum virtually identical with that of II (infrared contained some absorptions characteristic of I).

***trans*-4-Bromo-*t*-butylcyclohexane (IV) and *cis*-3-Bromo-*t*-butylcyclohexane (V).**—In a manner similar to that used for the photobromination of I, a mixture of IV and V was sealed in an ampoule with bromine (0.8 equiv.) and carbon tetrachloride. Irradiation using a 150-watt frosted bulb was accomplished for about 6 hr. (60–66°) and for about 2 hr. (45–60°). After this length of time, only a light yellow color remained. The hydrogen bromide and carbon tetrachloride were removed under reduced pressure and the crude product analyzed by v.p.c. The following peaks were observed: two peaks due to IV and V (retention times = 14–16 min.), two peaks representing 53% of product area (retention times = 11–12 min.), and ten peaks representing 47% of product area (retention times = 27–60 min.).

Competitive Bromination.—A mixture of *cis*-4-bromo-*t*-butylcyclohexane (I) and *trans*-4-bromo-*t*-butylcyclohexane (IV) containing 13% *trans* isomer was prepared from the mixed bromide product (brominative decarboxylation) by dilution with relatively pure *cis* isomer. A weighed sample of this material in CCl_4 and bromine (0.8 equiv.) were placed in a small flask equipped with a condenser and a magnetic stirring bar. The system was swept out with helium and maintained under positive helium pressure. The flask was immersed in a water bath (39–51°) and the stirred solution irradiated for 1 hr. with a 150-watt frosted bulb. The reaction was complete. The hydrogen bromide and the majority of the CCl_4 were removed under reduced pressure and the total weight of the product mixture obtained. A weighed portion of the product was mixed with a known weight of a standard (1,1-diphenylethylene), and v.p.c. analysis accomplished. From the area–weight relationship between the standard and *cis*- and *trans*-bromides, the quantity of each bromide remaining in the product was determined. The ratio of the rate constants for the reaction of each bromide with bromine was then calculated using the expression

$$k_{cis}/k_{trans} = \frac{\log \dfrac{[cis]\ \text{initial}}{[cis]\ \text{final}}}{\log \dfrac{[trans]\ \text{initial}}{[trans]\ \text{final}}}$$

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

Stereochemical Assignments for β-Ketols Formed by Aldol Addition of Three Simple Ketones to *p*-Nitrobenzaldehyde[1]

BY MARTIN STILES,[2a] ROBERT R. WINKLER,[2b] YU-LAN CHANG, AND LEE TRAYNOR[2c]

RECEIVED MARCH 14, 1964

The aldol reactions of cyclohexanone and desoxybenzoin with *p*-nitrobenzaldehyde gave both diastereoisomers of the expected ketols VII and VIII. From 2-butanone and *p*-nitrobenzaldehyde the two diastereomeric ketols II derived from reaction at the methylene group were obtained, in addition to the skeletal isomer I resulting from reaction at the methyl group. Stereochemical assignments for *erythro*- and *threo*-II were based upon the reaction scheme in Fig. 1. The stereochemistry of isomer pairs VII and VIII was determined by means of infrared and n.m.r. spectroscopy.

The general features of the aldol reaction are so well understood that it stands as the mechanistic prototype of many reactions in which carbon–carbon bonds are formed. The fundamental studies by Bonhoeffer and Walters[3] and Bell[4] firmly established the two-step enolization–addition mechanism, through kinetic and deuterium exchange experiments with acetaldehyde. The results of a number of related researches which confirm this mechanism have been discussed by Bartlett.[5]

The enolization of aldehydes and ketones has been subjected to unusually detailed scrutiny, which will not be reviewed here.[6] By contrast, the second step of the

(1) Taken in part from the Ph.D. theses of R. R. Winkler (1961) and L. Traynor (1964) at the University of Michigan.

(2) (a) Fellow of the Alfred P. Sloan Foundation. (b) E. C. Britton Fellow (Dow Chemical Co.) 1959–1960; Sun Oil Co. Fellow 1960–1961. (c) Rohm and Haas Fellow 1962–1964.

(3) K. F. Bonhoeffer and W. D. Walters, *Z. physik. Chem.*, **A181**, 441 (1938).

(4) R. P. Bell, *J. Chem. Soc.*, 1637 (1937); R. P. Bell and M. J. Smith, *ibid.*, 1691 (1958). See also A. Broche and R. Gibert, *Bull. soc. chim. France*, 131 (1955).

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(6) A recent important paper by H. O. House and K. K. Kramar (*J. Org. Chem.*, **28**, 3362 (1963)) discusses the enolization of unsymmetrical ketones, particularly with regard to the position of attack by base and to the question of *cis–trans* isomerism of enolates. The transition state for enolization has been discussed in considerable detail with respect to both extent of bond breakage[7] and preferred geometry.[8,9]

(7) C. G. Swain and A. S. Rosenberg, *J. Am. Chem. Soc.*, **83**, 2154 (1961), and other papers cited there.

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