and rehydrogenated with platinum oxide as catalyst. The infrared spectrum (0.02 mm. neat film) of the product ($n_D^{20.2}$ 1.4479) was identical to *t*-butylcyclohexane except for an extraneous band at 9.0μ. An infrared spectrum in a 0.2 mm. cell revealed however also extraneous bands at 9.4, 13.1, and 14.3μ. These bands can be assigned to *t*-butylbenzene.

Reaction of a Mixture of 3-trans-4-cis- and 3-cis-4-trans-dibromo-t-butylcyclohexane with sodium hydroxide. The dibromide mixture obtained from the reaction of commercial 4-*t*-butylcyclohexanol and phosphorus pentabromide (24.1 g.), was treated with 50% of the calculated amount of sodium hydroxide in 200 ml. 85% ethanol. It was left standing at room temperature for 2 weeks. The alcoholic solution was then poured into water and extracted with pentane. The pentane solution was washed dried and stripped. Twenty g. of residue were obtained. The infrared spectrum of the crude residue showed that appreciable amounts of the diaxial isomer were still present. The crude residue was then boiled with a solution of 3 g. sodium hydroxide in 200 ml. ethanol for 3 hr. It was worked up as before and 15 g. of crude residue was obtained. The material was distilled at 15 mm.

Fraction 1, b.p. 64–90°; fraction 2, b.p. 90–99°; fraction 3, residue. Fraction 1 was an olefinic mixture with bands in the 9μ region and characteristic bands at 12.9, 13.1, 13.6, 14.9, and 15.4μ.

Fraction 2 was a different olefinic mixture with characteristic bands at 12.8, 13.8, and 15.03μ.

Fraction 3 (residue) was mainly diequatorial dibromide with some diaxial isomer and at least one further product, probably an ether. No further attempts were made to separate this complex mixture.

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NOTRE DAME, IND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Conformational Analysis. VI. The Hunsdiecker Reaction with *cis*- and *trans*-4-*t*-Butylcyclohexanecarboxylic Acid[1]

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Reaction of the silver salts of *cis*- and *trans*-4-*t*-butylcyclohexanecarboxylic acid with bromine in boiling carbon tetrachloride gave identical mixtures of 4-*t*-butylcyclohexyl bromides containing 65 ± 3% of the *trans* isomer. Neither the *cis* acid nor the *cis*-bromide is appreciably epimerized under the conditions of the reaction.

The reaction of the silver salt of an organic acid with bromine to give an alkyl bromide, carbon dioxide, and silver bromide: $RCOOAg + Br_2 \rightarrow RBr + CO_2 + AgBr$ is generally known as the Hunsdiecker Reaction.[2] The likely mechanism of this reaction has been discussed extensively[2b–d–4] and it appears that a mechanism involving free radicals as intermediates best fits most of the known facts.[5]

Among the evidence favoring a free radical mechanism are optical studies in systems where the group R is asymmetric at its point of attachment to the carboxylate group.[3,6–10] In all but two[6,7] of these cases an active acid RCOOH gave rise to a racemic bromide R—Br, as is to be expected if the reaction proceeds *via* the radical R·.[11] Of the two remaining cases,[6,7] one,[6] the conversion of silver hydratropate $C_6H_5CH(CH_3)COOAg$ to α-phenethyl bromide, $C_6H_5CHBrCH_3$, is beclouded by the fact that at least three investigators[3,7,12] could not repeat the reaction even with racemic starting material, and that the active bromide, if obtained, should have racemized extensively under the conditions of the reaction.[6,13] In the other instance,[7] the activity of the product was so slight that a small amount of asymmetric induction may be responsible for it.

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[1] Paper V: *J. Org. Chem.*, **24**, 143 (1959).

[2] For reviews, see (a) J. Kleinberg, *Chem. Revs.*, **40**, 381 (1947); (b) R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956); (c) C. V. Wilson in R. Adams, "Organic Reactions", Vol. 9, John Wiley & Sons, Inc., New York, 1957, pp. 332–387; (d) V. Franzen, "Reaktionsmechanismen. Erste Folge," Dr. Alfred Hüthig Verlag, Heidelberg, Germany, 1958, pp. 148–153.

[3] C. E. Berr, Ph.D. Dissertation, University of California, Los Angeles, 1952.

[4] R. E. Krall, Ph.D. Dissertation, University of Colorado, Boulder, 1956; *cf.* Dissertation Abstr., **17**, 2421 (1957).

[5] Some difficulties with this interpretation along with alternative suggestions are discussed in Ref. 4. See also K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955).

[6] C. L. Arcus, A. Campbell, and J. Kenyon, *J. Chem. Soc.*, 1510 (1949).

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

[8] F. Bell and I. F. B. Smyth, *J. Chem. Soc.*, 2372 (1949). One nonreproducible case of formation of an active bromide is reported, along with two reproducible cases yielding inactive bromides.

[9] R. T. Arnold and P. Morgan, *J Am. Chem. Soc.*, **70**, 4248 (1948).

[10] M. Heintzeler, *Ann.*, **569**, 102 (1950). This case refers to a chloride.

[11] *Cf.* E. L. Eliel in M. Newman's *Steric Effects in Organic Chemistry*, John Wiley & Sons, Inc., New York, N. Y., 1956, pp. 140–142; also D. F. DeTar and C. Weis, *J. Am. Chem. Soc.*, **79**, 3045 (1957).

[12] J. Cason, M. J. Kalm, and R. H. Mills, *J. Org. Chem.*, **18**, 1670 (1953).

[13] C. L. Arcus and G. V. Boyd, *J. Chem. Soc.*, 1580 (1951).

Studies involving optically active bromides as products are complicated by the fact that these bromides are apt to racemize quite rapidly under the conditions of the Hunsdiecker reaction[3,6,13] and that it is therefore often difficult to decide whether the obtention of racemic bromide really reflects on the mechanism of the Hunsdiecker reaction, or whether the bromide was racemized after the event. Another, minor, drawback of such studies is that the DL-bromide is both the product of greatest stability and the product of random attack on the radical. These difficulties might be avoided by the use of geometric instead of optical isomers. Four such studies are known. In one,[14] it was shown that both *cis*- and *trans*- cinnamic acid give rise to *trans*-β-bromostyrene in the Hunsdiecker reaction. It was not shown whether *cis*-β-bromostyrene is stable under the conditions of the reaction; demonstration of this point would have been complicated by the unavoidable addition of bromine to the β-bromostyrene. The cinnamic acid case is not strictly comparable with other instances of the Hunsdiecker reaction, since it involves an unsaturated group with sp^2 hybridization at the reaction center. Other pertinent cases are those of the *cis*- and *trans*- cyclohexane-1,2-dicarboxylic acids[15] and the corresponding cyclobutanedicarboxylic acids.[16] These acids gave, exclusively, *trans*-1,2-dibromocyclohexane and -cyclobutane, respectively. In the case of the cyclobutanedicarboxylic acid, the optically active *trans* isomer gave rise to an active *trans*-dibromide. This latter observation[16] precludes a symmetrical intermediate in the reaction—such as an olefin or a symmetrically bridged radical. The significance of the former finding (exclusive formation of *trans*-dibromides from both *cis*- and *trans*-diacids) is not clear. The difference in free energy between the *cis*- and *trans*-dibromides is not known,[17] and therefore one cannot tell to what extent this difference reflects itself in the difference in activation energy for the formation of the two dibromides in the Hunsdiecker reaction. There seems to be little doubt, however, that the diastereoisomeric homogeneity of the product in the reaction of the 1,2-dicarboxylic acids involves some sort of neighboring group effect[19] and therefore does not necessarily bear on the mechanism of the Hunsdiecker reaction in general. Finally, it has been claimed that *cis*- and *trans*-3-methylcyclohexanecarboxylic acids yield the corresponding bromides in the Hunsdiecker reaction with 70% and 95% retention of configuration, respectively.[20] Since the configurational assignments of the bromides used are probably uncertain,[1] and since other work pertaining to the acids[20] was later shown to be in error,[21] this claim should probably be viewed with much reserve.

Having available, in our laboratory, in connection with other problems, pure *cis*- and *trans*-4-*t*-butylcyclohexanecarboxylic acids[22] as well as the corresponding bromides,[18] we felt that a study of the Hunsdiecker reaction in this system would be of interest. Equilibrium between the bromides in this system, corresponding to *ca.* 77% *trans* and 23% *cis* isomer at 25°,[18,23] is neither random (50-50) nor all the way on one side. Moreover control experiments (see Experimental) indicated that the *cis* acid is configurationally stable under the conditions of the Hunsdiecker reaction and that a *cis*-rich bromide is epimerized only to a negligible extent by either silver bromide alone or silver bromide-bromine in carbon tetrachloride, the reaction solvent.[24]

Treatment of the dry silver salts of either *cis*- or *trans*-4-*t*-butylcyclohexanecarboxylic acid with an equivalent amount of bromine in boiling carbon tetrachloride gave a mixture of *cis*- and *trans*-4-*t*-butylcyclohexyl bromides contaminated with an ester (probably the "Simonini ester" 4-*t*-butylcyclohexyl 4-*t*-butylcyclohexanecarboxylate) which was removed by distillation or chromatography. The infrared spectra of the purified bromide frac-

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[14] C. C. Price and J. D. Berman, *J. Org. Chem.*, **23**, 102 (1958).

[15] P. I. Abell, *J. Org. Chem.*, **22**, 769 (1957).

[16] D. E. Applequist and A. S. Fox, *J. Org. Chem.*, **22**, 1751 (1957); see also footnote 2 in that communication.

[17] However, at least in the case of the 1,2-dibromocyclohexane, it would not appear that equilibrium lies all the way on the side of the *trans* compound. The *trans* compound is an equilibrium mixture of about equal amounts of the diequatorial and diaxial isomer [P. Bender, D. L. Flowers, and H. L. Goering, *J. Am. Chem. Soc.*, **77**, 3465 (1955)] and other references there cited—and the *cis* form is an equilibrium mixture of equal amounts of the two enantiomeric equatorial-axial isomers. Hence the geometric isomers differ by only one axial bromide (assuming perfect chair shapes throughout), which difference should not amount to more than about 0.7 kcal./mole.[18]

[18] E. L. Eliel and R. G. Haber, *Chem. & Ind. (London)*, 264 (1958); *J. Am. Chem. Soc.*, in press.

[19] For a similar effect in radical addition to olefins, *cf.* H. L. Goering and L. L. Sims, *J. Am. Chem. Soc.*, **77**, 3465 (1955).

[20] M. Mousseron and R. Jacquier, *Bull. soc. chim. France*, 80C(1951). To the best of our knowledge, experimental details supporting this claim have not been published up to now.

[21] H. L. Goering and F. H. McCarron, *J. Am. Chem. Soc.*, **80**, 2287 (1958).

[22] R. D. Stolow, Ph.D. dissertation, University of Illinois, Urbana, 1956; *cf. Dissertation Abstr.* **17**, 751 (1957). We are grateful to Professor David Y. Curtin for communicating the details of preparation of these acids to us well ahead of publication. We have also employed a modified method of preparation developed and kindly communicated by Professor Harold Hart, Michigan State University.

[23] This equilibrium measurement refers to 87% ethanol as a solvent. However, P. Klaeboe, J. L. Lothe, and K. Lunde, *Acta Chem. Scand.*, **10**, 1465 (1956) report that the relative intensity of the infrared absorption bands due to equatorial and axial bromine in cyclohexyl bromide does not vary when the solvent is changed from cyclohexane to nitromethane and is therefore independent of solvent polarity. Hence it may be assumed that the equilibrium composition is not much different in carbon tetrachloride.

[24] The *cis* isomers were chosen for the control experiments because they are the less stable of each pair.

tion from a number of runs employing *cis* or *trans* acid, or mixtures of the two as starting materials were virtually identical. Infrared analysis, employing the intensity of the 12.24μ, 11.4μ and 8.6μ bands as measure of the concentration of the *trans* isomer and the 11.7μ and 8.0μ bands for the *cis* isomer[1] indicated a composition of 65 ± 3% *trans* isomer for the products.

The fact that both diastereoisomeric silver salts generate the same mixture of bromides would seem to demand a common reaction intermediate from both starting materials. Concerted mechanisms involving rearward attack (whether heterolytic or homolytic) are ruled out, as they should have led to predominant inversion in the configuration of the product. Similarly, internal mechanisms involving frontal attack (similar to the S_Ni mechanism[25]) should have led to predominant retention of configuraion and are therefore inadmissible. A carbonium ion intermediate for the reaction, already ruled out on other grounds,[3,26] is also inconsistent with the present results, as it should have given rise to 3- as well as 4-*t*-butylcyclohexyl bromide.[1] An anion intermediate is unlikely, since there is no obvious reason why a cyclohexanecarboxylate anion should have lost carbon dioxide under the conditions of the Hunsdiecker reaction.[27] We therefore, in agreement with a number of other investigators and reviewers,[2b-d,3] favor a free radical intermediate for the Hunsdiecker reaction in the system and under the conditions of the present study. This does not mean that a different mechanism could not contribute, or even take over, in a different system or under different experimental conditions.

Our product composition (65% *trans*: 35% *cis*) differs from a random mixture (50:50) on the side of the equilibrium composition(77:23 at a slightly lower temperature and in a different solvent).[23] We take this to mean that the product-determining step in the reaction (*i.e.*, the reaction of the intermediate radical R· with bromine from an unspecified source) has an appreciable activation energy, so that the free energy difference of the products can reflect itself in the corresponding transition states to a considerable extent.[28] A radical chain mechanism of the type generally favored for the Hunsdiecker reaction[2b-d] would fulfill this condition.[29]

Careful scrutiny of the data for the one-hour runs in Table I suggests that possibly a little more *trans*-bromide resulted from the *cis* acid than did from the *trans* acid. This was also suggested by a visual inspection of the infrared spectra of the products. We therefore carried out[30] a kinetic analysis of the bromide mixture, using their reaction with thiophenolate in 87% ethanol. The rates of this reaction for the pure *cis*- and *trans*-bromides had been previously determined and differ by the substantial factor of 62.[18] The analysis indicated 57% *trans*-bromide in the product from the *trans* acid and 62% *trans*-bromide in the product from the *cis* acid. While the absolute accuracy of these figures is not so high as that of the infrared analysis, the *difference* between the two products is brought out more clearly by the kinetic analysis. Even so, it cannot be claimed that the trend (which is based on two single experiments) is of unequivocal significance. If real, it may show that in addition to the process involving a common intermediate, there may be a *very minor* contributing mechanism involving inversion of configuration, as claimed by Kenyon *et al.*[6]

TABLE I

SUMMARY OF HUNSDIECKER PRODUCTS

Starting Acid	Reaction Time, Hr.	Yield, %	*trans* Isomer in Product, % (A)[a]	(B)[a]	(C)[a]
cis	1	21.5	66–67	65	68
trans	1	23.9	65–66	60	65
cis	5	25.4	64–65	68	..
trans	5	24.1	68	69	..
Mixed	5	41.2	62–63	..	..
Mixed[b]	5	50.1	67	..	..

[a] 12.42μ and 11.7μ bands used for analysis; (B) based on 11.4μ and 11.7μ bands; (C) based on 8.6μ and 8.0μ bands. [b] Run carried out by Dr. Ralph G. Haber.

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(25) Ref. 11, pp. 79–83.

(26) W. T. Smith and R. L. Hull, *J. Am. Chem. Soc.*, **72**, 3309 (1950).

(27) *Cf.* J. Berman and C. C. Price, *J. Am. Chem. Soc.*, **79**, 5474 (1957).

(28) It is possible though unlikely that predominant formation of the more stable product may be fortuitous—in other words, that the activation energy of the product-forming step may not be related to the free energy of the products but be controlled in some other way. We feel that in cases where the more stable product is obtained predominantly, a causal connection between the activation energy of the product-controlling step and the free energy of the products may be presumed to exist unless there is compelling evidence to the contrary. In this connection, see G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(29) Professor Harold Hart, Michigan State University, has kindly informed us that the decomposition of *cis*- and *trans*-4-*t*-butylcyclohexanecarbonyl peroxides in tetrabromoethane at 50° gives, among other products, identical mixtures of *cis*- and *trans*-4-*t*-butylcyclohexyl bromides containing 52–55% of the *trans* isomer. Infrared comparison indicates the *trans* isomer content of this mixture to be slightly but significantly smaller than that of the Hunsdiecker product. This may be due to the differing nature of the product-forming step. In the reaction studied by H. Hart and H. Lau, this is reaction of the 4-*t*-butylcyclohexyl radical with tetrabromoethane at 50°. The nature of the product-determining step in the Hunsdiecker reaction is not known. It has been suggested to be reaction of the alkyl radical with bromine[2b,d] or with acyl hypobromite.[2c] It is not clear why either of these reactions should be more selective than the reaction of the radical with tetrabromoethane, since the Br—Br and O—Br bonds are weaker than C—Br.

(30) This part of the work was performed by E. L. E. at Harvard University while on a National Science Foundation Senior Postdoctoral Fellowship.

EXPERIMENTAL

Melting and boiling points are uncorrected. Infrared analyses were performed on a Baird double-beam instrument.

4-t-Butylcyclohexanecarboxylic Acids.[22] The *cis* acid melted at 116°, the *trans* acid at 174°. These melting points are in agreement with those reported by other investigators[22] and the infrared spectra of the acids were identical with spectra kindly provided by Professor Harold Hart. The mixed (*cis-trans*) acid employed in some experiments was obtained by catalytic reduction of 4-*t*-butylbenzoic acid over ruthenium oxide catalyst at 100° using a hydrogen pressure of 1000–1800 p.s.i.

Hunsdiecker reaction. Twenty g. (0.11 mole) of 4-*t*-butylcyclohexanecarboxylic acid was added slowly to a hot solution of 5 g. (0.12 mole) of sodium hydroxide in 50 ml. water and the mixture boiled until solution was complete. The solution was filtered, nitric acid was added dropwise to incipient turbidity, and a few drops of sodium hydroxide solution were then added just to clear up the solution again. Slow addition of a solution of 19 g. (0.11 mole) silver nitrate in 30 ml. water, with stirring, produced a copious precipitate of the silver salt which was collected, washed with water, and carefully dried in a vacuum desiccator. The yield of silver salt was quantitative.

To an ice-cooled suspension of 30 g. (0.10 mole) of the dry silver salt in 100 ml. of dry carbon tetrachloride in a three necked flask equipped with a reflux condenser, addition funnel, and efficient stirrer was added 5.4 ml. (15.8 g., 0.10 mole) of bromine dissolved in 20 ml. of carbon tetrachloride. The suspension was heated to boiling and stirred for periods ranging from 1 to 10 hr. It was then cooled and filtered, the silver bromide in the filter being washed with a fresh portion of carbon tetrachloride. The carbon tetrachloride layer was washed with sodium thiosulfate, sodium hydroxide, water, and brine, dried over sodium sulfate, and concentrated. The residue (12.5 g.) was distilled in a small Claisen flask and the product collected in three fractions, b.p. 82–86°/4.5 mm. (1.5 g.), 86–88°/4.5 mm. (7.8 g.), and 100–102°/4.5 mm. (2.0 g.). Fractions 1 and 2 were identical in infrared spectrum and were combined, yield 9.3 g. (41%). The combined fraction was subjected to infrared analysis (see below). In some instances, this fraction contained traces of ester (carbonyl band in infrared), in which case it was dissolved in petroleum ether, percolated through a small alumina column, recovered by concentration, and subjected to analysis.

The high-boiling fraction appeared to be mainly ester, as evidenced by the intensity of its carbonyl band in the infrared.

The above experiment is typical of a number which were carried out with different starting materials (*cis*, *trans*, and mixed) and for different lengths of time. Highest yields of bromide were obtained with the shortest reaction time (1 hr.). In the 10-hr. runs, and, to a much lesser extent, in the 5-hr. runs, the presence of extraneous products [probably 3-*t*-butylcyclohexyl bromide(s)[1]] manifested itself. For this reason, the products of the 10-hr. runs were not analyzed. The various runs are summarized in Table I above.

Infrared analyses. The bromide (0.100 g.) was dissolved in 0.50 ml. carbon disulfide and the infrared spectrum was recorded in a 0.1 mm. cell (using a similar cell filled with carbon disulfide for a blank). Calibration spectra were recorded in a similar way for synthetic mixtures ranging from 25% to 95% *trans* isomer. Compositions were calculated by interpolating the ratio of the intensity of two bands, one characteristic of the *trans* isomer, the other of the *cis* for the unknowns between the corresponding ratios for known mixtures. Combinations used were (A) 12.24μ (*trans*) and 11.7μ (*cis*), (B) 11.4μ (*trans*) and 11.7μ (*cis*), and (C) 8.6μ (*trans*) and 8.0μ (*cis*). The last combination could not be used in the 5-hr. runs, because of interference of the impurities present in these runs. The accuracy of the analysis was estimated as ±3% from the scatter of the data.

Kinetic analysis. Sodium was dissolved in 87% ethanol and the solution titrated against standard acid. Twenty-five ml. of this solution (0.57*N*) were pipetted into a 50-ml. volumetric flask and an excess of thiophenol (1.8 g.) was added. The solution was thermostatted at 25.1°, a weighed amount of the bromide sample was added, and the solution made up to the mark with 87% ethanol at 25.1° and thoroughly mixed. A 5-ml. sample was immediately withdrawn at time zero, quenched into excess standard (*ca.* 0.1*N*) hydrochloric acid, and titrated with standard (*ca.* 0.1*N*) base. The bulk of the solution was blanketed with nitrogen and placed in the thermostat. At appropriate intervals, 5-ml. samples were withdrawn from the flask and quenched and titrated as above, the time of quenching being recorded. The bulk of the solution was blanketed with nitrogen after each such withdrawal. Table II gives the pertinent data for the bromide from the *trans* acid and Table III for the bromide from the *cis* acid.

TABLE II

KINETIC ANALYSIS OF BROMIDE FROM *trans*-ACID

3.276 Millimoles Bromide and 14.25 Millimoles Base in 50 ml.

Time (min.)	0	1101	2460	4257	6069
% Reaction	0	36.1	44.0	46.8	51.3

TABLE III

KINETIC ANALYSIS OF BROMIDE FROM *cis*-ACID

3.892 Millimoles Bromide and 14.19 Millimoles Base in 50 ml.

Time (min.)	0	225	509	836	1423.5	1874.5	3287
% Reaction	0	11.9	22.9	29.8	35.7	37.5	41.0

Using k_{cis} 5.7 × 10^{-3} l. mole^{-1} min.$^{-1}$ and k_{trans} 0.09^{-3} l. mole^{-1} min.$^{-1}$, the data in Table I are best fitted by a composition of 57% *trans*-bromide and those in Table III by 62% *trans*-bromide (remainder *cis*-bromide). The fit was obtained by calculating, empirically, the per cent reaction to be expected for different initial concentrations of *cis*- and *trans*-bromide, corresponding to different compositions of the weighed amount of sample taken. The calculation was performed by means of the integrated form of the second-order rate equation, $\log \frac{a - x}{b - x} = \frac{k(a - b)t}{2.303} - \log \frac{b}{a}$. It was assumed that the two reactions are independent. This is not quite true (since both reactions consume base), but does not introduce a large error in the early stages of the reaction, since the contribution of the *trans* isomer to the total extent of reaction is so small, and since the base was in over 3:1 excess.

Control experiments. (a) The Hunsdiecker reaction was carried out as above, using the silver salt of the *cis* acid as starting material, but employing only half the theoretical amount of bromine. The mixed silver salts, filtered after 1 hr. reflux time, were dried and warmed with dilute hydrochloric acid. The resulting suspension was extracted with petroleum ether and the petroleum ether layer dried over sodium sulfate and evaporated. The residual acid melted at 114–115°, as compared with a melting point of 115–117° for the original *cis* acid. The infrared spectrum of the recovered acid was identical with that of the *cis* acid and did not show the characteristic bands corresponding to the *trans* acid.

(b) A suspension of 0.85 g. of dry silver acetate in 15 ml. of carbon tetrachloride was treated with 0.8 ml. bromine in 10 ml. carbon tetrachloride and stirred for 30 min. at room temperature followed by 30 min. at reflux. To the resulting suspension of silver bromide was added 1 g. of a 4-*t*-butylcyclohexyl bromide mixture very rich in the *cis* isomer.

Stirring was continued at reflux for 5 hr. and the bromide was then recovered in the usual way. The recovered bromide showed a slight increase in the amount of *trans* isomer, as evidenced by the diagnostic infrared bands of the latter, but was still very predominantly *cis*.

(c) The above experiment was repeated, expect that pure *cis*-bromide was used and the bromide was added to the silver acetate suspension one minute *before* bromine addition commenced. In this way, the *cis*-bromide was exposed to *both* bromine *and* silver bromide under the reaction conditions, rather than to silver bromide only. After 1 hr. boiling at reflux with stirring, the mixture was worked up as previously described. The product showed a marked ester band in the infrared at 5.77μ and very weak bands ascribable to the *trans* isomer, the one at 11.4μ being the most prominent (about six scale divisions). However, the recovered material was still very largely *cis*-bromide.

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NOTRE DAME, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CANTERBURY]

The Substituent Constant of the 3,4-Benzo Group

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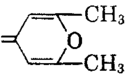
The effect of the 3,4-benzo substituent in different reactions has been examined by analyzing literature data, supplemented by further kinetic studies on the benzoylation of 2-naphthylamine, the alkaline hydrolysis of ethyl 2-naphthylacetate and of 2-naphthoic esters, and the acid-catalyzed esterification of 2-naphthoic acid. The substituent constant ($\sigma_{3,4\text{-benzo}}$) varies systematically with reaction type and it is possible to distinguish σ^-, σ and σ^+ values. The σ^- values display an unexpected anomaly, which is discernible also in the comparable data for the *p*-nitro substituent.

Hammett[1] calculated a value of 0.170 for the substituent constant of the 3,4-benzo substituent, using the dissociation constant of the 2-naphthylammonium ion. In testing this $\sigma_{3,4\text{-benzo}}$ value in nine other reactions he found a probable error of 0.102, one of the largest listed by him. Now for a number of reactions, plots of log k *vs.* σ show that the 3,4-benzo substituent is well removed from the best straight line and that a lower $\sigma_{3,4\text{-benzo}}$ value would provide a better fit. Examples of such reactions are (*a*) R-C_6H_4COOEt + OH^- in dioxane/water (Ref. 2, reaction 47L) (*b*) dissociation of R-$C_6H_4B(OH)_2$ in ethanol/water (Ref. 2, reaction 13) (*c*) R-$C_6H_4COCH_2Br$ + S=  in benzene (Ref. 2, reaction 105a) (*d*) dissociation of R-$C_5H_4NH^+$ in water (Ref. 14). For reaction (*a*) Jaffe[2] has already noted the marked deviation, from the linear plot, of this substituent.

Although a few independent determinations of $\sigma_{3,4\text{-benzo}}$ have been made, Hammett's value is still generally taken as the standard for reference. But if it be assumed that the benzo substituent has the ability to withdraw electrons by the conjugative mechanism (−T), then the substituent constant obtained by Hammett is likely to be a σ^- value. For reactions other than those of phenol or amine derivatives a normal σ value should apply although, with its weak conjugative withdrawal of electrons, this substituent is likely to have σ^- and σ values not greatly different in magnitude. However, it is clearly of interest to know whether such distinct values may be assigned to the 3,4-benzo group and also to learn whether, with its ability to donate electrons conjugatively (+T mechanism) in suitable circumstances, the group requires also a σ^+ value under these conditions. From the literature, data of sufficient accuracy have now been found for the calculation of over 20 sigma values for this substituent. In addition, in order to extend these values, and in one case to confirm a value derived from published data, further kinetic studies have been made.

EXPERIMENTAL

Benzoylation of naphthylamines. The reaction rates of many substituted anilines were measured at 25° by Stubbs and Hinshelwood,[3] and a smaller number of measurements were made by these workers at 40°. The data for 25° fit a Hammett plot exceptionally well in most cases but two amines, of which 2-naphthylamine is one, do not lie on the linear plot. Calculation gives the apparent $\sigma_{3,4\text{-benzo}}$ value as 0.06 (cf. Hammett's value of 0.17) and, to obtain confirmation of this value, the kinetics of reaction of 2-naphthylamine were re-examined using the same technique. Measurements were made over the temperature range 10–45°; the 1-naphthylamine reaction was similarly examined for general comparative purposes. Results are given in Tables I and II, and it will be seen that results at 25° agree well with those of the previous study.

Alkaline hydrolysis of ethyl naphthylacetates (in 87.83% ethanol/water). The only previous work is recorded by

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[1] L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, 1940, Ch. 7.

[2] H. H. Jaffé, *Chem. Revs.*, 53, 237 (1953).

[3] F. J. Stubbs and C. N. Hinshelwood, *J. Chem. Soc.*, 152, S.71 (1949).