TABLE II

RATE CONSTANTS FOR IODINATION IN TRIFLUOROACETIC ACID

$10^3(ArH)_i$, mole/l.	$10^3(ICl)_i$, mole/l.	$10^3k'_{obs}(ArH)_i$, sec.$^{-1}$	k'_{obs}, mole^{-1} l. sec.$^{-1}$
Toluene, t = 25.2°			
225.6	3.82	1.94	0.0086
228	3.82	2.11	.0092^a
112.8	3.82	1.36	.0120
56.4	3.82	0.844	.0149
56.4	7.64	.800	.0142
56.4	15.3	.790	.0140
235	4.00	1.62	.0070^b
224	4.00	1.72	.0075^b
t = 1.6°			
241	4.10	0.276	.00114^b
p-Xylene, t = 25.2°			
51.5	4.27	4.00	.078
25.8	4.27	2.48	.096
25.8	8.55	2.08	.081
25.7	7.96	2.10	.082
12.9	4.27	1.36	.105
2-Iodo-1,4-dimethylbenzene, t = 25.2°			
46.8	4.06	1.50	.032
23.4	4.06	0.865	.037

^{a} Initial HCl concentration of 0.0565 M. ^{b} A separately purified batch of solvent was used for these runs on which the reported activation energy is based.

ant rate constants, k'_{obs}, are reported in Table II. These values are a little less than one-half those obtained for p-xylene. Qualitatively, then, the mechanism of equations 11–13 appears to be satisfactory. Since k'_{obs} values for the aromatic hydrocarbons vary somewhat with the hydrocarbon concentration, a more quantitative test of the above mechanism would require a more elaborate series of rate measurements than has been made. Plans for such measurements were abandoned when the extent of corrosive action of the solvent fumes on the spectrophotometer, and also on the experimenters, became overwhelmingly objectionable.

The k'_{obs} values obtained for toluene were tested to see whether their variation with changing values of $(ArH)_i$ could be explained on the assumption that the equilibrium constant K_2 was large. Values of K_2 calculated from the rate constants, as explained elsewhere,[3] were found to be at least ten times as large as the measured equilibrium constant for the benzene–iodine monochloride complex in trifluoroacetic acid (see the Experimental section). It seems improbable that the equilibrium constants for the benzene and toluene complexes should differ by such a large factor. It seems preferable to ascribe the major share of the diminution in k'_{obs} with increasing aromatic hydrocarbon concentration to a solvent effect similar to that noted for the bromination of mesitylene in acetic acid solution.[4b]

The activation energy for the reaction of toluene with iodine monochloride was calculated from k'_{obs} values for runs at 25.2 and 1.6° as 12.7 kcal. This figure is several kilocalories less than that observed for zinc chloride catalyzed iodinations in acetic acid.[4c]

DAVIS, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Stereospecificity in Brominations of Bibenzyl and Acenaphthene with N-Bromosuccinimide

BY FREDERICK D. GREENE, WILLIAM A. REMERS AND JOSEPH W. WILSON

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Reaction of N-bromosuccinimide and bibenzyl or α-bromobibenzyl in carbon tetrachloride under peroxide initiation affords chiefly *meso*-α,α'-dibromobibenzyl in which the minimum ratio of *meso*- to *dl*-dibromide is 11 to 1. Reaction of N-bromosuccinimide and *erythro*-2-deutero-1,2-diphenylethyl bromide (IIa) affords chiefly *meso*-α,α'-dibromobibenzyl with a 60% loss of deuterium, corresponding to a preference for abstraction of Hb over Ha in IIc of 5 to 1. Reaction of N-bromosuccinimide and acenaphthene affords chiefly 1,2-dibromoacenaphthene for which the *trans*-structure has been established by partial resolution. The results are discussed in terms of the Bloomfield chain mechanism; the stereospecificity of the chain propagating steps is attributed to steric effects and to dipole interactions in the transition state.

The use of N-bromosuccinimide to effect the introduction of bromine at a carbon atom adjacent to an aromatic ring or to a double bond (the Wohl–Ziegler reaction) has been the subject of many investigations.[1] The generally accepted mechanism for this reaction is that proposed by Bloomfield,[2] involving a free radical chain mechanism.

$$\text{N-bromosuccinimide} \xrightarrow{\text{peroxide}} \text{succinimide radical} \quad (1)$$

$$\text{RH} + \text{succinimide radical} \longrightarrow \text{R}\cdot + \text{succinimide} \quad (2)$$

$$\text{R}\cdot + \text{N-bromosuccinimide} \longrightarrow \text{R-Br} + \text{succinimide radical} \quad (3)$$

Information on the initiating steps has been provided by Ford and Waters.[3] The influence of electrical effects on the side chain bromination[4a] and chlorination[4b] of m- and p-substituted toluenes[4] and the influence of steric effects on hydrogen

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(1) For reviews of this work up to 1951, see C. Djerassi, *Chem. Revs.*, **43**, 271 (1948); T. D. Waugh, "N-Bromosuccinimide, Its Reactions and Uses," Arapahoe Chemicals, Inc., Boulder, Colorado, May, 1951.

(2) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

(3) M. C. Ford and W. A. Waters, *J. Chem. Soc.*, 2240 (1952); M. C. Ford, *ibid.*, 2529 (1955).

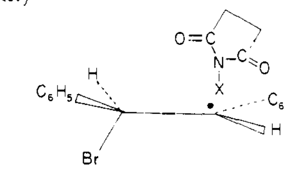
(4) (a) E. C. Kooyman, R. Van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **56B**, 75 (1953); (b) R. Van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954).

abstraction from alkylbenzenes[5] have been elucidated by the work of Kooyman and his collaborators. Much additional evidence, such as the conversion of dimethylaromatic compounds to bisbromomethyl compounds[6] and the conversion of 1,2,5,6-dibenzcycloöctadiene by N-bromosuccinimide to a single isomer of 3,7-dibromo-1,2,5,6-dibenzcycloöctadiene in 88% yield,[7] serve to define further the nature of this reaction. A preliminary report on the isotope effect in the reaction of N-bromosuccinimide on deuterated alkylbenzenes also has appeared recently.[8] The present paper presents evidence bearing on the stereospecificity of the reaction of N-bromosuccinimide with bibenzyl, α-bromobibenzyl and with acenaphthene.

Results and Discussion

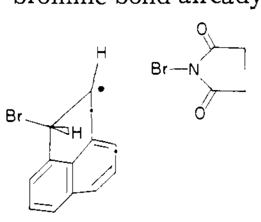
Stereospecificity in the Formation of the Carbon–Bromine Bond.—Bibenzyl has been found to react with two equivalents of N-bromosuccinimide in carbon tetrachloride under benzoyl peroxide initiation to give a 91% yield of *meso*-α,α′-dibromobibenzyl,[9] m.p. 238–239°. Both the *meso*- and the *dl*-isomers are known compounds, and the assigment of the *meso*-structure to the 239° compound and the *dl*-structure to the lower melting isomer of m.p. 113° rests on unequivocal grounds.[10] Analysis of the residual material from this reaction by infrared absorption and by combustion data enables one to set a maximum of 8% on the total possible amount of the *dl*-α,α′-dibromobibenzyl which may have been produced, corresponding to a minimum preference for formation of the *meso*-isomer of about eleven-to-one. This stereochemical result may arise in several different ways. In view of the fact that the *dl*-dibromide is converted to the *meso*-isomer by bromine in carbon tetrachloride in diffuse daylight,[11] the possibility of initial formation of the *dl*-dibromide in the N-bromosuccinimide reaction and subsequent conversion, either directly or indirectly, to the thermodynamically more stable *meso*-isomer was considered. This possibility has been eliminated by allowing bibenzyl to react with N-bromosuccinimide in the presence of added *dl*-dibromide. The amount of *meso*-isomer that was isolated from this experiment was exactly the same as that in the absence of added *dl*-dibromide, and the bulk of the *dl*-isomer was recovered unchanged.

The most probable source of the stereospecificity lies in the reaction of the radical derived from α-bromobibenzyl with N-bromosuccinimide. Of the many possible orientations for the groups in the transition state of this reaction, the one that appears most favorable is that in which the N-bromosuccinimide molecule approaches the radical from the least hindered side, and in which the phenyl groups are as far apart as possible[12] (I, X = Br). (It is overwhelmingly probable that the monobromide is an intermediate in this reaction, further indicated, though not rigorously proven, by the conversion of the monobromide to the *meso*-dibromide under the reaction conditions in the same high yield.)



I

Evidence on the nature of the steric effects operative in the production of *meso*-α,α′-dibromobibenzyl has been obtained by a study of the acenaphthene system (in which the two phenyl rings of bibenzyl are fused together). Reaction of acenaphthene with two equivalents of N-bromosuccinimide in carbon tetrachloride under peroxide initiation affords 1,2-dibromoacenaphthene, m.p. 124–125°, in 65% yield after two recrystallizations from pentane.[13] The assignment of the bromine atoms to the 1,2-positions has been established by oxidation to naphthalic acid[14] and by conversion of the dibromide to known derivatives of 1,2-dihydroxyacenaphthene.[15a] Only one isomer of 1,2-dibromoacenaphthene has been reported (by the bromination of acenaphthylene,[14] by the reaction of N-bromo compounds with acenaphthene[15a] and by the photochemical bromination of acenaphthene[15b]). The partial resolution of this dibromide has now been effected by incomplete reaction with brucine and recovery of the 1,2-dibromide. The optically active 1,2-dibromide has $[\alpha]^{28}\text{D}$ −78° (in chloroform) and possesses an infrared absorption spectrum which is identical with that of racemic material. This establishes the *trans*-structure for the 1,2-dibromide produced by the reaction of N-bromosuccinimide and acenaphthene. In the rigid 1-bromoacenaphthene system, the reaction is considered to proceed by hydrogen abstraction and reaction of the resultant radical with N-bromosuccinimide on the side opposite to the carbon–bromine bond already present.



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[5] E. C. Kooyman and A. Strang, *Rec. trav. chim.*, **72**, 329, 342 (1953); E. C. Kooyman, *Disc. Faraday Soc.*, **10**, 163 (1951).

[6] W. Wenner, *J. Org. Chem.*, **17**, 523 (1952).

[7] A. C. Cope and S. W. Fenton, THIS JOURNAL, **73**, 1668 (1951).

[8] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[9] Two earlier reports on this reaction indicated the formation of stilbene as the major product: Mousseron, *Bull. soc. chim. France*, 759 (1947); R. A. Barnes, THIS JOURNAL, **70**, 145 (1948).

[10] By kinetic data, W. G. Young, D. Pressman and C. D. Coryell, *ibid.*, **61**, 1640 (1939); by X-ray diffraction, J. D. McCullough, *ibid.*, **62**, 480 (1940); by dipole moment data, A. Weissberger, *ibid.*, **67**, 778 (1945).

[11] R. E. Buckles, W. E. Steinmetz and N. G. Wheeler, *ibid.*, **72**, 2496 (1950).

[12] See D. Y. Curtin, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **15**, 111 (1954), for a discussion of the importance of the "*cis* effect" in ionic reactions.

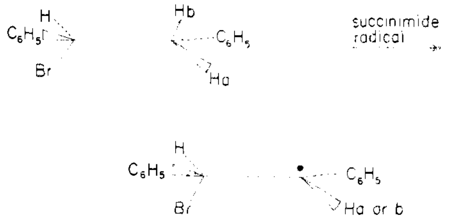
[13] The compound is unstable under the conditions of formation. The actual amount of this isomer that is produced in the reaction is probably considerably higher than the value given above. In addition, a 5% yield of a dibromoacenaphthylene of unknown structure was isolated.

[14] M. Blumenthal, *Chem. Ber.*, **7**, 1092 (1874).

[15] (a) O. O. Orazi and J. F. Salellas, *Anales asoc. quim., Argentina*, **38**, 309 (1950); (b) J. I. Jones, *J. Soc. Chem. Ind. (London)*, **68**, 225 (1949).

Stereospecificity in the Hydrogen Abstraction Step.—The stereospecificity of the step in which the carbon–bromine bond is formed has prompted us to investigate the stereospecificity of the step in which it is postulated that a succinimide radical removes a hydrogen atom from α-bromobibenzyl. The transition state in the conversion of II to III may be subject to the same forces responsible for the stereospecificity of the step in which the carbon–bromine bond is formed. In order to investigate this point, it is necessary to distinguish Ha from Hb. Curtin and Kellom[16] have prepared compound II and related compounds in which Hb was replaced by deuterium. This compound was prepared by their method, involving the ring-opening of *trans*-stilbene oxide with inversion of configuration by means of lithium aluminum deuteride and conversion of the resulting *erythro*-2-deutero-1,2-diphenylethanol to the corresponding bromide IIa, with retention of configuration by reaction of the alcohol with anhydrous hydrogen bromide in a pentane slurry at −78°. The proof of structure of the bromide lies in the stereospecific *trans*-elimination of deuterium bromide by sodium ethoxide in ethanol[16] to give *trans*-stilbene with a loss of 91% of the deuterium, in close accord with the reported loss of 87% of the deuterium content from the *erythro*-bromide prepared by Curtin and Kellom.[16] The residual deuterium in the *trans*-stilbene is most probably due to a small amount of inversion of configuration in the reaction of the *erythro*-alcohol with hydrogen bromide, resulting in formation of about 9% of the *threo*-2-deutero-1,2-diphenylethyl bromide, IIb.

II



III

IIa, Hb = D, Ha = H, *erythro*-bromide + succinimide
IIb, Hb = H, Ha = D, *threo*-bromide
IIc, Hb = Ha = H, α-bromobibenzyl

Reaction of *erythro*-bromide IIa with one equivalent of N-bromosuccinimide under peroxide initiation in carbon tetrachloride proceeded more slowly than in the case of the undeuterated monobromide. Under conditions in which the undeuterated compound afforded *meso*-α,α′-dibromobibenzyl in 91% yield, the *erythro*-deuterobromide gave a 68% yield of the *meso*-dibromide. That the difference in yield was primarily the result of a difference in rate rather than a difference in product composition was established in three ways: (1) conversion of the residue, consisting largely of the monobromide, to *trans*-stilbene; (2) conversion of part of the residue from a duplicate experiment to *meso*-dibromide by treatment with fresh N-bromosuccinimide; (3) conversion of monobromide to *meso*-dibromide in 82% yield from a reaction in which the reaction time and concentrations were increased.[17] The *meso*-dibromide obtained from the *erythro*-2-deuterobromide (IIa), contained only 40% of the original deuterium content.

The isotope effect for hydrogen abstraction from a benzyl carbon atom has been determined for a number of systems.[8] Examination of the limited data[18] reveals that the isotope effect for hydrogen atom removal shows some dependence on the abstracting radical (k_H/k_D for α-deuterotoluene: succinimide radical, 4.9; bromine atom, 4.6; radical derived from acetyl peroxide, 9.9) and on the structure of the substrate (k_H/k_D for radical derived from acetyl peroxide: toluene, 9.9; ethylbenzene, 6.5; diphenylmethane, 6.7). The isotope effect for hydrogen abstraction from α-deuteroethylbenzene by the succinimide radical in carbon tetrachloride is 2.65,[19] which value we shall use as a measure of what the isotope effect for hydrogen abstraction from *erythro*-2-deutero-1,2-diphenylethyl bromide (IIa) would be in the absence of stereochemical control.[20] The observed isotope effect for the reaction of N-bromosuccinimide with *erythro*-2-deutero-1,2-diphenylethyl bromide (IIa), $k_H/k_D = 0.50$,[21] coupled with the predicted isotope effect of $k_H/k_D = 2.65$ for the reaction in the absence of stereochemical control, amounts to *a preference for removal of Hb = H over Ha = H in II of about five-to-one.* It is also important to note that even in the case where Hb is deuterium and in which 40% of the hydrogen atoms Ha are removed in the course of reaction, the yield of *meso*-α,α′-dibromobibenzyl is over 85%. This observation constitutes proof of a two-step mechanism for side-chain bromination by N-bromosuccinimide and is powerful evidence in support of the Bloomfield mechanism.

The stereospecificity of the chain-propagating step in which the carbon–bromine bond is formed is greater than that in which the carbon–hydrogen bond is broken. These results are in accord with a transition state representation as in formula I, in which the greater stereospecificity is associated with the larger atom X. Although steric factors alone may be responsible for the stereospecificity of this N-bromosuccinimide reaction, a consideration of possible importance lies in the high ρ constant,[22] −1.55, reported for the reaction of N-bromosuccinimide with *m*- and *p*-substituted toluenes.[23] The magnitude and negative sign of this ρ constant, determined by competition experi-

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[16] D. Y. Curtin and D. B. Kellom, This Journal, **75**, 6011 (1953).

[17] Quantitative analysis of the products from the deuterobromide suffers from the competing decomposition of the dibromides under the reaction conditions necessary for complete reaction.

[18] Data of Urry and Wiberg, cited in Table 9, ref. 8.

[19] We wish to thank Professor Wiberg for this information.

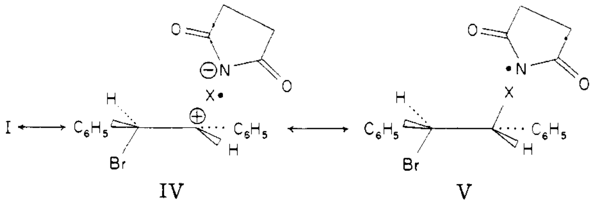
[20] The exact value of the isotope effect in this system could be determined by a study of the reaction of N-bromosuccinimide and the *threo*-deuterobromide (IIb).

[21] The *erythro*-deuterobromide contained about 9% of the *threo*-isomer. Although the rate of hydrogen abstraction from the *threo*-isomer is predicted to be greater than for the *erythro*-isomer, the fact that the concentration of *threo* was considerably less than that of the *erythro* means that roughly 9% of the deuterium in the *meso*-dibromide was derived from the *threo*-isomer even though the reaction had not gone to completion. This correction has been applied in calculating k_H/k_D for the *erythro*-isomer.

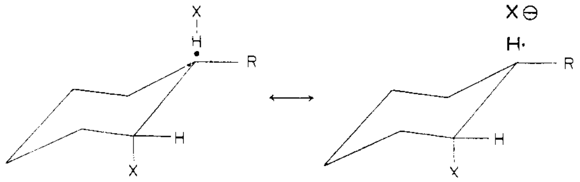
[22] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

[23] E. C. Kooyman, R. Van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **56B**, 75 (1953).

ments, imply a considerable degree of ionic character to the transition state for hydrogen abstraction, with the negative end of the incipient dipole directed away from the site of attack. In the present case, contributions of type IV (X = H) are indicated. The superficial similarity of the transition state for hydrogen abstraction (I ↔ IV ↔ V, X = H) to that for bromine addition (I ↔ IV ↔ V, X = Br) raises the possibility that the stereospecificity in both chain-propagating steps of this N-bromosuccinimide reaction may be dictated not only by the desirability of the placement of the phenyl groups as far apart as possible and approach of the attacking entity from the least hindered side but also by orientation of the newly-forming dipole in opposition to the carbon–bromine dipole already present. This possibility may have a bearing on the general question of the stereospecificity in free radical reactions.[24–29] The free radical additions of hydrogen bromide,[24] hydrogen sulfide,[25] thiophenol[26,27] and thioacetic acid[25,27] to 1-substituted cyclohexenes have been shown to involve predominantly *trans* addition. In all of these cases, the stereochemistry of the product may be partly ascribed to the kind of dipole interactions discussed here. (The original suggestion[24a] of neighboring group participation when X = Br has not been excluded.)



IV V



X = -Br, R = Cl, Br, CH_3
X = —SH, R = Cl
-SC_6H_5, R = Cl
$-\underset{\overset{\|}{S}}{\mathrm{SC}}\mathrm{H_3}$, R = Cl

The addition of a peroxy radical and an oxygen molecule to the double bond of indene has a very low stereospecificity.[29] This case is rather different in character from the ones discussed above, in that the stereochemically controlling step is one of very low activation energy; this case and others have been discussed[29] in terms of Hammond's Thermic Postulate.[30]

Experimental[31]

erythro-**1,2-Diphenyl-2-deuteroethanol** was prepared by a slight modification of the procedure of Curtin and Kellom[16,32] by the reaction of *trans*-stilbene oxide, 7 g. (m.p. 69–70°), with an excess of lithium aluminum deuteride in 90 ml. of ether. The reaction was run overnight at room temperature, diluted with water, and the mixture was extracted 3 times with ether. The ether layer was washed with water, dried over magnesium sulfate, filtered and solvent was removed. Crystallization of the residual oil from hexane yielded 5.72 g. of pure *erythro*-1,2-diphenyl-2-deuteroethanol, m.p. 66–67°. A second crop of 0.63 g., m.p. 65–66°, was obtained, corresponding to a total yield of 90%. *Anal.* 7.31 atom % deuterium, corresponding to 1.02 g. atom deuterium per mole.

erythro-**1,2-Diphenyl-2-deuteroethyl bromide** was prepared by the reaction of hydrogen bromide and the above alcohol in a pentane slurry at −80° according to the method of Curtin and Kellom.[16] The bromide was obtained as an unstable, colorless liquid, $n^{29}\mathrm{D}$ 1.5993.

Elimination of Deuterium Bromide from ***erythro*****-1,2-Diphenyl-2-deuteroethyl Bromide.**—A solution of 0.25 g. of the bromide in 25 ml. of 2 *N* ethanolic sodium ethoxide was heated at reflux for 1 hr. The mixture was diluted with water and extracted with ether. The ether layer was washed with water, dried over magnesium sulfate, filtered and the ether removed, leaving 0.16 g. (93%) of *trans*-stilbene, m.p. 123–124.5°. The infrared absorption spectrum of this material was identical with that of authentic *trans*-stilbene. *Anal.* 0.76 atom % deuterium, corresponding to 0.091 g. atom deuterium per mole.

Reaction of N-Bromosuccinimide and Bibenzyl.—A mixture of 0.67 g. (0.0037 mole) of bibenzyl (Eastman Organic Chemicals, recrystallized from hexane, m.p. 52.5–53.5°), 1.33 g. (0.0074 mole) of N-bromosuccinimide (recrystallized from water, purity 99.5% by titration) and 3 mg. of benzoyl peroxide in 10 ml. of carbon tetrachloride (reagent grade, distilled from phosphorus pentoxide) was heated at reflux for 45 min. The slightly yellow mixture was cooled and filtered. The residue was washed 5 times with 20-ml. portions of hot water to remove succinimide. The water-insoluble residue amounted to 1.14 g. (91.5% yield), m.p. 236–237°, practically pure *meso*-α,α′-dibromobibenzyl. One recrystallization from a large volume of benzene raised the m.p. to 238–239°. The original carbon tetrachloride filtrate was evaporated to dryness; 0.137 g. Trituration of the semi-solid residue with 2 ml. of carbon tetrachloride and filtration afforded 29 mg. of *meso*-α,α′-dibromobibenzyl, m.p. 230–233°, m.m.p. 234–236°. The filtrate was taken to dryness and dried under 0.1 mm. pressure for 24 hr., 0.108 g.

Anal. Calcd. for $C_{14}H_{12}Br_2$: Br, 47.0. Found: Br, 43.84.

Assuming that all of the bromine of this residue is in the form of *dl*-α,α′-dibromobibenzyl, these data set a maximum of 8% over-all yield of the *dl*-dibromide.

Reaction of N-Bromosuccinimide and Bibenzyl in the Presence of Excess N-Bromosuccinimide.—From an experiment identical to the one above, except that 4 equivalents of N-bromosuccinimide was added instead of 2 equivalents, *meso*-α,α′-dibromobibenzyl was isolated in 91% yield.

Reaction of N-Bromosuccinimide and Bibenzyl in the Presence of ***dl*****-α,α′-Dibromobibenzyl.**—An experiment was carried out on exactly the same scale as above with the inclusion of 0.63 g. (0.0018 mole) of *dl*-α,α′-dibromobibenzyl (m.p. 112–113°). The carbon tetrachloride-insoluble, water-insoluble portion weighed 1.11 g. (89% yield), m.p. 237–238°, pure *meso*-α,α′-dibromobibenzyl. The bulk of the *dl*-dibromide was recovered from the carbon tetrachloride filtrate.

Reaction of N-Bromosuccinimide and 1,2-Diphenylethyl Bromide.—A 1.93-g. sample of 1,2-diphenylethyl bromide

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[24] (a) H. L. Goering, P. I. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1952); (b) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

[25] H. L. Goering, D. I. Relyea and D. W. Larsen, *ibid.*, **78**, 348 (1956).

[26] S. J. Cristol and G. D. Brindell, *ibid.*, **76**, 5699 (1954).

[27] F. G. Bordwell and W. A. Hewett, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York City, September, 1954, p. 6-O.

[28] P. S. Skell and R. D. Woodworth, THIS JOURNAL, **77**, 4638 (1955).

[29] G. A. Russell, *ibid.*, **78**, 1035 (1956).

[30] G. S. Hammond, *ibid.*, **77**, 334 (1955).

[31] Melting points are corrected. We are indebted to Dr. S. M. Nagy and his associates for combustion analyses and infrared spectra, and to Jozsef Nemeth for the deuterium analyses.

[32] The procedure is described here in some detail because of the considerable improvement in yield.

was heated at reflux with 1 equivalent of N-bromosuccinimide and 3 mg. of benzoyl peroxide in 10 ml. of carbon tetrachloride for 45 minutes. The *meso*-α,α'-dibromobibenzyl was isolated as before in 89% yield.

Reaction of N-Bromosuccinimide and *erythro*-**1,2-Diphenyl-2-deuteroethyl Bromide.**—A 0.96-g. sample of the deuterium-containing bromide was treated with one equivalent of N-bromosuccinimide by the above procedure. Reaction proceeded more slowly than in the case of the undeuterated bromide. After 45 minutes at reflux, product isolation afforded 0.88 g. (71%) of *meso*-α,α'-dibromobibenzyl, m.p. 236–237°. *Anal.* 3.35 atom % deuterium, corresponding to 0.402 g. atom deuterium per mole.

The carbon tetrachloride-soluble material, 0.33 g., was redissolved in carbon tetrachloride, more N-bromosuccinimide and peroxide was added, and the material was refluxed an additional 30 minutes, affording 126 mg. of *meso*-α,α'-dibromobibenzyl, m.p. 232–234°, m.m.p. 233–235°. *Anal.* 3.18 atom % deuterium, corresponding to 0.382 g. atom of deuterium per mole.

In a duplicate experiment, the carbon tetrachloride-soluble material, 0.32 g., was dissolved in carbon tetrachloride and chromatographed on 6 g. of acid-washed alumina. The first two fractions were evaporated to dryness, 0.253 g., taken up in 2 *N* sodium ethoxide in ethanol and heated at reflux for 1 hour. Isolation by the procedure described previously afforded 115 mg. of impure *trans*-stilbene. Sublimation and recrystallization gave 50 mg. of *trans*-stilbene, m.p. 122–124°, m.m.p. 123–125°.

In one experiment, 0.623 g. of the deuterium-containing bromide was heated at reflux with 0.575 g. of N-bromosuccinimide and 10 mg. of peroxide in 2.5 ml. of carbon tetrachloride for 75 minutes. Product isolation afforded 0.65 g. (82% yield) of *meso*-α,α'-dibromobibenzyl, m.p. 235–236°.

Reaction of N-Bromosuccinimide and Acenaphthene.[15,33]—A mixture of 0.77 g. (0.005 mole) of acenaphthene (Eastman White Label, m.p. 93.5–95°), 1.78 g. (0.01 mole) of N-bromosuccinimide and 5 mg. of benzoyl peroxide in 10 ml. of carbon tetrachloride was heated at reflux for 30 minutes. The orange mixture was cooled and filtered (strong odor of hydrogen bromide) and the residue which consisted chiefly of succinimide was washed with carbon tetrachloride. The filtrate was taken to dryness under reduced pressure, affording 1.5 g. of pale yellow solid, m.p. 80–95°. Recrystallization of a 1.43-g. sample from pentane gave a first crop of 650 mg. of colorless solid, m.p. 118–121°, and a second crop of 310 mg. of less pure 1,2-dibromoacenaphthene, m.p. 90–100°. The filtrate was taken to dryness and treated with 2 ml. of ethanol, yielding 120 mg. of orange plates, m.p. 90–100°. Recrystallization of the first crop of colorless material afforded 1,2-dibromoacenaphthene of m.p. 124–125° (reported[15b] m.p. 124°).

Anal. Calcd. for $C_{12}H_8Br_2$: C, 46.19; H, 2.58. Found: C, 46.09; H, 2.78.

Recrystallization of the orange product from ethanol gave 50 mg. of orange plates, m.p. 113–114°. The compound is inert toward ethanolic silver nitrate solution and has an analysis corresponding to a dibromoacenaphthylene (probably the 1,5-dibromide).

Anal. Calcd. for $C_{12}H_6Br_2$: C, 46.49; H, 1.95; Br, 51.56. Found: C, 46.02; H, 2.14; Br, 51.03.

The ultraviolet absorption spectrum of the compound in ethanol has λ_{max} 351 mμ (log ϵ 4.18), 345 mμ (log ϵ 4.17), 327 mμ (log ϵ 4.54), 281 mμ (log ϵ 3.82), 270 mμ (log ϵ 3.89), 231 mμ (log ϵ 4.65) and two principal minima at 286 mμ (log ϵ 3.61) and 251 mμ (log ϵ 3.73). The positions of the principal maxima and minima are in close accord with those of acenaphthylene, although the values of log ϵ are higher for this dibromo derivative. The compound was converted to a picrate, orange needles from ethanol, m.p. 135–136°.

Partial Resolution of 1,2-Dibromoacenaphthene.—A solution of 1.56 g. (0.005 mole) of 1,2-dibromoacenaphthene and 1.16 g. (0.0025 mole) of brucine in 10 ml. of chloroform was left at room temperature for 64 hours. The chloroform was removed under reduced pressure and the residual oil was treated with ether and 2 *N* hydrochloric acid. The ether layer was extracted 2 times with 2 *N* hydrochloric acid, once with water, dried over magnesium sulfate, filtered and the solvent was removed, leaving a semi-solid. Trituration with 15 ml. of pentane and filtration gave a residue of 390 mg. Recrystallization from 25 ml. of pentane afforded a first crop of 100 mg. of *trans*-1,2-dibromoacenaphthene as colorless prisms, m.p. 125–127°, mixed m.p. with racemic material 125–126°, $[\alpha]^{29}\mathrm{D}$ −78° (3.65% in chloroform), and a second crop of 140 mg., m.p. 124–125°, $[\alpha]^{29}\mathrm{D}$ −23.3° (2.70% in chloroform). The infrared absorption spectra of the racemic and the optically active samples were identical in all respects.

Anal. Calcd. for $C_{12}H_8Br_2$: Br, 51.23. Found: Br, 51.20.

Reaction of *trans*-**1,2-Dibromoacenaphthene and Excess Brucine.**—A solution of 1.2 g. of the dibromide and 3.0 g. of brucine in 10 ml. of chloroform was heated at reflux for 15 hours. Isolation of the product by the above procedure afforded 0.4 g. of a dark oil, presumably 1-bromoacenaphthylene.[34] The material may be crystallized at low temperatures. The oil was converted to a picrate as long fine yellow needles from ethanol, m.p. 145–146.5°. The analysis of the picrate corresponds to a 1:1 complex of picric acid and 1-bromoacenaphthylene.

Anal. Calcd. for $C_{18}H_{10}BrN_3O_7$: C, 46.96; H, 2.19; Br, 17.37; N, 9.13. Found: C, 46.73; H, 2.48; Br, 17.35; N, 8.85.

The ultraviolet absorption spectrum of the picrate in ethanol has λ_{max} at 346 mμ (log ϵ 4.31) and at 324 mμ (log ϵ 4.30) and $\lambda_{min.}$ at 282 mμ (log ϵ 3.51), from which it may be calculated that 1-bromoacenaphthylene has λ_{max} at 324 mμ (log ϵ 4.14) and $\lambda_{min.}$ at 282 (log ϵ 3.23).

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[33] Ng. Ph. Buu-Hoi, *Ann.*, **556**, 1 (1944), has reported the isolation of 5-bromoacenaphthene from these reactants, but analytical data are lacking and the products were subjected to drastic conditions.

[34] This compound was first prepared by Blumenthal (ref. 14) who reported its conversion to a picrate but did not give the m.p.