

extraction with methylene chloride gave the ketonitrile as a pale yellow oil. Distillation from an oil-jacketed flask at 170° (0.001 mm.) gave 8.2 g. (41% yield) of product; 24% yield over-all from 4-benzoyloxycyclohexanone; 2,4-dinitrophenylhydrazone, m.p. 161–162°.

Anal. Calcd. for C₂₀H₁₈N₂O₃: C, 58.67; H, 4.68; N, 17.11. Found: C, 59.02; H, 4.83; N, 17.24.

b.—A solution of 6.0 g. (0.029 mole) of 4-benzoyloxycyclohexanone and 3.0 g. (0.042 mole) of pyrrolidine in 60 ml. of benzene was refluxed under nitrogen with an azeotropic water separator for 4 hours. The benzene and excess pyrrolidine were then removed *in vacuo* and the residual enamine dissolved in 50 ml. of dry dioxane. The solution was stirred in an ice-bath and a solution of 1.9 g. (0.031 mole) of cyanogen chloride in 8 ml. of dry ether was added in one portion.

After stirring the suspension for 3 hours in the cold, followed by gradual warming to room temperature, it was poured into 300 ml. of ice-water and 200 ml. of methylene chloride. After acidification to pH 4 the mixture was shaken for 20 minutes, separated and extracted twice more with methylene chloride. The combined methylene chloride solution was extracted 6 times with 100-ml. portions of iced 0.5% KOH, the combined basic solutions acidified to pH 4 and extracted thoroughly with methylene chloride. Evaporation and distillation as under a gave 1.7 g. (25% yield) of product with an infrared spectrum identical with that of the material under a. Repeating the reaction with 2.9 g. (0.029 mole) of triethylamine added to the enamine solution gave 3.7 g. (55% yield) of product.

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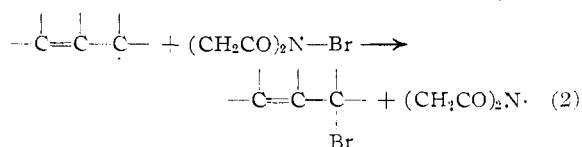
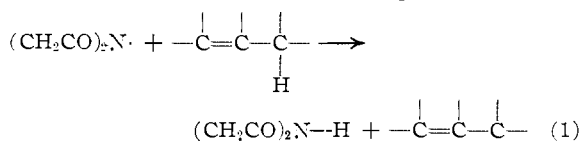
N-Bromosuccinimide. III. Stereochemical Course of Benzylic Bromination¹

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RECEIVED APRIL 6, 1959

While the general radical-chain nature of the allylic bromination reaction of alkenes by NBS is now well established, details of the mechanism such as the degree of freedom and the stereoconfiguration of the intermediate radical are not known. Use of the criteria of double bond migration (formation of isomeric allylic bromides) and of geometrical isomerization about the double bond in the reaction of alkenes with NBS has failed to provide conclusive evidence on these points. The present study utilizes a third criterion, stereochemical course with an optically-active reactant, for this purpose. (–)-α-Deuterioethylbenzene, prepared by the method of Eliel, has been shown to react with NBS in refluxing carbon tetrachloride with benzoyl peroxide initiation to produce phenylmethylcarbinyl bromide with at least 99.7% racemization. Since (+)-phenylmethylcarbinyl bromide has been found to be configurationally stable under the reaction and work-up conditions, this result is consonant only with the interpretation that the benzylic bromination reaction involves a completely free α-phenethyl radical intermediate that undergoes racemization at least 600 times faster than it displaces on NBS.

Considerable evidence has accumulated, since the discovery of the reaction by Ziegler and co-workers,³ that the N-bromosuccinimide (NBS) reacts with alkenes to form allylic bromide products by a radical chain mechanism involving initiation by various radical sources and propagation by steps 1 and 2.⁴ Certain other aspects of the reac-



tion, formation of isomeric allylic bromide products, geometrical isomerization about the double bond during the reaction and stereochemical course of the substitution, also have important bearing on more intimate details of the reaction mechanism, particularly in establishing the degree of freedom and the configuration of the intermediate allylic radical.

Formation of a free allylic radical intermediate in the reaction of an alkene with NBS would be

(1) (a) Taken from the Ph.D. Thesis of Layton L. McCoy, University of Washington, 1951. (b) Supported in part by research contract No. N8-onr-52007 with the Office of Naval Research, U. S. Navy.

(2) Predoctoral Fellow, Atomic Energy Commission, 1950–1951.

(3) K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 80 (1942).

(4) For a recent summary of evidence and pertinent references; see H. J. Dauben, Jr., and L. L. McCoy, *THIS JOURNAL*, **81**, 4863 (1959).

pected to lead to the formation of the two possible isomeric allylic bromide products (neglecting, for the present, geometrical isomers). In a number of cases (mainly 1-alkenes) mixtures of the isomeric allyl bromides have been shown to be formed, and in some other cases the only isolable allylic bromide product has been found to possess the isomerized structure.⁵ While such observations might be regarded as evidence for a mesomeric free radical intermediate, Bateman and co-workers⁶ have pointed out that this conclusion is justified only if it has been demonstrated that the isomeric allylic bromide products have been formed in kinetically-controlled, not thermodynamically-controlled, proportions. Since, in the only cases so far examined, these same workers⁶ have shown that the mixtures of allylic bromides formed from the reaction with NBS are the same as those produced by thermal equilibration of similar allylic bromides, it is obvious that the allylic isomerization criterion has not yet provided convincing evidence of a free radical intermediate in the NBS reaction.

The occurrence of geometrical isomerization during the reaction of NBS with the less stable alkene isomer would also indicate a mesomeric free radical

(5) References given in: (a) C. Djerassi, *Chem. Revs.*, **43**, 271 (1948); (b) T. D. Waugh, "NBS, Its Reactions and Uses," Arapahoe Chemicals, Inc., Boulder, Colo., 1951; (c) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 381–386. The report of F. L. Greenwood and M. D. Kellert (*THIS JOURNAL*, **75**, 4842 (1953)) that 2-heptene with NBS gave only 4-bromo-2-heptene apparently represents the only case in which a single unisomerized allylic bromide has been formed when isomeric allylic bromide products would have been expected.

(6) L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 941 (1950); L. Bateman, J. I. Cunneen, J. M. Fabian and H. P. Koch, *ibid.*, 936 (1950).

intermediate, provided prior isomerization of the alkene and subsequent isomerization of allylic bromide product could be excluded by appropriate control experiments. Studies of this type are simplified by the use of alkenes conjugated with carbonyl, nitrile or aryl groups to avoid the complication of double bond migration. Exploratory studies have shown that alkyl-substituted maleic esters are not suitable for this purpose, primarily because initiators needed for allylic bromination also effect prior geometrical isomerization.⁷ Soon thereafter, Couvreur and Bruylants reported that the benzoyl peroxide-initiated reaction of NBS with either *cis*- or *trans*-crotononitrile gave the same mixture of *cis*- and *trans*-bromocrotononitriles and claimed that this indicated a common mesomeric radical intermediate.⁸ Inasmuch as these workers established only that the product mixtures contained approximately equal quantities of the two isomeric products and failed to demonstrate the absence of prior or subsequent geometrical isomerization, this cannot be regarded as unequivocal evidence of a free radical intermediate in the allylic bromination reaction.

Determination of the steric course of a NBS substitution reaction might also be used to provide information about the nature of the reaction intermediate. Greene, Remers and Wilson⁹ have shown that brominations of bibenzyl and acenaphthene by NBS follow a stereospecific course to yield, predominantly, the more stable dibromide isomers. This stereospecificity, which arises in the introduction of the second bromine atom, was ascribed to control of the direction of approach of NBS by steric and dipolar repulsions of substituents on the intermediate radical. Similar arguments were evoked to explain the stereospecificity of the preceding chain step, attack of succinimidyl radical on α -bromobibenzyl, which could be demonstrated by the use of its α' -deuterio derivative. While these observations would appear to indicate a two-step radical chain mechanism for benzylic bromination by NBS, analogous to the propagation steps originally proposed by Bloomfield¹⁰ for allylic bromination, they fail to provide conclusive information about the freedom or the stereoconfiguration of the presumed radical intermediate in these NBS reactions. Due to the fact that the direction of substitution is dictated by steric and dipolar repulsions of substituent groups, the same stereospecific course would be expected from a radical intermediate with planar, inverting pyramidal or fixed pyram-

idal¹¹ configuration, as well as one with neighboring bromine group participation.¹²

Elucidation of the steric course of a displacement reaction or the stereoconfiguration of its intermediate usually is accomplished best by the use of an optically-active reacting center. Complications of induced asymmetric synthesis, formation of *meso*-DL mixtures, and control of substitution course by steric and dipolar interactions of adjacent substituents are avoided when the reactant has only a single asymmetric center. The structural requisites of a satisfactory allylic system, a double bond *trans*-substituted by a conjugated carbonyl, nitrile or aryl group (to avoid geometric and allylic isomerization) and an asymmetric carbon center, are fulfilled by such systems as ethyl 4-methyl-2-hexenoate and 3,7-dimethyl-1-phenyl-1-octene, both potentially available in optically-active forms from citronellal. Exploratory studies indicated that neither of these compounds would be satisfactory; with NBS the latter compound yielded addition dibromide but no isolable allylic bromide¹ and the former compound would be expected on the basis of studies on its lower homolog (ethyl 4-methyl-2-pentenoate),¹³ to yield a *t*-allylic bromide product insufficiently stable to be useful in the present type of study.

More successful results were obtained from the study of the benzylic bromination by NBS of optically-active α -deuterioethylbenzene (I), previously prepared by Eliel.¹⁴ Use of this reactant possessed several obvious advantages: (i) its optically-active forms are relatively easy to prepare, (ii) its structure precludes the possibility of geometrical or allylic isomerization, (iii) its bromination product phenylmethylcarbinyl bromide (II), being only a *secondary* benzylic bromide, is known to be relatively stable,¹⁵ (iv) the optically active forms of phenylmethylcarbinyl bromide are known^{15,16} and can be used to assess their optical stability under reaction and work-up conditions, and (v) the specific rotations and the absolute configurations¹⁷ of the enantiomeric bromides are known so that the amount of retention, inversion or racemization occurring in the NBS reaction can be evaluated.

Optically-active α -deuterioethylbenzene was prepared by the method of Eliel.¹⁴ D-(-)-Phenylmethylcarbinol (89.2% optical purity) with thi-

(7) H. J. Dauben, Jr., and L. L. McCoy; see ref. 1 for details of the following summary. Dimethyl maleate with NBS in refluxing carbon tetrachloride readily isomerizes to dimethyl fumarate in the presence of diffuse daylight or added benzoyl peroxide but is unchanged in their absence; under the latter conditions allylic bromination of stale cyclohexene is accomplished readily without isomerization of the maleic ester. Dimethyl methylmaleate with NBS in refluxing carbon tetrachloride and in the absence of light is recovered unchanged when peroxide-free but reacts slowly when stale to give dimethyl methylfumarate and its γ -bromination product. Under peroxide-free conditions even diffuse daylight is sufficient to initiate allylic bromination of dimethyl methylfumarate.

(8) P. Couvreur and A. Bruylants, *Bull. soc. chim. Belges*, **61**, 253 (1952).

(9) F. D. Greene, Jr., W. A. Remers and J. W. Wilson, *THIS JOURNAL*, **79**, 1416 (1957).

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

(11) The minimum energy conformation of ethyl or substituted ethyl radicals might be expected to have substituents on the trigonal carbon staggered with respect to those on the adjacent tetrahedral carbon (*cf.*, ref. 30a); in the present case benzylic resonance would tend to flatten the trigonal carbon atom more than in the unsubstituted ethyl radical.

(12) Similar to that originally suggested (by H. L. Goering, P. I. Abell and B. F. Aycock, *THIS JOURNAL*, **74**, 3588 (1952)) to explain the stereospecific addition of hydrogen bromide to alkenes by a radical mechanism.

(13) H. J. Dauben, Jr., and L. L. McCoy, *J. Org. Chem.*, **24**, in press (1959).

(14) E. Eliel, *THIS JOURNAL*, **71**, 3970 (1949).

(15) (a) C. L. Arcus, A. Campbell and J. Kenyon, *J. Chem. Soc.*, 1510 (1949); (b) C. L. Arcus and G. V. Boyd, *ibid.*, 1580 (1951).

(16) (a) W. Gerrard, *ibid.*, 848 (1945); (b) W. Gerrard, *ibid.*, 741 (1946).

(17) (-)-Phenylmethylcarbinyl bromide and (-)-phenylmethylcarbinyl chloride are both related to (-)-phenylmethylcarbinol which in turn is related to D-(+)-glyceraldehyde if its methyl group is regarded as derived from the aldehyde group of the latter (*cf.* J. A. Mills and W. Klyne, "Progress in Stereochemistry," Butterworth Scientific Publication, London, 1954, Vol. 1, pp. 186-187).

onyl chloride alone gave by a partial retention mechanism D(-)-phenylmethylcarbonyl chloride (42.2% optical purity). Treatment of the chloride with lithium deuteride-lithium aluminum deuteride in tetrahydrofuran furnished α -deuterioethylbenzene in 72% yield with $[\alpha]^{23D} - 0.293^\circ$ (1 dm., neat), in good agreement with the results of Eliel. Assuming that deuteride ion is introduced by a displacement mechanism, for which good evidence exists,¹⁸ the enantiomorph obtained has the L(-)-configuration and is 41.6% optically pure (corrected for 1.37% d_0 content).¹⁹

Initial attempts to prepare optically-active phenylmethylcarbonyl bromide, needed to establish its optical stability under the NBS bromination conditions, from optically-active phenylmethylcarbinol by the phosphorus tribromide-pyridine-carbon disulfide method of Gerrard¹⁶ were completely unsuccessful. Adaptation of his phosphorus oxychloride-pyridine-carbon disulfide method²⁰ by substitution of phosphorus oxybromide proved to be more satisfactory and D(-)-phenylmethylcarbinol (89.2% optical purity) was converted to L(+)-phenylmethylcarbonyl bromide (75.2% optical purity) in low yield. Subsequent to our work, Arcus and Boyd^{15b} used essentially the same method to obtain optically-pure phenylmethylcarbonyl bromide in 42% yield.

Previous studies²¹ had shown that benzylic bromination of toluene by NBS required the use of initiators, such as benzoyl peroxide, for rapid reaction; later work by Wiberg and Slaugh²² has demonstrated that equally satisfactory results are obtained when ultraviolet light initiation is used for benzylic brominations of toluene, ethylbenzene and cumene. In the present work it has been found that ethylbenzene readily undergoes benzylic bromination by NBS in refluxing carbon tetrachloride in the presence of 1 mole per cent. benzoyl peroxide to give 80-90% yields of phenylmethylcarbonyl bromide and quantitative yields of succinimide. Even though air-dried samples of NBS gave faster reactions (*ca.* 25 min.), material dried over phosphorus pentoxide reacted sufficiently rapidly (40-55 min.) and was used throughout this study to avoid possible side-reactions.

Control studies using optically-active phenylmethylcarbonyl bromide clearly indicated that any optically-active benzylic bromination product which might be formed from the reaction with optically-active α -deuterioethylbenzene would suffer at most slight racemization under reaction and work-up conditions. When heated under reflux with NBS in carbon tetrachloride, optically-

active phenylmethylcarbonyl bromide showed less than 2% racemization in 25 min.; this result is in good accord with the observation of Arcus, Campbell and Kenyon^{15a} that the same bromide undergoes only 0.6% racemization when heated under reflux with silver bromide in carbon tetrachloride for 1 hr. Furthermore, when bromination of ethylbenzene by NBS in refluxing carbon tetrachloride with benzoyl peroxide initiation was conducted in the presence of added optically-active phenylmethylcarbonyl bromide, yield and optical rotation of the isolated product defined a lower limit of 41% yield with 30% racemization and an upper limit of 72% yield with no racemization. Since yields in this bromination reaction were consistently in the range of 80-90%, only the upper limit is significant and little or no racemization of the optically-active bromide occurred in the reaction.

Reaction of L(-)- α -deuterioethylbenzene with $[\alpha]^{23D} - 0.293^\circ$ (41.6% optical purity) with dry NBS in dry, refluxing carbon tetrachloride containing 1 mole per cent. benzoyl peroxide occurred readily to give an 82% yield of isolated phenylmethylcarbonyl bromide with $[\alpha]^{23D} - 0.020 \pm 0.010^\circ$. The isotope effect, k_H/k_D , for the reaction of NBS with this sample of α -deuterioethylbenzene was found to be 2.67 ± 0.04 .²³ With the reasonable assumption that phenylmethylcarbonyl bromide and its α -deuterio analog have the same specific rotations,²⁴ the rotations of products expected by different substitution mechanisms may be estimated: (a) complete retention would give A and B in a ratio of 2.67:1.00 and have $[\alpha]_D - 18.3^\circ$; (b) complete inversion would give C and D in a ratio of 2.67:1.00 and have $[\alpha]_D + 18.3^\circ$; and (c) complete racemization would give A, B, C and D in a ratio of 2.67 (A + C): 1.00 (B + D) and have $[\alpha]_D 0.0^\circ$. Consequently, the bromo product from the reaction of NBS with this sample of α -deuterioethylbenzene was no more than 0.11% optically active and the reaction had occurred with at least 99.7% racemization.

Since it has been shown that optically-active phenylmethylcarbonyl bromide is essentially optically stable under the NBS reaction conditions, it must be concluded that complete racemization has occurred at some intermediate step in the substitution reaction. Considerable evidence has been obtained in support of a radical chain mechanism for the allylic bromination of alkenes by NBS⁴ and analogy,²⁵ as well as experimental observations,^{21,25}

(18) L. W. Trevoy and W. G. Brown, *THIS JOURNAL*, **71**, 1675 (1949).

(19) On this basis optically pure α -deuterioethylbenzene would be expected to have $[\alpha]^{23D} 0.70 \pm 0.03^\circ$ (1 dm., neat). The lower value ($[\alpha]^{23D} 0.33^\circ$) implied in the work of Eliel was based on the assumption, since proved incorrect,¹⁸ that optically pure phenylmethylcarbonyl chloride had $[\alpha]^{23D} 50.6^\circ$.

(20) W. Gerrard, *J. Chem. Soc.*, 106 (1945).

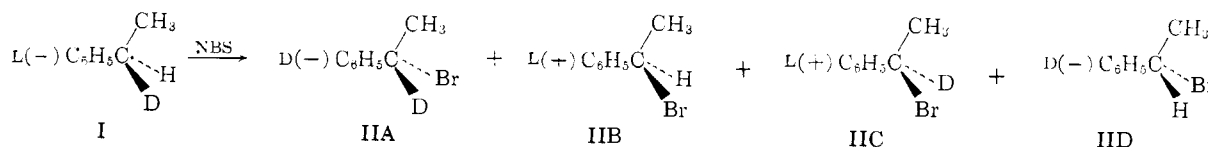
(21) Ng. Ph. Buu-Hoi, *Ann.*, **556**, 1 (1944); H. Schmid and P. Karrer, *Helv. Chim. Acta*, **31**, 1067 (1948). The apparent need of added initiators (*e.g.*, benzoyl peroxide, light) for successful benzylic brominations of simple alkylbenzenes by NBS is probably related to the fact that these hydrocarbons, in contrast to alkenes, do not form hydroperoxides readily on autoxidation (*cf.* ref. 5c, p. 408).

(22) K. B. Wiberg and L. H. Slaugh, *THIS JOURNAL*, **80**, 3033 (1958).

(23) We are indebted to Drs. K. B. Wiberg and L. H. Slaugh (ref. 22; L. H. Slaugh, Ph.D. Thesis, Univ. of Washington, 1956) for determinations of the deuterium content of our samples of α -deuterioethylbenzene and its bromination product.

(24) A. Streitwieser, *THIS JOURNAL*, **75**, 5014 (1953) and **77**, 1117 (1955) has found that samples of 2-octanol-2-d of "near optical purity" had maximum $[\alpha]_D \pm 9.54^\circ$ (1 dm., neat). Since the maximum reported rotations for non-deuterated 2-octanol are $[\alpha]^{23D} \pm 9.84^\circ$ (T. M. Lowry and E. M. Richards, *J. Chem. Soc.*, **125**, 1593 (1924)) and $[\alpha]^{20D} \pm 9.76^\circ$ or $[\alpha]^{25-5D} \pm 9.51^\circ$ (R. H. Pickard and J. Kenyon, *ibid.*, **99**, 45 (1911)), it is likely that 2-octanol and 2-octanol-2-d have the same, or nearly the same, rotations.

(25) Allylic and benzylic hydrogens have similar bond dissociation energies and the corresponding radicals have similar (extra) resonance energies (20-22 kcal. mole⁻¹). Both allylic and benzylic brominations by NBS are induced by light or by radical-forming initiators such as peroxides. The σ (E. C. Kooyman, R. Van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschappen Proc.*, **B56**, 75 (1953)) and k_H/k_D



strongly sustain a similar mechanism for benzylic bromination involving benzyl radicals as intermediates. Then on this basis racemization must have taken place on formation of the benzylic radical by abstraction of α -hydrogen or α -deuterium atoms from the optically-active α -deuterioethylbenzene by the chain-carrying succinimidyl radicals. The intermediate α -phenethyl radical, accordingly, must either be formed in a planar configuration or in a rapidly inverting trigonal pyramidal configuration with inversion occurring faster than reaction of the radical with NBS.²⁶ On the basis of the difference between observed and expected rotations it may be estimated that racemization of the α -phenethyl radical intermediate must have occurred at least 600 times faster than its displacement reaction on NBS.

It is now evident that complete, or essentially complete, racemization of a potentially optically-active radical intermediate has been demonstrated in at least five different cases: (i) chlorination of optically-active 1-chloro-1-methylbutane by sulfur chloride with peroxide and by chlorine with light,^{27a} (ii) *t*-butyl peroxide-induced decarbonylation of optically-active methylethylisobutylacetaldehyde,^{27b} (iii) thermal decomposition of optically-active α -methylbutyryl peroxide in carbon tetrachloride to yield racemic 2-chlorobutane,^{27c} (iv) thermal decomposition of optically-active β -phenylisobutyryl peroxide in carbon tetrachloride to give racemic 2-chloro-1-phenylpropane^{27d} and the present work (v) benzylic bromination of optically-active α -deuterioethylbenzene by NBS. While these reactions are of four different types and differ considerably in certain mechanistic details,²⁸ they all have two features in common, their potentially asymmetric radicals are produced singly, rather than in pairs, and these radicals stabilize

themselves by displacement reactions on another type of molecule which, in all but one case, is non-asymmetric.²⁹ The significance of the production of single radicals is that it not only assures free radicals but also avoids the complications of rapid recombination of radical pairs produced in a solvent cage. The importance of the second feature may be only complementary to that of the first, *i.e.*, displacement is merely one way by which a free radical may stabilize itself. However, some evidence exists which indicates that radical stabilization by displacement, rather than by addition or coupling, provides the most unambiguous information about the stereoconfiguration of the radical intermediate. Kharasch and Skell³⁰ have found that the acetyl peroxide-induced addition of ethyl (-)- α -bromopropionate to 1-butene gave ethyl α -methyl- γ -bromocaproate with low, but definite, levorotation. Inasmuch as radical addition reactions usually occur at about the same rate as radical displacement reactions, it would be expected that this intermediate α -carboethoxyethyl radical, which is also singly-produced, would be racemic; consequently, the low rotation of the adduct must have been due to induced asymmetric synthesis, as suggested by Skell.^{30a} It has also been reported^{30b,c} that Kharasch, Kuderna and Urry found that (-)- α -methylbutyric acid (or methyl ester) with acetyl peroxide yielded slightly dextrorotatory dimethyldiethylsuccinic acid (or dimethyl ester). This result may also be attributable to induced asymmetric synthesis, but since radical couplings are usually 10^4 - 10^5 times faster than radical displacements or additions the optically-active portion of the coupling product may have resulted from radicals that have not survived long enough to be statistically racemized. The asymmetry of such radicals need not arise from a pyramidal configuration as radicals with three bulky substituents, one or more of which is angularly disposed, could attain coplanarity of bonds to the trigonal carbon as formed but realize statistically symmetrical distribution of the substituent groups only relatively slowly, due to restricted rotations.

Experimental

Melting points and boiling points are uncorrected. Optical rotations were measured on an O. C. Rudolph and Sons, Caldwell, N. J., High Precision Polarimeter capable of reading 0.002° arc. Deuterium analyses were carried out in a Consolidated Electroynamics Corp. model 21-103 mass spectrometer.^{25,23}

(29) In the displacement of the potentially asymmetric methylethylisobutylmethyl radical on the hydrogen of the asymmetric methylethylisobutylacetaldehyde,^{27b} possible asymmetric synthesis may have been avoided by the use of high temperature but may be merely a consequence of the appreciable distance between the two asymmetric centers in the transition state.

(30) (a) *Cf.* P. S. Skell, R. C. Woodworth and J. H. McNamara, *THIS JOURNAL*, **79**, 1253 (1957). Previous brief reports ((b) L. E. Sutton, *Disc. Faraday Soc.*, **2**, 62 (1947); (c) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 714-715) of this unpublished work specified that the alkene used was 1-octene.

²⁶ k_D^{23} values for the reaction of NBS with toluenes indicates that benzylic bromination involves succinimidyl, and not bromine, radicals in the rate-determining, hydrogen abstraction step.

(26) Recent vacuum ultraviolet absorption (G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956); *cf.* G. Herzberg, *Ann. Rev. Phys. Chem.*, **9**, 327 (1958)) and paramagnetic resonance (T. Cole, H. O. Pritchard, N. R. Davidson and H. M. McConnell, *Molec. Phys.*, **1**, 406 (1958)) spectral results have provided strong evidence that methyl radicals possess a planar configuration.

(27) (a) H. C. Brown, M. S. Kharasch and T. H. Chao, *THIS JOURNAL*, **62**, 3435 (1940); (b) W. v. E. Doering, M. Farber, M. Sprecher and K. B. Wiberg, *ibid.*, **74**, 3000 (1952); (c) H. J. Dauben, Jr., and H.-T. Liang, unpublished results (H.-T. Liang, Ph.D. Thesis, University of Washington, 1952), thermal decomposition of optically-active α -methylbutyryl peroxide in refluxing carbon tetrachloride gave completely racemic 2-chlorobutane and *sec*-butyl α -methylbutyrate with complete retention in the acid part and at least 96% retention in the alcohol part of the ester; (d) D. F. DeTar and C. Weis, *ibid.*, **79**, 3045 (1957). Reactions involving possibly doubtful radical mechanisms (*e.g.*, Kolbe electrolyses) are not considered here but may provide additional examples.

(28) Some of the potentially asymmetric radicals are formed by displacement reactions and others from elimination processes; most of these radical intermediates stabilize themselves by displacements on different halogen donors but one displaces on a hydrogen donor. The radicals differ widely in type and have stabilization energies varying from 4-22 kcal. mole⁻¹; estimated exothermicities for their displacement reactions range from -4 to -20 kcal. mole⁻¹.

L-(+)- and D-(-)-Phenylmethylcarbinol.—Racemic phenylmethylcarbinol was converted to its acid phthalates by the method of Houssa and Kenyon³¹; a better yield (79% instead of 65%) was obtained by increasing the amount of pyridine used to 1.5 molar equivalents and the heating time to 3 hours. The recrystallized acid phthalate was transformed into its brucine salts and resolved, using seed crystals,³² as described by Downer and Kenyon.³³ The (+) and (-) acid phthalates were liberated from their brucine salts as done by Eliel,¹⁴ and isolated and purified in the manner reported by Downer and Kenyon³³; saponification,³³ using extractive steam distillation³⁴ with ether, yielded the enantiomeric carbinols: (+)-phenylmethylcarbinol, b.p. 94.5–95.0° (14 mm.), n_D^{25} 1.5258, α_D^{25} +41.68° (1 dm., neat) or with d_{25}^{25} 1.0116,³⁵ $[\alpha]_D^{25}$ +41.20° (94.8% optical purity); (-)-phenylmethylcarbinol, same b.p. and n_D values, α_D^{25} -39.20° (1 dm., neat) or $[\alpha]_D^{25}$ -38.78° (89.2% optical purity).

D-(-)-Phenylmethylcarbinyl Chloride.—Following the procedure of McKenzie and Clough,³⁵ (-)-phenylmethylcarbinol ($[\alpha]_D^{25}$ -38.78°, 89.2% optical purity) on reaction with thionyl chloride at about 20° and subsequent fractional distillation furnished (-)-phenylmethylcarbinyl chloride (85% yield, b.p. 76–77° (17 mm.), n_D^{25} 1.5260, α_D^{25} -46.2° (1 dm., neat), using d_{25}^{25} 1.0623³⁵ gives $[\alpha]_D^{25}$ -43.6° (42.2% optical purity); reported¹¹ b.p. 78° (16 mm.), n_D^{25} 1.5262).

L-(-)- α -Deuterioethylbenzene (I).—The procedure of Eliel¹⁴ was followed with minor modifications; the deuterium reactants, as supplied by Metal Hydrides, Inc., were reported to be 99% isotopically pure. (-)-Phenylmethylcarbinyl chloride (35.0 g., 0.236 mole, $[\alpha]_D^{25}$ -43.6°, 42.2% optical purity) was added rapidly to a well-stirred, refluxing suspension of lithium deuteride (3.00 g., 0.335 mole) and lithium aluminum deuteride (1.00 g., 0.024 mole) in tetrahydrofuran (75 ml., distilled from sodium and from lithium aluminum hydride) under an atmosphere of dry nitrogen. After 24 hr. of stirring and gentle refluxing, the reaction mixture was cooled, water (20 ml.) in tetrahydrofuran (30 ml.) was added dropwise with stirring and cooling, and the resultant mixture poured into ice-water (100 ml.) containing sulfuric acid (20 ml.). After complete dissolution of the solid material, the mixture was extracted with pentane (2 × 100 ml., b.p. < 65°) and the combined pentane extracts washed successively with water (2 × 100 ml.), 85% phosphoric acid (4 × 25 ml.), water (2 × 100 ml.), 10% aqueous sodium carbonate (1 × 100 ml.) and water (1 × 100 ml.). The pentane solution was dried (calcium chloride) and distilled at atmospheric pressure to give α -deuterioethylbenzene (18.0 g., 72% yield, b.p. 131–134°, n_D^{25}

1.4929, α_D^{25} -0.51 ± 0.02° (2 dm., neat), 98.63% d_1 and 1.37% d_0 content²³; reported¹⁴ 79% yield, b.p. 133–135° (747 mm.), n_D^{25} 1.4923 ± 0.0002, α_D^{25} -0.51 ± 0.02° (2 dm., neat), d_{25}^{25} 0.8712). Using d_{25}^{25} 0.8712, the product had $[\alpha]_D^{25}$ -0.293 (1 dm., neat); assuming that the deuterium displacement occurs with complete inversion¹⁵ and correcting for 1.37% d_0 content, the product is 41.6% optically pure. On the assumptions that phenylmethylcarbinyl chloride has maximum rotation of $[\alpha]_D^{25}$ ± 103.9°³⁶ and that the reduction is completely stereospecific, optically pure α -deuterioethylbenzene should have $[\alpha]_D^{25}$ ± 0.70 ± 0.03° (1 dm., neat). Solvents (pentane, tetrahydrofuran) used in this preparation were checked for optical activity and found to have rotations of < 0.02° (2 dm.).

L-(+)-Phenylmethylcarbinyl Bromide.—Reaction of (+)- or (-)-phenylmethylcarbinol with 1 molar equivalent of phosphorus tribromide and 2 molar equivalents of pyridine in carbon disulfide or ether, exactly as specified by Gerrard¹⁶ or with minor modifications, furnished no phenylmethylcarbinyl bromide in six attempts.

The phosphorus oxychloride method of Gerrard²⁰ was adapted to the preparation of bromide by substitution of phosphorus oxybromide. (-)-Phenylmethylcarbinol (3.66 g., 0.030 mole, $[\alpha]_D^{25}$ -38.78°, 89.2% optical purity) and pyridine (4.75 g., 0.060 mole) were dissolved in carbon disulfide (20 ml.) and cooled to 0°. Phosphorus oxybromide²⁷ (5.75 g., 0.02 mole, b.p. 185–189°, redistilled under reduced pressure just before use) in carbon disulfide (15 ml.) was added dropwise with swirling at 0° to the carbinol solution. The mixture was allowed to stand at about 20° for 11 hr., filtered, and the solid washed with carbon disulfide (2 × 5 ml.). The combined filtrate and washings were poured onto ice-water, the carbon disulfide layer separated, washed with dilute sodium carbonate solution, with water, and dried (sodium sulfate). Evaporation of the carbon disulfide and distillation of the residue gave (+)-phenylmethylcarbinyl bromide (0.50 g., 9% yield, b.p. 86–87° (15 mm.), n_D^{25} 1.5568, α_D^{25} +98.5° (1 dm., neat); using d_{25}^{25} 1.3590³⁸ gives $[\alpha]_D^{25}$ +72.5° (75.2% optical purity); reported^{15b} b.p. 86–87° (11 mm.) n_D^{25} 1.5595). Subsequent to our preparation, Arcus and Boyd^{15b} have used essentially the same method, except for initial mixing at a lower temperature (-10°), to obtain (+)-phenylmethylcarbinyl bromide, $[\alpha]_D^{25}$ +96.30°, in 42% yield from the (-)-carbinol, $[\alpha]_D^{25}$ -43.56°.

Bromination of Ethylbenzene by NBS.—A mixture of ethylbenzene (11.7 g., 0.11 mole), NBS (18.1 g., 0.10 mole based on 98.5% active bromine content; purified by method Aa⁴), benzoyl peroxide (0.24 g., 0.001 mole) and carbon tetrachloride (54 ml., C.P. grade) were heated under reflux until all of the NBS had been consumed (negative external test with moistened starch-iodide paper); reaction time, 25 min. During the reaction a pale orange color developed which disappeared just before the reaction was complete; when NBS was dried over phosphorus pentoxide at 25° (15 min.) for 5 days and the carbon tetrachloride distilled from the same drying agent, this color was very much less intense or did not develop at all but the reaction time was increased (40–55 min.) and the yield of the bromide product remained essentially the same. The reaction mixture was cooled in an ice-bath, filtered to remove succinimide (10.0 g., 100% yield), and carbon tetrachloride evaporated under reduced pressure from the filtrate. Distillation of the residue gave phenylmethylcarbinyl bromide (16.1 g., 87% yield, b.p. 87–90° (14 mm.), n_D^{25} 1.5588–1.5612 (several fractions); reported, b.p. 88° (14 mm.),^{15a} n_D^{25} 1.5595^{15b}). In four runs of this reaction, including those using carefully dried reactants, the yields of bromide product were consistently in the range of 80–90%.

Optical Stability Control Runs.—(A). (+)-Phenylmethylcarbinyl bromide (1.70 g., α_D^{25} +19.77° (1 dm., neat),

(37) H. S. Booth and C. G. Seegmiller, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. 2, p. 151.

(38) Estimated from d_{25}^{25} 1.3605 (W. Reppé, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 47 (1948)) using $d \cdot d_t/dt = -0.0003$ °C., assumed to be the same as for the chloride. The highest reported rotations for the bromide, using densities estimated in this way, are: α_D^{18} +131.4°^{15b} or $[\alpha]_D^{18}$ +96.53°; α_D^{20} +130.96°^{15b} or $[\alpha]_D^{20}$ +96.30°. Optical purity of our product was estimated by assuming that optically pure bromide had $[\alpha]_D^{25}$ 96.4° (2.20 times the rotation of the carbinol) and that temperature differences were insignificant.

(31) A. J. Houssa and J. Kenyon, *J. Chem. Soc.*, 2260 (1930).

(32) We are indebted to Dr. Nathan Kornblum, Purdue University, for pure samples of the (+) and (-) acid phthalates and their brucine salts.

(33) E. Downer and J. Kenyon, *J. Chem. Soc.*, 1156 (1930).

(34) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans-Green, London, 1st ed., 1948, p. 223.

(35) From the data of R. H. Pickard and J. Kenyon (*J. Chem. Soc.*, **99**, 45 (1911); **105**, 1115 (1914)) the carbinols have d_{25}^{25} 1.0140 and $d \cdot d_t/dt = -0.0008$ °C. may be used to estimate their densities in the range of 14–40°. Using these density values when needed to convert reported values to specific rotations, the highest specific rotations reported in the literature are: $[\alpha]_D^{20}$ +43.4° (A. McKenzie and G. W. Clough, *ibid.*, **103**, 687 (1913)). $[\alpha]_D^{17}$ +43.46°,³³ $[\alpha]_D^{17}$ -43.64°,^{15b} $[\alpha]_D$ -43.6°¹⁴; correcting these values to 20° by $d[\alpha]_D^{17}/dt = -0.012$ °/C. (from data of Pickard and Kenyon) gives average maximum specific rotation values of $[\alpha]_D^{20}$ 43.51° and $[\alpha]_D^{20}$ 43.45°, both ± 0.10°.

(36) McKenzie and Clough³⁵ report d_{25}^{25} 1.0632, and $d \cdot d_t/dt \cong -0.0003$ °/C., from their limited data, may be used to approximate densities at other temperatures needed to obtain specific rotations. Since the maximum specific rotations for the chlorides obtained by an inversion mechanism ((-)-carbinol with α_D^{25} -38.93° or $[\alpha]_D^{25}$ -38.54° (89.6% optical purity) gave chloride with α_D^{25} +97.4° or $[\alpha]_D^{25}$ +91.7°, or corrected to an optically pure basis, $[\alpha]_D^{25}$ +103.5°; R. L. Burwell, Jr., A. D. Shields and H. Hart, *THIS JOURNAL*, **76**, 909 (1954) and by a retention mechanism ((-)-carbinol, $[\alpha]_D^{25}$ -9.95° (22.9% optical purity) gave chloride (in dioxane) with $[\alpha]_D^{25}$ -23.83° or corrected to an optically pure basis, $[\alpha]_D^{25}$ -104.2°; K. B. Wiberg and T. M. Shryne, *ibid.*, **77**, 2774 (1955)) agree closely, it is very likely that optically pure phenylmethylcarbinyl chloride has $[\alpha]_D^{25}$ 103.9 ± 0.4° or 2.39 times the rotation of the carbinol (*cf.* Wiberg and Shryne).

$[\alpha]^{25D} + 14.55^\circ$, 15.1% optical purity, prepared by dilution of bromide with $[\alpha]^{25D} + 72.5^\circ$, NBS (1.50 g., dried over phosphorus pentoxide at 20° (15 mm.) for 5 days) and carbon tetrachloride (7.0 ml., distilled from phosphorus pentoxide) were heated under reflux for 25 min. The mixture was cooled in an ice-bath, filtered, the carbon tetrachloride removed under reduced pressure, and the residue distilled to give (+)-phenylmethylcarbonyl bromide (0.61 g., $\alpha^{25D} + 19.44^\circ$ (1 dm., neat) or $[\alpha]^{25D} + 14.31^\circ$, 14.8% optical purity) with less than 2% racemization.

(B). (+)-Phenylmethylcarbonyl bromide (0.61 g., 0.0033 mole, $\alpha^{25D} + 19.44^\circ$ (1 dm., neat), $[\alpha]^{25D} + 14.31^\circ$, 14.8% optical purity), NBS (1.81 g., 0.010 mole, dried as in A), ethylbenzene (1.17 g., 0.011 mole), benzoyl peroxide (0.024 g., 0.0001 mole) and carbon tetrachloride (65 ml., dried as in A) were heated under reflux until reaction was complete (35–45 min.). The mixture was cooled, filtered, the carbon tetrachloride removed under reduced pressure, and the residue distilled to give (+)-phenylmethylcarbonyl bromide (1.37 g., b.p. $90-91^\circ$ (19 mm.), $n^{25D} 1.5580$, $\alpha^{25D} + 6.10^\circ$ (1 dm., neat) or $[\alpha]^{25D} + 4.49^\circ$, 4.66% optical purity). From the amount of bromide isolated and its optical rotation the limits of a maximum of 72% benzylic substitution with no racemization or a minimum of 41% substitution with 30% racemization were estimated as follows: amount of bromide formed in the reaction = $1.37 - 0.61 = 0.76$ g. or 41% yield (lower limit); maximum possible rotation for isolated bromide = $19.44 (0.61/1.37) = 8.65^\circ$; amount of racemization = $[(8.65 - 6.10)/8.65] 100 = 30\%$ (lower limit); assume no racemization and let x = amount of bromide formed in the reaction, then from $19.44 [0.61/(0.61 - x)] = 6.10$, $x = 1.33$ g. or 72% yield (upper limit).

Bromination of (-)- α -Deuterioethylbenzene by NBS.—(-)- α -Deuterioethylbenzene (9.00 g., 0.084 mole, $\alpha^{25D} - 0.51^\circ$ (2 dm., neat), $[\alpha]^{25D} - 0.293^\circ$ (1 dm., neat)), NBS (13.9 g., 0.077 mole based on 98.5% active bromine, dried over phosphorus pentoxide at 20° (15 mm.) for 5 days), benzoyl peroxide (0.19 g., 0.00077 mole) and carbon tetrachloride (50 ml., distilled from phosphorus pentoxide) were heated under reflux until the bromination reaction was com-

plete (<10 min.). The mixture was cooled, filtered, and carbon tetrachloride removed under reduced pressure from the filtrate. Distillation of the residue gave the following fractions: (1) 0.13 g., b.p. to 91° (16 mm.), $n^{25D} 1.5530$; (2) 3.88 g., b.p. $91-92^\circ$ (16 mm.), $n^{25D} 1.5582$, $\alpha^{25D} - 0.07 \pm 0.02^\circ$ (2 dm., neat); (3) 4.57 g., b.p. 92° (16 mm.), $n^{25D} 1.5591$, $\alpha^{25D} - 0.07 \pm 0.03^\circ$ (2 dm., neat); (4) 3.24 g., b.p. $92-91^\circ$ (16 mm.), $n^{25D} 1.5596$, $\alpha^{25D} - 0.02 \pm 0.03^\circ$ (2 dm., neat); yield of bromo product (fractions 2–4) 11.69 g. (82.0% yield); weighted average for same fractions, $\alpha^{25D} - 0.056 \pm 0.026^\circ$ (2 dm., neat) or using $d^{25D} 1.3677$ (includes correction of $+0.0084$ for the deuterium content, assumed same as that for introduction of α -deuterium into ethylbenzene), $[\alpha]^{25D} - 0.020 \pm 0.01^\circ$ (1 dm., neat). The isotope effect, k_H/k_D , for the reaction of NBS with this sample of α -deuterioethylbenzene in refluxing carbon tetrachloride with benzoyl peroxide or ultraviolet light initiation was 2.67 ± 0.04 .^{22,23} With the reasonable assumption that phenylmethylcarbonyl bromide and its α -deuterio analog have the same specific rotations ($[\alpha]^{25D} 96.4^\circ$), it follows that substitution for hydrogen and for deuterium on (-)- α -deuterioethylbenzene will give enantiomeric bromide products. Then, using $k_H/k_D = 2.67$, the maximum specific rotations of the bromide products from the reaction of NBS with this sample of α -deuterioethylbenzene (41.6% optical purity) would be given by

$$[\alpha]^{25D} (\text{max.}) = (0.416)(96.4) \left[\pm \frac{2.67}{2.67 - 1.00} \pm \frac{1.00}{2.67 - 1.00} \right] = \pm 18.3^\circ$$

or -18.3° for complete retention, and $+18.3^\circ$ for complete inversion. Therefore, the bromide product obtained was no more than 0.11% optically pure, and the NBS reaction has occurred with at least $100 - (0.11/41.6) = 99.7\%$ racemization.

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[CONTRIBUTION FROM THE McPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Condensed Cyclobutane Aromatic Compounds. VII. Diels-Alder Adducts of Benzocyclobutadiene

BY M. P. CAVA AND M. J. MITCHELL

RECEIVED APRIL 14, 1959

Adducts of benzocyclobutadiene with two dienes, cyclopentadiene and furan, have been obtained. The structure of the cyclopentadiene adduct, as reported independently by Nenitzescu, has been confirmed by additional transformations. The reaction of benzocyclobutadiene with a typical dienophile, N-phenylmaleimide, has been achieved: a derivative of 1,2-dihydronaphthalene is formed.

Reactions which would be expected to generate benzocyclobutadiene (I)¹⁻³ produce, instead of the monomer I, the crystalline dimer II, shown^{1,2} to be 6a,10a-dihydrobenzo[a]biphenylene. The formation of II from two moles of benzocyclobutadiene has been envisaged² in its primary stage as a Diels-Alder reaction in which benzocyclobutadiene acts as both diene and dienophile. The results of some attempts to trap the elusive benzocyclobutadiene by reaction with other dienes and dienophiles are now reported.

During the course of this investigation, a report⁴ appeared describing the trapping of benzocyclobu-

tadiene⁵ by an active diene, cyclopentadiene. A liquid hydrocarbon, C₁₃H₁₂, was obtained which formed a crystalline phenyl azide adduct and which absorbed only *one* mole of hydrogen in the presence of a palladium catalyst.⁶ Largely on this basis the adduct was assigned structure III. The less likely structure IV, which might be expected if the cyclopentadiene had acted as a dienophile instead of a diene, was not compatible with the hydrogenation data.

(5) The benzocyclobutadiene was generated from 1,2-dibromobenzocyclobutene and lithium amalgam in ether. For a recent report on the preparation of the linear dimer of benzocyclobutadiene, 3:4-7:8-dibenzo-tricyclo[4.2.0.0^{2,3}]octadiene, see M. Avram, D. Dinu and C. D. Nenitzescu, *Chemistry & Industry*, 257 (1959).

(6) Reference 4, p. 2542: "Die katalytische Hydrierung zwecks Feststellung der Zahl der Doppelbindungen kam nach Aufnahme von einem Mol. Wasserstoff zum Stillstand" (italics supplied).

- (1) M. P. Cava and D. R. Napier, *THIS JOURNAL*, **78**, 500 (1956).
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- (4) C. D. Nenitzescu, M. Avram and D. Dinu, *Chem. Ber.*, **90**, 2541 (1957).