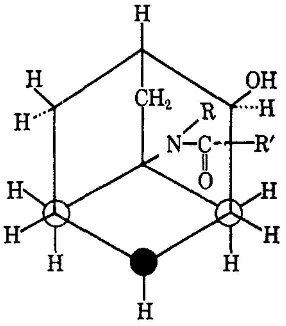
groups, *i.e.*, phenyl rather than methyl, for example. The increased size of the groups R and R′ will impart greater lipophilic character to the molecule and it may be that this is sufficient to allow a second attachment of the molecule to the enzyme following the first hydroxylation. In terms of the above orientation model, the product of dihydroxylation[5] will have the following projection formula. Rotation of the adamantane nucleus 120° around the C–N bond will present a second "face" of the nucleus to the enzyme surface identical with the first. A second hydroxylation of this orientation results in the di-α-OH products which are observed.



The above argument implies that dihydroxylation occurs as two discreet steps. This is supported by following the course of the fermentation by thin layer chromatography. When this is done, a single spot corresponding to the monohydroxy product is seen first. With increasing time a second spot, corresponding to the dihydroxy product, appears and becomes stronger at the expense of the monohydroxy product. It is also possible to isolate the monohydroxy product and then add it to a fresh *S. sulfurescens* culture, which converts it into the dihydroxy product.[5]

The oxygenation of some substrates gives only hydroxylated products while in other cases both hydroxy and ketonic products are obtained. In the latter cases, the hydroxyl groups and the ketone groups are found at the same position, suggesting that the hydroxy compound is probably an intermediate in the formation of the ketone. We have observed that molecules having a higher degree of conformational mobility tend to give more ketonic products when oxygenated with *S. sulfurescens*, while highly rigid molecules give exclusively hydroxylated products. As examples, the macrocyclic alcohols (C_{12}–C_{14}) are oxygenated to mixtures of dialcohols, keto alcohols, and diketones.[1] Similarly, oxygenation of 1-benzoylhexamethylenimine, 1-benzoylheptamethylenimine, and 1-benzoyloctamethylenimine gave mixtures of alcohols and ketones in each case.[3] All of these molecules have several conformations differing in energy to a relatively small degree. On the other hand, molecules such as N-acetyl-1-adamantanamine, 3-benzoyl-3-azabicyclo[3.3.1]nonane, 2-benzoyl-2-azabicyclo[2.2.2]octane, and 1-benzoyl-*trans*-decahydroquinoline have either a rigid structure or a highly preferred conformation. All of these compounds give only hydroxy products.[4–6] Intermediate in conformational mobility are the six- and seven-membered-ring compounds. Cyclohexane derivatives may flip from one chair conformation to a second but they prefer the one in which substituents are equatorial. Cyclohexyl compounds generally give only hydroxylated products.[1,2] Cycloheptyl derivatives have a slightly greater conformational freedom and are found to give both hydroxy and ketonic products. The compound 3-benzoyl-3-azabicyclo[3.2.2]nonane contains both six- and seven-membered rings and has some conformational freedom as judged from Dreiding models. This compound also gives both a hydroxy and a ketonic product.[4] It seems plausible that the greater conformational mobility of some molecules permits them to be adapted to the alcohol dehydrogenating enzymes of the microorganism with the result that they are more readily converted from alcohols into ketones.

Steric Requirements for Free-Radical Substitutions.
I. Phenyl Migration during Bromination[1]

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Steric hindrance can affect the course of free-radical brominations with N-bromosuccinimide (NBS) and with bromine. 1,1,1,2-Tetraphenylethane with NBS or Br_2 affords tetraphenylethylene resulting from a phenyl migration. 1,2,2-Triphenylpropane undergoes normal bromination with either reagent to give 1-bromo-1,2,2-triphenylpropane. 4,4,4-Triphenyl-1-butene, **11**, with NBS gives exclusively 1-bromo-4,4,4-triphenyl-2-butene, **12**, the product arising from allylic rearrangement. Both **11** and **12** give negative tests for unsaturation when treated with bromine in carbon tetrachloride.

The Wohl–Ziegler reaction[4] utilizing N-bromosuccinimide (NBS) is a valuable synthetic method for introducing a bromine atom at an allylic or benzylic position.[5] A free-radical chain sequence initiated by bromine atoms as suggested in 1953 by Goldfinger and coworkers[6] has been substantiated by others.[7] The

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[1] Presented in part at the 132nd National Meeting of the American Chemical Society in New York City, N. Y., Sept 1957.

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[3] Taken in part from theses submitted in partial completion for the M. A. degree: (a) Brooklyn College, 1956; (b) City College, 1966.

[4] (a) A. Wohl, *Ber.*, **52**, 51 (1919); (b) K. Ziegler, A. Spaeta, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 80 (1942).

[5] C. Djerassi, *Chem. Rev.*, **43**, 271 (1948).

[6] J. Adam, P. A. Gosselain, and P. Goldfinger, *Nature*, **171**, 704 (1953); *Bull. Soc. Chim. Belges*, **65**, 533 (1956).

[7] (a) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 1511 (1961); (b) C. Walling, A. L. Rieger, and D. Tanner, *J. Amer. Chem. Soc.*, **85**, 3129 (1963); (c) G. A. Russell and K. M. Desmond, *ibid.*, **85**, 3139 (1963); (d) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963).

chain-propagating steps (eq 1 and 2) require small amounts of bromine formed *in situ* from HBr and NBS, designated in eq 3 as S-Br.

$$\text{RH} + \text{Br}\cdot \longrightarrow \text{R}\cdot + \text{HBr} \qquad (1)$$

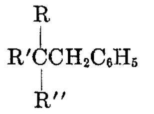
$$\text{R}\cdot + \text{Br}_2 \longrightarrow \text{RBr} + \text{Br}\cdot \qquad (2)$$

$$\underset{\text{(NBS)}}{\text{S-Br}} + \text{HBr} \longrightarrow \underset{\text{(succinimide)}}{\text{S-H}} + \text{Br}_2 \qquad (3)$$

Little attention has been given to the steric requirements for this type of reaction. There is some evidence that steric factors may control the course of the reaction. For example, although there is ample evidence[5] for suggesting that an active methylene group is more reactive than an active methyl group, it has been observed that 2,4,4-trimethyl-1-pentene reacts with NBS to give 2-bromomethyl-4,4-dimethyl-1-pentene.[4b] This product arises from bromination at a methyl group rather than at the sterically hindered neopentyl methylene group.

Although the presence of a bromine atom at an active site deters the insertion of a geminal bromine atom,[5] tetrabromination of [2.2]paracyclophane with NBS gives geminal rather than vicinal tetrabromide,[8] an occurrence attributed to steric strain associated with this unique ring system.

This work was undertaken to study the steric requirements of the NBS reaction. The substrates chosen possess only one active site which is also adjacent to a quaternary carbon atom. The substrates are of two broad types: (a) compounds **1**, **4**, and **7**, in which the active site is benzylic, and (b) 4,4,4-triphenyl-1-butene, compound **11**, in which the active site is allylic.



$$\text{R}'\overset{\overset{\text{R}}{|}}{\underset{\underset{\text{R}''}{|}}{\text{C}}}\text{CH}_2\text{C}_6\text{H}_5$$

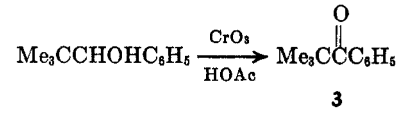
1, R = R′ = R″ = CH_3
4, R = R′ = R″ = C_6H_5
7, R = R′ = C_6H_5; R″ = CH_3

$(C_6H_5)_3CCH_2CH{=}CH_2$

11

Results and Discussion

Neopentylbenzene,[9] **1**, was allowed to react in carbon tetrachloride with NBS in ordinary light and without initiating catalysts; the reaction time for 0.1 mol was 2.5 hr. Vacuum distillation of the crude brominated product gave a main fraction (57%) having a boiling point, density, and refractive index expected for 1-bromo-2,2-dimethyl-1-phenylpropane (**2**). Further proof of structure of **2** was achieved by the sequence steps[10] in eq 4. *t*-Butyl phenyl ketone (**3**) was characterized by preparing its 2,4-dinitrophenylhydrazone.



$$\underset{\mathbf{2}}{\text{Me}_3\text{CCHBrC}_6\text{H}_5} \xrightarrow[\text{H}_2\text{O}]{\text{Ag}^+} \text{Me}_3\text{CCHOHC}_6\text{H}_5 \xrightarrow[\text{HOAc}]{\text{CrO}_3} \underset{\mathbf{3}}{\text{Me}_3\overset{\overset{\text{O}}{\|}}{\text{C}}\text{C}\text{C}_6\text{H}_5} \qquad (4)$$

The fact that **1** is brominated in the normal manner indicates that the mere presence of a quaternary carbon atom bonded to the benzylic carbon atom does not prevent normal reaction.

Steric hindrance could be augmented by replacing the methyl groups of **1** with bulkier phenyl groups. For this reason, 1,1,1,2-tetraphenylethane (**4**) was prepared from benzylmagnesium chloride and triphenylchloromethane.[11] As the reaction of **4** with NBS in refluxing carbon tetrachloride proceeded, an orange-brown vapor, identified as bromine, was observed. The appearance of bromine presages an elimination of hydrogen bromide as a result of the reaction shown in eq 3. The crude residue from the bromination reaction was separated by fractional crystallization into two solids, 51% starting material and 43% compound **5**, mp 220–221°. That **5** was tetraphenylethylene was confirmed by a mixture melting point determination with an authentic sample, by ultraviolet absorption [$\lambda_{\max}$ 310 mμ (log ϵ 4.20)], and by oxidative degradation to benzophenone, characterized as its 2,4-dinitrophenylhydrazone.

Formation of **5** requires a *migration of a phenyl group*. Aryl migration in free-radical intermediates is well known.[12] However, heretofore, they have not been observed during free-radical halogenations in solution.[13]

That free radicals were intermediates was shown by the absence of any reaction when **4** and NBS were refluxed in carbon tetrachloride in the dark under nitrogen. With a trace of benzoyl peroxide under nitrogen in the dark, the reaction was complete in 1 hr, giving a 48% yield of **5**.

It might be suggested that 2-bromo-1,1,1,2-tetraphenylethane (**6**), formed initially by a typical free-radical bromination, can rearrange *via* a carbonium ion intermediate engendered by succinimide acting as an electrophilic catalyst. This possibility is very remote in view of the fact that certain compounds react with NBS to give bromo derivatives which after isolation can be made to undergo rearrangement when converted into the corresponding carbonium ion. For example, 1,1,2-triphenylethanol reacts normally with NBS to give 1,1,2-triphenyl-2-bromoethanol; no phenyl benzhydryl ketone is obtained. The ketone, from a typical carbonium ion rearrangement, was isolated from the action of silver nitrate on the bromohydrin.[14]

Compound **5** is also obtained as the sole product when **4** is allowed to react with bromine in carbon tetrachloride at room temperature in ordinary light. It is suggested that **5** arises from **4** directly as the result of a free-radical phenyl migration as shown. No decision can be made as to whether the alkene arises by a chain-terminating step (eq 7) or a chain-propagating step (eq 8).

$$(\text{C}_6\text{H}_5)_3\text{CCH}_2\text{C}_6\text{H}_5 + \text{Br}\cdot \longrightarrow (\text{C}_6\text{H}_5)_3\text{C}\dot{\text{C}}\text{HC}_6\text{H}_5 + \text{HBr} \qquad (5)$$

$$(\text{C}_6\text{H}_5)_3\text{C}\dot{\text{C}}\text{HC}_6\text{H}_5 \xrightarrow{\sim\text{C}_6\text{H}_5\cdot} (\text{C}_6\text{H}_5)_2\dot{\text{C}}\text{CH}(\text{C}_6\text{H}_5)_2 \qquad (6)$$

$$(\text{C}_6\text{H}_5)_2\dot{\text{C}}\text{CH}(\text{C}_6\text{H}_5)_2 + \text{Br}\cdot \longrightarrow (\text{C}_6\text{H}_5)_2\text{C}{=}\text{C}(\text{C}_6\text{H}_5)_2 + \text{HBr} \qquad (7$$

or

$$(\text{C}_6\text{H}_5)_2\dot{\text{C}}\text{CH}(\text{C}_6\text{H}_5)_2 + \text{Br}_2 \longrightarrow \underset{\mathbf{5}}{(\text{C}_6\text{H}_5)_2\text{C}{=}\text{C}(\text{C}_6\text{H}_5)_2} + \text{HBr} + \text{Br}\cdot \qquad (8)$$

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[8] K. C. Dewhirst and D. J. Cram, *J. Amer. Chem. Soc.*, **80**, 3115 (1958).

[9] (a) A. Bygdèn, *Ber.*, **45**, 3479 (1912); (b) V. N. Ipatieff and L. Schmerling, *J. Amer. Chem. Soc.*, **60**, 1476 (1938).

[10] P. Skell and C. R. Hauser, *ibid.*, **64**, 2633 (1942).

[11] M. Gomberg, *Ber.*, **39**, 1463 (1906).

[12] C. Walling in "Molecular Rearrangements," Interscience Publishers, Inc., New York, N. Y., 1963, p 407–455.

[13] In the gas phase chlorination of *t*-butylbenzene at 190–245° at low concentration of halogen, a small amount of 1-chloro-2-methyl-3-phenylpropane was detected: J. D. Backhurst, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2742 (1959).

[14] J. F. Lane and D. R. Walters, *J. Amer. Chem. Soc.*, **73**, 4234 (1951).

Ordinarily, such free-radical migrations do not occur during halogenation reactions because of the low activation energy for eq 2. This step usually proceeds more rapidly than the migration which requires a higher energy of activation. However, in the halogenation of **4**, the bulky trityl group adjacent to the free-radical carbon atom retards eq 2, so that the migration (eq 6) becomes competitive. The free radical engendered in eq 5 has a relatively low-energy barrier for phenyl migration since it is a secondary free radical stabilized by one phenyl group, and the rearranged free radical in eq 6 is tertiary and stabilized by two phenyl groups. This combination of steric hindrance toward bromine insertion and formation of a much more stable radical resulting from phenyl migration enables the rearranged product to form.

It seemed pertinent to see if phenyl migration could stil occur with substrate **7**, having one of the phenyls of the trityl group replaced by a methyl group. 1,2,2-Triphenylpropane[15] (**7**) was allowed to react with NBS in carbon tetrachloride solution to yield a product (90–95%) which was analyzed as a compound in which one hydrogen of the starting material was replaced by a bromine. The crude reaction product was shown by thin layer chromatography to contain only the brominated product and starting material. Investigation of the ultraviolet spectrum of the crude reaction product gave no evidence for the presence of material containing a styrene or a 1,1-diphenylethylene-like conjugation in quantities greater than approximately 0.5%. The nmr spectrum of the purified bromination product shows a singlet at δ 1.81 integrating for three hydrogens, a singlet at 5.72 integrating for one hydrogen, and a complex multiplet of peaks from δ 6.9 to 7.4 integrating for 15 hydrogens. The interpretation of this spectrum indicates that the bromination product is either $(C_6H_5)_2CCH_3CHBrC_6H_5$ (**8**) or $(C_6H_5)_2CHC(CH_3)BrC_6H_5$ (**9**), the latter compound resulting from a rearrangement. To distinguish between these compounds, the product was reduced with lithium aluminum hydride. From the reduction was isolated a product in 52.5% yield, the remainder being unreacted starting material. The reduced product was identical with **6** by mixture melting point, thin layer R_f values, and identity of ultraviolet, infrared and nmr spectra. Furthermore, prolonged treatment of the brominated product with N,N-diethylaniline gave no reaction. These results lead to the conclusion that the brominated product is the unrearranged compound, 1-bromo-1,2,2-triphenylpropane (**8**), rather than the rearranged one, **9**. The incomplete reduction of **8** with lithium aluminum hydride is explainable by the fact that **8** is a neopentyl-type halide and hence would react sluggishly in SN2-type displacements.

$$\begin{tikzcd}[column sep=large] & \underset{\mathbf{8}}{(C_6H_5)_2CCH_3CHBrC_6H_5} \\ \underset{\mathbf{7}}{(C_6H_5)_2CCH_3CH_2C_6H_5} \arrow[ur, "NBS"] \arrow[dr, "\times"'] & \\ & \underset{\mathbf{9}}{(C_6H_5)_2CHC(CH_3)BrC_6H_5} \end{tikzcd} \qquad (9)$$

The free-radical intermediate arising by hydrogen abstraction from **7** is not so sterically hindered toward bromine insertion as is the free-radical intermediate arising from **4** because a methyl group has less space requirement than a phenyl group. The energy of activation for migration of a phenyl group of the radical intermediate from **7** is greater than that for the radical intermediate from **4** because, although the rearranged radical is tertiary in both cases, the former is stabilized by only one rather than by two phenyl groups. The combination of these two factors precludes rearrangement during the bromination of **7**.

The isolation of **8** from the reaction of **7** with NBS can be used as further circumstantial evidence that **5** is formed from **4** by a free-radical rearrangement rather than by a carbonium ion rearrangement of **6**. If under the conditions of the NBS reaction **6** had been formed and had been converted into a carbonium ion, there is no reason why a carbonium ion could not likewise be formed from **8**. The 1,1,2-triphenylethyl carbonium ion undergoes phenyl migration,[16,17] and a 1,2,2-triphenylpropyl carbonium ion would be expected to behave similarly.

We hope to arrive at a definitive answer as to the free-radical character of the rearrangement observed during the bromination of **4** by studying migratory aptitudes of properly phenyl-substituted derivatives of **4**.

To examine the effect on the course of free-radical brominations of compounds having a trityl group bonded to an allylic position, 4,4,4-triphenyl-1-butene (**11**) was prepared. The coupling of triphenylmethylmagnesium bromide with allyl bromide[18] did not afford good yields. The reaction of tritylsodium with allyl bromide gave erratic yields (91–50%). The most consistently good yields (75%) were obtained by the method of Nesmeyanov and Perevalov,[19] involving the addition of a mixture of triphenylchloromethane and allyl bromide to activated magnesium and some allylmagnesium bromide. The reaction of **11** with NBS under ordinary conditions was complete after 4 hr. After one recrystallization of the crude product, there was obtained in 85.1% yield, a white needlelike solid (**12**) having a molecular formula of $C_{22}H_{19}Br$, as determined by elemental analysis. Ozonolysis of **12** afforded triphenylacetic acid, identified by melting point and as its amide, and bromoacetaldehyde, characterized as its 2,4-dinitrophenylhydrazone derivative. Formaldehyde was absent as shown by the very sensitive chromotropic acid test.[20] Hence, the structure of 1-bromo-4,4,4-triphenyl-2-butene was assigned to **12**. Confirmation of the structure and assignment of the *trans* geometry was made possible by infrared and nmr spectroscopy. The nmr spectrum of $(C_6H_5)_3CCH_A{=}CH_BCH_{C_2}Br$ has (a) a singlet at δ 7.15 integrating for 15 protons (three phenyl rings), (b) a doublet centered at 6.79 (J = 18 cps) integrating for one proton (H_A *trans* to H_B), (c) a quintet in the ratio of 1:2:2:2:1 centered at 5.48 (J_{AB} = 18 cps and J_{BC} = 9 cps) integrating for 1 proton (H_B), and (d) a doublet at 3.95 (J_{BC} = 9 cps) integrating for two pro-

$$\underset{\mathbf{11}}{(C_6H_5)_3CCH_2CH{=}CH_2} \xrightarrow{NBS} \underset{\mathbf{12}}{(C_6H_5)_3CCH{=}CHCH_2Br} \qquad (10)$$

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[15] C. B. Wooster and J. F. Ryan, *J. Amer. Chem. Soc.*, **56**, 1133 (1934).

[16] C. J. Collins, W. A. Bonner, and C. T. Lester,, *ibid.*, **81**, 466 (1959).

[17] C. J. Collins and B. M. Benjamin, *ibid.*, **85**, 2519 (1963).

[18] W. E. Bachman and R. F. Cockerill, *ibid.*, **55**, 2932 (1933).

[19] A. N. Nesmeyanov and E. G. Perevalov, *Izv. Akad. Nauk SSSR, Otd. Khim Nauk*, 1002 (1954).

[20] F. Feigl, "Manual of Spot Tests," Reinhold Publishing Co., New York, N. Y., 1943.

tons. The infrared spectrum shows a band at 975 cm^{-1}, typical of a *trans*-dialkyl-substituted alkene.

Allylic rearrangement during bromination with NBS of terminal alkenes is to be expected. The predominant product usually results from the allylic shift but *some of the unrearranged product also is isolated.* For example, the reaction of 1-octene gives a 20% yield of the normal bromination product, 3-bromo-1-octene, and an 80% yield of the allylic rearranged product, 1-bromo-2-octene.[21] In only one case, the isolation of 3-bromo-1-phenylpropene from the reaction of allylbenzene with NBS, is complete allylic rearrangement observed.[22] In this case, total allylic rearrangement is attributable to conjugation of the newly positioned double bond and the benzene ring.

The absence of any impurity with a terminal vinyl group in once-recrystallized **12**, as evidenced by the negative test for formaldehyde in the products from ozonolysis, prompted the conclusion that the reaction of **11** with NBS might be another *instance of complete allylic rearrangement.* Hence, the infrared spectrum of the crude product from the reaction of **11** with NBS was compared with that of pure **11**, pure **12**, and mixtures of **11** and **12**. The characteristic peak at 915 cm^{-1} for a terminal vinyl group was absent in once-recrystallized **12**, but was present in **11**. It was present in crude **12**, but had an exceedingly low intensity. By comparing relative intensities of the bands at 975 (*trans*-dialkyl-substituted alkene) and at 915 cm^{-1} (terminal vinyl group), the amount of terminal unsaturation in crude **12** was determined to be less than 5%, and this slight absorption may have been due to unreacted **11**. Analysis of crude **12** by thin layer chromatography showed the presence of only **12** and **11**. Hence, it is concluded that little or no "normal" (unrearranged) bromination occurred, a fact attributable to severe steric hindrance of "normal" bromination, but not of "allylic" (rearranged) bromination.

In characterizing **12**, it was observed that bromine in carbon tetrachloride gives a negative test for unsaturation. A 2% solution of potassium permanganate was decolorized, but only after long standing and warming. Starting material (**11**) behaves in a similar manner toward these reagents. Since there is no direct conjugation between the phenyl groups and the double bond, these results were unexpected. However, the same phenomenon was observed with similarly constituted compounds. Both 2,2-diphenyl-3-pentenenitrile (**13**) and 2,2-diphenyl-3-methylbutenenitrile (**14**) are reported to give negative tests for unsaturation.[23]

$$N{\equiv}CC(C_6H_5)_2CH{=}CHCH_3 \qquad N{\equiv}CC(C_6H_5)_2C(CH_3){=}CH_2$$

13 **14**

These results are considered to be in accord with the hindered position of the double bond. There is, however, a possibility that some sort of long-range electronic interaction between the π bond of the double bond and the π bonds of any one of the three phenyl groups in **11** and **12**, or the nitrile and the two phenyl groups in **13** and **14**, may affect the reactivity of the double bond. The reason for this unexpected loss of "unsaturation" is now under study.

Experimental Section

Melting points were taken in capillaries and are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Crobaugh Laboratories, Charleston, W. V. Ultraviolet absorption measurements were taken using both the Beckman Model DU spectrophotometer and the Cary Model 15 recording spectrophotometer. A 5×10^{-5} *M* solution in ethanol was used in most cases. Infrared measurements were taken using both the Baird double-beam Infrared spectrophotometer and the Perkin-Elmer Model 137 Infracord spectrometer. Carbon tetrachloride was used as the solvent in all cases. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer, and taken in carbon tetrachloride, unless specified otherwise, with an internal standard of tetramethylsilane. Densities were taken with a Davidson Densitometer, and indices of refraction were taken with an Abbe refractometer. Thin layer plates were 400 μ thick, and were prepared from Merck silica gel HF_{254}. Materials to be analyzed were spotted in ether solvent, and the chromatograms were developed in 97% petroleum ether (bp 30–60°)–3% diethyl ether.

All solvents were dried and distilled before use. Reagent grade NBS was used and recrystallized from anhydrous benzene if the color was yellow.

Neopentylbenzene (**1**) was prepared by the method of Bygdèn[9] from benzylmagnesium chloride and *t*-butyl chloride. The crude material (76% yield) was distilled at atmospheric pressure to give a colorless, sweet-smelling oil (31%) in the boiling range 185–193°. This oil was then fractionally distilled giving **1**: bp 185–186.5°; $n^{20}{}_D$ 1.4888 (lit.[9b] bp 185–188°, $n^{20}{}_D$ 1.4884).

Reaction of 1 with NBS. Preparation of α-Bromoneopentylbenzene.—A mixture of 14.8 g (0.1 mol) of **1** and 17.8 g (0.1 mol) of NBS in 200 ml of carbon tetrachloride was refluxed for 2.5 hr after which time the reaction was complete. The content of the flask was cooled and the succinimide (9.8 g, 99%, mp 124–126°) was removed by filtration. The filtrate was concentrated and the residue was vacuum distilled. The main fraction (57%) was collected: bp 78–80° (2 mm); $d^{21.7}{}_4$ 1.244; $n^{20}{}_D$ 1.538 [for α-bromoneopentylbenzene (**2**), lit.[24] bp 89° (3–4 mm), $d^{25}{}_4$ 1.237, and $n^{20}{}_D$ 1.540].

Conversion of 2 into Phenyl *t*-Butyl Ketone (3).—The bromo compound **2** was converted into the corresponding alcohol with aqueous silver nitrate.[10] The crude alcohol (0.164 g, 0.001 mol) in 0.5 ml of glacial acetic acid was oxidized with chromic acid according to the method of Cheronis.[25] An oil was obtained which, when dissolved in methanol and warmed with 2,4-dinitrophenylhydrazine reagent, gave upon cooling 0.12 g (34%) of a yellow-orange solid, mp 165–170°. The solid was recrystallized from methanol to give pure material, mp 191–193° (ref 10 reports mp 190–191° for the DNPH of phenyl *t*-butyl ketone).

Reaction of 1,1,1,2-Tetraphenylethane (4) with NBS. A.—A mixture of 3.82 g (0.0114 mol) of **4**, mp 142–143° (lit.[11] mp 144°), and 1.98 g (0.0111 mol) of NBS in 45 ml of carbon tetrachloride was refluxed in ordinary light. After 1 hr the carbon tetrachloride developed a light orange color which deepened. After 2 hr, orange-brown vapors, identified as bromine, were present in the condenser. The reaction was complete after 4.5 hr. The succinimide (1.0 g, 91%) was removed by filtration and the bromine was removed from the filtrate by a current of warm dry air. The filtrate was concentrated in stages to give two main solid fractions which, on recrystallization from 1:1 benzene-methanol, gave 1.95 g (51%) of starting material **4**, mp 137–140° (no depression in melting point on admixture with authentic sample), and 1.62 g (43%) of another compound, mp 220–221°, uv max 310 mμ (log ϵ 4.20). This compound was characterized as tetraphenylethylene (**5**) (lit.[26] mp 221°). Compound **5** was oxidized with potassium permanganate affording an oil which gave an orange 2,4-dinitrophenylhydrazone derivative melting at 233–235° (lit.[27] mp 237° for the DNPH of benzophenone). Admixture of this with an authentic 2,4-DNPH derivative of benzophenone gave no depression.

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[21] L. C. Bateman, *Nature*, **164**, 242 (1949).

[22] E. A. Braude and E. S. Waight, *J. Chem. Soc.*, 1116 (1952).

[23] E. M. Schultz, C. M. Robb, and J. M. Sprague, *J. Amer. Chem. Soc.*, 69, 2454 (1947).

[24] S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952).

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B.—When **4** was refluxed with NBS in carbon tetrachloride under nitrogen in the dark, no reaction was observed after 8 hr. When a few milligrams of benzoyl peroxide was added and refluxing was continued, excluding light and air, the reaction was complete after 1 hr, and **5** was isolated as the product in 48.2% yield.

Reaction of 4 with Bromine.—A solution of 1.7 g (0.0050 mol) of **4** and 1.6 g (0.010 g-atom) of bromine in carbon tetrachloride (50 ml) was warmed by a sun lamp for 12 hr. A quantitative yield of **5** was obtained.

Preparation of 1,2,2-Triphenylpropane (7).[16]—1,1,2-Triphenylethylene (5.00 g, 19.5 mmol) was added to 5 ml of liquid ammonia under a nitrogen atmosphere in an insulated flask fitted with a magnetic stirring bar, a Dry Ice condenser, and an ammonia inlet tube. Approximately 200 ml of ammonia was then added to the flask. Sodium (1.21 g, 53 mg-atoms) was added in small portions over a period of 2 hr, and the resulting black solution was stirred for an additional 0.5 hr. A solution of dimethyl sulfate (5.5 ml, 2.34 g, 58 mmol) in 15 ml of sodium-dried ether was added dropwise with stirring to the ammonia solution. The ammonia was permitted to evaporate at room temperature and the remaining white precipitate was triturated with water and filtered to yield 4.8 g of a white precipitate, mp 60–110°. An additional 0.2 g of white product was recovered by ether extraction from the water used in the trituration. After two recrystallizations of the crude reaction product (5.0 g) from absolute ethanol, 2.0 g (38% yield) of white crystals, mp 115–116.1° (lit.[28] mp 116–117°), was obtained. This purified material gave a single spot when subjected to analysis by thin layer chromatography.

Reaction of 7 with NBS. Preparation of 1-Bromo-1,2,2-triphenylpropane (8).—A mixture of **7** (1.00 g, 3.68 mmol) in 30 ml of carbon tetrachloride and NBS (0.65 g, 3.68 mmol) was refluxed under an atmosphere of nitrogen in a flask fitted with an Allihn condenser and a calcium chloride drying tube while being illuminated by a 100-W incandescent lamp. The course of the reaction was followed by thin layer chromatography, and was tested periodically for unreacted NBS with potassium iodide–starch paper. After 2 hr of refluxing, the mixture contained a small amount of starting material and no NBS. The colorless solution was cooled and succinimide (0.375 g, 102% yield) was removed by filtration. The solvent was evaporated to yield a thick yellow oil (1.434 g, 111% yield). By comparing the relative intensities of the peaks in the nmr spectrum of the crude oil at δ 1.51, assigned to the methyl group of **7**, and at 1.81, assigned to the methyl group of the product **8**, the ratio of product to starting material was found to be 94:6.

The oil (6.250 g from a larger scale reaction) was dissolved in 25 ml of *n*-hexane and the solution was kept at room temperature for 11 days. A first crop of colorless crystals (2.78 g), mp 93.5–96.5°, was obtained. On further standing, the solution deposited three additional fractions of 1.30 g (mp 94–96.8°), 0.92 g and 0.31 g (mp 95–96°). The four fractions totaled 5.31 g (87% over-all yield). Each crop was found to be contaminated by a trace of starting material as shown by thin layer chromatography. The first crop was recrystallized from 13 ml of *n*-hexane to give 2.08 g of colorless crystals of **8**: mp 94.7–96°; ir (KBr), 3050, 1597, 1577, 1493, 1443 and 1070 (C_6H_5), 760 and 705 (monsubstituted C_6H_5), 1380 (CH_3), and 2995–2850 cm^{-1} (CH_3 and C–H); nmr (CCl_4), δ 1.81 (s, 3, CH_3), 5.72 (s, 1, CHBr), and 6.97–7.4 ppm (m, 15, C_6H_5).

Anal. Calcd for $C_{21}H_{19}Br$: C, 71.80; H, 5.45; Br, 22.75. Found: C, 71.75; H, 5.62; Br, 22.92.

Lithium Aluminum Hydride Reduction of 8.—Lithium aluminum hydride (0.19 g, 5.0 mmol) was slurried in 20 ml of anhydrous tetrahydrofuran in a three-necked, 100-ml round-bottom flask, fitted with an air stirrer, condenser, drying tube, and dropping funnel. The apparatus had been flushed with dry nitrogen to remove traces of moisture prior to addition of reagents. The flask was heated in an oil bath until the gray suspension began to boil and then a solution of **8** (1.75 g, 5.0 mmol) in 10 ml of anhydrous tetrahydrofuran was added dropwise to the stirred reaction mixture. Gas was evolved following each addition of **8**. After the addition had been completed, the mixture was stirred and refluxed for 1 hr. The oil bath was removed and 10 ml of ethanol was added slowly, followed by 2 ml of water and 5 ml of 5 *N* sodium hydroxide. The solution, which turned white, was concentrated to a volume of approximately 50 ml, and an equal volume of water was added. The mixture was extracted with 500 ml of ether, and the ethereal extract was dried ($MgSO_4$) and concentrated to yield 1.29 g of off-white solid, which was dissolved in 30 ml of *n*-hexane, filtered from a trace of insoluble material, and concentrated to 20 ml. When cooled, the pale yellow solution deposited 17 mg of colorless needles (mp 160–163°) giving a negative Beilstein test and shown to be pure by thin layer chromatography. The hexane filtrate was concentrated to 15 ml and cooled to deposit large clusters of needles on standing. The solid was removed by filtration, washed with 4 ml of cold *n*-hexane, and dried to yield 471 mg, mp 115.3–116.2°. This second crop of crystals was identified as 1,2,2-triphenylpropane (**7**) by melting point, by mixture melting point, and by infrared and nmr spectra. On further concentration of the hexane solution, an additional 244 mg of **7** (mp 112–115°) was obtained. The total yield of **7** was 715 mg (52.5%). Much of the remaining solid was starting material **8**.

Reaction of 4,4,4-Triphenyl-1-butene[19] (11) with NBS. Preparation of 1-Bromo-4,4,4-triphenyl-2-butene (12).—A mixture of 10.0 g (0.0352 mol) of **11**, mp 68–70°, and 6.12 g (0.0352 mol) of NBS was added to 100 ml of carbon tetrachloride in a 250-ml, round-bottom flask. The reflux condenser was protected by a calcium chloride drying tube, and the mixture was refluxed for 4 hr. The reaction mixture was cooled and filtered leaving 3.45 g (98%) of succinimide (mp 124–126°). By removing the solvent from the filtered mother liquor there was obtained 12.0 g (94.1%) of crude solid which when recrystallized from acetonitrile gave white needles (85.1%) of **12**: mp 145–147°; ir (CCl_4), 975 cm^{-1} (*trans* RCH=CHR); nmr (CCl_4), δ 7.15 (s, 15, C_6H_5), 6.79 (d, 1, J_{AB} = 18 cps, *trans* CH=CH), 5.48 [quintet (ratio 1:2:2:2:1), 1, J_{AB} = 18 cps and J_{BC} = 9 cps, $CH{=}CHCH_2$], and 3.95 ppm (d, 2, J_{BC} = 9 cps, CH_2Br).

Anal. Calcd for $C_{22}H_{19}Br$: C, 72.72; H, 5.27; Br, 22.01. Found: C, 72.70; H, 5.56; Br, 21.85.

Compound **12** gave an immediate precipitate with alcoholic silver nitrate, gave a negative test for unsaturation with bromine in carbon tetrachloride, and decolorized a 2% potassium permanganate solution in acetone only after long standing or heating.

Ozonolysis of 12.—In a Welsbach ozonizer, ozone was bubbled for approximately 30 min through a solution of 0.45 g (0.00124 mol) of **12** in ethyl acetate in a flask immersed in a Dry Ice–acetone bath. The solution was hydrogenated at atmospheric pressure using palladium on charcoal as a catalyst. The chromotropic acid test[20] for formaldehyde on the solution after reduction was negative.

When mixed with water and concentrated under vacuum with a current of air bubbling through it, the ethyl acetate solution yielded a white solid, 0.094 g (30%, mp 190–200°), which when recrystallized from methanol gave white crystals, mp 257–262°, identified as triphenylacetic acid (lit.[29] mp 264–265°). The triphenylacetic acid was further characterized as the amide in the usual manner.[27] When recrystallized from toluene, white crystals were obtained, mp 238–240° (lit.[26] mp 238).

To the aqueous mother liquor of the filtration of triphenylacetic acid was added 2,4-dinitrophenylhydrazine reagent, and an immediate orange precipitate was obtained, mp 147–150°, corresponding to the DNPH derivative of bromoacetaldehyde (lit.[26] mp 150°). A mixture of the DNPH derivative of bromoacetaldehyde with that of acetaldehyde (lit.[26] mp 147°) gave a depressed melting point at 125–127°.

Registry No.—NBS, 128-08-5; bromine, 7726-95-6; **1**, 1007-26-7; **4**, 2294-94-2; **7**, 16876-18-9; **8**, 16876-19-0; **11**, 16876-20-3; **12**, 16876-21-4.

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