several times with 30–60° petroleum ether, leaving an insoluble residue (0.91 g.) of sulfone VI (identified by melting point and infrared spectrum). The petroleum ether extract, after treatment with charcoal (Darco), was concentrated and cooled to give white prisms of naphtho[b]-cyclobutene, m.p. 84.5–86° (3.49 g., 61% based on unrecovered sulfone). In a number of similar preparations the yield of III varied from 60 to 75%. Chromatographic investigation of the dark pot residues from the pyrolysis of sulfone VI afforded no crystalline by-products. The analytical sample of III, m.p. 86.5° (cor.), was obtained by decomposition (on alumina) of the purified picrate (see below); ultraviolet spectrum(ethanol): λ_{max} 223 (log *E* 4.88), 267 (3.68), 278 (3.78), 290 (3.63), 304 (3.06), 311 (2.85), 318 (3.21); shoulders at 250, 259 and 286 mμ (see Fig. 1).

Anal. Calcd. for $C_{12}H_{10}$: C, 93.46; H, 6.54; mol. wt., 154. Found: C, 93.37; H, 6.65; mol. wt. (isothermal distillation in methylene chloride), 154.

The picrate of III, m.p. 139.5–140.5°, crystallized from ethanol in long yellow needles.

Anal. Calcd. for $C_{18}H_{13}O_7N_3$: C, 56.40; H, 3.43; N, 10.96. Found: C, 56.26; H, 3.45; N, 10.82.

The orange **2,4,7-trinitrofluorenone complex of III**, m.p. 146–148°, was crystallized from benzene–petroleum ether.

Anal. Calcd. for $C_{25}H_{15}O_7N_3$: C, 63.97; H, 3.22; N, 8.95. Found: C, 63.78; H, 3.25; N, 9.08.

N-Phenyl-1,2,3,4-tetrahydro-*cis*-2,3-anthracenedicarboximide (X).—A mixture of sulfone VI (2.00 g.), N-phenylmaleimide (2.40 g.) and diethyl phthalate (25 ml.) was heated to boiling and distilled slowly until almost 20 ml. of distillate was collected. The distillation residue was cooled in the refrigerator; the white solid which crystallized was triturated with cold benzene, filtered, washed with cold benzene and dissolved in methylene chloride. The solution was placed on a column of alumina (neutral Woelm, activity 1) and the column eluted with methylene chloride. Passage of the product through the column was observed easily as the movement of a bluish fluorescent zone. Concentration of the eluate and crystallization from methylene chloride–benzene afforded the imide X as tiny white crystals (2.30 g., 82%), m.p. 230–233°. The analytical sample, m.p. 233–234.5°, was recrystallized from chloroform–benzene.

The identical imide X was obtained in 61% yield by pyrolysis of a mixture of sulfone VI and N-phenylmaleimide in the absence of diethyl phthalate. The ultraviolet spectrum of X (Fig. 2) was very similar to that of 2,3-dimethylnaphthalene (Fig. 1).

Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.71; H, 5.24; N, 4.28. Found: C, 81.14; H, 5.18; N, 4.77.

N-Phenyl-2,3-anthracenedicarboximide (XI).—A mixture of imide X (0.33 g.), N-bromosuccinimide (0.36 g.), benzoyl peroxide (*ca.* 20 mg.) and chloroform (4 ml.) was refluxed for 15 hours while irradiated by an ordinary 100-watt lamp. The chloroform was evaporated and the solid residue was crystallized twice from dimethylformamide to give imide XI as fine orange–yellow leaflets (0.22 g., 68%), m.p. 355–358°. A dilute benzene solution of XI exhibited an intense blue fluorescence; its ultraviolet spectrum (Fig. 2) revealed an intensely absorbing chromophore different from that of imide X.

Anal. Calcd. for $C_{22}H_{13}O_2N$: C, 81.72; H, 4.05; N, 4.33. Found: C, 81.63; H, 4.23; N, 4.40.

COLUMBUS 10, OHIO

[CONTRIBUTION OF THE CHEMISTRY DEPARTMENT, OHIO UNIVERSITY]

Some Evidence Regarding Free Radical Rearrangement Reactions

BY WILLIAM B. SMITH AND JAMES D. ANDERSON

RECEIVED JULY 8, 1959

Treatment of 2-phenyl-1-bromopropane and 2-phenyl-1-bromoethane-1-C^{14} with magnesium and cobaltous bromide in refluxing ether has been used to produce the respective free radicals. In the former case the monomeric products showed 40% rearrangement, while in the latter case rearrangement amounted to *ca.* 20%. The mechanistic implications of these results are considered.

Introduction

A number of free radical rearrangement reactions are now known which proceed at least to a certain extent with the 1,2-shift of an aryl group. It has been well established in analogous carbonium ion rearrangements that the neighboring aryl group may contribute to the driving force for the reaction through aryl-bridged transitions states and subsequent formation of "non-classical" aryl-bridged carbonium ions. While qualitative considerations suggest that neighboring aryl-group participation should be equally likely in free radical rearrangement reactions, the fact remains that existent evidence in the literature strongly argues against the formation of such "non-classical" radical intermediates except as possible stages in the conversion of one conventional open radical to another.

The first evidence of phenyl migration during a free radical reaction was obtained by Urry and Kharasch[1] who found that the treatment of 1-chloro-2-phenyl-2-methylpropane (neophyl chloride) with phenylmagnesium bromide and cobaltous bromide produced a mixture of hydrocarbons corresponding to about 50% migration of the phenyl group. Winstein and Seubold[2] subsequently obtained essentially the same result during the decarbonylation of 3-phenyl-3-methylbutanal. Arguments in favor of a phenyl-bridged intermediate were refuted by Seubold[3] who showed that the precentage rearrangement in the decarbonylation reaction was a function of the life time of the radical intermediate, increasing beyond 50% when the reaction mixture was diluted with an inert solvent.

Further evidence regarding the nature of the radical intermediate in reactions involving the migration of an aryl group was reported by Urry and Nicolaides[4] who found that the 2-*p*-tolyl-2-methylpropyl radical produced either from the bromide *via* the Grignard reagent–cobaltous halide reaction or by the decarbonylation of the appropriate aldehyde formed monomeric prod-

---

[1] W. H. Urry and M. S. Kharasch, THIS JOURNAL, **66**, 1438 (1944).

[2] S. Winstein and F. H. Seubold, *ibid.*, **69**, 2916 (1947).

[3] F. H. Seubold, *ibid.*, **75**, 2432 (1953).

[4] W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).

ucts again showing 50% aryl migration. However, the decarbonylation of 2,2-dimethyl-3-phenylpropionaldehyde led only to isopropylbenzene. These results, coupled with those above, were interpreted as indicating again only the formation of classical open free radicals which then may or may not undergo further rearrangement.

Recently, Slaugh[5] has shown that the decarbonylation of 3-phenylpropanal-2-C^{14} produced a 2-phenylethyl radical which underwent only slight rearrangement (2–5%) in forming ethylbenzene. It is evident here where the interconversion of a primary to a primary radical would have to occur that no significant amount of phenyl migration takes place and phenyl bridging is not an important factor in the reaction.

In order to extend our knowledge of the role of the phenyl group in free radical rearrangement reactions we have investigated the treatment of 2-phenyl-1-bromopropane and 2-phenyl-1-bromoethane-1-C^{14}, respectively, with magnesium and cobaltous bromide.

Discussion

The reaction of 2-phenyl-1-bromopropane with magnesium and an equivalent amount of cobaltous bromide resulted in a 17% yield of monomeric products which were analyzed by vapor phase chromatography as: isopropylbenzene 38%, α-methylstyrene 22%, *n*-propylbenzene 15%, allylbenzene 8%, and β-methylstyrene 17%. This corresponds to 40% rearrangement in the monomeric products.

The reaction of 2-phenyl-1-bromoethane-1-C^{14} with magnesium and cobaltous bromide gave a 44% yield of product consisting of 43% styrene and 57% ethylbenzene. A portion of the crude monomer mixture was hydrogenated to give pure ethylbenzene which then was oxidized to *p*-nitrobenzoic acid.[6] The percentage phenyl migration was determined in this fashion to be 18.9%. The styrene was isolated as the dibromide from another portion of the reaction product. Regeneration and oxidation to *p*-nitrobenzoic acid gave material with 20.6% of the initial activity.

The most reasonable mechanism for the formation of β-arylethyl free radicals from β-arylethyl halides magnesium, and cobaltous bromide would seem to be an adaptation of the mechanism of Kharasch, Lewis and Reynolds[7] where R may be CH_3 or H.

$$ArCR_2CH_2Br + Mg \longrightarrow ArCR_2CH_2MgBr \quad (1)$$

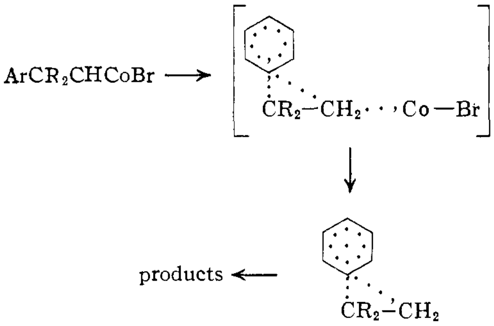
$$ArCR_2CH_2MgBr + CoBr_2 \longrightarrow ArCR_2CH_2CoBr + MgBr_2 \quad (2)$$

$$ArCR_2CH_2CoBr \longrightarrow \underset{A}{ArCR_2CH_2\cdot} + \cdot CoBr \quad (3)$$

Two schemes may be suggested to account for the rearrangement found in the 2-phenylethyl radical (R is H). First, the classical radical may be formed as in (3) above. The radical A may then react partially by direct disproportionation and partially by rearrangement to B then disproportionation.

$$\underset{A}{Ar{-}CR_2{-}CH_2\cdot} \longrightarrow \underset{B}{\cdot CR_2{-}CH_2{-}Ar}$$

A second possibility involves the decomposition of the organocobalt halide through an unsymmetrically bridged transition state to form an unsymmetrically bridged intermediate which then reacts to form products with partial rearrangement.



(3′)

No firm decision regarding the correct alternative is possible. The significantly larger amount of phenyl migration observed in the 2-phenylethyl radical produced by the bromide, magnesium, cobaltous bromide reaction as opposed to the decarbonylation reaction reported by Slaugh[5] is indicative of a clear-cut alteration in one or more of the factors controlling the course of the reaction. If one includes the observation of Urry and Kharasch,[1] it is seen that the effect of increasing methyl substitution on the carbon adjacent to the site of radical formation increases the amount of phenyl migration in the order 2-phenylethyl < 2-phenylpropyl < 2-phenyl-2,2-dimethylethyl. Since the steric crowding and electronic effects of increasing methyl substitution at the β-carbon would be expected to operate to cause greater phenyl migration in either scheme, no argument can be based on this observation.

Slaugh[5] reported that the rearrangement of 2-phenylethyl free radical increased from 3.3 to 5.1% with an increase in temperature from 145 to 165°, indicating that the energy of activation for the rearrangement process is somewhat higher than that for hydrogen abstraction. Furthermore, the addition of an active hydrogen donor to the system decreased the amount of phenyl migration by increasing the hydrogen abstraction reaction at the expense of the life time of the radical.

It is evident that any explanation of the increased amount of phenyl migration observed in this study must take into account the relative rates of disproportionation or hydrogen abstraction as compared to the rate of phenyl migration in the system under consideration. Unfortunately, these terms are not directly accessible by experiment in this system. Product analysis indicates that 86% of the radicals produced by the bromide, magnesium, cobaltous bromide reaction react by disproportionation while 14% react by hydrogen abstracting from the solvent. This finding is in

[5] L. H. Slaugh, This Journal, **81**, 2262 (1959).

[6] R. M. Roberts, G. A. Ropp and O. K. Neville, *ibid.*, **77**, 1764 (1955).

[7] (a) M. S. Kharasch, D. W. Lewis and W. B. Reynolds, *ibid.*, **65**, 495 (1943); (b) W. B. Smith, *J. Org. Chem.*, **24**, 703 (1959).

keeping with the speculation of Steacie[8] that the activation energy for disproportionation of a free radical is considerably less than that for hydrogen abstraction from the solvent. While no quantitative statement may be made about rates of rearrangement *versus* disproportionation, the experimental observation of greater rearrangement in our system runs counter to that expected on the basis of the above considerations and the observations made by Slaugh.[5]

The possibility of the formation of a phenyl-bridged intermediate cannot be dismissed. It is reasonable to expect that the formation of the 2-phenylethyl free radical by the decarbonylation of the aldehyde in a step involving the formation of stable carbon monoxide will require less energy of activation than the rupture of a carbon–cobalt bond. Since no data on the strengths of such bonds are available, this matter remains in the realm of speculation. However, if true, then the driving force provided by the formation of a non-classical transition state (3′) will be more significant in determining the course of the reaction when the radical is produced *via* the bromide, magnesium cobaltous bromide route. The ultimate criterion for a "non-classical" intermediate is the observation of a stereospecific migration. A test of this point is planned in the near future in this laboratory. Until the appearance of such data the question of the existence of a bridged free radical must be considered unsolved.

Acknowledgment.—The authors wish to thank the Ohio University Research Fund for their generous support of this work.

Experimental

Product analysis was accomplished by means of vapor phase chromatography (v.p.c.) using a column of tricresyl phosphate on firebrick with helium as eluting gas. Compounds were identified by a comparison of retention times with those of known compounds. The method of radiocarbon analysis has been described elsewhere.[9]

Reaction of 2-Phenyl-1-bromopropane.—The method of Cohen, Marshall and Woodman was used to prepare 2-phenyl-1-bromopropane.[10] A mixture of 3.8 g. of magnesium and 34.0 g. of anhydrous cobaltous bromide was stirred in 300 ml. of ether. The mixture was brought to reflux, and a solution of 25.6 g. of 2-phenyl-1-bromopropane in 250 ml. of ether was added dropwise. After about one-fourth of the bromide solution was added the reaction mixture turned dark, and the reaction proceeded vigorously throughout the remainder of the addition without external heating. Upon completion of the addition, the mixture was refluxed for 5 hours. After cooling, the mixture was poured into iced dilute hydrochloric acid. The ether layer was separated, dried over anhydrous magnesium sulfate, and the ether distilled off. The oily residue was vacuum distilled through a semi-micro column. The fraction, b.p. 37–50° (20 mm.), contained all of the monomeric products; yield 2.68 g. (17%). On v.p.c. at 145° five peaks were obtained. The composition was computed from the areas under the peaks to give these results in order of appearance: isopropylbenzene 38%, *n*-propylbenzene 15%, allylbenzene 8%, β-methylstyrene 17%, and α-methylstyrene 22%.

Preparation of 2-Phenyl-1-bromoethane-1-C^{14}.—Reduction of phenylacetic acid-1-C^{14} with lithium aluminum hydride produced 2-phenylethanol-1-C^{14}. This alcohol (10 g.) was stirred in an ice-cooled flask while 10.5 g. of phosphorus tribromide was added dropwise over a one-hour period. The mixture was stirred in the cold for *ca.* 6 hours. It then was warmed on the steam-bath for 0.5 hour. The reaction mixture now was poured into ice-water, extracted with ether, dried over magnesium sulfate, and the ether distilled off. Distillation of the residue produced 10.2 g. (67%) of 2-phenyl-1-bromoethane-1-C^{14}, b.p. 95–96° (13 mm.), n^{25}D 1.5548 (reported[11] for 2-phenyl-1-bromoethane b.p. 96° (13 mm.) n^{25}D 1.5543).

A sample of the bromide (1.508 ± 0.008 mc./mole) prepared by the above method was converted to hydrocinnamic acid which then was oxidized to benzoic acid, 0.022 ± 0.001 mc./mole, in the manner of Lee and Spinks.[12] Thus, the amount of isotope position rearrangement produced during the formation of the bromide was 1.46%. This was applied as a correction in computing the amount of phenyl rearrangement in the reaction below.

Reaction of 2-Phenyl-1-bromoethane-1-C^{14}.—A solution of 2-phenyl-1-bromoethane-1-C^{14} (1.388 ± 0.003 mc./mole) in 90 ml. of ether was allowed to react with a mixture of 1.7 g. of magnesium, 14.5 g. of cobaltous bromide and 270 ml. of ether in a fashion analogous to that described above. The product was worked up as before. The monomer fraction, b.p. 47–51° (22 mm.), amounted to 2.51 g. (44%). This fraction was analyzed by v.p.c. at 127° and found to consist of 57% ethylbenzene and 43% styrene.

A small sample of this material was hydrogenated at room temperature and pressure over Adams platinum catalyst. The amount of hydrogen absorbed corresponded to 96% of that calculated on the basis of the v.p.c. analysis. The hydrogenated material checked on v.p.c. as pure ethylbenzene. This material was oxidized to *p*-nitrobenzoic acid (0.271 ± 0.003 mc./mole) by the method of Roberts, Ropp and Neville.[6]

Another portion of the reaction product was treated with the calculated amount of bromine dissolved in carbon tetrachloride. After the reaction was complete, the mixture was washed with dilute sodium bisulfite, and the solvent evaporated. Styrene dibromide was recrystallized from ethanol, m.p. 73–74°, 1.396 ± 0.008 mc./mole (reported[13] for styrene dibromide m.p. 73–74°).

Styrene was regenerated from the dibromide by refluxing the latter (0.9 g.) with *ca.* 25 ml. of acetone saturated with sodium iodide. After several hours heating, the mixture was poured into dilute sodium bisulfite and then extracted with ether. The ether solution was dried over magnesium sulfate and then distilled off. The oily residue was oxidized to *p*-nitrobenzoic acid as above, 0.287 ± 0.003 mc./mole.

ATHENS, OHIO

---

[8] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, Vol. II, p. 508.

[9] W. B. Smith, R. E. Bowman and T. J. Kmet, THIS JOURNAL, **81**, 997 (1959).

[10] J. B. Cohen, J. Marshall and H. E. Woodman, *J. Chem. Soc.*, **107**, 897 (1915).

[11] D. Perlman, D. Davidson and M. T. Bogert, *J. Org. Chem.*, **1**, 288 (1936).

[12] C. C. Lee and J. W. T. Spinks, *Can. J. Chem.*, **31**, 765 (1953).

[13] R. E. Buckles, THIS JOURNAL, **71**, 1157 (1949).