Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.2; H, 4.6. Found: C, 79.6; H, 4.4.

Registry No.—Va, 16526-86-6; Vb, 16526-87-7; Vc, 16526-88-8; VIa, 16526-89-9; diphenylacetylene, 501-65-5.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Institutes of Health (GM 1394) for partial support of this research.

Factors Governing the Reaction of the Benzyl Grignard Reagent. III. The Formation of *ortho* and *para* Products in Reactions with Alkyl Sulfates *via* Triene Intermediates

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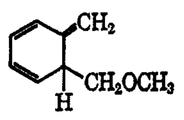
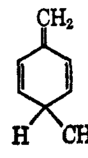
Benzylmagnesium chloride was treated with dimethyl, diethyl, and di-*n*-propyl sulfate as well as *n*-propyl tosylate under standardized conditions. In all cases the principal product was an alkylbenzene accompanied by smaller amounts of *both ortho-* and *para*-substituted toluenes. Under identical conditions the same Grignard reagent reacts with methyl iodide to form only ethylbenzene, but at a much slower rate. Likewise, benzyllithium forms only *n*-butylbenzene with di-*n*-propyl sulfate in a tetrahydrofuran solvent. When benzylmagnesium chloride is treated with diethyl sulfate and the reaction mixture hydrolyzed with deuterium chloride in deuterium oxide, the *o*- and *p*-ethyltoluenes produced contain a large percentage of molecules with one deuterium atom incorporated in the methyl group attached to the ring. This is rationalized in terms of triene intermediates which are aromatized during hydrolysis. Attention is directed to the fact that *para*-substituted products are formed in displacement reactions of the benzyl Grignard but usually not in carbonyl additions. Contrary to earlier literature reports, no *para* products were found when benzylmagnesium chloride reacts with either ethyl chlorocarbonate or ethyl formate.

It was recently disclosed[1] that, in displacement reactions between the benzyl Grignard reagent and chloromethyl methyl ether, triene intermediates like I, and probably II, exist in the reaction mixture prior to hydrolysis. Such intermediates are protonated by strong acids during hydrolysis to form, in this instance, *o*- and *p*-methylbenzyl methyl ether.


I


II

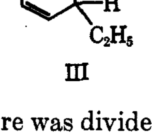
It seemed reasonable that intermediates like I and II should be formed in other displacement reactions also in which the benzyl Grignard participates. To this end we turned our attention to the preparation of *n*-propylbenzene from the reaction of the benzyl Grignard with diethyl sulfate.[2] It had been pointed out[3] that this preparation produced *p*-ethyltoluene as a by-product, but no *o*-ethyltoluene could be detected. When we repeated this reaction, it was found that *both* *o*- and *p*-ethyltoluene are indeed produced in this case as shown in Table I. Likewise, when our study was extended to dimethyl and di-*n*-propyl sulfate, small amounts of both the *ortho*- and *para*-substituted toluenes were again produced (Table I). This was also true when *n*-propyl *p*-toluenesulfonate was substituted for di-*n*-propyl sulfate as the alkylating agent. Of interest was the observation that no ring-substituted products were produced in the reaction between benzyllithium and di-*n*-propyl sulfate or between the benzyl Grignard and methyl iodide. A summary of all of these results is in Table I.

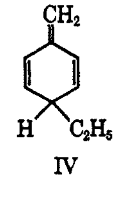
TABLE I

REACTION OF BENZYLMAGNESIUM CHLORIDE AND BENZYLLITHIUM WITH VARIOUS ALKYLATING AGENTS[a]

Run	Organometallic[c]	Alkylating agent	Products, %[b]		
			$C_6H_5CH_2R$	o-$CH_3C_6H_4R$	p-$CH_3C_6H_4R$
1	$PhCH_2MgCl$	$(CH_3)_2SO_4$	74[d]	0.5	0.3
2	$PhCH_2MgCl$	$(C_2H_5)_2SO_4$	71[e]	7	2.3
3	$PhCH_2MgCl$	$(n\text{-}C_3H_7)_2SO_4$	77[f]	8	0.8
4	$PhCH_2MgCl$	$n\text{-}C_3H_7OTs$	77[g]	1	0.8
5	$PhCH_2Li$	$(n\text{-}C_3H_7)_2SO_4$	72[h]	...	...
6	$PhCH_2MgCl$	CH_3I	49[i]	...	...

[a] In all cases the initial concentration of the organometallic was 0.4 *M*. The benzyllithium reaction (run 5) was carried out in tetrahydrofuran; all others were in diethyl ether. [b] These values represent the percentage distribution of product in the distilled fraction and in most cases are the average of two runs. [c] In every case (except run 6) the reaction mixture was stirred at room temperature for 1 hr after the alkylating agent had been added. [d] There was an average of 9% toluene also isolated in this run. [e] About 15% toluene was also isolated. [f] There was also isolated in this run about 2% isobutylbenzene, 1% each of *o*- and *p*-cymene, and 5% toluene. [g] Also 5% toluene was isolated. [h] About 27% toluene was also recovered along with 1% isobutylbenzene. [i] This reaction was carried out for 3 days. In addition to ethylbenzene, 26% toluene was also obtained.


III


IV

To demonstrate the existence of intermediates like III and IV in the reaction with diethyl sulfate, a reaction mixture was divided into two equal parts just prior to hydrolysis. One of the parts was hydrolyzed with aqueous hydrochloric acid and the other part with saturated ammonium chloride solution. The latter

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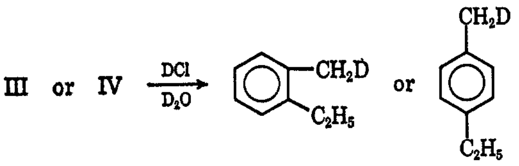
(1) R. A. Benkeser and W. DeTalvo, *J. Amer. Chem. Soc.*, **89**, 2141 (1967).

(2) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 471.

(3) J. G. Burtle and R. L. Shriner, *J. Amer. Chem. Soc.*, **69**, 2059 (1947).

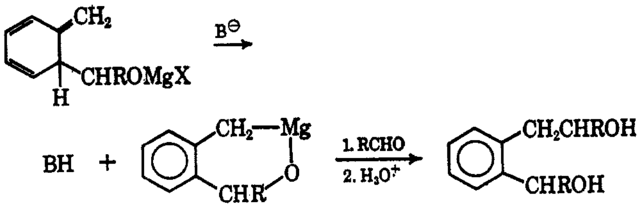
portion produced only half as much of the *o*- and *p*-ethyltoluenes as the portion hydrolyzed with the hydrochloric acid. This was identical with our findings with chloromethylmethyl ether and can be rationalized in the same way.[1] Apparently intermediates like I–IV are aromatized by mineral acids during hydrolysis, but are much less reactive toward weaker acids like ammonium chloride. In the latter instance they survive the hydrolysis step only to be destroyed during distillation.

Much more positive evidence for the existence of intermediates III and IV was obtained by hydrolyzing another reaction mixture with DCl in D_2O. Analysis of the *o*- and *p*-ethyltoluenes thus produced by nmr confirmed the presence of considerable deuterium in the methyl groups bonded to the aromatic ring. Mass spectral analysis of the same material established the incorporation of only one deuterium atom at this position and gave values of 48–55% deuterium enrichment. Clearly, a considerable portion of the *o*- and *p*-ethyltoluenes produced in this reaction is arising during hydrolysis and can best be rationalized in terms of intermediates like III and IV.



In a blank experiment it was shown that this uptake of deuterium was not the result of any exchange between the alkyltoluenes and the DCl during hydrolysis. When *p*-ethyltoluene in ether was stirred with DCl in D_2O to simulate hydrolysis conditions, no deuterium exchange occurred.

There is still another way to rationalize the incorporation of deuterium during hydrolysis. It has been amply demonstrated that in certain carbonyl addition reactions of the benzyl Grignard reagent[4] as well as in certain other displacement reactions,[1] bis products often result from reaction of 1 equiv of the organometallic with 2 equiv of the alkylating or carbonyl reagent. In the case of the carbonyl reactions, such products have been explained[4b,5] by a reaction sequence as follows.



V

In essence, a base (B^-) which could conceivably be another molecule of benzyl Grignard abstracts an allylic proton to form a new organometallic, V, which reacts in conventional fashion with more carbonyl reagent to form biscarbinols. It is conceivable that in our system intermediates like III and IV might react with more Grignard reagent (by allylic hydrogen abstraction) to form new organometallic intermediates, which, upon reaction with DCl would result in deuterium incorporation. We do not consider such a sequence likely in our case because no trace of either *o*- or *p*-ethyl-*n*-propylbenzene could be detected in our reaction products. It certainly seems that the same organometallic intermediate which is capable of deuteration with DCl should also be capable of reaction with diethyl sulfate to form products like *o*- or *p*-ethyl-*n*-propylbenzene. Hence, we believe the monodeuterated products we observed came about by reaction of intermediates III and IV with DCl.

Discussion of Results

Certain comments are in order with regard to the data in Table I. In the first four entries there are some differences to be noted with regard to the *ortho* and *para* isomers obtained. For example, these so-called "abnormal" products seem less in the case of the dimethyl sulfate reaction (entry 1) and the *n*-propyl tosylate (entry 4). However, since the differences are small, we prefer to reserve comment at this time as to their possible significance. That the alkylating agent probably plays a role, however, in determining whether such "abnormal" products are formed is indicated by the methyl iodide reaction (entry 6). While this reaction is very slow (requiring 3 days), it seems significant that no *o*- or *p*-ethyltoluene is formed in this case.

The reaction with di-*n*-propyl sulfate (entry 3, Table I) proved interesting in that small amounts of isobutylbenzene as well as *o*- and *p*-cymene were detected among the products. While conclusive proof is lacking, we feel that our *n*-propyl sulfate, although prepared by well-established reactions, was probably contaminated with small amounts of the isopropyl isomer produced during the multistep preparative sequence employed.[6] These branched-chain impurities did not show up when *n*-propyl tosylate was substituted for the *n*-propyl sulfate (entry 4) suggesting that they were caused by impurities in the sulfate. It is also noteworthy that 1% isobutylbenzene again appeared when this same sample of *n*-propyl sulfate was treated with benzyllithium (entry 5), suggesting again that the sulfate was slightly impure.

Again, it will be noted that the "abnormal" *ortho* and *para* products were eliminated when benzyllithium was used (entry 5). Some caution must be exerted in comparing this result with the others in Table I since tetrahydrofuran was used as the solvent rather than the usual diethyl ether. However, it was our previous[1] experience, also, that benzyllithium reacts almost exclusively at the α position during such displacements.

When the data in Table I are considered in conjunction with the existing literature[7] on the subject, it becomes apparent that *para*-substituted products result almost exclusively from displacement reactions of the benzyl Grignard reagent. When the latter reacts with carbonyl reagents, *para* products almost never are formed. There seemed to be possibly two exceptions

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[4] (a) J. Schmidlin and A. Garcia-Banus, *Ber.*, **45**, 3193 (1912); (b) W. G. Young and S. Siegel, *J. Amer. Chem. Soc.*, **66**, 354 (1944); (c) S. Siegel, S. K. Coburn, and D. R. Levering, *ibid.*, **73**, 3163 (1951); (d) R. A. Benkeser and T. E. Johnston, *ibid.*, **88**, 2220 (1966).

[5] S. Siegel, W. M. Boyer, and R. R. Jay, *ibid.*, **73**, 3237 (1951).

[6] There was no isopropyl alcohol in the *n*-propyl alcohol we used as the starting material in this reaction sequence.

[7] See M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p 1134, for pertinent references.

to this statement, namely the reaction between benzylmagnesium chloride and ethyl chlorocarbonate and ethyl formate[8] wherein small amounts of *para* products were found. Using an excess of carbonyl compound,[9] we found neither of these reactions to be particularly clean-cut. Numerous products were produced in addition to considerable amounts of polymeric material, especially in the case of ethyl formate. Most significant, however, was our inability to detect any *para*-substitution products in either the crude or distilled reaction mixtures. This was true even when oxidation of the crude products was attempted with permanganate followed by subsequent conversion of the acids to esters with diazomethane. Analysis of these esters by vpc disclosed no trace of dimethyl terephthalate.

Hence, the generalization seems to be evolving that *para, ortho,* and normal products are formed in displacement reactions of the benzyl[10] Grignard reagent. Carbonyl addition reactions of this reagent result in normal and *ortho* products only.

Experimental Section

o-(n-Propyl)ethylbenzene.—A solution of *o*-ethylphenylmagnesium bromide was prepared in 200 ml of dry tetrahydrofuran from 8 g (0.33 g-atom) of magnesium and 55.5 g (0.3 mol) of *o*-ethylbromobenzene (Eastman). To this solution was added 51.0 g (0.3 mol) of *n*-propyl iodide. The mixture was refluxed for 3 hr and hydrolyzed with 100 ml of 3 *N* hydrochloric acid. After the customary work-up, the product was distilled through a short Vigreux column and 8.4 g (18%) of product was collected boiling at 200–204°. An analytical sample ($n^{20}{}_{D}$ 1.4970) was collected by vpc (20 ft, 20% dibutyl tetrachlorophthalate on Chromosorb P, 60–80 mesh, at 140°).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.37; H, 11.07.

Reaction of Benzylmagnesium Chloride with Various Alkyl Sulfates and Sulfonates.—Since the conditions employed in these reactions were nearly identical, the directions given below for methyl sulfate can be considered typical for all. The results of all these runs are in Table I.

A. Methyl Sulfate.—To a three-necked flask equipped with a mercury-sealed stirrer, pressure-equalizing dropping funnel with nitrogen inlet, and reflux condenser was added 313 ml of an ethereal solution of benzylmagnesium chloride containing 0.3 mol of the organometallic. Then 437 ml of anhydrous ether was added to produce 750 ml of a 0.4 *M* solution. To this solution was added dropwise 75.6 g (0.6 mol) of methyl sulfate in 50 ml of ether over a 40-min period. After stirring for 1 hr, the mixture was hydrolyzed with 3 *N* hydrochloric acid. The aqueous layer was washed twice with ether, and the ethereal solutions were combined. Most of the solvent was removed, and the residue was refluxed with 50 ml of a 30% potassium hydroxide solution for 1 hr. After the usual work-up, the product was distilled and 25.6 g was collected boiling at 90–145°. Analysis by vpc (see Table I) using a 20 ft × 0.125 in. column of 2.5% dibutyltetrachlorophthalate +2.5% Bentone 34 on Chromosorb W, 80–100 mesh, at 100° showed no trace of the *o*- or *p*-ethyltoluenes.

B. Ethyl Sulfate.—There was obtained 25.9 g of product boiling at 140–155°. Analysis by vpc (see Table I) using the same column as was used for methyl sulfate showed no trace of either *o*- or *p*-(*n*-propyl)ethylbenzene.[11] Authentic samples of the latter compound, as well as *o*-[12] and *p*-ethyltoluene,[12b] were at hand for a comparison of retention times.

C. n-Propyl Sulfate.[13]—There was obtained 12.6 g of material boiling at 80–200°. Complete separation of the products of this reaction [toluene, isobutylbenzene, *n*-butylbenzene, *o*- and *p*-cymene, and *o*-[14] and *p*-(*n*-propyl)toluene] was achieved using a Golay capillary column of Squalene at 80° and a hydrogen pressure of 14 psi.

D. n-Propyl p-Toluenesulfonate.[15]—Conditions for this reaction were essentially the same as those described for the methyl sulfate case except that 0.1 mol of Grignard was used and 0.2 mol of the sulfonate. There was obtained 11.0 g of product which contained only toluene, *n*-butylbenzene, and *o*- and *p*-(*n*-propyl)toluene.

Benzyllithium with n-Propyl Sulfate.—To 193 ml of tetrahydrofuran containing 0.0772 mol of benzyllithium[16] was added dropwise 60.0 g (0.33 mol) of *n*-propyl sulfate in 50 ml of dry tetrahydrofuran over a period of 40 min. After stirring at room temperature for 1 hr, the mixture was hydrolyzed with 3 *N* hydrochloric acid and then worked up in the customary manner. Distillation yielded 12.4 g of material boiling at 80–200°. See Table I for results.

Benzylmagnesium Chloride with Methyl Iodide.—To 750 ml of ether containing 0.3 mol of benzylmagnesium chloride was added dropwise 44.9 g (0.3 mol) of methyl iodide in 50 ml of ether over a 40-min period. The mixture was stirred for 3 days before it was hydrolyzed and worked up in the customary fashion. Distillation afforded 22.7 g of product boiling at 90–140°, which contained 49% ethylbenzene and 26% toluene (analysis by vpc).

Benzylmagnesium Chloride with Diethyl Sulfate. Hydrolysis with Saturated Ammonium Chloride and Aqueous Hydrochloric Acid.—To a solution (0.4 *M*) of 0.3 mol of benzylmagnesium chloride in 750 ml of anhydrous ether was added 46.2 g (0.3 mol) of diethyl sulfate in 100 ml of ether in a 20-min period. After stirring at room temperature for 1 hr, the mixture was divided into two parts. One portion was hydrolyzed with 50 ml of 15% HCl solution and 50 ml of water, the other portion with 50 ml of saturated ammonium chloride solution and 50 ml of water. Both portions were worked up in the usual manner, distilled, and analyzed by vpc (12 ft × 0.25 in. stainless steel column packed with Apiezon L on 60–80 mesh Chromosorb W at 130°). The portion hydrolyzed with hydrochloric acid contained 7% *o*-ethyltoluene and 6% *p*-ethyltoluene; that hydrolyzed with ammonium chloride contained 3% each of these two compounds.

None of the bis-substituted products (*e.g.*, the *n*-propylethylbenzenes) could be detected.

Benzylmagnesium Chloride with Diethyl Sulfate. Hydrolysis with DCl in D_2O.—A reaction was carried out under identical conditions to those described directly above. A portion (150 ml) of the reaction mixture was hydrolyzed with 20 ml of 10% DCl in D_2O and 20 ml of D_2O.[17] After the customary work-up, a sample of the *ortho*-substituted compound (*i.e.*, partially deuterated *o*-ethyltoluene) was collected by vpc (same column and conditions as above). Analysis of this sample for deuterium by mass spectroscopy indicated there was 55% of *o*-$DCH_2C_6H_4C_2H_5$ and 45% of the protium analog.[18] A pure sample of the *para* compound was collected by gc by reinjecting an initially collected[19] sample. Mass spectral analysis of this sample showed 48% deuterium enrichment.

Attempted Deuterium Exchange of p-Ethyltoluene with DCl in D_2O.—In a 200-ml flask was placed 2 g of *p*-ethyltoluene in 50 ml of ether. To the flask was added 5 ml of 20% DCl in D_2O and 5 ml of D_2O followed by 10 ml of D_2O. The mixture was stirred for 15 min.

The aqueous layer was separated and washed several times with Et_2O. The washings and organic layer were combined and dried over Drierite. The solvent was distilled by using a 12-in. Vigreux column. A sample of *p*-ethyltoluene was collected by vpc using a 4 ft × 0.25 in. stainless steel column packed with Apiezon L on 60–80 mesh Chromosorb W.

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[8] H. Gilman and J. E. Kirby, *J. Amer. Chem. Soc.*, **54**, 345 (1932).

[9] Apparently this condition was employed originally[8] to minimize carbinol formation which is known to occur if the Grignard is in excess; see P. R. Austin and J. R. Johnson, *ibid.*, **54**, 647 (1932).

[10] It should be noted that this statement is made in connection with the *unsubstituted* benzylic Grignard. Additional research will be needed to ascertain whether substituents in the aromatic ring or on the side chain play a role in determining orientation.

[11] V. N. Ipatiev, N. A. Orlov, and A. D. Petrov, *Compt. Rend. Acad. Sci., URSS, Ser. A*, 255 (1928).

[12] K. v. Auwers, *Ann. Chim.*, **419**, 109 (1919); (b) *ibid.*, **419**, 110 (1919).

[13] C. M. Suter and H. L. Gerhart, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 111.

[14] A. Claus and H. Hansen, *Ber.*, **13**, 897 (1880).

[15] F. L. Hahn and H. Walter, *ibid.*, **54**, 1541 (1921).

[16] H. Gilman, H. A. McNinch, and D. Wittenberg, *J. Org. Chem.*, **23**, 2044 (1958).

[17] The DCl was 99% isomerically pure and the D_2O was 99.5%.

[18] Analysis of the sample by nmr generally corroborated these results.

[19] The retention times of *n*-propylbenzene and the *para* compound are very close. A rough separation of these two materials was achieved by the first gc collection and final purification by the second.

Analysis of this sample for deuterium by nmr spectroscopy indicated that *no* deuterium exchange had occurred.

Benzylmagnesium Chloride and Ethyl Chlorocarbonate.—To ethyl chlorocarbonate (65.1 g, 0.6 mol) in 100 ml of anhydrous ether was added slowly 750 ml of a 0.4 *M* solution of benzylmagnesium chloride in ether. The temperature of the reaction mixture was kept at 0 to −5° by a Dry Ice–acetone bath. After this addition was completed, the mixture was stirred for 1 hr and then hydrolyzed with 100 ml of 15% hydrochloric acid followed by 100 ml of water. Following the usual work-up, the solvent was removed and the residue analyzed by vpc (4 ft × 0.25 in. stainless steel column packed with Apiezon L on 60–80 mesh Chromosorb W). The following products[20] were identified: ethyl phenylacetate (31%), tribenzylcarbinol (21%), ethyl *o*-toluate (12%), β,β-bis(benzyl)styrene (13%), and diethyl homophthalate (1%). Neither ethyl *p*-toluate nor diethyl homoterephthate could be detected by vpc.

To 3 g of the crude reaction product in 250 ml of boiling water containing 25 g of KOH was slowly added 13 g of finely powdered potassium permanganate. The mixture was refluxed 4 hr, and then the excess permanganate was destroyed by adding a small amount of ethanol. The heavy manganese dioxide precipitate was washed with a small amount of dilute alkali, and the filtrate and washings were combined and acidified with hydrochloric acid. The organic acids were extracted with ether and then esterified with diazomethane. Analysis by vpc (4 ft × 0.25 in. Apiezon L on Chromosorb W) showed the products to be methyl benzoate and dimethyl phthalate in that their nmr and infrared spectra matched those of an authentic sample. No dimethyl terephthalate could be detected.

Benzylmagnesium Chloride and Ethyl Formate.—The procedure was the same as that described for ethyl chlorocarbonate except that 44.4 g (0.6 mol) of ethyl formate was used. Analysis of the product was by vpc (5 ft × 0.25 in. column packed with 5% FFAP on 60–80 mesh Chromosorb W). Only phenylacetaldehyde was formed in any quantity (14%) in addition to considerable amounts of tar (25 g). The following materials were also identified: benzaldehyde (3%), benzyl formate (5%), β-phenylethyl formate (3%), benzyl alcohol (4%), and β-phenylethanol (1%).[21]

The crude mixture obtained from this reaction was oxidized by permanganate in essentially the same way as for ethyl chlorocarbonate. After work-up and esterification with diazomethane, the methyl esters were again analyzed by gc. Only methyl benzoate and dimethyl phthalate were found; no dimethyl terephthalate could be detected.

Registry No.—Benzylmagnesium chloride, 6921-34-2; benzyllithium, 766-04-1; *o*-(*n*-propyl)ethylbenzene, 16021-20-8.

Acknowledgment.—This research was supported by the U. S. Army Research Office (Durham) to whom the authors are deeply indebted.

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[20] Each of these materials was isolated by gc and were identical in retention time, nmr, and infrared spectra with authentic samples. The percentages listed are yields based on benzylmagnesium chloride and were determined by vpc using ethyl benzoate as an internal standard.

[21] The yields given are based on benzylmagnesium chloride and were obtained by gc using *o*-bromotoluene as an internal standard.

Metal–Ammonia Reduction. III. Stepwise Transformation of Polycyclic Aromatic Hydrocarbons[1,2]

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Received October 3, 1967

Reduction of benz[*a*]anthracene to dodecahydrobenz[*a*]anthracene in controlled stages *via* di-, tetra-, hexa-, octa-, and decahydrobenz[*a*]anthracene is achieved by means of lithium dissolved in liquid ammonia or liquid amine solvents. Utilization of nuclear magnetic resonance spectra and mass spectra to distinguish isomeric hydroaromatic structures is described.

Although the reduction of aromatic ring systems by alkali metals dissolved in liquid ammonia was observed by LeBeau and Picon[3] in 1914, it was not until the elegant investigations of Birch[4] and his collaborators that the method achieved acceptance as a major synthetic tool. The state of current knowledge, summarized in an excellent comprehensive monograph by Smith,[5] is surprisingly deficient regarding substances other than monobenzenoid molecules. Naphthalene,[3,6,7] anthracene,[8–10] phenanthrene,[7,11] pyrene,[12] fluorene,[13] and acenaphthene[8] are apparently the only polycyclic aromatic hydrocarbons to be investigated. Precautions for the exclusion of impurities known to affect the course of such reactions (trace metals,[2,14] peroxides, oxygen[15]) are seldom mentioned in the earlier literature, and characterization of the hydroaromatic products is often unsatisfactory by modern standards. Extensive reduction, often accompanied by disproportionation of products, is common. Also, the stepwise reduction of compounds possessing three or more fused aromatic rings had not been described prior to our studies in this field.[2,16]

Since controlled transformation of polycyclic aromatic hydrocarbons would provide hydroaromatic substances of considerable interest as synthetic intermediates,[17] we undertook to reinvestigate the

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[1] This investigation was supported in part by U. S. Public Health Service Research Grant CA-08674 from the National Cancer Institute. Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] Part II: R. G. Harvey and K. Urberg, *J. Org. Chem.*, **33**, 2571 (1968).

[3] P. LeBeau and M. Picon, *Compt. Rend.*, **158**, 1514 (1914).

[4] A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

[5] H. Smith, "Organic Reactions in Liquid Ammonia," Vol. 1, part 2, John Wiley and Sons, Inc., New York, N. Y., 1963.

[6] C. B. Wooster and F. B. Smith, *J. Amer. Chem. Soc.*, **53**, 179 (1931); A. J. Birch, A. R. Murray and H. Smith, *J. Chem. Soc.*, 1945 (1951); W. Hückel and H. Schlee, *Ber.*, **88**, 346 (1955).

[7] W. Hückel and H. Bretschneider, *Ann.*, **540**, 157 (1939).

[8] P. LeBeau and M. Picon, *Compt. Rend.*, **159**, 70 (1914).

[9] H. F. Miller and G. B. Bachman, *J. Amer. Chem. Soc.*, **57**, 768 (1935).

[10] A. J. Birch, *et al.*, *J. Chem. Soc.*, 2209 (1963); J. Runge, *Z. Chem.*, **2**, 374 (1962); *J. Prakt. Chem.*, [4] **31**, 280 (1966).

[11] S. Mejer, *Bull. Acad. Polon. Sci., Chim.*, **9**, 773 (1961).

[12] O. Neunhoeffer and H. Woggon, *Ann.*, **600**, 34 (1956); O. Neunhoeffer, H. Woggon, and S. Dähne, *ibid.*, **612**, 98 (1958).

[13] W. Hückel and R. Schwen, *Ber.*, **89**, 481 (1956).

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[17] For example, compounds with an internal double bond, such as V and VI, may serve as precursors to polycyclic hydrocarbons having a cyclopropyl ring fused along the ring juncture. Synthesis of several such unusual molecules will be reported shortly.