product was very soluble in water, ethanol, methanol and acetic acid at room temperature. Purification of this crude product was unsuccessful. It either separated as a sticky solid or formed two liquid layers in a number of solvents.

Triphenyl-*p*-bromophenyltin.—Triphenyl-*p*-bromophenyltin was prepared by Krause and Weinberg[6] from the reaction of *p*-dibromobenzene, magnesium and triphenyltin bromide. No yield was given in this paper, and they reported the melting point of this compound to be 224°, which seemed to be abnormally high for compounds of this type. Accordingly, the preparation of triphenyl-*p*-bromophenyltin was reinvestigated.

Several attempts were first made to prepare triphenyl-*p*-bromophenyltin essentially using the published procedure for the preparation of the silicon analog.[10]

In one experiment 0.10 mole of *n*-butyllithium was added, over a period of 10 minutes, to 25.8 g. (0.11 mole) of *p*-dibromobenzene suspended in 50 ml. of ether at 0°. A negative Color Test II-A[11] was obtained immediately after the addition. Thirty-four and seven-tenths grams (0.09 mole) of triphenyltin chloride dissolved in ether was added to the organolithium compound thus formed. The reaction mixture was warmed by the heat of reaction while a large amount of white precipitate formed. After 2 hours of refluxing the reaction mixture was hydrolyzed with ammonium chloride solution and filtered by suction. There was obtained 20.5 g. of white solid melting at 190–212°. Two recrystallizations from benzene yielded 15.2 g. of tetraphenyltin (mixed melting point) melting at 223–225°. The ethereal solution from the reaction mixture was separated, dried over sodium sulfate, filtered, and distilled to give a yellow gummy residue. This was shaken with hot 95% ethanol, cooled, and filtered to separate 19.9 g. of cream-colored, sticky solid melting at 103–110°. Two recrystallizations from a mixture of benzene and ethanol raised the melting point to 117–119°. This product contained halogen and tin, but the structure was not investigated. The experiment was repeated twice under different conditions. In all these experiments no triphenyl-*p*-bromophenyltin was isolated.

Triphenyl-*p*-bromophenyltin can be prepared by first converting *p*-bromophenyllithium into the Grignard reagent prior to the reaction with triphenyltin chloride. Thus, to 11.8 g. (0.05 mole) of *p*-dibromobenzene was added 0.05 mole of *n*-butyllithium at 0°. Ten minutes later 0.05 mole of magnesium iodide (prepared by treating magnesium with iodine in anhydrous ether) was added rapidly to the organolithium compound and was stirred for 10 minutes; meanwhile, the reaction mixture was cooled to −20°. Then 19.3 g. (0.05 mole) of triphenyltin chloride dissolved in 75 ml. of dry benzene was added rapidly to the Grignard reagent thus prepared. Color Test I[12] at the end of the addition was negative. Three minutes later the reaction mixture was hydrolyzed with cold, aqueous ammonium chloride solution. The ethereal solution was separated, dried over sodium sulfate, filtered and distilled to give 21.7 g. (86%) of white solid melting at 132–135°. One recrystallization from a solution containing 150 ml. of ethanol and 50 ml. of benzene gave 18.1 g. (72%) of colorless crystals melting at 133–135°. Further recrystallizations from a solution of ethanol and benzene or from ethanol alone did not change the melting point. Since the melting point found was very different from that described in the literature,[6] the compound was analyzed.

Anal. Calcd. for $C_{24}H_{19}BrSn$: Br, 15.79; Sn, 23.46. Found: Br, 15.64, 15.70; Sn, 23.58, 23.64.

AMES, IOWA

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[10] H. Gilman and H. W. Melvin, THIS JOURNAL, **72**, 995 (1950).

[11] H. Gilman and J. Swiss, *ibid.*, **62**, 1847 (1940).

[12] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

Reduction of Organic Compounds by Lithium in Low Molecular Weight Amines. I. Selective Reduction of Aromatic Hydrocarbons to Monoölefins

BY ROBERT A. BENKESER, ROBERT E. ROBINSON, DALE M. SAUVE AND OWEN H. THOMAS

RECEIVED DECEMBER 11, 1954

Lithium in low molecular weight aliphatic amines is uniquely suited for reducing aromatic hydrocarbons selectively to monoölefins. Thus, naphthalene and tetralin are reduced in a one-step operation in 50 to 70% yield to $\Delta^{9,10}$- and $\Delta^{1,9}$-octalins (50:1 ratio) by lithium in methyl-, ethyl- or *n*-propylamine. The small amount of $\Delta^{1,9}$-octalin formed can be isomerized to the 9,10-isomer with phosphorus pentoxide. Benzene is reduced similarly to cyclohexene and cyclohexane; biphenyl to a mixture of 1-cyclohexylcyclohexene and bicyclohexyl. Ethylbenzene at 17° is reduced to 1-ethylcyclohexene and ethylcyclohexane, while at −78°, 1-ethylcyclohexene is formed. It is proposed that these reactions involve a rapid 1,4-reduction, with isomerization of the resulting dihydro compound to a conjugated system. The final 1,2-reduction is slow, thus permitting good yields of monoölefins.

In a previous communication from this Laboratory,[1] the absorption of large quantities of lithium by various aromatic compounds dissolved in anhydrous ethylamine was reported. The formation of an organolithium intermediate is strongly suggested by the definite ratio of lithium absorbed to aromatic compound even in the presence of excess lithium; the intensely colored solutions which result; the fact that hydrolysis of the reaction mixtures did not result in the evolution of hydrogen. If an organolithium intermediate is involved, the hydrolysis product should be an extensively reduced hydrocarbon. Thus, naphthalene in ethylamine was observed to absorb eight atoms of lithium per mole of hydrocarbon. The expected reduction product should thus be one or more of the isomeric octahydronaphthalenes. In accord with this prediction we were able to isolate a mixture of $\Delta^{9,10}$- and $\Delta^{1,9}$-octalin (50:1 ratio) from this reaction.

In view of the encouraging results obtained with naphthalene, we became interested in exploring the applicability and limitations of lithium in ethylamine as a reducing agent. An excellent and very convenient procedure now has been developed whereby extensive reductions may be carried out in this system. The purpose of this paper is to report the selective nature of this reduction in producing monoölefins from aromatic hydrocarbons.

Naphthalene and Tetralin.—Naphthalene and tetralin are reduced by lithium in ethylamine to a mixture of $\Delta^{9,10}$- and $\Delta^{1,9}$-octalin (50:1 ratio). A small amount of decalin also is produced (see Table I). Identification of the olefins was accomplished by way of the nitrosochloride derivatives.

Biphenyl.—Employing similar techniques, biphenyl was reduced to a mixture of 1-cyclohexyl-

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[1] R. A. Benkeser, R. E. Robinson and H. Landesman, THIS JOURNAL, **74**, 5699 (1952).

cyclohexene and bicyclohexyl (see Table II). The olefin was identified through its nitrosochloride which gave an undepressed mixed melting point with an authentic sample.[2,3]

Benzene.—Benzene was reduced in ethylamine to a mixture of cyclohexene and cyclohexane. A 2,4-dinitrobenzenesulfenyl chloride adduct of this product was not depressed in melting point by a similar derivative prepared from authentic cyclohexene. The identification was confirmed by an infrared spectrum.

Ethylbenzene.—Ethylbenzene, when reduced at the reflux temperature of ethylamine (17°), gave a mixture of 1-ethylcyclohexene (45%) and ethylcyclohexane (55%) as determined by bromine titration of the reduction mixture (see Experimental for this procedure). A nitrosyl chloride adduct of the olefin did not depress the melting point of an authentic sample.

When the reduction was carried out at −78°, 1-ethylcyclohexene was produced (75% yield) with but trace amounts of the completely saturated compound.

The utility of several low molecular weight amines other than ethylamine as solvents for these reductions has been investigated. Methyl and *n*-propylamine have been found to give the same products from naphthalene, biphenyl and tetralin as were obtained using ethylamine. Although reductions with naphthalene and biphenyl also occur in isopropyl, *n*-butyl and diethylamine, the reactions are considerably slower, and the products consist of mixtures of less extensively reduced hydrocarbons than are obtained with methyl-, ethyl- and *n*-propylamines. This is probably due to the limited solubility of lithium in these solvents.

The marked difference between the lithium–amine and the sodium–ammonia systems is seen clearly by comparing the reduction products obtained from the individual reducing agents. Naphthalene is reduced by the lithium–amine reagent to the isomeric $\Delta^{9,10}$- and $\Delta^{1,9}$-octalin, whereas sodium–ammonia reduces it to tetralin.[4] Similarly, biphenyl is reduced by the lithium–amine system to 1-cyclohexylcyclohexene and by sodium–ammonia to 1-phenyl-1-cyclohexene.[5] While benzene[6] is unaffected by sodium–ammonia, the lithium–amine system reduces it to cyclohexene and cyclohexane. We also have shown that lithium in ammonia reduces naphthalene to tetralin. Several attempts to effect reduction of naphthalene by sodium in ethylamine resulted in unidentified polymeric materials. These results serve to point out the potency and uniqueness of the *lithium–amine combination* in reducing aromatic hydrocarbons to monoölefins. In this regard the lithium–amine system resembles the calcium–ammonia[7] system, but from our experience differs from it in being more convenient to handle and, in at least one instance, superior.[8]

Discussion

The above cases represent one of the few recorded instances in which reduction of an aromatic nucleus by a chemical reducing agent was effectively halted at the monoölefin stage.

It is interesting to speculate on the reason for the selectivity of this reaction. We are currently investigating the possibility that these reductions proceed initially by some type of *rapid* 1,4-addition of lithium. The organometallic thus produced reacts with the solvent to form a 1,4-dihydro product which then rearranges in the basic medium to a more stable conjugated olefinic system. The latter undergoes further 1,4-reduction until ultimately a monoölefin is formed. A *much slower* 1,2-reduction then ensues, but this can be virtually stopped at low temperatures.

Experimental

General Procedure for Lithium–Amine Reductions.—All reductions were carried out under a nitrogen atmosphere in a 500-cc. three-necked flask equipped with mechanical stirrer, Dry Ice condenser or Friedrich condenser at the reflux temperature of ethylamine and methylamine unless otherwise stated, and at room temperature with propyl, isopropyl and *n*-butylamines. In cases where the material to be reduced was a liquid, a separatory funnel also was employed. The liquid was added dropwise to the blue solution of the amine containing the lithium wire or ribbon cut up in small pieces. When the material to be added was a solid, it was placed in the flask with the metal. The amine was then added and stirring commenced. Various color changes ranging from green to dark red were observed in all cases in which reduction occurred. With ethylamine and *n*-propylamine, these colors developed within 5 minutes; the reactions in isopropyl and *n*-butylamine were considerably slower. The reduction using ethylamine and *n*-propylamine required periodic cooling. The total reaction time was usually 8 to 10 hours. At the end of this time, the excess lithium, which usually became fused into one piece, was removed mechanically with the aid of forceps. The solution then was decomposed by the cautious addition of solid ammonium chloride. This addition was halted when the solution became colorless. The solvent then was allowed to evaporate, and water was added dropwise to the residue with external cooling. The organic layer was taken up into ether and separated. The aqueous layer was extracted with ether and the combined ether extracts were dried over magnesium sulfate. The ether was stripped off and the product isolated by distillation.

Determination of Total Olefin Content in Reaction Mixtures.—The total amount of olefinic material in the reduction products of biphenyl, naphthalene and tetralin in methyl-, ethyl- and *n*-propylamines was determined by titration of a known amount of the mixture with a standard bromine–acetic acid solution as described by Uhrig and Levin.[9] The method was estimated to be accurate within 4% as checked with mixtures of known composition.

The mixtures obtained from the reduction of benzene and ethylbenzene in ethylamine were analyzed for total olefin by the procedure described by Siggia.[10] Check determinations on known standard cyclohexene solutions showed this method had an accuracy of ±3%. In all cases, the amount of saturated hydrocarbon was obtained by difference.

Reduction of Naphthalene in Ethylamine (Table I, Run a).—In a typical run, 12.8 g. (0.1 mole) of naphthalene was reduced by 8.3 g. (1.2 g. atoms) of lithium in 250 cc. of anhydrous ethylamine. Upon working up, there resulted 10.2 g. of distillate (75%), b.p. 190–193° (753 mm.), $n^{20}{}_{\mathrm{D}}$ 1.4972. *Anal.* total olefin, 95%; decalin, 5%. Con-

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[2] R. Criegee, E. Vogel and H. Hoger, *Chem. Ber.*, **85**, 144 (1952).

[3] W. Hückel and I. Neunhoeffer, *Ann.*, **477**, 106 (1930).

[4] P. Lebeau and M. Picon, *Compt. rend.*, **158**, 1514 (1914). See also C. B. Wooster and F. B. Smith, THIS JOURNAL, **53**, 179 (1931).

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

[6] P. Lebeau and M. Picon, *Compt. rend.*, **159**, 70 (1915).

[7] B. A. Kazanskii and N. F. Glushnev, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 642 (1938); *C. A.*, **33**, 1280 (1939).

[8] Whereas Kazanskii reports that mesitylene is reduced difficultly by calcium–ammonia, we have found that mesitylene is reduced smoothly by the lithium–amine system to 1,3,5-trimethylcyclohexene. These results will appear in a later publication.

[9] K. Uhrig and H. Levin, *Ind. Eng. Chem. Anal. Ed.*, **13**, 90 (1941).

[10] S. Siggia, "Quantitative Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 33–37.

TABLE I

REDUCTION OF NAPHTHALENE AND TETRALIN

	Hydrocarbon (mole)	Metal (g. atom)	Solvent	Time, hr.	n^{20}D (crude product)	Yield, % Octalins	Decalin	Ratio octalins (approx.) $\Delta^{9,10}/\Delta^{1,9}$
a	$C_{10}H_8$(0.1)	Li(1.2)	$EtNH_2$	10	1.4972	71	5	50/1
b	$C_{10}H_8$(0.1)	Li(1.2)	$MeNH_2$	5	1.4925	56	4	7–10/1
c	$C_{10}H_8$(0.1)	Li(1.2)	*n*-$PrNH_2$	10	1.4986	49	10	45–50/1
d	$C_{10}H_8$(0.05)	Li(0.45)	*i*-$PrNH_2$	10	1.5257	No octalins obsd.		.....
e	$C_{10}H_8$(0.05)	Li(0.45)	*n*-$BuNH_2$	10	1.5127	..	..	28/1
f	$C_{10}H_8$(0.05)	Li(0.45)	Et_2NH	10	1.5320	Tetralin observed		.....
g	$C_{10}H_{12}$(0.1)	Li(0.7)	$EtNH_2$	10	1.4988	56	12	40/1
h	$C_{10}H_{12}$(0.1)	Li(0.7)	*n*-$PrNH_2$	30	1.4970	54	..	80–85/1
i	$C_{10}H_8$(0.1)	Li(0.9)	NH_3	12	1.5403	Tetralin, 66%		.....
j	$C_{10}H_8$(0.05)	Na(0.45)	$EtNH_2$	10	....	Polymeric material		.....

version to the nitrosochloride derivatives showed the olefins to be $\Delta^{9,10}$- and $\Delta^{1,9}$-octalin in an approximate ratio of 50:1. The blue 9-chloro-10-nitrosodecahydronaphthalene after crystallization from acetone melted at 90–91° alone or in a mixed melting point with an authentic specimen (reported[11] m.p. 91°).

The white 9-chloro-1-oximinodecahydronaphthalene melted at 127° when a capillary containing the compound was inserted into a melting point bath preheated to 120°. Melting points taken in the usual way were always lower. This derivative has been reported to melt at 114–115,[7] 121,[11] 127,[12] 135,[13] 142–143.[12] It had been noted previously that its melting point depends on the method of heating.[11] Treatment of the $\Delta^{1,9}$-octalin nitrosochloride with piperidine converted it to the corresponding nitrolpiperidine which melted at 176–177° when inserted into a bath preheated to 170°. This derivative has been reported to melt at 173°,[14] 179,[12] 181,[13] and 178–179.[12] Its melting point also has been reported to depend on the method of heating.[12] The $\Delta^{1,9}$-octalin nitrosochloride also was converted to the expected $\Delta^{9,10}$-1-ketoöctahydronaphthalene 2,4-dinitrophenylhydrazone by treatment with 2,4-dinitrophenylhydrazine in alcohol containing hydrochloric acid. Crystallization from xylene yielded small, dark red crystals, m.p. 266–267° dec., reported[15,16] m.p. 266.5–267° dec.

Neither the nitrosochloride or the nitropiperidine depressed the m.p. of the corresponding derivatives obtained from the $\Delta^{1,9}$-octalin prepared by the method of Kazanskii and Glushnev.[7]

Comparison of the infrared spectrum of this mixture with the spectra of authentic $\Delta^{9,10}$-, $\Delta^{1,9}$- and *cis*- and *trans*-$\Delta^{1,2}$-octalins further established the presence of the 1,9- and 9,10-isomers and conveniently eliminated the presence of *cis*- and *trans*-$\Delta^{1,2}$-octalin.

A 2,4-dinitrobenzenesulfenyl chloride adduct of the reduction product was prepared following the procedure of Kharasch and Buess.[17] The yellow adduct crystallized from absolute ethanol as yellow needles, m.p. 142–143°.

Anal. Calcd. for $C_{16}H_{19}N_2O_4SCl$: C, 51.82; H, 5.14; N, 7.56. Found: C, 51.57; H, 5.46; N, 7.65.

Pure $\Delta^{9,10}$-octalin regenerated from 9-chloro-10-nitrosodecahydronaphthalene by treatment with sodium methoxide in methanol failed to give a 2,4-dinitrobenzenesulfenyl chloride adduct. The adduct proved to be 9-chloro-1-decahydronaphthyl 2′,4′-dinitrophenyl sulfide formed from $\Delta^{1,9}$-octalin. This was identical (mixed m.p.) with the corresponding derivative obtained from a mixture of $\Delta^{9,10}$- and $\Delta^{1,9}$-octalin prepared by the method of Kazanskii and Glushnev.[7]

The results obtained by reducing this compound in other amines are summarized in Table I.

Isomerization of $\Delta^{1,9}$- to $\Delta^{9,10}$-Octalin.—In a 100-ml. 3-necked flask equipped with a mechanical stirrer and reflux condenser, 7.0 g. (9,10 to 1,9 ratio 45–50:1) of the isomeric octalins was added to 4 g. of phosphorus pentoxide. The mixture was heated for 2 hours at 140°. The flask was cooled and ice was added to react with the phosphorus pentoxide. The organic material was taken up into ether and after washing and drying the solvent was distilled. Distillation of the residue gave 6.6 g. of product, b.p. 192–193° (760 mm.); the 9,10 to 1,9 ratio was now 95:1.

Reduction of Tetralin in Ethylamine (Table I, Run g).—Following the general procedure, 13.2 g. (0.1 mole) of tetralin was reduced by 4.83 g. (0.7 g. atom) of lithium in 250 cc. of ethylamine. Upon working up the reaction mixture, 9.25 g. of distillate (68%) was isolated, b.p. 193–194.5° (755 mm.), n^{20}D 1.4988. *Anal.* total olefin, 82%; decalin, 18%. Preparation of the nitrosochloride showed the olefins to be $\Delta^{9,10}$- and $\Delta^{1,9}$-octalin in an approximate ratio of 40:1.

Another reduction of this compound using *n*-propylamine as a solvent is summarized in Table I.

Reduction of Biphenyl in Methylamine (Table II, Run a).—In a typical reduction, 15.4 g. (0.1 mole) of biphenyl was reduced by 9.0 g. (1.3 g. atoms) of lithium in 300 cc. of anhydrous methylamine. The reaction mixture was worked up as usual. Distillation gave two fractions after a small forerun, 10.60 g., 108.5–110° (14 mm.), n^{20}D 1.4958; 3.80 g., 111–112.5° (15 mm.), n^{20}D 1.4962. This was shown to be a mixture (87%) of 1-cyclohexylcyclohexene and bicyclohexyl by conversion of the olefin to its nitrosochloride and formation of two layers with fuming sulfuric acid. *Anal.* total olefin, 94%; bicyclohexyl, 6%. After crystallization from acetone, the white nitrosochloride melted at 140° alone or in a mixed m.p. with an authentic sample (reported[18] for 1-cyclohexylcyclohexene, n^{20}D 1.4969, nitrosochloride,[2,3] 140°). Isolation of a small amount of the acid-insoluble hydrocarbon showed it to have a refractive index of 1.4820 (reported[18] for bicyclohexyl, 1.4794). Other reductions of this compound are summarized in Table II.

TABLE II

REDUCTION OF BIPHENYL

	Hydrocarbon, mole	Li, g. atoms	Solvent	Yield, % 1-Cyclohexylcyclohexene	Bicyclohexyl
a	0.1	1.3	$MeNH_2$	82	5
b	.018	0.20	$EtNH_2$	66	..
c	.1	1.3	*n*-$PrNH_2$	48	3
d	.05	0.65	*i*-$PrNH_2$	1–2[a]	
e	.1	1.3	*n*-$BuNH_2$	10–15[a]	

[a] Estimated yields based on yield of nitrosochloride obtained from reduction mixture.

Reduction of Benzene in Ethylamine.—Following the general procedure for reductions, 11.7 g. (0.15 mole) of benzene was reduced by 7.4 g. (1.05 g. atoms) of lithium in 250 cc. of anhydrous ethylamine. During the evaporation of

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[11] (a) W. Hückel, R. Danneel, A. Schwartz and A. Gercke, *Ann.*, **474**, 132 (1929); (b) P. D. Bartlett, F. E. Condon and A. Schneider, THIS JOURNAL, **66**, 1538 (1944).

[12] (a) W. Hückel and H. Naab, *Ann.*, **502**, 136 (1933); (b) see also A. C. Cope and G. Holzman, THIS JOURNAL, **72**, 3067 (1950).

[13] W. Hückel, R. Danneel, A. Schwartz and A. Gercke, *Ann.*, **474**, 121 (1929).

[14] W. Huckel and M. Blohm, *ibid.*, **502**, 134 (1933).

[15] A. L. Wilds and N. A. Nelson, THIS JOURNAL, **75**, 5365 (1953).

[16] J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 817 (1937).

[17] N. Kharasch and C. Buess, THIS JOURNAL, **71**, 2724 (1949).

[18] N. D. Zelinskii, N. I. Shuikin and L. M. Fateev, *J. Gen. Chem.* (*U.S.S.R.*), **2**, 671 (1932); *C. A.*, **27**, 2430 (1933).

the solvent, a Friedrich condenser was attached to the flask as a special precautionary measure to minimize the loss of product due to entrainment. The run was worked up as usual to yield 8.4 g. (68%) of reduction product, b.p. 81–81.5° (752 mm.), $n^{20}\text{D}$ 1.4380. This proved to be a mixture of cyclohexene (75%) and cyclohexane (25%). The former was identified by conversion to 2-chlorocyclohexyl 2′,4′-dinitrophenyl sulfide by reaction with 2,4-dinitrobenzenesulfenyl chloride. After crystallization from 95% ethanol, the derivative melted at 118.5–119° (reported[17] 117–118°). The infrared spectrum of an authentic cyclohexane–cyclohexene mixture was identical with the spectrum of the reduction mixture.

Reduction of Ethylbenzene by Lithium in Ethylamine. A. At 17°.—The reduction of 10.6 g. (0.1 mole) of ethylbenzene by 5.6 g. (0.8 g. atom) of lithium in ethylamine resulted in 7.0 g. of distillate (68%), b.p. 129°, $n^{20}\text{D}$ 1.4438. This product proved to be a mixture of ethylcyclohexane and 1-ethylcyclohexene by comparison of the infrared spectrum with the spectrum of an authentic mixture of ethylcyclohexane and 1-ethylcyclohexene; the isolation of the nitrosyl chloride derivative of the olefin from the mixture which melted at 102° alone or in a mixed m.p. with an authentic specimen,[7] and the formation of two layers with fuming sulfuric acid. Bromine titration showed this mixture contained 42–45% 1-ethylcyclohexene and 55–58% ethylcyclohexane. A plot of refractive index *versus* percentage composition for known concentrations of ethylcyclohexane and 1-ethylcyclohexene followed a linear relationship. Analysis of the mixture by this refractometric method checked well with the value from the titration.

B. At −78°.—From the reduction of 10.6 g. (0.1 mole) of ethylbenzene by 5.6 g. (0.8 g. atom) of lithium in ethylamine kept at −78° by a Dry Ice slurry, there resulted 8.3 g. (75%) of 1-ethylcyclohexene, b.p. 131°, $n^{20}\text{D}$ 1.4572 (reported[19] 1.4570). The nitrosyl chloride melted at 101–102°. No depression was observed in a mixed m.p. determination with an authentic sample.

Acknowledgment.—The authors gratefully acknowledge the assistance of Dr. Arthur Cope in interpreting the infrared absorption spectra of the octalin mixture. We also wish to express our appreciation to the Purdue Research Foundation and the Research Corporation for their financial assistance.

[19] G. Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1940, p. 329.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Air Oxidation of Hydrocarbons.[1] II. The Stoichiometry and Fate of Inhibitors in Benzene and Chlorobenzene

BY CHARLES E. BOOZER, GEORGE S. HAMMOND, CHESTER E. HAMILTON AND JYOTIRINDRA N. SEN

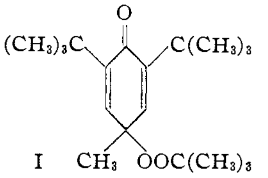
RECEIVED NOVEMBER 6, 1954

The inhibitory effects of 17 phenols and amines on the autoöxidation of cumene initiated by azo-bis-isobutyronitrile have been studied. By the measurement of the duration of the inhibition periods the relative chain-stopping capacities of the antioxidants have been determined. These relative values are then put on an absolute basis by the identification of the products derived from two of the inhibitors. The efficiency of chain initiation indicated by the stoichiometric factors thus assigned is in good agreement with initiator efficiencies measured by other methods. The significance of the individual stoichiometric factors is discussed.

Variously substituted phenols and aromatic amines are well known antioxidants for hydrocarbons. The efficiency of such antioxidants has been measured for a wide variety of substrates and experimental conditions.[2]

It is generally conceded that most such inhibitors function by reacting with alkyl peroxy radicals ($RO_2\cdot$) rather than alkyl radicals except at low oxygen pressures since oxidation rates become independent of the oxygen pressure at partial pressures well below one atmosphere.[3] It is, therefore, to be expected that the reactions of antioxidants may be quite unlike those of substances which are known to react with carbon radicals. Despite this fact relatively little has been done to establish the nature of these reactions.

Bolland and ten Haave[4] suggest that hydroquinones react only with $RO_2\cdot$ radicals produced in the benzoyl peroxide initiated oxidation of ethyl linoleate. Each molecule of hydroquinone was assumed to react with two radicals to produce benzoquinone and two molecules of hydroperoxide. Campbell and Coppinger[5] reported that compound I was produced as a consequence of carrying out the decomposition of *tert*-butylhydroperoxide in the presence 2,6-di-*t*-butyl-*p*-cresol. They suggested that this compound was



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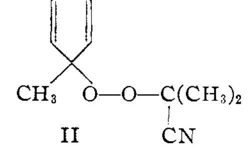
the product of the reaction(s) of two *t*-butylperoxy radicals with the phenol and drew the further inference that the reaction(s) of two $RO_2\cdot$ with this antioxidant should, in general, give analogous products. This presumption was further confirmed by the observation, which we had also made, that II



II

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[1] Part I of this series is C. E. Boozer and G. S. Hammond, THIS JOURNAL, **76**, 3861 (1954).

[2] (a) R. H. Rosenwald, J. R. Hoatson and J. A. Chenicek, *Ind. Eng. Chem.*, **42**, 162 (1950); (b) E. M. Bickoff, *J. Am. Oil Chem. Soc.*, **28**, 65 (1951); (c) R. H. Rosenwald and J. A. Chenick, *ibid.*, **28**, 185 (1951); (d) J. L. Bolland and P. ten Haave, *Disc. Faraday Soc.*, **2**, 252 (1947); (e) C. D. Lowry, Jr., G. Egloff, J. C. Morrell and C. G. Dryer, *Ind. Eng. Chem.*, **25**, 804 (1933).

[3] L. Bateman, *Quart. Revs.*, **8**, 147 (1954).

[4] J. L. Bolland and P. ten Haave, *Trans. Faraday Soc.*, **43**, 2011 (1947).

[5] T. W. Campbell and G. M. Coppinger, THIS JOURNAL, **74**, 1469 (1952).