[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXXV. The Reactions of the Sodium Derivative of Allylbenzene in *n*-Pentane with Methanol, Alkyl and Allylic Halides[1a]

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The reactions of the sodium derivative of allylbenzene, $[C_6H_5CH\overset{\cdots}{-}CH_2\overset{\cdots}{-}CH_2]^{\ominus}$, in *n*-pentane with methanol, methyl bromide, *n*-amyl chloride, allyl chloride, allyl iodide, 1-chloro-2-butene, 3-chloro-1-butene, 1-bromo-2-butene and 3-bromo-1 butene have been studied and compared to the analogous reactions in liquid ammonia. The action of methanol with the sodium derivative of 1-phenylcyclohexene has also been studied in liquid ammonia. A correlation is presented for the reactions of a number of allylic-metallic compounds with various catoinoid agents in several media.

In the reactions of organosodium compounds with chlorobutenes, it has been shown that there are two mechanisms possible, apparently depending either upon the medium or the organosodium compound involved. In a non-polar medium, such as *n*-pentane, ethylsodium reacted with 3-chloro-1-butene and 1-chloro-2-butene to give identical results.[2] This was considered evidence for a carbonium-ion process (SN1). Similar results were obtained with phenylsodium,[3a] phenyllithium,[3b] butyllithium[3b] and butylmagnesium chloride.[4]

When liquid ammonia was used as a polar medium, the reaction of phenylallylsodium with the same chlorobutenes showed that a direct-displacement process (SN2) occurred without rearrangement of the butenyl moiety.[5,6] It was these differences in reaction mechanism that prompted the study of the reactions of the sodium derivative of allylbenzene in *n*-pentane with methanol (a proton donor) and various alkyl and allylic halides.

Reactions with Methanol.—The reactions of the organosodium derivative of allylbenzene in *n*-pentane with methanol gave strikingly different product compositions depending upon the order of addition.

$$\underset{\text{I}}{[C_6H_5CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2]^{\ominus}\,Na^{\oplus}} + CH_3OH \longrightarrow \begin{matrix} C_6H_5CH{=}CHCH_3 \\ C_6H_5CH_2CH{=}CH_2 \end{matrix} + CH_3ONa \quad (1)$$

These results are shown in Table I. In method A, the slurry of the organosodium compound in *n*-pentane was added to a large excess of methanol in pentane. In method B, the methanol was added to organosodium compound in *n*-pentane (or in liquid ammonia). In all of the reactions carried out in *n*-pentane the organosodium derivative was prepared by a proton–metal interchange between amylsodium and allylbenzene; however, in these reactions with methanol an excess of amylsodium

$$C_5H_{11}Na + C_6H_5CH_2CH{=}CH_2 \longrightarrow C_5H_{12} + [C_6H_5CH\overset{\cdots}{-}C\overset{\cdots}{-}CH_2]^{\ominus}\,Na^{\oplus} \quad (2)$$

was used to ensure that none of the original unreacted allylbenzene would be in the products. The results can be explained on the basis of the excess amylsodium, or possibly phenylallylsodium, being present. In method B, as the methanol is being added, the excess organosodium or amylsodium has an opportunity to react with the newly formed allylpropenylbenzene mixture regenerating the phenylallyl anion. If the organosodium compound reacts preferentially with the more acidic hydrocarbon, allylbenzene, as expected, then propenylbenzene should be the major component. In method A, where the amylsodium–phenylallylsodium slurry is added to methanol, the amylsodium can only react with the methanol. Sodium methoxide in pentane was shown not to affect the rearrangement of allylbenzene to propenylbenzene in contrast with the results in liquid ammonia.[8] It becomes apparent that results of method A give a better indication of the true reaction course. In liquid ammonia the major component of the reaction mixture was shown to be propenylbenzene.[8]

TABLE I

YIELD AND PRODUCT COMPOSITION FOR THE REACTIONS OF THE SODIUM SALT OF ALLYLBENZENE WITH METHANOL

Medium	*n*-Pentane		Liquid ammonia	
Method of addition	A	B	B[6]	A[7]
Yield of hydrocarbons, %	84	81	70	80
Composition (by wt.)				
Allylbenzene, %	74	16.5	15	7
cis-Propenylbenzene, %	26	14.5	85	93
trans-Propenylbenzene, %		69		

Azeotropes of *cis*- and *trans*-propenylbenzene with *n*-decane were encountered during the distillation of the products of the above reactions in *n*-pentane. Their composition and physical properties have been reported.[9]

The reaction of the sodium salt of 1-phenylcyclohexene in liquid ammonia with methanol was carried out as an extension of the studies of the sodium derivative of allylbenzene to see what effect the cyclohexene ring might have on the mesomeric anion and its reaction products. Under the assumption that 1- and 3-phenylcyclohexane would be the products of this reaction, it was anticipated that the 1-phenylcyclohexene would be the major

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(1) (a) The authors wish to acknowledge the helpful criticism of Dr. Dorothy Semenow. (b) Standard Oil Co. of California Fellow, 1950–1952.

(2) S. E. Ulrich and J. F. Lane, THIS JOURNAL, **72**, 5130 (1950).

(3) (a) S. J. Cristol and W. C. Overhults, *ibid.*, **73**, 2932 (1951); (b) S. J. Cristol, W. C. Overhults and J. S. Meek, *ibid.*, **73**, 813 (1951).

(4) A. L. Henne, H. Chanan and A. Turk, *ibid.*, **63**, 3473 (1941).

(5) H. Levy and A. C. Cope, *ibid.*, **66**, 1684 (1944).

(6) W. G. Young, M. Kosmin, R. Y. Mixer and T. W. Campbell, *ibid.*, **74**, 608 (1952).

(7) D. E. Johnson, unpublished work, University of California at Los Angeles.

(8) T. W. Campbell and W. G. Young, THIS JOURNAL, **69**, 688 (1947).

(9) R. Y. Mixer, R. F. Heck, S. Winstein and W. G. Young, *ibid.*, **75**, 4094 (1953).

component (*cf.* phenylallylsodium in liquid ammonia, Table I).

The composition observed was 64% 1-phenylcyclohexene and 36% 3-phenylcyclohexene and not 85 and 15%, respectively, as predicted by the results from phenylallylsodium in liquid ammonia (see Table I).

The refractive index of the 1-phenylcyclohexene that was obtained was 1.5692 as compared to the literature value of $n^{20}D$ 1.5670.[10] The analytical and optical data offered ample proof that the compound obtained was, in fact, 1-phenylcyclohexene. The principal infrared absorption bands of 1- and 3-phenylcyclohexene are presented in Table II.

TABLE II

PRINCIPAL INFRARED ABSORPTION BANDS OF 1- AND 3-PHENYLCYCLOHEXENE

s = strong, m = medium and w = weak intensities

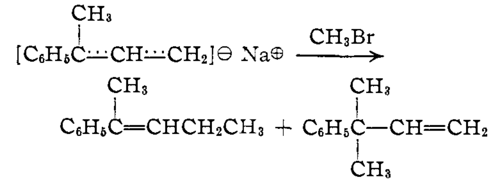
Cyclohexenes, frequency, cm.$^{-1}$ 1-Phenyl-	3-Phenyl-	1-Phenyl-	3-Phenyl-
	675s		
696s	701s	1248w	1264w
	725s	1284w	
744s			1312w
760s	755s	1350m	1346w
	790m	1443s	1456s
805m		1495m	1502m
850m	847m	1597m	1613m
	883m	1645w	1664w
906m	895m	1733w	1761w
921s	912m	1799w	1825w
1007w	986w	1876w	1894w
1037w	1036w	1949w	1972w
1080w	1081w	2874s	2941s
1142w	1143w	2924s	2994s
		3058s	3105s

Reactions with Allyl Halides.—In the reactions of the sodium derivative of allylbenzene with methyl bromide, it is possible to formulate two monoalkylated and four dialkylated products. These could arise by the reactions

$$I + CH_3Br \longrightarrow \underset{III}{C_6H_5CH=CHCH_2CH_3} + \underset{IV}{C_6H_5CH(CH_3)CH=CH_2} \quad (4)$$

$$III + Na^{\oplus}A^{\ominus} \longrightarrow [C_6H_5CH\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CHCH_3]^{\ominus}Na^{\oplus} \xrightarrow{CH_3Br} C_6H_5CH=CHCH(CH_3)_2 + C_6H_5CH(CH_3)CH=CHCH_3 \quad (5)$$

$IV + Na^{\oplus}\ A^{\ominus} \longrightarrow$



$$[C_6H_5\overset{CH_3}{\overset{|}{C}}\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CH_2]^{\ominus}\ Na^{\oplus} \xrightarrow{CH_3Br} C_6H_5\overset{CH_3}{\overset{|}{C}}=CHCH_2CH_3 + C_6H_5\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH=CH_2 \quad (6)$$

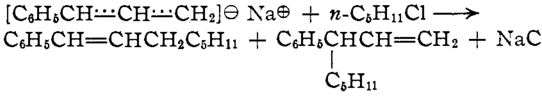
where $A^{\ominus}$ represents any anion capable of bringing about the acid–salt interchange and is most likely the phenylallyl anion. The results of the reactions of the sodium derivative of allylbenzene in *n*-pentane with methyl bromide are compared in Table III with those previously reported[6] for the same reactions in liquid ammonia. Here method A and B imply the same order of addition as for the reactions with methanol. It is interesting to note that there is very little difference in the results for methods A and B when *n*-pentane is used as the medium. This is in contrast to the large difference in liquid ammonia. The results in liquid ammonia were partially explained[6] by assuming that when the phenylallylsodium was in excess (method B) reactions 5 and 6 had a chance to occur. The only dialkylated product isolated in liquid ammonia was 3-methyl-3-phenyl-1-butene. The absence of dialkylated products in *n*-pentane indicated that reactions 5 and 6 had little tendency to occur in a non-polar medium. In view of expected greater acidity of allylbenzene as compared to the phenyl-1-butenes[11,12] this would indicate that the acid–salt interchange is more sensitive to differences in acid strength in *n*-pentane than in liquid ammonia. The increased sensitivity may be the result of a change in the nucleophilic character of the phenylallyl anion, $[C_6H_5CH\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CH_2]^{\ominus}$.

TABLE III

YIELD AND PRODUCT COMPOSITION FOR THE REACTIONS OF THE SODIUM DERIVATIVE OF ALLYLBENZENE WITH METHYL BROMIDE

Medium	*n*-Pentane		Liquid ammonia[6]	
Method of addition	A	B	A	B
Yield, %	35	24	70	42
3-Phenyl-1-butene, %	58	55	91.5	38
cis-1-Phenyl-1-butene, %	42	45	8.5	12
trans-1-Phenyl-1-butene, %				14
3-Methyl-3-phenyl-1-butene, %	..	..	..	36

The reaction of the sodium derivative of allylbenzene with *n*-amyl chloride in *n*-pentane was studied to determine the reaction course when a relatively unreactive alkyl halide was used and to determine the physical constants of the expected products, 1- and 3-phenyl-1-octenes.



$$[C_6H_5CH\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CH_2]^{\ominus}\ Na^{\oplus} + n\text{-}C_5H_{11}Cl \longrightarrow C_6H_5CH=CHCH_2C_5H_{11} + C_6H_5\underset{C_5H_{11}}{\underset{|}{C}}HCH=CH_2 + NaCl \quad (7)$$

It was anticipated that in the other reactions the 3-phenyl-1-octene might be found as a side reaction from the unreacted *n*-amyl chloride (used in preparing the amylsodium), and that this compound was interfering with the product analyses of the reactions of the sodium derivative of allylbenzene with the butenyl halides (see Experimental).

It was found necessary to raise the temperature from −10° (at which the reactions were normally run) to +20° in order to have the reactions with *n*-amyl chloride proceed at a reasonable rate. This would have been expected of relatively unreactive *n*-alkyl chlorides. The expected products were found in the proportions of 70% 3-phenyl-1-octene and 30% 1-phenyl-1-octene. Only the 1-phenyl-1-octene had been reported previously,[13] but the refractive index did not agree with that found in this investigation. There was substantial physical (see

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(10) C. C. Price and J. V. Karabinos, THIS JOURNAL, **62**, 1159 (1940).

(11) A. A. Morton, *Chem. Revs.*, **35**, 1 (1944).

(12) A. J. Birch, *Disc. Faraday Soc.*, **2**, 246 (1951).

(13) S. Reich, *et al.*, *Helv. Chim. Acta*, **4**, 242 (1921).

Experimental) and optical evidence to support the claim that the compounds were, in fact, *trans*-1-phenyl-1-octene and 3-phenyl-1-octene. The ultraviolet absorption maxima of these compounds are almost identical with those of *trans*-propenylbenzene and allylbenzene, respectively (Table IV). Koch[14] found a small but definite batho- and hyperchromic shift of the ultraviolet absorption maximum (in the 250 mμ region) of 1,10-diphenyl-1,9-decadiene as compared to 1,6-diphenyl-1,5-hexadiene. He ascribed this shift to the increased weight or length of the carbon chain. A similar effect was noted for *trans*-1-phenyl-1-octene as compared to *trans*-propenylbenzene (*cf.* Table IV). This effect is also shown in the molar exaltations of the two compounds (*trans*-1-phenyl-1-octene, 2.46; *trans*-propenylbenzene, 1.87[9]). The infrared absorption spectrum of 1-phenyl-1-octene (Table V) showed the typical, strong band of the asymmetrical out-of-plane hydrogen deformations of the *trans*-CH—CH— grouping[15,16] at 967 cm.$^{-1}$. The corresponding deformations in the vinyl group[15,16] were found for 3-phenyl-1-octene (Table V) as strong bands at 911 and 948 cm.$^{-1}$. The infrared absorption spectrum of the 3-phenyl-1-octene was almost identical (as expected) with that of 3-phenyl-1-butene.[17]

TABLE IV

ULTRAVIOLET ABSORPTION MAXIMA OF 1- AND 3-PHENYL-1-OCTENE COMPARED TO THAT OF PROPENYLBENZENE (*cis* AND *trans*)[a] AND ALLYLBENZENE, RESPECTIVELY, IN 95% ETHANOL

1-Phenyl-1-octene		Propenylbenzene			
		trans-		*cis*-	
λ, mμ	εm	λ, mμ	εm	λ, mμ	εm
251	18,400	250	17,300	240.6	13,800
284	1,430	284	1,100	279	Sh.
293	1,000	293	780	290	120

3-Phenyl-1-octene		Allylbenzene	
λ, mμ	εm	λ, mμ	εm
248	177	249	Sh.
251.3	227	253.8	225
254.5	Sh.	255.3	223
258.5	255	259.2	276
261.3	244	261.6	288
264.4	193	264.4	205
268.2	174	268.5	212

[a] Reference 9.

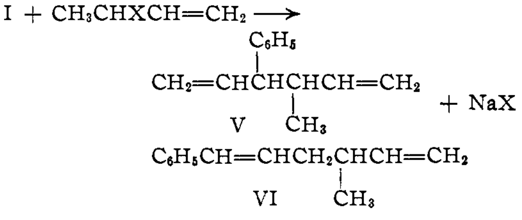
Reactions with Allyl Halides.—The reactions with the allylic halides were run to determine whether the expected change in the reaction mechanism (from SN2 to SN1) was due to a change in medium or a change in organometallic compound or both. The sodium derivative of allylbenzene is unique in comparison to the other organometallics studied in that it can exist in all three media (pentane, ether[7] and liquid ammonia). The allylic halides chosen for these studies were allyl chloride, allyl iodide, 1-chloro-2-butene, 3-chloro-1-butene, 1-bromo-2-butene and 3-bromo-1-butene. The results of their reactions with phenylallylsodium in *n*-pentane are compared with those in liquid ammonia[6] in Table VI. Even though one could not detect a change in mechanism for the allyl halides[18] in the two media there was a moderately large difference in product composition. However, with the halobutenes[19] the change in mechanism is easily seen. In liquid ammonia only two of the possible four products were formed from each halide, whereas in pentane all four products were found. The reactions involved in liquid ammonia were shown to be of the SN2 type[6]; however, in *n*-pentane the compositions were significantly different from those in ammonia and similar (maximum product spread 23%) for all of the 1- and 3-butenyl halides. Thus, in the non-polar solvent, *n*-pentane, the reaction, which is heterogeneous, appears to proceed to some extent by a carbonium ion process, SN1. These results correspond to those for the reactions of ethylsodium,[2] phenylsodium,[3a] phenyllithium,[3b] butyllithium[3b] and butylmagnesium chloride[4] with the same chlorobutenes. The reaction studied in this investigation can be formulated as

TABLE V

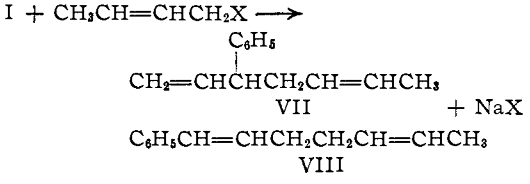
PRINCIPAL INFRARED ABSORPTION BANDS OF 1- AND 3-PHENYL-1-OCTENE

s = strong, m = medium and w = weak intensities

1-Octenes, frequency, cm.$^{-1}$			
1-Phenyl-	3-Phenyl-	1-Phenyl-	3-Phenyl-
	678m	1389m	1391m
694s	702s		1429m
715m		1468s	1471s
	727m	1506m	1504m
744s		1613m	1613m
	759s	1667w	1653m
892w		1718w	1754w
911w	911s	1815w	1842w
967s		1898w	1894w
	998s	1972w	1972w
1033w	1034w	2933s	2941s
1078w	1078w	3003s	2994s
1321w	1314w	3096s	3115s



$$\mathrm{I} + CH_3CHXCH{=}CH_2 \longrightarrow \underset{\mathrm{V}}{CH_2{=}CH\overset{C_6H_5}{\overset{|}{C}}H\underset{\underset{CH_3}{|}}{C}HCH{=}CH_2} \quad \underset{\mathrm{VI}}{C_6H_5CH{=}CHCH_2\underset{\underset{CH_3}{|}}{C}HCH{=}CH_2} + NaX \quad (8)$$



$$\mathrm{I} + CH_3CH{=}CHCH_2X \longrightarrow \underset{\mathrm{VII}}{CH_2{=}CH\overset{C_6H_5}{\overset{|}{C}}HCH_2CH{=}CHCH_3} \quad \underset{\mathrm{VIII}}{C_6H_5CH{=}CHCH_2CH_2CH{=}CHCH_3} + NaX \quad (9)$$

$$\begin{matrix} CH_3CHXCH{=}CH_2 \\ \text{or} \\ CH_3CH{=}CHCH_3X \end{matrix} \xrightarrow{([C_6H_5CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2]^{\ominus}\ Na^{\oplus})} [CH_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH]^{\oplus}X^{\ominus} \xrightarrow{[C_6H_5CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2]^{\ominus}\ Na^{\oplus}} \mathrm{V.\ VI,\ VII,\ VIII} \quad (10)$$

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(14) H. P. Koch, *J. Chem. Soc.*, 1123 (1948).

(15) N. Sheppard and D. M. Simpson, *Quart. Revs.*, **6**, 1 (1952).

(16) G. B. B. M. Sutherland, *Rec. Chem. Prog.*, **13**, 79 (1952).

(17) D. J. Cram, THIS JOURNAL, **74**, 2137 (1952).

(18) The products from an SN1 or SN2 attack on an allyl halide are the same, because in the SN1 process the carbonium ion is symmetrical.

(19) Halobutenes is used to denote only 1-chloro-2-butene and 3-chloro-1-butene.

Table VI

Yield and Product Composition for the Reactions of Phenylallylsodium with Allylic Halides

Medium →	*n*-Pentane						Liquid ammonia[6]		
Allylic halide →	Allyl chloride	Allyl iodine	1-Chloro-2-butene	3-Chloro-1-butene	1-Bromo-2-butene	3-Bromo-1-butene	Allyl bromide	1-Chloro-2-butene	3-Chloro-1-butene
Yield, %	32	20	40	33	34	33	67	86	86
Composition (by wt.)									
3-Phenyl-1,5-hexadiene, %	60	49					91		
1-Phenyl-1,5-hexadiene, %	40	51					9		
3-Methyl-4-phenyl-1,5-hexadiene, %			..	..	Trace	20		..	95
3-Phenyl-1,5-heptadiene, %			39	27	49	37		86	..
4-Methyl-1-phenyl-1,5-hexadiene, %			18	23	13	16		..	5
1-Phenyl-1,5-heptadiene, %			43	50	38	27		14	..

It would appear[3b,20] that in these reactions in pentane (and in the similar reactions of organolithium and Grignard compounds in ether) the electrophilic character of the cation portion of the organometallic compound is quite important. In liquid ammonia, a medium of high dielectric constant and good solvating power for ions, phenylallylsodium acts less like an ion pair and exhibits more of the properties of a dissociated salt. Due to the solvation of the ions, the electrophilic character of the sodium is no longer effective in producing the loosening of the halogen of the halobutenes with the result that the nucleophilic character of the anion governs the course of the reaction.

Experimental[21,22]

Preparation of *n*-Amyl Chloride.—Two gallons of commercial *n*-amyl alcohol (Sharples Chemical Co.) were distilled through a 40-plate, one-inch, Oldershaw column at 40:1 reflux ratio. A center cut (50%) was selected which had a boiling range of 138–138.5° and n^{20}_D 1.4104–1.4107.

A mixture of 655 g. (5.5 moles) of purified thionyl chloride[23] and 20 ml. (*ca.* 0.25 mole) of anhydrous pyridine was heated to reflux with stirring and 440 g. (5.0 moles) of purified *n*-amyl alcohol containing 20 ml. (*ca.* 0.25 mole) of anhydrous pyridine was added over a period of 4.5 hours. The heating and stirring were continued (*ca.* two hours) until the temperature rose to 105°. The reaction mixture was cooled, decanted into a 2-l. flask and distilled rapidly at *ca.* 300 mm. The distillate was washed four times with 100 ml. of concentrated sulfuric acid, with distilled water and twice with 100 ml. of a 10% potassium carbonate solution and then dried over anhydrous potassium carbonate. The yield of the colorless, crude *n*-amyl chloride was 88–90%. The combined products (3.5 liters) of several runs were distilled through an 80-plate, one-inch Oldershaw column at 60:1 reflux ratio taking a cut (2.2 liters) boiling 108–108.5° and n^{25}_D 1.4106–1.4108. The procedure based upon Gerrard's studies on the thermal decomposition of alkyl chlorosulfides in the presence of bases[24] was found more convenient than Whitmore's method.[25]

A final purification (suggested by Morton[26]) was obtained by passing the amyl chloride through a 1 × 36-inch column packed in three sections with calcium chloride (at the top), alumina and Drierite. In accord with a report by Morton we found that traces of hydrochloric acid in the amyl chloride seriously affected the starting of the Wurtz reaction.[27]

Preparation of Phenylallylsodium in *n*-Pentane.—One gram atom of sodium sand in 500 ml. of pure *n*-decane (Humphrey–Wilkinson Co.) in a 1-l. flask of the Morton high-speed stirring apparatus was made by stirring at 120° under nitrogen for one minute at 10,000 r.p.m.[28] The cooled liquid was siphoned off, the sand washed three times with 250 ml. of dry *n*-pentane and 500 ml. of *n*-pentane was added as the medium for subsequent reactions. The *n*-pentane (from Phillips Petroleum Co.), which was used in all of these experiments, was purified by passing it through a column of silica gel and was stored over sodium hydride.

The amylsodium was prepared by the addition of 5 ml. of 53.3 g. (0.50 mole) of the purified amyl chloride to the sodium sand in *n*-pentane at −10° while stirring at *ca.* 6000 r.p.m. When the reaction had started, as indicated by the darkening of the contents to a deep black-purple, the remaining amyl chloride was added dropwise over a 2–3 hour period. After an additional hour of stirring, 59.0 g. (0.50 mole) of allylbenzene, n^{25}_D 1.5086–1.5090, was added dropwise over a one-hour period. The color of the reaction mixture turned to a dark olive drab. The phenylallylsodium was stirred one-half hour longer before the reactant was added. In all cases, except where indicated, these same amounts of sodium, *n*-amyl chloride and allylbenzene were used to prepare the "standard 0.5 mole" of phenylallylsodium in *n*-pentane.

Reactions of Phenylallylsodium in *n*-Pentane with Methanol. Method A.—In the standard manner, 0.25 mole of phenylallylsodium in *n*-pentane was prepared from one gram-atom of sodium, 0.5 mole of amyl chloride and 0.25 mole of allylbenzene. This reaction mixture was then forced over under nitrogen pressure into a mixture of 250 ml. (6.2 moles) of methanol (Baker C.P.) and 750 ml. of *n*-pentane. The addition took 30 minutes and the temperature was held between 8 and 10°.

After the addition was complete, water was added and the layers carefully separated. The pentane layer was washed with water and dried over anhydrous magnesium sulfate and the solvent carefully removed through a short column. The yield of the crude product was 31.8 g. (108%). This material was very carefully distilled at 20 mm. pressure with the use of a 30-inch twisted, stainless-steel wire gauze column[29] equipped with an electrically heated jacket over a silvered vacuum jacket. The boil-up rate was 3 ml./min. and reflux ratio 160:1. The results are given in Table I under method A.

The allylbenzene fraction had a low refractive index and, on the basis of a bromine titration, contained some non-olefinic material. Analysis of this fraction using refractive indices indicated approximately 8% *n*-propylbenzene. All of the allylbenzene fractions in subsequent distillations showed a similar lowering of the refractive index.

Method B.—In the same manner as in method A, 0.25 mole of phenylallylsodium in *n*-pentane was prepared and to this was added 8.0 g. (0.25 mole) of methanol (Baker C.P., dissolved in 50 ml. of *n*-pentane) over a one-half hour period while maintaining the temperature about −10°. Following an additional half-hour of stirring, the reaction mixture was poured onto Dry Ice and worked up in the same manner as in method A.

The pentane solution, after removal of the solvent, yielded 35.8 g. (121%) of crude products. This material was carefully distilled in the wire gauze column under the same conditions as described under method A. The results are given in Table I under method B in *n*-pentane.

It was interesting to note that sodium methoxide did not

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[20] A. A. Morton, This Journal, **69**, 969 (1947).

[21] All m.p.'s and b.p.'s are uncorrected except where indicated.

[22] All microanalyses were run by Dr. Adalbert Elek of Elek Microanalytical Laboratories, Los Angeles, Calif.

[23] D. L. Cottle, This Journal, **68**, 1380 (1946).

[24] W. Gerrard, *J. Chem. Soc.*, 99 (1939); 218 (1940).

[25] F. C. Whitmore, F. A. Karnatz and A. H. Popkin, This Journal, **60**, 2540 (1938).

[26] A. A. Morton, a private communication.

[27] A. A. Morton, J. B. Davidson and H. A. Navey, This Journal, **64**, 2240 (1942).

[28] A. A. Morton and L. M. Redman, *Ind. Eng. Chem.*, **40**, 1190 (1948).

[29] J. R. Bower and L. M. Cooke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 290 (1943).

cause the rearrangement of allylbenzene to propenylbenzene under the reaction conditions employed above, whereas in liquid ammonia it did produce the rearrangement.[8]

In the distillations of the reaction products from both methods, *trans*-propenylbenzene was observed to form an azeotrope with *n*-decane.[9] In method B, the *cis*-propenylbenzene came over as an azeotrope with *n*-decane. There was no evidence of azeotrope formation for allylbenzene and *n*-decane.

Reactions of Phenylallylsodium in *n*-Pentane with Methyl Bromide. Method A.—The standard 0.5 mole of phenylallylsodium in *n*-pentane was forced over into 400 ml. (690 g., 7.3 moles) of anhydrous liquid methyl bromide in a 2-l., 3-necked flask equipped with a stirrer and Dry Ice condenser. The addition required 30 minutes and left a gray-blue, semi-pasty mixture, which was forced over onto Dry Ice. After remaining overnight, the slurry was filtered and the salts washed with more pentane. The salts were dissolved in water and extracted with pentane. All pentane solutions were combined, dried over anhydrous magnesium sulfate and the solvent removed. The residue was distilled in a Hickman vacuum still under reduced pressure. The yield of crude products was 65.0 g. (99%). A portion of this distillate was very carefully distilled through an 8 mm. × 18-inch Podbielniak Heligrid column at 145 mm. pressure, boil-up rate *ca.* 3 ml./min. and reflux ratios from 150 to 350:1. The results of this distillation are given in Table II.

Method B.—To the standard 0.5 mole of phenylallylsodium in *n*-pentane at −10° was added 32 ml. (0.57 mole) of anhydrous liquid methyl bromide over a 50-minute period. The color changed to a greenish-gray when 25 ml. (0.45 mole) had been added. The reaction mixture was stirred an additional 30 minutes and then worked up and distilled in the same manner as in method A. The yield of crude material prior to the fractional distillation was 62.0 g. (94%). Table II shows the results of this distillation.

There was very little dimer of allylbenzene formed in these reactions in *n*-pentane as compared to the same reactions run in liquid ammonia[6] where 14–16% was formed.

In this distillation as well as in the one in method A, the 3-phenyl-1-butene was found to form an azeotrope with *n*-decane. The azeotrope was conveniently separated into its components by adsorption on silica gel and desorption with methanol. The azeotrope was confirmed by carefully distilling a synthetic mixture of 3-phenyl-1-butene and *n*-decane on the Podbielniak column; this also gave an accurate value of the refractive index of the azeotrope. From the non-linear, refractive index–composition curve drawn from the refractive indices of synthetic mixtures, the composition of the azeotrope was determined. The data on the azeotrope are summarized as follows: b.p., 118.5–119° (152 mm.), $n^{25}\text{D}$ 1.4606; composition (by wt.): *n*-decane, 40.0%; 3-phenyl-1-butene, 60.0%. There was no evidence of *n*-decane azeotrope formation with the other product of the reaction, 1-phenyl-1-butene.

Reactions of Phenylallylsodium in *n*-Pentane with *n*-Amyl Chloride.—One half-mole of phenylallylsodium was prepared in *n*-pentane in the standard manner; however, this particular batch was too viscous[30] for the stirrer to handle safely, so approximately one-half of the slurry was transferred to a nitrogen-filled flask and stoppered. An additional 100 ml. of pentane was added to the remaining slurry and then 53.3 g. (0.5 mole) of pure *n*-amyl chloride was added to the remaining slurry and then 53.3 g. (0.5 mole) of pure *n*-amyl chloride was added at −10° over a two-hour period. No reaction appeared to be taking place, so the temperature was gradually raised to +20°. At this temperature the reaction appeared to go quite normally. This portion of the reaction mixture was carbonated by pouring into Dry Ice. The second half of the phenylallylsodium slurry was returned to the reaction flask and 60 ml. (*ca.* 0.5 mole) of *n*-amyl chloride was added at +20°. This second portion was carbonated and combined with the first fraction. The combined fractions were filtered and the salts washed with more pentane. The salts were then dissolved in water and extracted with pentane. All of the pentane solutions were combined, dried over anhydrous magnesium sulfate and the solvent removed through a short column. This procedure for working up the products was employed on all subsequent reaction mixtures. The yield of crude product after removal of the solvent and excess amyl chloride was 86.6 g. (92%). A portion of this material was carefully distilled through the twisted wire gauze column described above. There was obtained a 60% yield of the phenyloctenes, of which 70% was 3-phenyl-1-octene and 30% was 1-phenyl-1-octene.

The physical properties of 3-phenyl-1-octene were b.p. 114° (10 mm.), $n^{25}\text{D}$ 1.4946, $d^{25}{}_4$ 0.8667; *MR*D calcd. 62.78, found 63.31; exaltation, 0.53; molecular weight by olefin determination calcd. 188, found 189.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.36; H, 10.71.

The physical properties of 1-phenyl-1-octene were b.p. 144° (10 mm.), $n^{25}\text{D}$ 1.5180, $d^{25}{}_4$ 0.8744; *MR*D calcd. 62.78, found 65.24; exaltation, 2.46; molecular weight by olefin determination calcd. 188, found 189.6. The refractive index does not agree with that previously reported.[10]

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.21; H, 10.77.

The ultraviolet absorption maxima of the phenyl-1-octenes in 95% ethanol using the Cary spectrophotometer, model 11-PMS, are given in Table III and are compared with allylbenzene and *cis*- and *trans*-propenylbenzenes.[9] The principal infrared absorption bands of the pure liquids as determined in the Beckman IR-2 spectrophotometer are presented in Table IV.

Reactions of Phenylallylsodium in *n*-Pentane with Allylic Halides.—All of these reactions were run by adding dropwise approximately 0.5 mole of the freshly distilled allylic halide over an hour period to the standard 0.5 mole of phenylallylsodium in *n*-pentane at 0° in the high-speed stirring apparatus while stirring at *ca.* 6000 r.p.m. The reaction mixtures were worked up as described above and the crude products carefully distilled at 10 mm. pressure through the twisted wire gauze column. The results of distillation of products from the reaction with the allyl halides and those from the reaction with the halobutenes are given in Table VI. In the distillation of the products from the reaction of phenylallylsodium with the bromo- and chlorobutenes, the refractive index of the fraction supposed to be for 4-methyl-1-phenyl-1,5-hexadiene was much too low. It was found that 3-phenyl-1-octene (boiling in virtually the same place as 4-methyl-1-phenyl-1,5-hexadiene) was responsible for this discrepancy and that refractometry was satisfactory for analysis of the distillation cuts in this region.

The refractive indexes of the butenyl halides were measured prior to addition and were for 3-chloro-1-butene, $n^{25}\text{D}$ 1.4126; 1-chloro-1-butene, $n^{25}\text{D}$ 1.4327; 3-bromo-1-butene, $n^{25}\text{D}$ 1.4602; and 1-bromo-2-butene, $n^{25}\text{D}$ 1.4768. The butenyl bromides were kept cold to prevent rearrangement during the addition by means of Dry Ice packed around the addition funnel.

Reaction of Phenylallylsodium in *n*-Pentane with Excess 3-Chloro-1-butene.—To the standard of 0.5 mole of phenylallylsodium in *n*-pentane at 0° was added 84.5 g. (0.935 mole) of 3-chloro-1-butene over a 45-minute period. Approximately 72% of the unreacted chlorobutenes was recovered, of which 27% was 3-chloro-1-butene and 73% was 1-chloro-2-butene. This composition approximates that of the equilibrium mixture and thus provides proof that the rearrangement of the halobutenes does occur under these conditions.

Reaction of Phenylcyclohexenylsodium in Liquid Ammonia with Methanol.—Crude 3-phenylcyclohexene[31] was carefully distilled at 15 mm. pressure through an 8-mm. × 36-inch Heli-Pak column rated at 90 theoretical plates under total reflux. A center cut was collected having b.p. 113.5–114.5°, $n^{20}\text{D}$ 1.5444, $n^{25}\text{D}$ 1.5424, and the following ultraviolet absorption maxima when dissolved in 95% ethanol: λ, mμ, 248.1 ($\epsilon_{\max}$ 634), 2530(653), 258.0(620), 261.4(598), 264.0 (452) and 268.2 (402). The principal infrared absorption bands are shown in Table II.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.17; H, 8.87.

To *ca.* 300 ml. of anhydrous liquid ammonia 4.6 g. (0.2 gram atom) of sodium was added with stirring, converted to sodamide and 29.9 g. (0.190 mole) of 3-phenylcyclohexene was added dropwise. The stirring was continued for one

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[30] Morton also ran into this same viscosity problem on several occasions, *cf.*, A. A. Morton, J. B. Davidson and B. L. Hakan, THIS JOURNAL, **64**, 2242 (1942).

[31] Kindly provided by Dr. R. H. Heck of these laboratories.

hour before all of the sodamide had reacted, and then 16 ml. (0.4 mole) of methanol (Baker C.P.) was added very rapidly. As soon as the deep red color of the 3-phenylcyclohexenyl anion had disappeared, 15 g. (0.28 mole) of ammonium chloride was added to neutralize the sodium methoxide that was formed.[8] Approximately 100 ml. of ether was added and the ammonia allowed to evaporate. The hydrocarbon products were recovered in the same manner as in the reactions of phenylallylsodium with methanol above and distilled in a Hickman vacuum still. A colorless distillate (n^{20}_{D} 1.5603, λ_{max} 247 mμ, ϵ_{max} 8410) was recovered in 92% yield. Careful distillation through the twisted wire gauze column at 15 mm. pressure gave 33% 3-phenylcyclohexene and 67% 1-phenylcyclohexene.

The refractive index of the 1-phenylcyclohexene was 1.5692 as compared to the literature value[11] of n^{20}_{D} 1.5670. Based on d^{20}_{4} 0.9934[11] and n^{20}_{D} 1.5692, the molar refraction for 1-phenylcyclohexene was found to be 52.17, calcd. 51.35. The exaltation was 0.82. The ultraviolet absorption showed only one maximum at 247 mμ (ϵ_{max} 12940) and the 283 and 292 mμ peaks normally found in compounds of the type $C_6H_5CH{=}CHR$ were absent. The principal infrared absorption bands are given in Table II.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.09; H, 8.94.

Based on ultraviolet absorption spectra, refractive indexes and fractional distillation, the amounts of 1-phenylcyclohexene present in the reaction products were 63, 64 and 67%, respectively, and 3-phenylcyclohexene, 37, 36 and 33%, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Persulfate-initiated Oxidation of Vinyl Monomers in Aqueous Solutions[1]

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The reaction of oxygen with vinyl monomers in aqueous solution in the presence of potassium persulfate has been studied in detail. Rates of oxygen absorption have been obtained for acrylonitrile, methyl vinyl ketone and methacrylonitrile, and rates of monomer disappearance for the first two. The experimental data support the proposal that the reaction is a simplified copolymerization, involving the direct attack of persulfate on the monomer as one of the initiation steps. A comparison of rates of oxygen absorption gives the order of reactivity of monomers toward the peroxy free radical, which is in line with *Q*-values for these monomers. A study of the oxidation products shows that the polymeric peroxide resulting from the copolymerization may not always survive the aqueous media, but the monomeric products may be explained as arising from the decomposition of the peroxide, followed by further oxidation of some primary products.

In an earlier paper[2] the effect of oxygen on the polymerization of acrylonitrile in aqueous solution was investigated by following the rates of absorption of oxygen and determining the products of the oxidation. The results gave evidence for the formation of a polymeric peroxide, which subsequently decomposed to give a variety of products of low molecular weight. A tentative mechanism was suggested, but it could not be rigorously correlated with experimental results because of the lack of information concerning the kinetics of acrylonitrile disappearance.

A suitable method of analysis for acrylonitrile has now been developed,[3] which has made possible more detailed study of the oxidation of acrylonitrile by simultaneous determination of the rates of absorption of oxygen and disappearance of monomer. It was also desired to extend the investigation of the oxidation products of acrylonitrile and to study other vinyl monomers, such as methyl vinyl ketone and methacrylonitrile.

Experimental and Results

Apparatus for Kinetic Experiments.—For the kinetic studies with acrylonitrile and methyl vinyl ketone the reaction flask was immersed in a water-bath at 50 ± 0.1° and was connected to constant pressure equipment of the type described by McBurney.[4] A minimum of connecting tubing was used, joints were of glass wherever possible, and water from the constant temperature bath was circulated through the jacket of the gas buret.

In the kinetic experiments with methacrylonitrile the pressure adjustment was manual, rather than automatic, and the gas buret was maintained at 50 ± 0.2° by means of an electrically-heated air jacket.

Polarographic Equipment.—The Heyrovsky polarograph, Sargent Co., model XII, was used for all analyses for acrylonitrile and methyl vinyl ketone. The dropping mercury electrode was of the Heyrovsky type. The drop time (*t*) in 0.02 *M* tetramethylammonium iodide was 5.11 sec. The mercury mass (*m*) was 1.0467 mg. per sec. The value of $m^{2/3}t^{1/6}$ was 1.35 mg.$^{2/3}$sec.$^{-1/2}$. The Sargent–Heyrovsky erlenmeyer type electrolysis vessel was placed in a circulating water-bath at 25.0 ± 0.1°. Mercury was purified to pass the foam test when shaken with distilled water.

Materials. Acrylonitrile.—Eastman Kodak Co. material was dried over calcium chloride, distilled through a 50-cm. Vigreux column, and stored over calcium chloride. Portions were redistilled immediately before use; n^{25}_{D} 1.3886.

Methyl Vinyl Ketone.[5]—The 85% azeotrope with water was treated with anhydrous potassium carbonate and calcium chloride during cooling, followed by distillation at a pressure of 2 to 3 mm.; n^{22}_{D} 1.400.

Methacrylonitrile.[6]—The inhibitor was removed by washing with 1% sodium hydroxide, water, drying over calcium chloride and redistilling. The fraction boiling at 90–90.3° was used at once.

Potassium Persulfate.—Baker and Adamson Reagent Grade was recrystallized from water at 50°. Iodometric analysis indicated a purity of better than 99.5%.

Other Materials.—Eastman Kodak Co. tetramethylammonium iodide was recrystallized twice from 50% aqueous ethanol. Methyl isopropenyl ketone dimer was depolymerized by heating at 200°, and the monomeric form was redistilled under reduced pressure immediately before use. Acrylamide[7] was used without recrystallization.

Procedures for Kinetic Experiments.—The following procedure was used for experiments with acrylonitrile and methyl vinyl ketone. With the reaction system and gas buret at 50°, an accurately weighed amount of potassium persulfate and 50 ml. of distilled water were added to the

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(1) From the Ph.D. Theses of Oscar A. Pickett, Jr., and Sterling F. Strause (1955) and the M.S. Theses of Sterling F. Strause (1953) and Howard E. Worrell, Jr. (1950). Supported in part by grants NSF-G193 and NSF-G578 from the National Science Foundation.

(2) K. C. Smeltz and E. Dyer, THIS JOURNAL, **74**, 623 (1952).

(3) S. F. Strause and E. Dyer, *Anal. Chem.*, **27**, 1906 (1955).

(4) L. F. McBurney, *Ind. Eng. Chem.*, **41**, 1251 (1949).

(5) Kindly supplied by the Jackson Laboratory of E. I. du Pont de Nemours and Co., Inc.

(6) Kindly furnished by the Shell Development Company.

(7) Supplied through the courtesy of Dr. W. M. Thomas, American Cyanamid Co.