Table II shows that the influence of the CF_3 group on the dissociating groups of the amino acids is in each case, where data are available, of about the same magnitude as in monofunctional compounds of equal distance between groups. The pK for the hydroxyl group of 4,4,4-trifluorothreonine, 12.7, may be compared with $pK = 12.3$ for 2,2,2-trifluoroethanol.[7]

Comparison of 6,6,6-trifluoronorleucine(pK_1 2.16, pK_2 9.46) with ornithine (2,5-diaminopentanoic acid, pK_1 1.84, pK_2 8.65), and 2-amino-4,4,4-trifluorobutyric (pK_1 1.60, pK_2 8.17) with 2,3-diaminopropionic acid (pK_1 1.33, pK_2 6.80) gives some measure of the relative effect of the strong dipole[19] CF_3 and the charged group, $^+NH_3$. A similar comparison is available in ω-CF_3 and ω-$^+NH_3$ aliphatic carboxylic acids. As would be expected, the effect of the charged group is considerably the greater, especially when close to the dissociating group.

[19] J. D. Roberts, R. L. Webb and E. A. McElhill, THIS JOURNAL, **72**, 408 (1950); J. J. Conradi and N. C. Li, *ibid.*, **75**, 1785 (1953).

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Carbanions Additions in the Reaction of Aromatic Hydrocarbons with Monoölefins[1a,b,c]

BY HERMAN PINES AND VICTOR MARK[2]

RECEIVED MARCH 14, 1956

Alkylaromatic hydrocarbons which contain a benzylic hydrogen atom react with monosubstituted ethylenes, such as propylene, 1-butene and 1-octene in the presence of alkali, and an organoalkali compound prepared *in situ* at about 250–320° to form 1:1 adducts. Propylene reacts with toluene, ethylbenzene, isopropylbenzene and diphenylmethane yielding isobutylbenzene, 2-phenyl-3-methylbutane, 2-phenyl-2,3-dimethylbutane and 1,1-diphenyl-2-methylpropane, respectively. 1-Butene and 1-octene with toluene give 2-benzylbutane and 2-benzyloctane. Under similar conditions toluene and isobutylene react to give neopentylbenzene. Benzene reacts with ethylene to form small amounts of ethylbenzene, *sec*-butylbenzene and biphenyl. *t*-Butylbenzene on reaction with ethylene under similar conditions forms *o*-, *m*- and *p*-*t*-butylethylbenzene. The reaction of benzene with isobutylene yields *t*-butylbenzene, isobutylbenzene and biphenyl. The experimental results, which are interpreted by a carbanion chain mechanism, indicate that the mode of addition of carbanions to unsymmetrical olefins is determined entirely by polar rather than by steric factors. The mode of addition reveals that the primary alkylcarbanions are more stable and more easily formed than the secondary and tertiary ones. Several aspects of the carbanions and of their reaction mechanism are discussed.

There are only a few reports in the literature in which organoalkali compounds were added to monoölefins. Ziegler and Gellert[3] described the reaction of primary alkyllithium compounds with ethylene under pressure to yield a series of adducts. The reaction failed, however, with other olefins. Bartlett and co-workers[4] reported the addition of isopropyllithium and *t*-butyllithium to ethylene at atmospheric pressure and low temperature. When propylene was substituted for ethylene only a small amount of an unidentified polymeric material was obtained. The reaction of several alkylaromatic hydrocarbons, which have at least one benzylic hydrogen, with ethylene in the presence of sodium and a "promoter" recently has been described.[5] There are also a few patents in which similar reactions are claimed to take place in the presence of sodium[6] or organosodium compounds.[7]

The purpose of the present study was to investigate the reaction of alkylaromatic hydrocarbons containing a benzylic hydrogen with simple monoolefins other than ethylene, in the presence of sodium and a substance capable of forming an organosodium compound. Another objective of the present experiments was to determine whether benzene and *t*-butylbenzene under similar conditions would react with olefins.

Results

Propylene and Aromatic Hydrocarbons.—The experimental condition used and the results obtained are summarized in Tables I and II. The "promoters" employed were anthracene, *o*-chlorotoluene and dimethylmercury. The yield of isobutylbenzene produced from the reaction of toluene with propylene, amounting to about 10 to 23 mole per cent., was based on the propylene charge and not on the propylene reacted.[8]

Ethylbenzene, isopropylbenzene and diphenylmethane yielded on reaction with propylene, respectively, 2-phenyl-3-methylbutane (3-methyl-2-butyl)-benzene, 2-phenyl-2,3-dimethylbutane (2,3-dimethyl-2-butyl)-benzene and 1,1-diphenyl-2-methylpropane. The yield of the latter amounted to 51%. The adducts obtained from the interaction of one mole of aromatic hydrocarbons with one mole of propylene were comparable in purity, according to infrared spectra, with the respective

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[1] (a) Paper V of the series of Base Catalyzed Reactions. For IV see H. Pines and H. E. Eschinazi, THIS JOURNAL, **78**, 1178 (1956). (b) Taken in part from a dissertation submitted by Victor Mark to the graduate school in partial fulfillment of the requirements for the Ph.D. degree, October, 1955. (c) Presented in part before the Division of Organic Chemistry, American Chemical Society Meeting, March 29–April 7, 1955.

[2] Predoctoral Fellow, Universal Oil Products Co. 1953–54; E. I. du Pont de Nemours and Co., 1954–1955.

[3] K. Ziegler and H. G. Gellert, *Ann.*, **567**, 195 (1950).

[4] P. D. Bartlett, S. Friedman and M. Stiles, THIS JOURNAL, **75**, 1771 (1953).

[5] H. Pines, J. A. Vesely and V. N. Ipatieff, *ibid.*, **77**, 554 (1955).

[6] G. M. Whitman, U. S. Patent, 2,448,641 (1948); *C.A.*, **43**, 1057 (1949).

[7] E. L. Little, Jr., U. S. Patent, 2,548,803 (1951); *C.A.*, **45**, 8554 (1951).

[8] A 4% yield of isobutylbenzene based on propylene charged, was previously found by treating 1 mole of toluene with 0.8 mole of propylene in the presence of 0.27 g. atom of sodium and 0.014 mole of di-*t*-butyl peroxide at 200°. Unpublished work by H. Pines and J. A. Vesely from the Universal Oil Products Co., Riverside, Ill.

TABLE I

REACTION OF TOLUENE WITH PROPYLENE

One mole of toluene and one mole of propylene[a] were used in each experiment[b]

Experiment	1	2	3	4
Chain initiator precursor, g. (mole)	←Anthracene→		Dimethylmercury	o-Chlorotoluene
	←0.9(0.005)→		2.5(0.0114)	8.0(0.063)
Sodium g. (atom)	1.0(0.043)	5.0(0.215)	1.0(0.043)	4.6(0.2)
Temp. of pressure drop, °C.	291	292	291	290
Highest temp., °C.	297	306	304	300
Highest pressure, atm.	90	135	86	82
Duration, hours	20	19.5	27	15
Product obtained				
2-Methyl-*x*-pentene, g. (mole)	6.2(0.074)	5.3(0.063)	2.5(0.03)	1.7(0.02)
Isobutylbenzene, g. (mole)	13.0(0.097)	29.4(0.22)	13(0.097)	22(0.165)
Bottoms and/or holdup, g.	2.4	4.0	2.5	3.3
Gaseous product recovered, mole				
Hydrogen	0.012	0.0085		
Methane	.0164	.023		
Ethane	.0025	.0054		
Propylene	.350	.01		
Propane	.163	.33		

[a] Composition, mole per cent.: propylene 96, propane 3, ethane 1. [b] The reaction was made in a 250-ml. capacity Magne-Dash autoclave.

TABLE II

REACTION OF AROMATIC HYDROCARBONS WITH PROPYLENE

Experiment	5	6	7	8
Propylene, g. (mole)	42(1.0)	38(0.91)	42(1.0)	27(0.64)
Aromatic hydrocarbon, g. (moles)	Ethylbenzene	←Isopropylbenzene→		Diphenylmethane
	92(0.87)	←120(1.0)→		108(0.64)
Chain initiator precursor, g. (moles)	Anthracene	o-Chlorotoluene	None	o-Chlorotoluene
	0.9(0.005)	8.0(0.063)	...	5.6(0.04)
Sodium, g. (atom)	5.0(0.215)	4.6(0.2)	None	3.0(0.13)
Temp. of pressure drop °C.	282	270		250
Highest temp., °C.	291	280	302	270
Highest pressure, atm.	153	95	238	42
Duration, hours	10	13	14	7
Product obtained				
2-Methyl-*x*-pentene	3.7(0.044)		None	
Aromatic hydrocarbon[a]	2-Phenyl-3-methylbutane	2-Phenyl-2,3-dimethylbutane	None	1,1-Diphenyl-2-methylpropane
g. (moles)	21.4(0.145)	12.1(0.075)		66(0.314)
Yield, Mole %	16.7	7.8		51
Bottoms and/or holdup, g.	5.0	3.4	0	6.3

[a] Product of the interaction of 1 mole of charged aromatic hydrocarbon with 1 mole of propylene.

aromatic hydrocarbons reported by the API Project 44.[9]

The reaction of propylene with aromatic hydrocarbons was in most of the experiments accompanied by dimerization of propylene to form 2-methyl-*x*-pentene.

The organosodium compounds required for the above reactions were generated *in situ* by using as chain initiator precursors anthracene,[5] *o*-chlorotoluene[5] and dimethylmercury.[7,10] No particular attempt was made in any of these or the following reactions to determine optimum reaction conditions.

Isobutylene and Aromatic Hydrocarbons.—The reaction of toluene with isobutylene proceeded sluggishly. The temperature necessary to assure a reaction was considerably higher than in the experiments in which propylene was used. The pentylbenzenes obtained from the reaction consisted of neopentylbenzene and of 3-methylbutylbenzene, the latter resulting from a thermal, free radical, reaction. The presence of 2-benzylbutane (2-methylbutylbenzene) in the reaction product resulted from the catalytic reaction of toluene with *n*-butylene present as a contaminant in isobutylene.

The carbanion reactions are not specific to sodium, and lithium and potassium[11] gave similar results. The use of sodium hydride as a chain initiator also was demonstrated. The results are summarized in Table III.

In the reaction products of isopropylbenzene

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(9) Catalogue of Infrared Spectra, American Petroleum Institute Project 44.

(10) H. Gilman and H. A. Pacevitz, THIS JOURNAL, **62**, 673 (1940).

(11) L. Schaap, unpublished results from this Laboratory.

TABLE III

REACTION OF TOLUENE WITH ISOBUTYLENE

Experiment	9	10	11	12
Isobutylene,^{a} g. (moles)	56(1.0)	45(0.8)	56(1.0)	89(1.58)
Toluene, g. (moles)	92(1.0)	69(0.75)	92(1.0)	135(1.47)
Chain initiator precursor,	←o-Chlorotoluene→		NaH	None
g. (mole)	←8.0(0.063)→		2.4(0.1)	...
Alkali metal	Sodium	Lithium	...	None
g. (atom)	4.6(0.2)	1.4(0.2)	...	...
Temp. of pressure drop, °C.	323	380	320	332
Highest temp., °C.	348	386	334	354
Highest pressure, atm.	207	104	222	210
Duration, hours	14.5	27	14	24
Product obtained, g. (moles)				
Neopentylbenzene	9.4(0.063)	2.7(0.018)	2.2(0.015)	0
3-Methylbutylbenzene	Present	6.4(0.043)	Traces	18.2(0.123)
2-Benzylbutane	2.0(0.0135)	Present	0.4(0.003)	0
Bottoms and/or holdup	13.2		1.5	25

[a] Composition: 99% isobutylene, 1% butenes.

TABLE IV

REACTION OF AROMATIC HYDROCARBONS WITH ISOBUTYLENE

Experiment	13	14	15
Isobutylene, g. (mole)	47(0.85)	50(0.89)	20.5(0.37)
Aromatic hydrocarbon	←Isopropylbenzene→		Diphenylmethane
g. (mole)	120(1.0)	103(0.86)	100(0.59)
Chain initiator precursor	o-Chloroisopropylbenzene		o-Chlorotoluene
g. (mole)	8.2(0.05)	8.2(0.05)	5.6(0.04)
Alkali metal	Sodium	Potassium	Sodium
g. (atom)	4.6(0.2)	3.9(0.1)	3.0(0.13)
Temp. of pressure drop, °C.	280		
Highest temp., °C.	293	292	317
Highest pressure, atm.	182	103	110
Duration, hours	16	26	10
Product, g.	4.9^{a,b}	2.5^{c}	9.8^{d}
Bottoms and/or holdup, g.	10.4	3.2	6.0

[a] Corresponds to a fraction of the boiling range between 192 and 231°; 2-phenyl-2,4-dimethylpentane was present in the fraction. [b] A lower boiling product was also obtained from which 3 g. (0.027 mole) of 2,4,4-trimethyl-*x*-pentene was isolated. [c] Corresponds to a fraction boiling between 211 and 219°; it contained 2-phenyl-2,4-dimethylpentane. [d] Corresponds to a fraction boiling between 270 and 294°; 1,1-diphenyl-3-methylbutane was identified in this fraction.

and diphenylmethane with isobutylene the presence of only the thermal adducts was detectable, Table IV.

Toluene with 1-Butene and 1-Octene.—The presence of 2-benzylbutane in the reaction product from toluene with isobutylene was attributed to *n*-butylenes present as impurities in isobutylene used. In order to confirm the validity of such an assumption an experiment was made in which 1-butene and toluene were used as reactants. 2-Benzylbutane was the only pentylbenzene formed (Table V).

The reaction of 1-octene with toluene in the presence of sodium and anthracene as chain precursor yielded 2-benzyloctane as the adduct. The recovered octenes consisted predominantly of *trans*-octenes, which shows that migration of the double bond took place.

Toluene and Cyclohexene.—A reaction between these two hydrocarbons (one mole of each) was attempted under experimental conditions used for expt. 9. Only one gram of a product boiling between 218 and 282° was obtained. Infrared spectral analysis indicated the presence of only a small amount of benzylcyclohexane, contaminated with an unsaturated hydrocarbon. Experiments along this line were therefore not pursued.

TABLE V

REACTION OF TOLUENE WITH 1-BUTENE AND 1-OCTENE

Experiment	16	17
Olefin	1-Butene	1-Octene
g. (moles)	62(1.1)	39.5(0.35)
Toluene, g. (mole)	92(1.0)	92(1.0)
Anthracene, g. (mole)	0.9(0.005)	0.9(0.005)
Sodium, g. (mole)	5.0(0.215)	4.0(0.174)
Temp. of pres. drop, °C.	290	
Highest temp., °C.	299	289
Highest pressure, atm.	173	22
Duration, hours	23	50
Product, g. (mole)	^{a} 14(0.095)	^{b} 5.1(0.025)
Bottoms and/or holdup, g.	6.8	3.0

[a] 2-Benzylbutane. The presence of low boiling hydrocarbons was not investigated. [b] 2-Benzyloctane. Recovered olefins were composed predominantly of *trans*-octenes.

Benzene and *t*-Butylbenzene with Olefins.—The reaction of benzene with ethylene and isobutylene and of *t*-butylbenzene with ethylene was investi-

TABLE VI

REACTION OF BENZENE AND *t*-BUTYLBENZENE WITH OLEFINS

Experiment	18	19	20	21
Olefin	←Ethylene→		Isobutylene	Ethylene
g. (mole)	14(0.5)	14(0.5)	56(1.0)	14(0.5)
Aromatic hydrocarbons	←Benzene→			*t*-Butylbenzene
g. (moles)	110(1.41)	78(1.0)	105(1.35)	104(0.78)
Chain initiator precursor	Bromobenzene	Anthracene	←1-Chlorocyclohexene→	
g. (mole)	15(0.095)	0.9(0.005)	←7.0(0.06)→	
Sodium, g. (atoms)	4.6(0.2)	5.0(0.215)	←4.6(0.2)→	
Temp. of pressure drop, °C.			300	265
Highest temp., °C.	300	349	310	304
Highest pressure, atm.	42	83	52	36
Duration, hours	8	33	22	20
Product, g. (mole)	[a] 1.0(0.009)	[c] 0.6(0.004)	[e] 0.87	[g] 0.7(0.004)
Bottoms and/or holdup, g.	5.0[b]	4.0[d]	1.8[f]	1.1

[a] Ethylbenzene. [b] Contained *sec*-butylbenzene, 3-phenyl-3-methylpentane and biphenyl. [c] *sec*-Butylbenzene. [d] Biphenyl, 0.026 mole. [e] *t*-Butylbenzene, 0.13 g. (0.001 mole); isobutylbenzene, 0.74 g. (0.006 mole). [f] Biphenyl, 0.012 mole. [g] *o*-, *m*- and *p*-*t*-butylethylbenzene.

gated because alkali alkyls metalate the aromatic ring, as first reported by Schorigin.[12] The experimental results are summarized in Table VI.

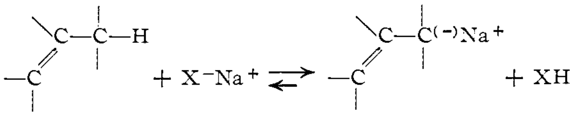
Discussion and Mechanism

The results which are summarized in Tables I-III demonstrate the strictly selective mode of addition of the alkylaromatic entity to unsymmetrical olefins. This mode of addition in itself shows that the reactive species is a carbanion and at the same time indicates the relative order of stability, *viz.*, reactivity of the alkyl carbanions. This order of stability is the opposite to that of the carbonium ions and of free radicals.

The observation of Bartlett and co-workers[4] relative to the enhanced reactivity of the secondary and tertiary alkyl lithium compounds indicated that secondary and tertiary carbanions are more reactive than primary ones. In competitive metalation experiments of arylalkanes Bryce-Smith[13] found that the release of a proton from a benzylic carbon–hydrogen bond is hindered by the presence of methyl groups, *e.g.*, toluene is more reactive than ethylbenzene, and the latter is more reactive than isopropylbenzene. In line with these findings the present data also show that whenever the intermediate benzylic carbanion is added to an unsymmetrical olefin such as propylene or isobutylene, a primary instead of a secondary or a tertiary intermediate carbanion was produced. This mode of addition indicates the higher anionic stability of the primary alkyl sodium compounds and that the mode of addition is determined by polar rather than by steric factors. Steric factors may account to some extent for the reluctance of isobutylene and of propylene, as compared with ethylene, to accept a benzylic carbanion. It was found that under similar experimental conditions isobutylene reacts with toluene at a higher temperature than with propylene, which in turn requires a higher temperature than ethylene. In all these cases, however, a parallel effect, the electron density of the acceptor olefin is operating. Bryce-Smith[13] and Shatenstein and co-workers[14] found that alkyl substitution deactivates the aromatic nucleus toward metalation by ethylpotassium and potassium amide, respectively, whereas electronegative substituents increase the rate of nuclear metalation.[15] A similar inductive effect of the methyl groups apparently renders the isobutylene and propylene poorer reagents toward the nucleophilic carbanion than ethylene proper.

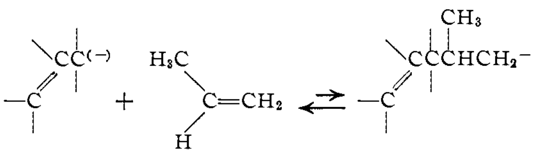
The addition of alkylaromatic hydrocarbons to propylene and isobutylene in the presence of an organosodium chain initiator can be explained by a mechanism similar to the one described previously.[5] The organosodium compounds, carbanions subsequently, are best considered as polar, undissociated ion pairs; the role of the metal cation in these, as apparently in all other reactions, is purely electrostatic.[13]

The carbanion chain initiator abstracts a proton from a benzylic carbon in an acid–base equilibrium. This equilibrium is shifted the more to the right the larger the difference between the *pK*$_a$ of the conjugate acid of X^- and the reacting hydrocarbon.



(1)

Through the addition of the resonance stabilized benzylic carbanion to the olefin a resonance nonstabilized carbanion is produced



(2)

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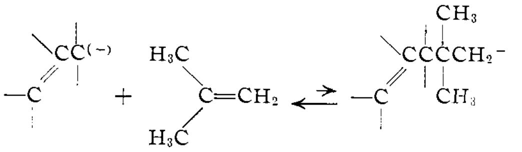
[12] P. Schorigin, *Ber.*, **41**, 2711, 2723 (1908); **43**, 1938 (1910).

[13] D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

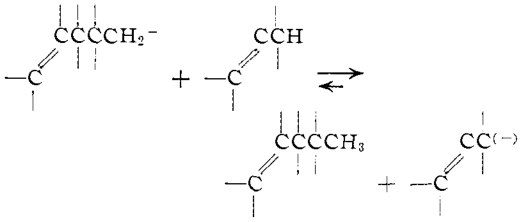
[14] A. I. Shatenshtein, L. N. Vasil'eva, N. M. Dykhno and E. A. Izrailevich, *Doklady Akad. Nauk S.S.S.R.*, **85**, 381 (1952); *C.A.* **46**, 9954 (1952).

[15] G. E. Hall, R. Piccolini and J. D. Roberts, THIS JOURNAL, **77**, 4540 (1955).


(2a)

It is assumed that this addition is an energetically unfavorable step, as indicated by the short arrow in the forward direction. This assumption is supported by the observation made by Wooster and Morse[16] who found that 1,1,1-triphenyl-3-iodopropane decomposed in the presence of sodium in liquid ammonia to yield triphenylmethylsodium, ethylene and sodium iodide.

Even though steps 2 and 2a are energetically unfavorable ones, the carbanions thus formed can react again with acidic reagents. The latter are the parent alkylaromatic hydrocarbons, which are in great excess in the reaction mixture.

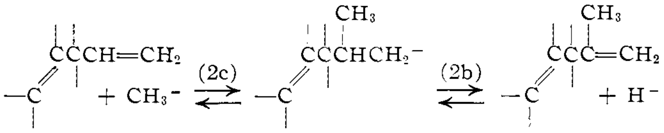

(3)

Step 3 is similar to step 1. By this reaction the benzylic carbanion is generated and the whole reaction sequence is thus repeated.

Since triphenylmethylsodium in Wooster and Morse's[16] experiment may represent an extreme case as far as resonance stabilization is concerned, the reverse step, that is the addition of ethylene to triphenylmethane in the presence of sodium and *o*-chlorotoluene as an organosodium precursor, was investigated. It was found that under pressure at 300° ethylation of triphenylmethane occurred resulting in the formation of 1,1,1-triphenylpropane. In the absence of the catalyst but under similar experimental conditions triphenylmethane did not react with ethylene.

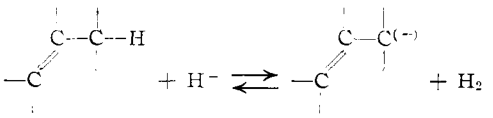
The relatively high yield in the reaction of diphenylmethane with propylene (expt. 8) emphasizes the importance of the acidity[17,18] of the parent hydrocarbon in these steps.

The adduct formed in step 2 may undergo other competitive reactions. Bryce-Smith[19] has shown that alkali alkyls, unstable at temperatures above 100°, decompose by an ionic mechanism to yield alkali hydrides and olefins. Since present reactions were carried out at relatively high temperatures, the fate of the aralkyl carbanion formed in step 2 is best represented by the following competitive reactions



The hydride formed in step 2b can add to propylene to form ultimately propane (expt. 1,2), according to the mechanism described previously.[5]

Gas analysis also indicated the production of hydrogen during the reaction, resulting apparently from an acid–base reaction of the hydride ion.[20,21]



Since sodium hydride apparently can either add to an olefin,[5] thus producing an alkylsodium chain initiator, or can abstract a proton from a benzylic carbon, thus forming the reagent carbanion, it seemed desirable to carry out a reaction of toluene with isobutylene in the presence of sodium hydride alone. This was done in expt. 11; neopentylbenzene was obtained.

The decomposition of the aralkyl carbanion according to 2c was indicated by the formation of methane (expt. 1 and 2). Since propane and hydrogen were formed through the hydride ion (2b), whereas the methane through the methide ion (2c) the ratio of these products indicates the relative energetics of these steps. The ratio of propane plus hydrogen to methane is 10.6 and 14.7, respectively, thus indicating that a hydride ion is a more stable species than a methyl carbanion.

By either of these steps (2b and 2c) an allylbenzene is produced, which is known to isomerize readily to a propenylbenzene.[22] The beneficial effect of the excess of sodium (expt. 1 and 2) is most probably due to the formation of new chain initiators through the interaction of the substituted styrenes with the sodium, according to a reaction previously described.[23,24]

Since the reaction of isobutylene with toluene occurred at about 320° it was suspected that the presence of small amounts of 1-phenyl-3-methylbutane in the neopentylbenzene fraction was due to a thermal, free radical, reaction. For that reason toluene and isobutylene were heated at 300–350° in the absence of sodium; 3-methylbutylbenzene, free from neopentylbenzene, was obtained (expt. 12). In the reactions of isopropylbenzene and diphenylmethane with isobutylene the presence of only the similarly derivable thermal adducts, namely, 2-phenyl-2,4-dimethylpentane and 1,1-diphenyl-3-methylbutane, respectively were detectable.

The small amounts of 2-benzylbutane found in the neopentylbenzene fractions (expt. 9–11) were due to the presence of 1% of *n*-butenes in the isobutylene used. The material balance of the reaction product indicated that the *n*-butenes reacted preferentially. It was subsequently found that 1-butene reacts with toluene in the presence of sodium and anthracene (Table V, expt. 16) to form pure 2-benzylbutane in a yield comparable to that of the propylene reactions.

Olefin dimers were separated and identified in many of the experiments described herein.

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(16) C. B. Wooster and R. A. Morse, THIS JOURNAL, **56**, 1735 (1934).

(17) J. B. Conant and G. W. Wheland, *ibid.*, **54**, 1212 (1932).

(18) W. K. McEwen, *ibid.*, **58**, 1124 (1936).

(19) D. Bryce-Smith, *J. Chem. Soc.*, 1712 (1955).

(20) H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 347 (1955).

(21) H. Pines and H. E. Eschinazi, *ibid.*, **77**, 6314 (1955).

(22) M. Tiffeneau, *Compt. rend.*, **139**, 482 (1904).

(23) J. B. Conant and A. H. Blatt, THIS JOURNAL, **50**, 551 (1928).

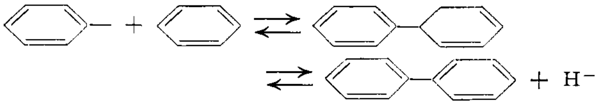
(24) For general literature survey see Franz Runge, "Organometallverbindungen," Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1944.

In the reactions of propylene the carbon skeleton of the olefin dimer was shown to be that of pure 2-methylpentane, whereas isobutylene dimer after hydrogenation yielded pure 2,2,4-trimethylpentane. Although a more detailed study of the dimerization reaction will be described in a subsequent paper it can be stated here that the polymerization is due to the metalation of the allylic carbon of the parent olefin. The allylic carbanion thus produced adds to another olefin molecule in the same way as the benzylic carbanion did.

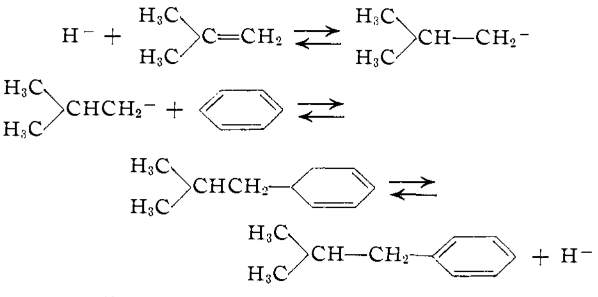
The relative stability of a primary carbanion over a secondary one also was demonstrated in the reaction of 1-octene with toluene (Table V); the adduct consisted of 2-benzyloctane.

Reactions using benzene and *t*-butylbenzene were carried out because alkyl-sodium metalates an aromatic nucleus[12] and it was expected that phenyl carbanions thus formed would add to olefins the same way as benzylic carbanions did. Although the yields were very small, the expected additions did take place (Table VI). Benzene and ethylene formed ethylbenzene as the primary adduct. The *sec*-butylbenzene which was formed apparently resulted from the reaction of ethylbenzene with ethylene.

The reaction of benzene with isobutylene yielded a mixture of *t*-butylbenzene and isobutylbenzene in 1:5 ratio. The formation of the latter compound, owing to the relatively low temperature, could not be attributed to the thermal reaction of benzene and isobutylene. However, the consistent occurrence of biphenyl in all of the carbanion reactions of benzene and an observation made by Bryce-Smith and Turner[25] offers a plausible interpretation for this reaction. The above authors[25] found that in the metalation of benzene by alkali alkyls at 65°, but not at 20°, the corresponding alkylbenzenes were always produced. The formation of biphenyl in the present experiments is apparently the result of the addition of phenylcarbanion to benzene followed by the loss of a hydride ion



Due to the relatively poor protophilic activity of the hydride ion (expt. 1 and 2) it adds preferentially to isobutylene to form isobutyl carbanion followed by the alkylation of benzene



t-Butylbenzene under similar conditions reacted with ethylene to give a mixture of *t*-butylethylbenzenes. Besides the *meta* and *para* isomers the presence of *o*-*t*-butylethylbenzene is also indicated by the strong infrared band in the 13.0–13.6 μ region, although the spectrum of the *ortho* isomer has not yet been published. Because alkyl substituents deactivate the aromatic ring toward nuclear metalation,[13] the yield with *t*-butylbenzene was expectedly lower than with benzene itself.

Experimental

Reagents.—*o*-Chloroisopropylbenzene was obtained by the chlorination of isopropylbenzene in the presence of iron powder.[26] The sample boiled at 191°, n^{20}_{D} 1.5150. The infrared spectrum showed strong bands at 13.1–13.3 and 14.3 μ.

1-Chlorocyclohexene was prepared from cyclohexanone and phosphorus pentachloride[27]; b.p. 59° at 48 mm., n^{20}_{D} 1.4795.

Dimethylmercury was prepared by the method of Gilman and Brown[28] in 55% yield, b.p. 90–91°, n^{20}_{D} 1.5450.

Analytical Procedure.—Infrared spectroscopy was used throughout the work for qualitative and quantitative analysis. Individual hydrocarbons were identified by matching their spectra with those of synthetic specimens. Quantitative analysis was done by matching band intensities. The infrared spectra were run on a double-beam infrared spectrophotometer, product of Baird Associates, Inc., Cambridge, Mass.

Displacement chromatography on silica gel (Davison Chemical Co., Baltimore, Md.) was used to separate hydrocarbon mixtures into paraffinc, olefinic and aromatic fractions, respectively.[29] Often *n*-pentane was used to "wet" the silica gel and to speed up the operation. Absolute ethyl alcohol was used to displace the hydrocarbon fraction.

Refractive indices were determined at 20°. In some cases quantitative estimations were made using the linear relationship in the refractive indices of mixtures of hydrocarbons.[30]

Unless indicated otherwise, distillations were carried out on a 40 × 1 cm. column, packed with stainless steel gauze.

Gas analysis was made by means of mass spectrometry.

Apparatus and Procedure.—A mixture of the reactants, the chain initiator precursor and the alkali metal was charged into a 250-ml. capacity Magne-Dash autoclave.[31] Propylene, 1-butene and isobutylene were charged in liquid from a pressure charger provided with a calibrated glass gage. The amount of ethylene added was estimated from *PVT* relationship. The air in the autoclave was displaced with hydrogen or nitrogen before the olefins were added. The agitated mixture was heated to the reaction temperature which was usually indicated by a commencing pressure drop, and maintained at this or slightly higher temperature by means of a temperature controller. The end of reaction was usually indicated by a steady or leveling-off pressure. The reaction mixture was cooled to room temperature, forced from the reaction vessel by means of nitrogen pressure through a sintered glass funnel with the simultaneous application of suction. The reaction vessel was rinsed with a solvent, usually the parent alkyl-aromatic hydrocarbon. The black residue, collected on the filter funnel, was kept wet with the solvent till it was decomposed with methyl alcohol. The filtered reaction product, a clear, sometimes yellow liquid, was then fractionated.

Experiments 1–4.—A fraction boiling between 55 and 100° was selectively hydrogenated over PtO_2 and the hydrogenated product separated from the contaminant toluene through chromatography; it had an n^{20}_{D} 1.3728 and its spectrum was identical with that of 2-methylpentane (NBS standard; API Project 44, spectrum 551). After distilling off unreacted toluene, the reaction product boiled between

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[25] D. Bryce-Smith and E. E. Turner, *J. Chem. Soc.* 861 (1953).

[26] R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2875 (1949).

[27] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2014 (1950).

[28] H. Gilman and R. E. Brown, THIS JOURNAL, **52**, 3315 (1930).

[29] B. J. Mair, *J. Research Natl. Bur. Standards*, **34**, 435 (1945).

[30] B. T. Brooks, S. S. Kurtz, Jr., C. E. Boord and L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1954, p. 315.

[31] Autoclave Engineers, Inc., Erie, Pennsylvania.

169–170°, n^{20}_{D} 1.4862. The spectrum of the product was indistinguishable from the spectrum of isobutylbenzene (NBS standard, API spectrum 469). For experiment 1, 12.2 liter (S.T.P.) and for expt. 2, 8.7 liter (S.T.P.) of gas was collected. The composition of the gas is shown in Table I.

Experiment 5.—Propylene dimer was collected between 61 and 66°, n^{20}_{D} 1.3950. The alkylaromatic reaction product distilled at 187–190°, n^{20}_{D} 1.4902; infrared spectrum of the product was identical with that of synthetic 2-phenyl-3-methylbutane, b.p. 181–190°, n^{20}_{D} 1.4913.[32]

Experiment 6.—The reaction product, after distilling off unreacted isopropylbenzene, boiled between 212.5–215.5°, n^{20}_{D} 1.4978; infrared spectrum of the cut was identical with that of a synthetic sample of 2-phenyl-2,3-dimethylbutane, n^{20}_{D} 1.4998.[33]

Experiment 8.—The reaction product distilled at 125° at 3.5 mm., b.p. 292° at 760 mm. (cor.), m.p. 15.0–16.0°, n^{20}_{D} 1.5576. Infrared spectrum of the product was identical with that of synthetic 1,1-diphenyl-2-methylpropane. The reference sample was prepared by a conventional procedure[34] from ethyl isobutyrate and phenylmagnesium bromide, dehydrating the resulting 1,1-diphenyl-2-methylpropanol over activated alumina (The Harshaw Chemical Co.) at 275° and hydrogenating the obtained 1,1-diphenyl-2-methyl-1-propene (b.p. 125–126° at 3.5 mm., n^{20}_{D} 1.5885) over copper chromite in absolute ethanol solution at 200°. The 1,1-diphenyl-2-methylpropane thus prepared distilled at 292° (cor.), n^{20}_{D} 1.5585.

Experiments 9–12.—The reference neopentylbenzene was prepared by the method of Bygdèn,[35,36] n^{20}_{D} 1.4885. 2-Benzylbutane,[37] n^{20}_{D} 1.4879, was obtained from Professor Letsinger. 1-Phenyl-3-methylbutane, b.p. 195–197° at 760 mm. (cor.), n^{20}_{D} 1.4860, prepared by conventional procedure, was available in this Laboratory.

Experiments 13–14.—A fraction, 3 g., boiling between 70 and 100°, n^{20}_{D} 1.4155, after selective hydrogenation over platinum oxide and chromatography, had n^{20}_{D} 1.3925 and an infrared spectrum identical with that of pure 2,2,4-trimethylpentane.

Synthesis of 2-Phenyl-2,4-dimethylpentane.—4-Phenyl-4-methyl-2-pentanone, b.p. 91.8–95.5° at 3.5 mm., n^{20}_{D} 1.5106–1.5109, was prepared from mesityl oxide and benzene[38] in 68% yield. Methylmagnesium iodide added to this ketone yielded 4-phenyl-2,4-dimethyl-2-pentanol, which was dehydrated in the presence of *p*-toluenesulfonic acid in toluene solution to a mixture of 4-phenyl-2,4-dimethyl-1-pentene and 4-phenyl-2,4-dimethyl-2-pentene; b.p. 68–69° at 3.8 mm., n^{20}_{D} 1.5086, yield 78%. Infrared spectra of the cuts indicated that the trisubstituted olefin boils at a lower temperature than the vinylidene compound. The mixture of olefins was selectively hydrogenated in the presence of copper chromite at 125° and 157 atm. hydrogen pressure in quantitative yield to pure 2-phenyl-2,4-dimethylpentane, b.p. 67° at 3.5 mm. (b.p. 215° at 760 mm., cor.), n^{20}_{D} 1.4932; literature[39] b.p. 216–218°, $n^{16.5}_{D}$ 1.4938.

Synthesis of 2-Phenyl-2,3,3-trimethylbutane.—Benzene, 2.86 moles, was alkylated with 29 g. (0.296 mole) of 2,3,3-trimethyl-1-butene (triptene) in the presence of 70 g. of anhydrous hydrogen fluoride at 0°. The reaction product boiled between 70 and 74° at 3.5 mm. (b.p. 219–223° at 760 mm., cor.), n^{20}_{D} 1.5030–1.5041, yield 5.2 g., 10%. Chromatography of the product gave a heart-cut of n^{20}_{D} 1.5055 (literature[40] b.p. 224–226°, n^{20}_{D} 1.5019).

Experiment 15.—1,1-Diphenyl-3-methylbutane was prepared by the method of Sabatier[34]; b.p. 305°, n^{20}_{D} 1.5482; lit.[34] b.p. 297°, n^{20}_{D} 1.551.

1,1-Diphenyl-2,2-dimethylpropane was prepared by the procedure described by Skerrett and Woodcock[41]; b.p. 132° at 3.5 mm. m.p. 55°.

Experiment 16.—The reaction product, 14 g., boiled at 52° at 4 mm., n^{20}_{D} 1.4874; literature[37] for 2-benzylbutane, b.p. 86–87° at 20 mm., n^{20}_{D} 1.4879.

Experiment 17.—A fraction, 5.1 g., boiling between 107 and 117° at 4 mm., after chromatography gave a heart-cut of n^{20}_{D} 1.4854. The spectrum of this cut was essentially identical with that of a synthetic sample of 2-benzyloctane.[37]

The recovered olefins, after separation from toluene by chromatography, were shown by infrared spectrum to be a mixture of *trans*- (major), *cis*- and α-olefins (minor). Infrared bands of medium intensity at 9.3–9.5 μ indicate that the *trans*-olefin is probably a mixture of *trans*-2-, 3- and/or 4-octenes.

Experiment 21.—The product of the reaction was collected from a Piros–Glover column between 61.2 and 90° at 1 mm., n^{20}_{D} 1.4906–1.5012. Infrared spectra of the cuts indicated that the product was a mixture of *o*-, *m*- and *p*-disubstituted benzenes and that the *m*-isomer had the lowest and the *o*-isomer the highest boiling point. *t*-Butyltoluenes also followed the same order in boiling points[42]; literature[42] for *m*-*t*-butylethylbenzene, b.p. 205.4°, n^{20}_{D} 1.4928; for *p*-*t*-butylethylbenzene, b.p. 212.1°, n^{20}_{D} 1.4933.

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[32] Patterson, M. S. Thesis, Purdue University, 1952, p. 35.

[33] L. Schmerling and J. P. West, THIS JOURNAL, **76**, 1917 (1954).

[34] P. Sabatier and M. Murat, *Ann. chim.*, [9] **4**, 294 (1915).

[35] A. Bygdèn, *Ber.*, **45**, 3479 (1912).

[36] V. N. Ipatieff and L. Schmerling, THIS JOURNAL, **60**, 1476 (1938).

[37] R. L. Letsinger, *ibid.*, **70**, 406 (1948).

[38] A. Hoffman, *ibid.*, **51**, 2542 (1929).

[39] Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946, p. 145.

[40] R. C. Huston, W. B. Fox and M. N. Binder, *J. Org. Chem.*, **3**, 251 (1938).

[41] E. J. Skerrett and D. Woodcock, *J. Chem. Soc.*, 2804 (1952).

[42] M. J. Schlatter and R. D. Clark, THIS JOURNAL, **75**, 361 (1953).