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Carbanion and Thermal Reactions of Some Simple Olefins[1]

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Several simple olefins or olefin pairs were subjected to a reaction in the presence and the absence of organosodium compounds, in order to demonstrate the role and importance of the relative stability of the ionic and radical species in determining the structure of the ultimate product. The carbon skeleton of the resulting dimeric hydrocarbons indicated that the order of alkylcarbanion stabilities, I > II > III, accounts for the structure of the products resulting from the reactions carried out in the presence of organosodium compounds. The order of stability of alkyl free radicals, III > II > I, accounts for the structure of the products resulting from the purely thermal reactions. The ratios of cycloalkanes to the open chain hydrocarbons in the dimer fractions of propylene, 1-butene and isobutylene are 1:13, 1:6 and 3:1, respectively.

Carbanion reactions of alkylaromatic hydrocarbons with unsymmetrical monoölefins show a selective mode of addition[1a] as a result of the order of intrinsic carbanion stability, which for alkylcarbanions appears to be I > II > III. It is known that the order of stability of alkyl free radicals follows the reverse sequence: III > II > I.[4] Therefore, it is expected that an unsymmetrical system will yield different products, depending on whether the reaction takes place free radical wise or carbanion wise.

Some simple olefins, which can give both allylic carbanions and allylic free radicals, were selected to demonstrate the role of the relative stability of the ionic or free radical species in determining the ultimate products. In predicting products the "activity" of the reacting species was also taken into consideration. The most stable (*i.e.*, the least reactive) reagent, a primary carbanion or a tertiary free radical, is expected to exert the greatest selectivity in the mode of addition to an unsymmetrical substrate.[5]

TABLE I

CARBANION REACTIONS

Chain initiator precursor: 0.9 g. (0.005 mole) of anthracene and 5.0 g. (0.215 g. atom) of sodium

Experiment	1	2	3	4	5	6
Olefin I	Propylene	Isobutylene	Cyclohexene	Ethylene	Propylene	Isobutylene
Moles	1.67	1.5	1.0	0.5	1.0	0.75
Olefin II	...	...	...	←Cyclohexene→		
Mole	...	...	...	1.0	1.0	1.0
Temp. of pressure drop, °C.	250	280	...	280	278	282
Highest temp., °C.	280	285	298	300	287	287
Highest press., atm.	225	215	43	70	175	121
Duration, hours	4.5	25.5	34	8.5	14	41
Hydrogenated 1:1 adduct mole	0.2	0.082	0.009	0.036	0.036	0.020
Yield, mole %	24	11	1.8	7.2	3.6	2.7
Bottoms and/or holdup, g.	...	...	0.8	3.4	1.5	3.2

Expt. 1.: Fifty ml. of decalin was used as solvent. The dimeric fractions, b.p. 61–64°, $n^{20}\mathrm{D}$ 1.3950-1.3990, consisted of *trans*-4-methyl-2-pentene (minor), 4-methyl-1-pentene (small), 2-methyl-1-pentene and 2-methyl 2-pentene (major). The hydrogenated product was 2-methylpentane.

Expt. 2: Fifty ml. of decalin was used as solvent. The dimeric fraction, b.p. 100-104°, $n^{20}\mathrm{D}$ 1.4096–1.4116, was composed of 78% 2,4,4-trimethyl-1-pentene and 22% 2,4,4-trimethyl-2-pentene. On hydrogenation it absorbed the quantitative amount of hydrogen to form 2,2,4-trimethylpentane.

Expt. 3: The recovered cyclohexene contained 0.09 mole of benzene. The dimeric fraction, amounting to 1.5 g., was composed of 65% 1-cyclohexylcyclohexene out of a mixture of biphenyl and phenylcyclohexane. The dimeric fraction yielded on hydrogenation bicyclohexyl.

Ext. 4: The recovered cyclohexene contained 0.06 mole of benzene. The adduct, b.p. 134–136°, $n^{20}\mathrm{D}$ 1.4577, was composed of trisubstituted olefins and of ethylbenzene, 7%. After chromatography 1-ethylcyclohexene was separated, $n^{20}\mathrm{D}$ 1.4528. A portion of the original, 1.24 g., adduct on selective hydrogenation over platinum oxide catalyst absorbed 93% of the theoretical amount of hydrogen. The saturated hydrocarbons, after chromatography, were composed of ethylcyclohexane only.

Ext. 5: The catalytic sludge of the reaction, owing to a high reactivity, was decomposed stepwise, first with benzene (suggested by Mr. Luke Schaap), then with alcohol. A vigorous exothermic reaction probably indicated the easy metalation of benzene by the cyclohexenyl sodium. The adduct, b.p. 150–155°, $n^{20}\mathrm{D}$ 1.4554–1.4606, was selectively hydrogenated. It was composed of 72% isopropylcyclohexane, 18% *n*-propylcyclohexane, 7% isopropylbenzene and 3% *n*-propylbenzene.

Expt. 6: The adduct, 2.8 g., which distilled at 56° at 12 mm., $n^{20}\mathrm{D}$ 1.4563, was composed of aromatic hydrocarbons, of trisubstituted olefin, of *cis*-olefin and of vinylidene olefin. On selective hydrogenation the adduct absorbed 0.9 mole of hydrogen per mole of hydrocarbon. The hydrogenated product was composed of 86% isobutylcyclohexane, 10% *t*-butylcyclohexane and 4% of a mixture of iso- and *t*-butylbenzene.

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[1] (a) Paper VI of the series of Base Catalyzed Reactions. For V see H. Pines and V. Mark, THIS JOURNAL, **78**, 4316 (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.

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

[3] To whom requests for reprints should be addressed.

[4] For general references see Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954.

[5] A quantitative correlation between the reactivity of the reagent and the isomer distribution ratios of the product was presented in the electrophilic aromatic substitution by H. C. Brown and coworkers: (a) THIS JOURNAL, **75**, 6292 (1953); (b) **77**, 2300, 2310 (1955).

TABLE II

THERMAL REACTIONS OF OLEFINS

Experiment	7	8	9	10
Olefin	Propylene	Isobutylene	1-Butene	Cyclopentene
Moles	4.0	3.8	3.8	1.47
Temp. of pressure drop, °C.	330	335	315	. . .
Highest temp., °C.	360	345	355	375
Highest press., atm.	71	68	69	24
Duration, hours	16	33	44	23
Hydrogenated dimer				
Mole	0.1330	0.395	0.244	0.068
Yield, mole %	6.6	20.8	12.9	9.3
Bottoms and/or holdup, g.	54	37	71	7.5
Conversion of olefin, mole %	39	38	46	68
Dimer content of product, wt. %	17.4	54.5	27.8	55

Expt. 7: The dimeric product was composed of *n*-hexane 22%, 2-methylpentane 27%, methylcyclopentane 7%, *n*-x-hexene 13% and 2-methyl-x-pentene 31%.

Expt. 8: Composition of the dimeric product: 1,1,3-trimethylcyclopentane 76%, 2,5-dimethylhexane 18%, 2,5-dimethyl-x-hexene 6%.

Expt. 9: Dimeric product was composed of a hydrocarbon corresponding most probably to 1-methyl-3-ethylcyclopentane 15%, 3-methylheptane (*n*-octane?) 26%, 3-methyl-x-heptene (*n*-x-octene?) 59%. The saturated hydrocarbons which were separated from the olefins by means of silica gel chromatography were analyzed: Calcd. for C_8H_{16}: C, 85.63; H, 14.37. Calcd. for C_8H_{18}: C, 84.16; H, 15.84. Found: C, 85.05; H, 14.98; $n^{20}\mathrm{D}$ 1.4041.

Expt. 10: The reaction was accompanied by the formation of carbonaceous material. The recovered cyclopentene fraction contained 0.15 *M* of cyclopentane. The dimeric fractions distilled at 48–62° at 4 mm. (corrected b.p. 186–205°); 95% of the product boiled at 186–191 (corrected), $n^{20}\mathrm{D}$ 1.4744 – 1.4788. On hydrogenation only 0.26 mole of hydrogen per mole of the hydrocarbons was absorbed. The infrared spectrum of the hydrogenated dimeric fraction was identical with the spectrum of pure bicyclopentyl (A.P.I. spectrum 1088).

TABLE III

THERMAL REACTIONS OF ALKENES WITH CYCLOHEXENE

Experiment	11	12	13	14
Olefin I	. . .	Ethylene	Propylene	Isobutylene
Mole	. . .	1.0	0.93	0.75
Olefin II	Cyclohexene			
Moles	1.38	1.0	0.85	1.0
Temp. of pressure drop, °C.	. . .	350	340	350
Highest temp., °C.	370	381	356	364
Highest press., atm.	82	90	187	161
Duration, hr.	30	66	66	45
Hydrogenated I and II adduct mole	0.095	0.09	0.127	0.091
Yield, mole %	13.8	8.9	15	12
Bottoms and/or hold-up, g.	8.5	27	48.5	31.6

Expt. 11: The recovered cyclohexene contained traces of benzene. The dimeric fraction distilled between 70 and 83° at 3.5 mm. (corrected b.p. 220–236°), $n^{20}\mathrm{D}$ 1.4916–1.4957; 72% of the dimers distilled at 228–230°, $n^{20}\mathrm{D}$ 1.4947. Infrared spectrum of the product showed the strong bands of a *cis*-olefin at 6.05 and 13.82 μ; this olefin consisted most probably of 3-cyclohexylcyclohexene. On hydrogenation bicyclohexyl was obtained, the infrared spectrum of which was undistinguishable from that of a synthetic specimen made by the hydrogenation of pure biphenyl.

Expt. 12: The adduct which distilled between 132 and 134° at 752 mm., $n^{20}\mathrm{D}$ 1.4530, was composed mainly of 3-ethylcyclohexene admixed with small amounts of 1-ethylcyclohexene and with 5% of ethylbenzene. On selective hydrogenation ethylcyclohexane having 5% of ethylbenzene was obtained. The bottoms contained 0.06 mole of 3-cyclohexylcyclohexene.

Expt. 13: The adduct, distilled at 151–158°, $n^{20}\mathrm{D}$ 1.4475 – 1.4546, 15.7 g., and was composed of 3-alkylcyclohexene as the major and allylcyclohexane as a minor constituent. The hydrogenated adduct consisted of 85% *n*-propyl- and 15% isopropylcyclohexane.

Expt. 14: The adduct distilled at 170–180°, $n^{20}\mathrm{D}$ 1.4520–1.4530, 12.5 g. Its infrared spectrum was almost identical with the spectrum of synthetic 3-isobutylcyclohexene, except for some weaker bands, characteristic of a vinylidene compound, presumably methallylcyclohexane. The adduct contained also 2% of isobutylbenzene. About 0.06 mole of 3-cyclohexylcyclohexene was present in the bottoms.

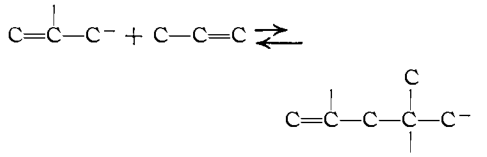
The carbanion reactions were carried out by generating the organosodium chain initiator *in situ*[1a,6]; the free radical reactions were carried out by generating the chain initiators by the pyrolysis of the olefinic hydrocarbons. The experimental conditions used and the results obtained are summarized in Tables I, II and III.

Discussion and Mechanism

Carbanion Reactions.—A reaction mechanism similar to the one suggested for the addition of alkylaromatic hydrocarbons to unsymmetrical olefins[1a] accounts also for the formation of the olefin adducts. An organosodium chain initiator (in present experiments the addition product of sodium and anthracene or the alkylsodium compound formed by the reaction of this organometallic adduct with an olefin) metalates the olefin to yield a resonance-stabilized allylic carbanion.

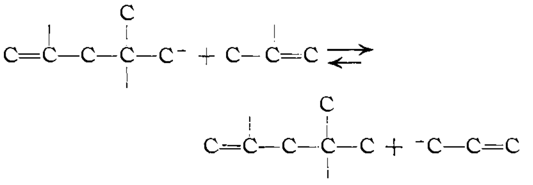
Under the experimental conditions used the allylic carbanion may add to an olefin to form a nonresonance stabilized adduct. If the substrate is an unsymmetrical olefin, the addition takes place in such a way as to yield the most stable carbanion.

If by this addition a primary allylic carbanion yields a primary carbanion adduct, then the addition step is an uphill process, because of the loss of the allylic resonance energy in this step. This energetically unfavorable addition still will lead to products if an excess of an olefin is present, with



$$C{=}\overset{|}{C}{-}C^- + C{-}C{=}C \rightleftarrows C{=}\overset{|}{C}{-}C{-}\underset{|}{\overset{\overset{C}{|}}{C}}{-}C^- \quad (2)$$

which the labile adduct can react in a presumably fast, acid–base equilibrium reaction



$$C{=}\overset{|}{C}{-}C{-}\underset{|}{\overset{\overset{C}{|}}{C}}{-}C^- + C{-}\overset{|}{C}{=}C \rightleftarrows C{=}\overset{|}{C}{-}C{-}\underset{|}{\overset{\overset{C}{|}}{C}}{-}C + {}^-C{-}C{=}C \quad (3)$$

Through this step the allylic carbanion is regenerated. The primary reaction product, a terminal olefin, may undergo double-bond isomerization under the influence of the organosodium compound, but the carbon skeleton is not changed. Hydrogenation, therefore, of propylene dimer yields pure

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(6) H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 554 (1955).

2-methylpentane, and that of isobutylene dimer yields pure 2,2,4-trimethylpentane.

In the reaction of cyclohexene with ethylene, propylene and isobutylene the cyclohexenylcarbanion is postulated as the reacting species.

The decreasing yields of ethyl-, isopropyl- and *t*-butylcyclohexene apparently are the result of: (1) increasing steric hindrance and (2) increasing inductive effect of the methyl group. Bryce-Smith[7] observed that alkyl substitution on a benzene ring deactivates the molecule toward nuclear metalation. A similar correlation was found by Shatenshtein and co-workers[8] in the toluene–benzene and tetrahydronaphthalene–naphthalene systems, whereas Hall, Piccolini and Roberts[9] have shown that electronegative substituents increase the rate of nuclear metalation. Due to the increased electron density, propylene, and especially isobutylene, are apparently more reluctant than ethylene to accept carbanions: the conditions of the addition are more drastic (a higher temperature is required[1a]) and the yields are smaller.

In the cyclohexene–propylene and cyclohexene–isobutylene systems, however, considering other things to be equal, the preferential formation of allyl- and methallylcarbanions (primary) rather than cyclohexenylcarbanion (secondary) is expected. *n*-Propyl- and isobutylcyclohexane would be the reaction products after hydrogenation if allyl and methallyl carbanions added to cyclohexene. The ratio of isopropyl- to *n*-propylcyclohexane obtained from the reaction after hydrogenation was 4:1, indicating that the addition of cyclohexenylcarbanion to propylene is the energetically favored one. This result was predicted on the basis that in the competitive metalation of propylene and cyclohexene there is less discrimination, due to resonance, between the primary and secondary allylic position than in the addition step proper. Therefore selectivity between the formation of a primary and a secondary carbanion adduct should be enhanced.

The high ratio (9:1) of isobutylcyclohexane/*t*-butylcyclohexane is apparently the result of several factors. Isobutylene may exert considerable steric hindrance and, due to the inductive effect of the methyl groups, certain reluctance in accepting a carbanion; a methallylcarbanion, however, if formed, should exert a greater reactivity than allylcarbanion in adding to an olefin molecule, due again to the inductive effect of the methyl groups.

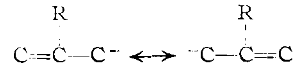
In all of the carbanion reactions of cyclohexene the recovered starting material contained benzene (6–8%) and the reaction product contained alkylaromatic hydrocarbons (5–10%). These results indicate that a cyclohexenylcarbanion loses a hydride ion with considerable ease, yielding ultimately an aromatic hydrocarbon.[10]

A similar metalation–elimination sequence accounts also for the formation of phenylcyclohexane and biphenyl (expt. 3).

Biphenyl may also result from the metalation of the formed benzene, followed by the addition of the phenylcarbanion to benzene.[1a]

There are several examples in the literature which appear to confirm the order of stability of carbanions as the one found from the mode of addition of alkylaromatic hydrocarbons[1a] or of allylic hydrocarbons to unsymmetrical olefins and which can be best interpreted by considering that primary carbanions are more stable and formed in preference to secondary or tertiary ones.

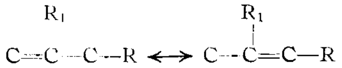
Morton and co-workers[11] reported that propylene, isobutylene and 2-methyl-1-butene are metalated faster than 1-butene, 2-butene, 1-pentene and 2-methyl-2-butene by pentyl sodium. In accordance with the order of stability of carbanions, I > II > III, highly reactive olefins are those which can form a primary allylic carbanion. The resonance structures involve primary carbanions only.



$$\mathrm{C{=}\overset{R}{C}{-}C^- \longleftrightarrow {}^-C{-}\overset{R}{\underset{}{C}}{=}C}$$

R is hydrogen, methyl or ethyl

Moderately reactive olefins are those which either cannot be metalated on a primary allylic carbon, or, if they can, whose resonance structures also involve a secondary carbanion



$$\mathrm{C{=}\overset{R_1}{C}{-}\overset{-}{C}{-}R \longleftrightarrow C{-}\overset{R_1}{C}{=}C{-}R}$$

R is methyl or ethyl; R_1 is hydrogen or methyl

Shatenshtein and co-workers[8] found in the metalation of saturated hydrocarbons by potassium amide in the presence of deuterated ammonia that *n*-heptane exchanged two hydrogen atoms while decahydronaphthalene exchanged only 0.7 atom hydrogen for deuterium. These results indicate that alkanes containing primary carbon atoms are metalated more readily than saturated hydrocarbons containing secondary or tertiary carbon atoms only. It is for this reason that in experiments 1 and 2 decalin was selected as the high boiling solvent.

Thermal Reactions.—Chain initiators were most probably generated *in situ* by the pyrolysis of the olefins. Bond dissociation energies[4] indicate a C–H homolysis for propylene and isobutylene and a C–C homolysis for 1-butene. A C–H cleavage was assumed also for the cyclic alkenes.

The carbon skeleton of the olefin dimers or adducts substantiated the predictions based upon the order of stability of free radicals: III > II > I. The structure of the unsymmetrical olefin adducts was different from that of the base-catalyzed products and in the case of isobutylene dimers a practically 100% selectivity was found in both types of reactions.

The dimers of propylene, isobutylene and 1-butene consisted of both the open chain alkenes and

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

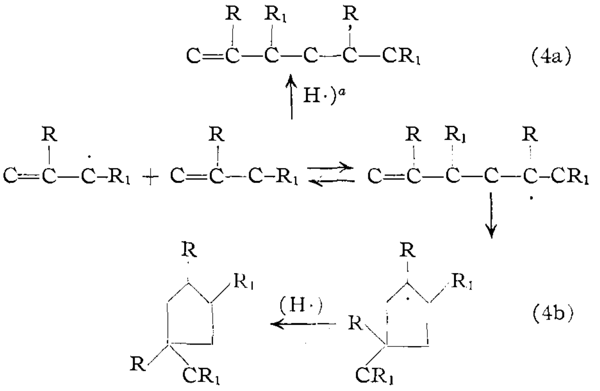
[8] A. I. Shatenshtein, L. N. Vasil'eva, N. M. Dykhno and E. A. Izrailevich, *Doklady Akad. Nauk., S.S.S.R.*, **85**, 381 (1952); *C. A.*, **46**, 9954 (1952).

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

[10] Aromatization of menthadienes by organosodium reagents was reported previously: (a) H. Pines, J. A. Vesely and V. N. Ipatieff, *ibid.*, **77**, 347 (1955); (b) H. Pines and H. E. Eschinazi, *ibid.*, **77**, 6314 (1955).

[11] A. A. Morton, M. L. Brown, M. E. T. Holden, R. L. Letsinger and E. E. Magat, *ibid.*, **67**, 2224 (1945).

the cycloparaffins.[12] These products apparently result from an intermolecular addition reaction, followed by either the abstraction of a hydrogen or an intramolecular addition reaction. The postulated alkenyl radical could be formed either by a C–H homolysis or by the abstraction of an allylic hydrogen atom by a free radical. This type of cyclization mechanism was previously suggested by Schmerling and Ipatieff.[13]



R and R_1 = H or CH_3

[a] The H· in parentheses indicates the abstraction of a hydrogen atom from an allylic position (in a chain reaction) rather than a reaction with free hydrogen atoms.

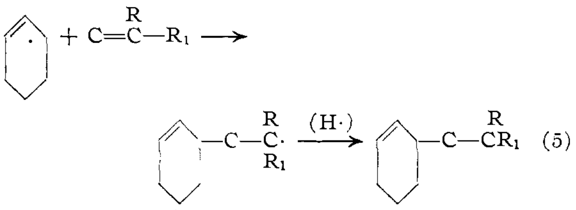
The dimer fractions from the three olefins also contained the corresponding alkanes which were probably formed by the addition of alkyl radicals to the parent olefins or by the hydrogenation of the dimeric alkenes by hydrogen atoms, products of a C–H homolysis. The monomeric alkyl radicals were most probably formed by a hydrogen transfer reaction in which the parent olefin acted as the acceptor of the hydrogen atom and a free radical, obtained from an addition reaction, as the donor of the hydrogen atom. The higher boiling hydrocarbons produced in this reaction were not investigated; they may, however, contain compounds of the general formula of C_nH_{2n-2} as previously reported.[14]

The ratios of cycloalkanes to the open chain hydrocarbons in the dimer fractions of propylene, 1-butene and isobutylene are 1:13, 1:6 and 3:1, respectively. These results also can best be interpreted by considering the order of reactivities of free radicals. There are indications that, *e.g.*, the addition of a primary free radical to an olefin to form a secondary radical has a lower activation energy than the abstraction of a secondary hydrogen atom by a primary radical.[4] Thus the least reactive tertiary radicals are less likely to abstract a hydrogen atom than the more reactive secondary radicals.[5b] Instead, the intramolecular addition may take place preferentially, resulting in the formation of a cyclopentane hydrocarbon.

The dimer fraction of propylene yielded compounds having the 2-methylpentane skeleton as well as the expected hexane. The non-selective mode of addition can be attributed to the high reactivity (*i.e.*, the none too great selectivity) of primary free radicals[15] at the temperature at which the polymerization was carried out and to a smaller extent to the high reactivity of primary free radicals.

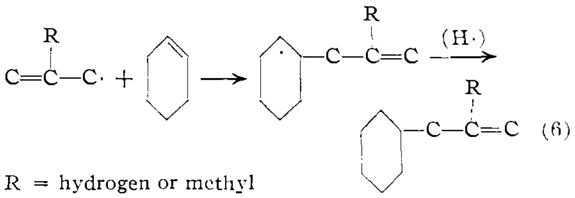
Both cyclopentene and cyclohexene yielded on thermal reaction the expected bicyclic compounds. Some cyclopentene and cyclopentylcyclopentane was also converted to the corresponding cycloalkanes. The formation of the cycloparaffins suggests that hydrogenation of the cycloölefins by hydrogen atoms, products of C–H homolysis, has taken place. It is not excluded, however, that cyclopentylcyclopentane might also have been produced by the addition of cyclopentyl free radical to the cyclopentene, followed by an abstraction of another hydrogen atom from a C–H homolysis.

A selective mode of addition of cyclohexenyl radicals to ethylene, propylene and isobutylene would give rise to 3-ethyl, 3-*n*-propyl- and 3-isobutylcyclohexene, respectively.



R and R_1 are hydrogen or methyl

The addition of an allyl or methallyl radical to cyclohexene would result in the formation of allyl- and methallylcyclohexane, respectively



R = hydrogen or methyl

The presence of both types of adducts in the reaction mixture was indicated by the characteristic infrared bands of the *cis*-, vinyl- and vinylidene olefins. The presence in only minor amounts of the alkenylcyclohexanes was indicated by the relatively weak vinyl and vinylidene bands and also by the comparison of the spectra of the reaction products of, *e.g.*, cyclohexene and isobutylene, with the spectrum of a synthetic 3-isobutylcyclohexene. Except for the presence of the vinylidene bands, the two spectra were identical.

The small amounts of alkyl aromatic hydrocarbons present in the reaction products of cyclohexene may result from consecutive hydrogen elimination steps.

The fact that aromatic hydrocarbons are formed to a smaller extent than in the corresponding carbanion reactions may indicate that the elimination of a hydrogen atom takes place with greater difficulty than the extrusion of the hydride ion.

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(12) J. B. McKinley, D. R. Stevens and W. E. Baldwin, *ibid.*, **67**, 1455 (1945), studied the thermal reaction of isobutylene and found that the dimer fraction contained large amounts of 1,1,3-trimethylcyclopentane; the nature of the other products was not investigated.

(13) L. Schmerling and V. N. Ipatieff in "Advances in Catalysis," Vol. II, Academic Press, Inc., New York, N. Y., 1950, p. 27.

(14) V. N. Ipatieff and H. Pines, *Ind. Eng. Chem.*, **28**, 684 (1936).

(15) H. Pines and J. T. Arrigo, unpublished results. In the thermal addition of toluene to propylene the ratio *n*-butylbenzene to isobutylbenzene produced was 5.1 at 430°; in the case of ethylbenzene the ratio of 2-phenylpentane to 2-methyl-3-phenylbutane was 6.6.

In the reaction of cyclohexene with ethylene both the carbanion and the free radical mechanisms were postulated to yield 3-ethylcyclohexene. However, ethylcyclohexene originating from the carbanion reaction showed a strong infrared band which is characteristic of a trisubstituted olefin, whereas the ethylcyclohexene resulting from the thermal reaction was predominantly a *cis*-olefin. A similar trend was found also in the carbanion and free radical reactions of the other alkylcyclohexenes. These results are not entirely unexpected since it was observed previously that the catalyst used in the carbanion reactions catalyses migration of double bonds.[8,10a,b,16,17]

Experimental Part

Materials.—Ethylene, propylene, 1-butene and isobutylene were of 99.0% purity (The Matheson Co., Inc.).

Cyclohexene (Eastman Organic Chemicals) was purified by treating with acidic ferrous ammonium sulfate, drying and distilling.

Cyclopentene was prepared by dehydrating cyclopentanol over activated alumina (The Harshaw Chemical Co.) at 420–430°, yield 77%, b.p. 43°, n^{20}_{D} 1.4230.

Apparatus and Procedure.—Carbanion reactions were carried out in a 250-ml. capacity Magne–Dash autoclave[18] using the procedure described previously.[1a] Thermal reactions also were carried out in the same autoclave, except for experiments 7–10 in which a rocking autoclave[19] of one liter capacity was used.

Analytical Procedure.—Infrared spectroscopy was used for qualitative and quantitative analysis. Individual hydrocarbons were identified by matching their spectra with those of synthetic specimens. Quantitative determinations were made by matching band intensities. A double beam spectrophotometer[20] was used in this work.

Displacement chromatography on silica gel[21] (Davison Chemical Co.) was used to separate hydrocarbon mixtures into saturated, olefinic and aromatic fractions, respectively.

Refractive indices were determined at 20°. In some cases quantitative determinations of mixtures of hydrocarbons were made using the linear relationships in the refractive indices.[22]

Distillations were made, in most of the experiments, in a 40 × 1 cm. column which was packed with stainless steel gauze.

Gaseous compounds were analyzed by means of a mass spectrometer.

3-Isobutylcyclohexene was prepared from 3-bromocyclohexene and isobutylmagnesium bromide.

3-Bromocyclohexene was prepared by the method of Ziegler[23] from 2.5 moles of freshly distilled cyclohexene, 0.5 mole of N-bromosuccinimide and 370 ml. of carbon tetrachloride as solvent. The product distilled at 62° at 28 mm., n^{20}_{D} 1.5300, yield 71%.

The reaction of isobutylmagnesium bromide (prepared from 0.4 mole of isobutyl bromide, 0.4 g. atom of magnesium in 180 ml. of dry ether with 3-bromocyclohexene (0.35 mole in 50 ml. of ether)) yielded 0.15 mole, 43%, of 3-isobutylcyclohexene, b.p. 53° at 10 mm., n^{20}_{D} 1.4550, and 8.7 g. of a product, b.p. 85° at 4 mm., n^{20}_{D} 1.5090. The higher boiling compound is believed to be 3-(2-cyclohexenyl)-cyclohexene.

The crude 3-isobutylcyclohexene after passing over silica gel yielded a bromine free hydrocarbon of n^{20}_{D} 1.4530.

Alkylcyclohexanes.—The reference alkylcyclohexanes, which were required for infrared spectral analyses, were made by hydrogenation of the corresponding aromatic hydrocarbons.

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Study in the Terpene Series. XXIX.[1] Sodium-catalyzed Aromatization of Geminal Alkylcyclohexadienes. Synthesis of 5-Methyl-5-ethyl-1,3-cyclohexadiene[2,3]

BY HERMAN PINES AND H. E. ESCHINAZI[4]

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Geminal alkylcyclohexadienes or their double bond isomers underwent aromatization with the loss of an alkane when refluxed in the presence of a sodium–organosodium catalyst. 5,5-Dimethyl-3-methylenecyclohexene and the conjugated 1,1,3-trimethylcyclohexadienes underwent a reversible isomerization and aromatization to *m*-xylene with a loss of methane. α-Pyronene was converted to 1,2,3-trimethylbenzene and methane when refluxed in the presence of sodium–benzylsodium catalyst. 5-Methyl-5-ethyl-1,3-cyclohexadiene underwent a competitive reaction; toluene and ethylbenzene were formed, the latter predominating. The gases were composed of methane and of a smaller amount of ethane. The mechanism of aromatization is discussed. The synthesis of 5-methyl-5-ethyl-1,3-cyclohexadiene is described.

It was previously shown that monocyclic terpenes such as limonene,[5,6] *l*-α-phellandrene,[6] 2,4(8)- and 3,8(9)-*p*-menthadiene[6] undergo isomerization and dehydrogenation to *p*-cymene when refluxed in the presence of sodium and an organosodium compound. Monocyclic dihydroterpenes, namely, *p*-menthenes, undergo racemization and reversible isomerization but not dehydrogenation.[7] Inasmuch as some of the monocyclic terpenes which are being studied in our laboratory contain a geminal carbon atom in the cyclohexadiene ring,[1,8] it was of interest

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(1) For paper XXVIII of this series see H. Pines and R. H. Kozlowski, This Journal, **78**, 3776 (1956).

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