Carbanion Chemistry. I. Propylene Dimerization to 4-Methyl-1-pentene

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The dimerization of propylene in the presence of potassium and higher atomic weight alkali metals leads in high selectivity to 4-methyl-1-pentene, which is slowly converted to 4-methyl-2-pentene but not readily to 2-methyl-1- or -2-pentene. In contrast to this behavior, dimerization of propylene in the presence of sodium leads to a mixture of methylpentene isomers approaching thermodynamic equilibrium. The effects of the nature of the alkali metal and of various process variables are discussed in the light of a possible mechanism.

The condensation of olefins to form higher molecular weight olefins in the presence of alkali metals is a well-known reaction.[1] Such reactions are believed to proceed through the formation of intermediate carbanions.[2] Condensations of low molecular weight olefins in the presence of sodium or potassium are generally selective for formation of low molecular weight products (oligomers). Recently, additional selectivity effects have been recognized in that certain double-bond isomers are produced in unexpectedly large amounts. Thus, the potassium-catalyzed dimerization of propylene yields relatively large amounts of 4-methyl-1-pentene and *cis*- and *trans*-4-methyl-2-pentene.[3]

We have studied the alkali metal catalyzed condensation of propylene in considerable detail in order to elucidate the selectivity effects in this reaction.

Selectivity Control by Alkali Metal.—In the course of our work, it was found that the rate and selectivity of carbanionic reactions of olefins was strongly dependent on the catalyst system. While reactions of olefins catalyzed by alkali metals had been noted previously in the literature,[2] the degree of specificity indicated was much less than that observed in our studies. This was partly due to the lack of complete structural studies in the earlier work as well as to the fact that many of the products produced depend very critically on the experimental conditions and the nature of the alkali metal used.

The propylene dimerization reaction takes place rapidly in a hydrocarbon solvent in the presence of an alkali metal catalyst at 100–200° and under several hundred pounds per square inch pressure. The alkali metal is a separate liquid phase dispersed in the solvent; therefore the physical processes associated with heterogeneous catalytic reactions may have an important bearing on this system.

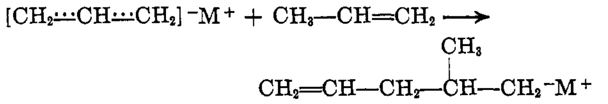
In Table I are presented data comparing the individual alkali metals, sodium, potassium, and cesium, for propylene dimerization and double-bond isomerization of methylpentenes in benzene solvent. The significant products of propylene dimerization in benzene solvent in decreasing order of importance appear to be monomethylpentenes (methyl branching next to the terminal carbon atom), solid residual material, propane, and normal C_6 olefins. The less important products are cracked fragments (C_1, C_2, C_4, and C_5), 2-methylpentane, methylcyclopentane, and C_9 olefins.

It should be pointed out that, when benzene is employed as solvent in alkali metal catalyzed condensation of olefins, condensations of the olefin with the aromatic nucleus occur, yielding small quantities of alkylbenzenes and, frequently, large quantities of intractable, coke-like material which deactivates the alkali metal by encapsulation. For these reasons, paraffinic solvents are to be preferred as reaction media, but the use of either paraffinic or aromatic solvent has little effect on the selectivity of the olefin condensation reaction *per se*.

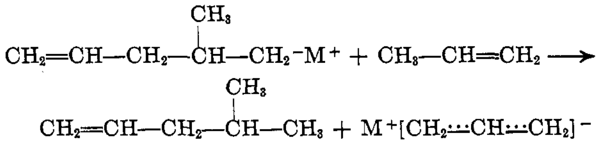
Selectivity of conversion of propylene to 4-methyl-1-pentene follows the order Cs $\sim$ K $\gg$ Na. A significant difference in the distribution of monomethylpentenes is seen between K and Cs on the one hand and Na on the other.[4] These data reveal a marked deviation of the observed distributions from the thermodynamic equilibrium composition.

This selectivity (for 4-methyl-1- and -2-pentenes *via* alkali metal catalyzed condensations as contrasted with the near-equilibrium distribution in acid-catalyzed condensations) can be understood by a consideration of the probable mechanism of dimerization of propylene in the presence of alkali metals. It is believed that the reaction proceeds through the initial formation of an organoalkali compound, shown in generalized form in eq. 1. This compound behaves as a source of allyl carbanion, which makes a nucleophilic attack on propylene, giving rise to an isohexenyl carbanion as shown in eq. 2. The isohexenyl carbanion is, with reference to the immediate surroundings of the negative charge, essentially a paraffinic carbanion. It is many orders of magnitude more basic than an allyl carbanion; consequently a proton transfer reaction occurs between propylene and the isohexenyl carbanion, eq. 3. In this manner 4-methyl-1-pentene is generated as the primary product and the allyl carbanion resulting from

$$\mathrm{CH_2{=}CH{-}CH_3} \xrightarrow{\mathrm{M}} [\mathrm{CH_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH_2}]^-\mathrm{M}^+ \qquad (1)$$



$$[\mathrm{CH_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH_2}]^-\mathrm{M}^+ + \mathrm{CH_3{-}CH{=}CH_2} \longrightarrow \mathrm{CH_2{=}CH{-}CH_2{-}}\underset{}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}\mathrm{H{-}CH_2}^-\mathrm{M}^+ \qquad (2)$$



$$\mathrm{CH_2{=}CH{-}CH_2{-}}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H{-}CH_2}^-\mathrm{M}^+ + \mathrm{CH_3{-}CH{=}CH_2} \longrightarrow \mathrm{CH_2{=}CH{-}CH_2{-}}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H{-}CH_3} + \mathrm{M}^+[\mathrm{CH_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH_2}]^- \qquad (3)$$

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[1] G. Egloff and C. I. Parrish, *Chem. Ind.* (London), 321 (1937); W. V. Freed (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,466,694 (April 12, 1949).

[2] V. Mark and H. Pines, *J. Am. Chem. Soc.*, **78**, 5946 (1956).

[3] R. M. Schramm (to California Research Corp.), U. S. Patent 2,986,588 (May 20, 1961); A. W. Shaw and G. Holzman (to Shell Oil Co.), U. S. Patent 2,994,725 (Aug. 1, 1961); A. W. Shaw, G. Holzman, and W. V. Bush (to Shell Oil Co.), U. S. Patent 3,006,976 (Oct. 31, 1961).

[4] C. D. Broaddus, *J. Org. Chem.*, **29**, 2689 (1964); see also C. D. Broaddus, T. J. Logan, and T. J. Flautt, *ibid.*, **28**, 1174 (1963).

TABLE I

EFFECT OF ALKALI METALS ON PROPYLENE DIMERIZATION AND DOUBLE-BOND ISOMERIZATION OF METHYLPENTENES

	Expt. no.								Thermodynamic equilibrium
	1	2	3	4	5	6	7	8	
Conditions									
Temp., °C.	196	211	218	214	200	190	196	192	200
Time, hr.	4.0	4.3	4.0	4.0	3.1	4.1	4.2	4.1	
Pressure, p.s.i.g., maximum	2300	1775	2350	2750	1650	200	650	820	
Pressure, p.s.i.g., final	1750	750	650	760	1200	200	450	625	
Charge									
Reactant, moles	C_3H_6 1.54	C_3H_6, 1.50	C_3H_6, 1.51	C_3H_6, 1.53	C_3H_6, 1.55	4-Methyl-1-pentene, 1.00	1.00	4-Methyl-2-pentene, 1.00	
Moles of benzene (solvent)	1.00	1.00	1.00	1.01	1.00	1.01	1.01	1.00	
Catalyst, g.	Na, 1.5	K, 0.5	K, 3.9	K, 3.9	Cs, 3.5	Na, 2.3	K, 3.9	K, 3.9	
Alkali metal, g.-atom	0.065	0.013	0.100	0.100	0.026	0.100	0.100	0.100	
Grams of anthracene (promoter)	1.8	...	...	1.8	...	1.8	...	...	
% conversion of reactant	20	34	61	58	39	97	65	11	
Products, wt. % of reactant converted									
$C_1 + C_2 + C_4 + C_5$	4	1	1	0	2				
C_3H_6	...	...	...	...	...	0	Trace	0	
C_3H_8	13	10	21	16	13				
4-Methyl-1-pentene	11	51	24	32	46	...	...	36	
4-Methyl-2-pentene	31	21	13	15	17	97	78	...	
2-Methyl-2-pentene	21	1	1	Trace	Trace	2	7	27	
2-Methyl-1-pentene	5	0	Trace	1	Trace		1	2	
n-C_6 olefins	...	7	4	5	3				
2-Methylpentane	...	Trace	1	1	Trace	0	5	4	
Methylcyclopentane	...	1	2	Trace	1				
C_9	...	1	1	1	1				
Residue	15	7	32	29	17	1	9	31	
	100	100	100	100	100	100	100	100	
Composition of branched hexenes, %									
4-Methyl-1-pentene	16	70	62	67	73	3	39	4	0.6
4-Methyl-2-pentene	45	29	34	31	26	95	56	93	15.5
2-Methyl-2-pentene	32	1	3	1	0	2	5	3	60.8
2-Methyl-1-pentene	7	0	1	1	1	0	Trace	Trace	23.1

proton abstraction from propylene adds to another propylene molecule, thus continuing the chain reaction.

Possibly, n-C_6 olefins are formed by a similar reaction sequence with the allyl carbanion adding to the terminal carbon atom of propylene which results in a secondary hexenyl carbanion. The ratio of the secondary carbanion formed by this path relative to the primary carbanion formed by addition to the central carbon atom of propylene probably depends on the relative stabilities of the two carbanions. Alternatively, allylic radicals may be generated, which upon addition to propylene would produce normal olefin. In any event, 1-hexene is the primary product of this reaction, and 2- and 3-hexenes result from isomerization of this α-olefin; it has been found that a high concentration of 4-methyl-1-pentene in the branched olefins is accompanied by a high relative concentration of 1-hexene among the normal olefins.

The preceding outline suggests the major kinds of intermediates involved but makes no attempt to account for all the details of the individual steps of the mechanism. For example, the organoalkali initiator may arise by several possible routes including carbon–hydrogen cleavage as well as by way of an unstable intermediate generated by electron transfer from the alkali metal to the antibonding π orbitals of the olefin. The latter possibility may be described schematically as follows. Propane is indeed found among the products

$$CH_2{=}CH{-}CH_3 + K \rightleftharpoons K^+[\ddot{C}H_2{-}\dot{C}H{-}CH_3]^-$$

$$K^+[\ddot{C}H_2{-}\dot{C}H{-}CH_3]^- + CH_3{-}CH{=}CH_2 \longrightarrow CH_3{-}\dot{C}H{-}CH_3 + K^+[CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} CH_2]^-$$

$$CH_3{-}\dot{C}H{-}CH_3 + K \rightleftharpoons K^+[CH_3{-}\ddot{C}H{-}CH_3]^-$$

$$K^+[CH_3{-}\ddot{C}H{-}CH_3]^- + CH_3{-}CH{=}CH_2 \longrightarrow CH_3{-}CH_2{-}CH_3 + K^+[CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} CH_2]^-$$

of the reaction, in increasing proportion as the amount of coke-like residue increases. This is undoubtedly due in part to the action of some hydrogen-transfer mechanism, not necessarily involving alkali metal. However, the presence of 5–10% propane observed among the reaction products even at very low residue formation would seem to lend support to the proposed mechanism.

C_9 olefins, formed by further additions to propylene, and high boiling residual material have not been characterized in any detail. Multiple addition proceeds at a much slower rate than the original dimerization as

TABLE II

EFFECT OF AMOUNT OF POTASSIUM METAL ON PROPYLENE DIMERIZATION

	Expt. no.					
	2	9	3	10	11	12
Conditions						
Temp., °C.	211	202	218	203	203	202
Time, hr.	4.3	1.1	4.0	2.2	0.8	0.5
Pressure, p.s.i.g., maximum	1700	1550	2350	940	930	990
Pressure, p.s.i.g., final	750	860	650	400	500	410
Minutes from P_{max} to $P_{max}/2$	92	>34	33–37	120	47	27
Charge						
C_3H_6, moles	1.50	1.49	1.51	1.12	1.15	1.15
Solvent, moles	1.00[a]	1.00[a]	1.00[a]	0.30[b]	0.30[b]	0.30[b]
Catalyst, g.	0.5	1.0	3.9	1.0	3.9	15.2
% conversion of C_3H_6	34	41	61	70	73	81
Products, wt. % C_3H_6 converted						
$C_1 + C_2 + C_4 + C_5$	1	0	1	0	0	0
C_3H_8	10	5	21	6	15	16
4-Methyl-1-pentene	51	62	24	61	53	38
4-Methyl-2-pentene	21	9	13	18	16	14
2-Methyl-2-pentene	1	6	1	8		
2-Methyl-1-pentene	0		Trace		5	5
n-C_6 olefins	7		4			
2-Methylpentane	Trace		1	...	...	...
Methylcyclopentane	1		2	...	...	...
C_9	1	1	1	1	1	1
Residue	7	17	32	6	10	26
	100	100	100	100	100	100
4-Methyl-1-pentene/4-methyl-2-pentene ratio	2.4	6.9	1.8	3.4	3.3	2.7

[a] Benzene. [b] Cetane.

shown by the virtual absence of tetramers and higher polymers.[5]

Selectivity Control by Metal/Propylene Ratio.—As was expected, raising the concentration of the alkali metal resulted in an increased rate of conversion of propylene to products. However, selectivity for dimer, and 4-methyl-1-pentene in particular, was highest at low concentrations of metal. Table II summarizes the results found with potassium in benzene and in cetane reaction media.

The data of Table II suggest that the loss of selectivity with increasing conversion may result from the increasing importance of remetalation and subsequent isomerization of the initial product to 4-methyl-2-pentene when higher concentrations of potassium metal are present. The apparent exception to this general trend is expt. 9. However, in this experiment the reaction time was much shorter than in expt. 2. Related experiments conducted at somewhat longer times indicate that the 4-methyl-1-pentene/4-methyl-2-pentene ratio at 4 hr. in the presence of 1 g. of potassium metal would be approximately 2.

Similar experiments carried out in heptane showed a similar trend of increasing rate of conversion with decreasing selectivity as potassium concentration was increased. However, when methyl t-butyl ether was employed as solvent, it exhibited an inhibiting effect on conversion; only 18% conversion of 1.24 moles of propylene was observed after 4 hr. in the presence of 3.9 g. of potassium. The 4-methyl-1-pentene/4-methyl-2-pentene ratio was 3.7.

Selectivity Control by Reaction Temperature.—Reaction temperature was found to have a large effect upon the rate of propylene conversion and upon product distribution. In Table III the results of varying the temperature over the range 175–300° are shown. The rate increases significantly as the temperature is raised over this range. Thus, at 175°, it requires over 3 hr. to obtain 70% conversion. The reaction rate is essentially equivalent at 200 and 250° and results in 70% conversion in about 1 hr. At 300° the rate is faster than at the lower temperatures but conversion does not readily go above 50%; the conversion may be limited by rapid deactivation of the catalyst due to excessive residue formation. At the higher tempera-

TABLE III

EFFECT OF TEMPERATURE OF PROPYLENE DIMERIZATION

	Expt. no.				
	13	14	15	16	17
Conditions					
Temp., °C.	175	200	254	252	300
Pressure, p.s.i.g., maximum	890	975	1300	1320	1350
Pressure, p.s.i.g., final	220	400	600	800	1080
Time, hr.	4.0	1.2	2.6	0.65	0.7
Charge					
C_3H_6, moles	1.09	1.14	1.34	1.14	1.11
Cetane, mole	0.30	0.30	0.30	0.30	0.30
Potassium, g.	3.6	3.9	3.9	3.6	3.9
% conversion of C_3H_6	90	70	69	75	54
Products, wt. % C_3H_6 converted					
$C_1 + C_2 + C_4 + C_5$	Trace	Trace	1	Trace	1
C_3H_8	5	7	24	18	41
4-Methyl-1-pentene	59	47	29	40	13
4-Methyl-2-pentene	19	22	20	21	11
2-Methyl-2-pentene	Trace	2	1	1	1
Other C_6 olefins	7	9	5	5	4
2-Methylpentane	1	1	1	1	1
C_9	3	3	2	2	1
Residue	6	9	17	12	27
	100	100	100	100	100
4-Methyl-1-pentene/4-methyl-2-pentene ratio	3.1	2.1	1.4	1.9	1.1

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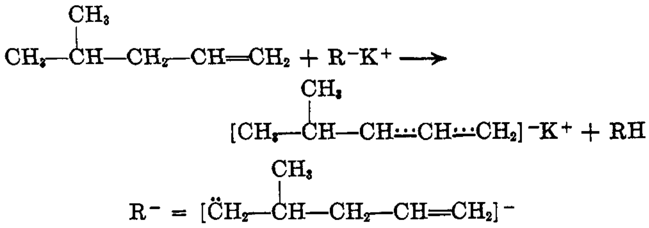
(5) Paper II: W. V. Bush, G. Holzman, and A. W. Shaw, *ibid.*, **30**, 3290 (1965).

tures double-bond isomerization was more rapid and consequently rather large amounts of 4-methyl-1-pentene were converted into *cis*- and *trans*-4-methyl-2-pentene.

The isomerization reaction is believed to occur by way of a proton-transfer reaction generating an allylic carbanion with a delocalized double bond, as follows.



$$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH{=}CH_2 + R^-K^+ \longrightarrow [CH_3-\overset{CH_3}{\overset{|}{C}}H-CH\mathrel{\overset{\cdots}{-}}CH\mathrel{\overset{\cdots}{-}}CH_2]^-K^+ + RH$$

$$R^- = [\ddot{C}H_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH{=}CH_2]^-$$

Upon protonation, this carbanion gives rise to the more thermodynamically stable *cis*- and *trans*-4-methyl-2-pentene isomers. Interestingly, the most thermodynamically stable methylpentene isomers are 2-methyl-2-pentene and 2-methyl-1-pentene, and these are not produced in any significant quantity by the isomerization reaction when Na and alkali metals of higher atomic weight are employed (see Table I, expt. 6, 7, and 8). Formation of 2-methyl-1- and -2-pentene *via* allylic metalation would require metalation at a tertiary position; this appears to be a relatively slow reaction. However, sodium causes the formation of significant amounts of these isomers during the dimerization reaction (see Table I, expt. 1). Thus, the 2-methylpentene isomers produced by sodium during the dimerization of propylene are probably formed from a transition intermediate not present when potassium and cesium are employed as the condensation catalyst.[6]

Experimental Section

The experiments were conducted in a 250-ml., 316 stainless steel Magne Dash autoclave[7] in the following manner.

The autoclave was placed into a drybox which was flushed with dry nitrogen until the oxygen partial pressure was below 5 mm. (generally *ca.* 1 mm.). The solvent and alkali metal, and promoter, if used, were weighed into the autoclave; the autoclave was then closed to prevent inward leakage of air. The autoclave was removed from the drybox and charged with the desired amount of propylene by forcing in liquid hydrocarbon with dry nitrogen under pressure.

The autoclave charge was heated as rapidly as possible (*ca.* 5 min.) to the desired reaction temperature with the dasher operating; a specially constructed 220-v. electric furnace permitted this rapid temperature rise and also permitted maintenance of the reaction temperature within ±2° of that desired. At the end of the reaction period (generally determined as the time required for the observed pressure to fall to one-half of its maximum value at run temperature), the autoclave and contents were cooled to room temperature within 10 min. by means of water circulation through coils in the furnace.

Reaction products and solvent were removed by heating the autoclave contents to 200° under 5-mm. pressure, and collected in a system consisting of a Dry Ice cooled flask, liquid nitrogen cooled cold finger traps, and a gas holder. The autoclave containing solid residue and alkali metal was placed in the drybox, and the metal was destroyed by reaction with a toluene–isopropyl alcohol mixture (1:1 v./v.), ethanol, and water in succession.

Reagents.—Propylene (Matheson C.P. grade[8]) was dried over Linde Molecular Sieves.[9] Mass spectrographic (m.s.) and gas chromatographic (g.c.) analyses indicated a purity of greater than 99.3% propylene (balance propane). Benzene was Baker Analyzed reagent[10] dried over Linde Molecular Sieves and sodium wire. Cetane was Humphrey–Wilkinson ASTM grade[11] dried over sodium wire. Sodium and potassium were Mallinckrodt reagent grade.[12] The portions of metal used in each experiment were cut from the center of a lump to remove scale, and washed free of hydrocarbon oil with *n*-hexane. Cesium[13] was poured into the autoclave from a small glass ampoule. Anthracene was Eastman grade.[14]

Analytical.—The gas samples were analyzed routinely by m.s. and g.c.; components of molecular weight up to about 86 (C_6H_{14} were identified and concentrations as low as 0.1 mole % were detected. The g.c. analyses were made on a 50 ft. × 0.25 in. column of dimethylsulfolane on firebrick, 50 cc./min. helium carrier, column at 40°. Results obtained by the two methods were in agreement within 1–2%. Liquid samples were kept refrigerated at −20° until analyzed by g.c. on dimethylsulfolane (as above) and on a 50-ft. column of SF-96 (a silicone oil)[15] on firebrick at 125°. The dimethylsulfolane column was capable of distinguishing and estimating 0.1 mole % of individual hydrocarbons through C_6; the SF-96 column separated components of the liquid mixture through C_{15} essentially according to boiling point. As in the case of the gas analyses, close agreement between the two chromatograms was observed within the range of overlap. Confirmation of structural assignments made on the basis of g.c. was obtained by routine application of m.s. and infrared methods. Individual isomers of C_9 and heavier material remain unidentified.

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[6] The possibility of isomerization from 4-methyl-1- and -2-pentenes to 2-methyl-1- and -2-pentenes *via* a vinylic metalation by sodium on an olefin (*cf.* ref. 4), followed by intermolecular proton transfer from the tertiary position of 4-methyl-2-pentene is not excluded, but seems unlikely.

[7] Autoclave Engineers, Inc., Erie, Pa.

[8] The Matheson Co., Inc., Newark, Calif.

[9] Linde Co., Division of Union Carbide Corp., Tonawanda, N. Y.

[10] J. T. Baker Chemical Co., Phillipsburg, N. J.

[11] Humphrey-Wilkinson, Inc., North Haven, Conn.

[12] Mallinckrodt Chemical Works, St. Louis, Mo.

[13] A. D. MacKay, Inc., New York, N. Y.

[14] Distillation Products Industries, Rochester, N. Y.

[15] Wilkens Instrument and Research, Inc., Walnut Creek, Calif.