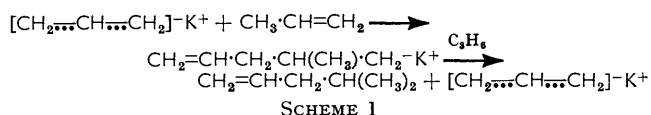


Reactions of Mono-olefins in the Presence of Alkali Metals. The Effect of Lithium and Group 2A Metals

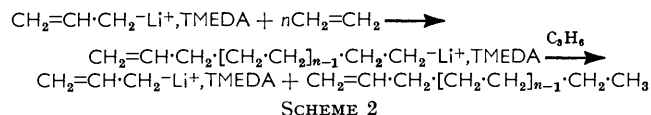
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Co-dimerisation of ethylene with propene and pentenes has been studied with a variety of alkali metal catalysts comprising dispersions of lithium hydride, and sodium and potassium metals on carbonates of metals of Groups 1A and 2A. Catalysts containing lithium and Group 2A metals showed an unexpectedly high selectivity for formation of linear heptenes and nonenes in comparison with catalysts containing only sodium and higher Group 1A metals. The difference in selectivity is explained by the nature of the bonding between the metals and anion intermediates

ALKALI metals react with olefins to yield allyl anions.¹ The subsequent addition of the anions to free olefin molecules has led to the development of supported alkali metal catalysts for the selective dimerisation of mono-olefins,^{2,3} for example the dimerisation of propene to 4-methylpent-1-ene (Scheme 1).



Ethylene is unreactive in the presence of alkali metals on account of the absence of an allyl position for metallation, but adds readily to preformed organo-alkali metal compounds. Ziegler⁴ showed that ethylene adds to butyl-lithium by insertion to give a mixture of long-chain alkyl lithiums. Bartlett⁵ observed addition of ethylene to secondary and tertiary alkyl-lithiums in the presence of ether at temperatures below 0 °C. The addition of chelating amines such as tetramethylethylenediamine (TMEDA) to alkyl-lithiums results in a much more active polymerisation catalyst which is best known for the so-called 'telomerisation' reaction of benzene and its derivatives with ethylene to give long-chain alkylbenzenes.⁶⁻⁸ Olefins such as propene and butenes may replace benzene in this reaction to give a mixture of α -olefins (Scheme 2).



The co-reaction of ethylene with higher mono-olefins

- ¹ A. A. Morton, M. L. Brown, M. E. T. Holden, R. L. Letsinger, and E. E. Magat, *J. Amer. Chem. Soc.*, 1945, **67**, 2224.
² V. Mark and H. Pines, *J. Amer. Chem. Soc.*, 1956, **78**, 5946;
 H. Pines and L. A. Schapp, *Adv. Catalysis*, 1960, **12**, 117.
³ J. K. Hambling, *Chem. in Britain*, 1969, **5**, 354.
⁴ K. Ziegler and H. G. Gellert, *Annalen*, 1950, **567**, 195.

is also very fast in the presence of free alkali metals or their hydrides. Hambling³ has shown that pent-1-ene is formed selectively from ethylene and propene, while ethylene and n-butenes yield 3-methylpent-1-ene as the major product and hex-2-ene as by-product. Shaw⁹ has also examined ethylation reactions. With a mixed lithium-potassium metal catalyst both pent-1-ene and pent-2-ene reacted with ethylene to yield a mixture of 3-ethylpent-1-ene and hept-3-ene, the branched isomer predominating. However, the reaction of both hex-1-ene and hex-2-ene with ethylene gave n-octenes and 3-ethylhexenes with the linear products predominating. This variation in selectivity between linear and branched products is not readily explained on the basis of addition to free allyl anions. Other reports of the co-reaction of mixtures of ethylene and propene and of ethylene and n-pentenes in the presence of supported sodium and potassium catalysts have shown that the principal heptene product is the branched olefin 3-ethylpent-1-ene.^{10,11}

We have now shown that alkali metal catalysts containing lithium or the alkaline earth metals induce a different selectivity in the mode of olefin addition compared with catalysts containing only the heavier alkali metals, and attribute the difference to the nature of the bonding between alkali metals and the anions involved.

⁵ P. D. Bartlett, S. Friedman, and M. Stiles, *J. Amer. Chem. Soc.*, 1953, **75**, 1771; P. D. Bartlett, S. J. Tauber, and W. P. Weber, *ibid.*, 1969, **91**, 6362; P. D. Bartlett, C. V. Goebel, and W. P. Weber, *ibid.*, p. 7425.

⁶ G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, 1964, **29**, 2928.

⁷ G. G. Eberhardt and W. R. Davis, *J. Polymer Sci., Part A*, 1965, **3**, 3753.

⁸ A. W. Langer, *Trans. New York Acad. Sci.*, 1965, **27**, 741.

⁹ A. W. Shaw, C. W. Bittner, W. V. Bush, and G. Holzmann, *J. Org. Chem.*, 1965, **30**, 3286.

¹⁰ B.P. 1,216,277; 1,221,709.

¹¹ U.S.P. 3,432,572.

EXPERIMENTAL

Materials.—Ethylene and propene were Polymerisation Grade (>99.5%) from BP Chemicals, Grangemouth, and I.C.I., respectively. Pentenes (92% pent-2-ene, 8% pent-1-ene, <0.5% other olefins) produced by co-dimerisation of ethylene and propene and subsequent isomerisation, were distilled from sodium-potassium alloy under dry argon before use.

Catalyst Preparation.—The support, used as a powder, was dried in vacuum at 200 °C for up to 100 h; sodium and potassium were dispersed by stirring the clean metal into the support at 150–200 °C under dried high-purity argon. In a typical preparation dried lithium carbonate (25 g) was heated to 150 °C; potassium metal (1.75 g) was added and the mixture was stirred vigorously for 2 h to achieve an even dispersion. The product, a mobile powder, was allowed to cool and was normally used within 24 h, although storage for several days was possible without significant deactivation.

Attempts to prepare lithium catalysts by this technique using lithium metal and potassium carbonate had to be

water at all times. The autoclave was rocked throughout the reaction period (17–24 h). Products were then vented slowly into flasks immersed in solid carbon dioxide-acetone. Entrained unconverted ethylene and propene were allowed to evaporate slowly; the liquid residue was weighed and distilled into fractions for g.l.c. analysis.

Product Analysis.—C₅–C₆ products were analysed on a 50 m squalane-coated capillary column at 0 °C. Individual heptenes were identified and analysed on a 100 m glass capillary column coated with silicone oil, at 25 °C. Olefins up to C₁₃ were analysed after hydrogenation on a 4 m × 3 mm (diam) column of 10% Apiezon L on 60–80 mesh Phasesep P at 160 °C. Heptenes were also analysed after hydrogenation as a cross-check.

RESULTS AND DISCUSSION

Ethylene-Propene Co-oligomerisation.—Typical results of co-reaction of ethylene and propene over a variety of alkali metal catalysts are summarised in Table I. With these carbonate-supported catalysts it appears that potassium, rubidium, or caesium must be present, either

TABLE I
Co-oligomerisation of 3 : 1 molar ethylene-propene mixtures

Catalyst	Metal content % (w/w)	Temp. (°C)	Rate (g oligomer per 100 g catalyst per h)	Product analysis				
				Pentenes % (w/w)	Heptenes		Nonenes	
					% (w/w)	% Linear *	% (w/w)	% Linear
Li/K ₂ CO ₃	2.2% Li	150	96	49	32	64	11	35
Li/Rb ₂ CO ₃	1.6% Li	150	91	60	23	63	7	48
Li/Cs ₂ CO ₃	1.3% Li	150	25	44	32	54	11	30
K/Li ₂ CO ₃	7.0% K	150	50	58	24	54	<5	
K/CaCO ₃	7.0% K	180	16	52	27	58	5	48
K/SrCO ₃	7.0% K	180	15	71	24	58	1	
K/BaCO ₃	7.0% K	180	24	50	30	51	8	34
K/BaCO ₃	8.0% K	150	46	48	35	54	5	
Na/K ₂ CO ₃	4.5% Na	150	21	14	57	20	12	7
K/K ₂ CO ₃	17.0% K	150	192	33	53	20	7	1
Na/Cs ₂ CO ₃	8.0% Na	150	77	45	46	32	4	<1
K/Cs ₂ CO ₃	7.0% K	150	70	51	32	28	8	4
K/Cs ₂ CO ₃	8.0% K	180	97	22	57	24	12	3

* Mainly hept-3-ene with <5% hept-2-ene; other heptenes mainly 3-ethylpent-1-ene with 2–10% 4-methylhex-2-ene.

abandoned on account of the ensuing vigorous reaction. Supported lithium catalysts were prepared by heating the support with the appropriate quantity of a ca. 20% (w/w) solution of butyl-lithium in n-hexane or cyclohexane. The mixture was heated with stirring under a dry argon purge; at about 100 °C, after solvent removal was complete, a black dispersion was formed and white fumes appeared demonstrating decomposition of the alkyl. The catalysts were finally heated at 150–200 °C for 2 h.

Butyl-lithium-TMEDA catalyst was prepared in solution by direct mixing of the components under dry nitrogen.

Oligomerisation Procedure.—Catalysts (ca. 25 g) were heated in a stainless steel autoclave under dry argon or nitrogen to the reaction temperature. Premixed ethylene and propene were dried in the liquid phase over molecular sieves (Laporte grade 3A) and introduced from a reservoir under a constant pressure of nitrogen between 70 and 105 bar maintained throughout each experiment. For the pentene-ethylene experiments, pentene was run into the autoclave before heating and ethylene was introduced from a compressor. Precautions were taken to exclude air and

added as free metal or hydride or in the support, for initial formation of anions. No reaction was observed in the presence of materials prepared from butyl-lithium on supports such as lithium carbonate, sodium carbonate, magnesium carbonate, barium carbonate, and lithium chloride. The environment of the alkali metal is clearly important in determining its effectiveness for initiation. Other workers have shown, for example, that sodium is an effective initiator when promoted by anthracene, graphite, or alumina.^{2,3} The less electro-positive metals are effective in propagation reactions whether promoted or not.

The reaction rates in the Tables give an approximate comparison of catalyst activity but allowance must be made for induction periods (anion formation) which reduce activity during the first few hours (sometimes days) of reaction. Conversion of free alkali metal into the hydride has previously been shown to promote anion formation and reduce induction periods by as

much as two thirds.¹² This benefit would be expected to apply to the catalysts prepared by decomposition of butyl-lithium which are presumed to contain the metal in the hydride form.

Products from the catalysts containing lithium and the Group 2A metals consistently showed a greater degree of linearity than those from catalysts containing

TABLE 2

Product distribution from 1:1 molar ethylene-propene co-oligomerisation with a butyl-lithium-TMEDA catalyst (reaction conditions: 100 °C, 70 bar, 15 h)

Olefin carbon number	Wt %	Linear %	Olefin carbon number	Wt %	Linear %
4	1.0	100	12	3.0	1.5
5	22.0	99	13	7.6	85
6	3.4	5	14	2.6	1.5
7	20.2	42.5	15	6.3	77.5
8	3.1	1.5	16	2.0	2
9	10.9	89	17	2.0	66
10	2.9	1.5	>17	4.5	—
11	8.5	89			

only the more electropositive Group 1A metals. This linearity appears in the ratio of linear heptenes (mainly hept-3-ene) to branched heptenes (mainly 3-ethylpent-1-ene) and more strikingly in the unexpected linearity of

extent of reaction is limited by side reactions leading to tar formation.

Results for ethylene-propene co-reaction in the presence of the homogeneous butyl-lithium-TMEDA system under typical conditions are shown in Table 2 for comparison.

The selective formation of olefins of odd carbon number is consistent with the performance of the heterogeneous catalysts of Table 1 but two important differences in product selectivity are apparent: (i) the much wider molecular weight range of the products, and (ii) the generally higher selectivity to linear olefin formation. The anomalously low selectivity to linear heptenes is due to the formation of methylcyclohexane, a product not observed to a significant extent in the heterogeneous systems, by anion cyclisation (Scheme 3). This cyclisation of hept-6-enyl-lithium in the presence of butyl-lithium-TMEDA has been reported by Drozd *et al.*¹³

The addition of TMEDA to a potassium-lithium carbonate catalyst had no effect on product selectivity.

Ethylene-Pentene Co-oligomerisation.—Results of the co-reaction of ethylene with a mixture of n-pentenes over a variety of catalysts are summarised in Table 3. The increased selectivity to linear addition of the

TABLE 3

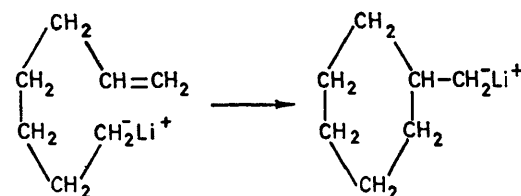
Ethylene-pentene co-oligomerisation

Catalyst	Metal content % (w/w)	Pentenes (ml)	Conditions		Rate (g oligomer per 100 g catalyst per h)	Product analysis			
			Temp. (°C)	Pressure (bar)		Heptenes		Nonenes	
						% (w/w)	% Linear *	% (w/w)	% Linear
Li/K ₂ CO ₃	1.1% Li	500	180	70	107	80	55	11	28
Li/Rb ₂ CO ₃	2.5% Li	500	180	80	53	91	51	8	12
Li/Cs ₂ CO ₃	1.7% Li	500	150	110	86	75	42	15	10
K/Li ₂ CO ₃	10.0% K	700	150	105	23	87	41		
K/BaCO ₃	17.0% K	500	180	70	41	71	43	23	10
K/Cs ₂ CO ₃	8.5% K	500	150	65	145	80	27	19	1
K/Cs ₂ CO ₃	11.8% K	500	180	65	175	49	15	33	7

* Mainly hept-3-ene with <5% hept-2-ene; other heptenes mainly 3-ethylpent-1-ene with *ca.* 15% 4-methylhex-2-ene (22% with K/Li₂CO₃).

the C₉ products from lithium and Group 2A metal catalysts. Maximum selectivity to linear products was observed with the catalysts prepared with butyl-lithium. The lithium catalysts were found to be consistent in their selectivities over the temperature range of maximum activity (120–180 °C). Variation in potassium content affected activity proportionately, but had little if any effect on selectivity. The potassium-calcium carbonate and potassium-strontium carbonate catalysts required to be used at 180 °C for linear addition to predominate; selectivity to n-heptenes was only 30% in each case at 150 °C. The high branched-to-linear ratio shown by the Group 1A catalysts containing no lithium was not significantly affected by increased reaction temperature up to 180 °C. At higher temperatures the

catalysts containing lithium and barium is again apparent, although the proportion of linear products is generally lower than in the ethylene-propene products.



SCHEME 3

The relatively low yields of 4-methylhex-2-ene by-product show that the use of the more reactive pent-2-ene in place of pent-1-ene only accounts in part for the lower selectivity to linear heptenes.

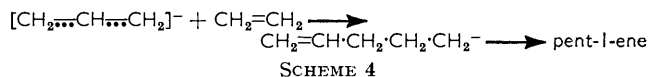
The lithium catalysts gave consistent results at 150 °C

¹² B.P. 1,066,113.

¹³ V. N. Drozd, Yu. A. Ustynyuk, M. A. Tsel'eva, and L. B. Dmitriev, *Zhur. obshchei Khim.*, 1969, **34**, 1951.

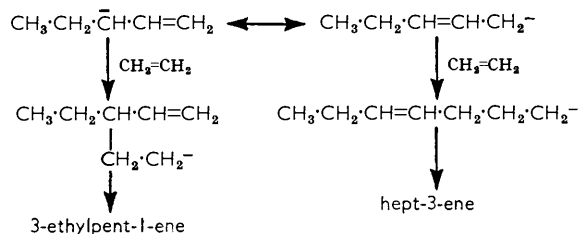
but the potassium–barium carbonate system required the higher temperature of 180 °C to achieve high selectivity to formation of linear heptenes. At temperatures below 110 °C the linearity of products from potassium–lithium carbonate was also lower but this effect was associated with much reduced catalyst activity and conclusions are therefore difficult to draw.

Reaction Mechanism.—The co-reaction of ethylene and propene in equimolar mixture in the presence of heterogeneous alkali metal catalysts was shown by



Hambling³ to lead to the formation of pent-1-ene in 92% selectivity (Scheme 4). The relative absence of higher oligomers shows that the exchange reaction between the pent-1-ene anion and propene is faster than the addition of ethylene. This contrasts with results obtained from the butyl-lithium–TMEDA system (Scheme 2) in which the further addition of ethylene is much faster leading to the production of hept-1-ene, non-1-ene, *etc.* Here the lower anionic character of the allyl group linked to lithium reduces the relative rate of exchange with propene.

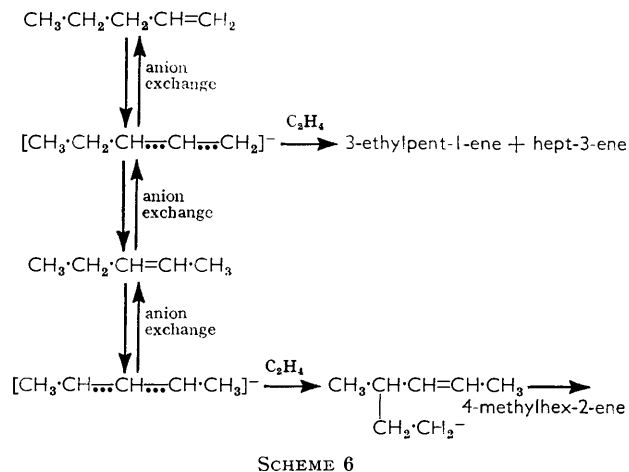
Under the conditions of more limited availability of propene in the present work further addition of ethylene to pentene is observed with the heterogeneous catalysts. The ‘free’ pentene anion may add in two different ways (Scheme 5).



Pent-2-ene, formed to a limited extent by isomerisation of pent-1-ene, leads to the formation of 4-methylhex-2-ene as a by-product (Scheme 6).

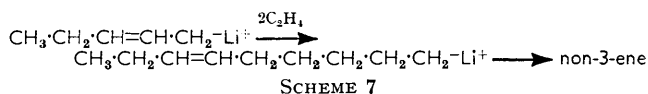
Under given conditions the relative rates of linear and branched addition of ethylene to ‘free’ pentene anions should be independent of the catalyst employed. The preponderance of linear addition in the presence of lithium and Group 2A metals indicates a greater degree of covalent bonding with the ‘anion’ or at least suffi-

ciently close ion pair formation to polarise the anion preferentially in one of its mesomeric forms. The greater stability of primary alkyl compounds of lithium over secondary alkyls is consistent with preferential



cient bonding of lithium, *etc.* with the terminal position of the pent-1-ene anion, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{CH}_2^-\text{Li}^+$, leading to increased selectivity to hept-3-ene.

The formation of linear nonenes from hept-3-ene is difficult to explain except by a series of anion exchange/isomerisation reactions. Two other possibilities are more likely. First the heptene anion formed by addition of ethylene to pentene may add a second ethylene molecule before the exchange reaction with a free olefin molecule occurs. This is analogous with the telomerisation reaction induced by butyl-lithium–TMEDA (Scheme 7). The second possibility is that nonenes are



formed directly from ethylene–propene in a side reaction (Scheme 2). The two observations: (i) formation of linear nonenes from ethylene–pentene mixtures, and (ii) the greater selectivity to both linear heptenes and nonenes from ethylene–propene mixtures, suggest that both types of reaction are occurring.

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