

ORGANIC REACTIONS INVOLVING TRANSITION METALS III*. THE PALLADIUM(II)-CATALYSED DIMERIZATION OF OLEFINIC COMPOUNDS

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SUMMARY

The palladium(II)-catalysed dimerization of olefins has been investigated. The olefinic compounds, ethylene, propene, n-butenes, methyl acrylate, and styrene, have been successfully dimerized, and the pairs of olefinic compounds, ethylene and propene, propene and 1-butene, ethylene and cyclopentene, ethylene and methyl acrylate, ethylene and styrene, and methyl acrylate and styrene successfully codimerized, using dichlorobis(benzonitrile)palladium or palladium dichloride as catalyst. In all cases, high proportions of straight-chain dimers are formed, and olefin-isomerization is a closely associated feature of the reaction. A mechanism involving a hydridopalladium(II) compound as the catalytically active species is suggested.

INTRODUCTION

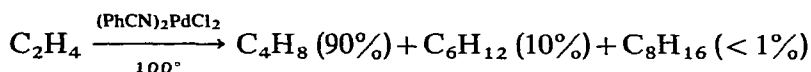
The catalytic dimerization and oligomerization of olefins by transition metal containing systems has recently excited much interest. Extremely active nickel-based systems for the dimerization of ethylene and propene have been described^{2,3}. Other systems which have been reported for this dimerization include ones based on cobalt⁴, rhodium⁵, and ruthenium⁵. In all cases, methylpentenes comprise the major product from propene dimerizations, straight-chain hexenes being formed in lesser amounts; heterogeneous systems based on cobalt oxide⁶ give no more than 52% n-hexenes, and anionic systems based on alkali metals give methylpentenes almost exclusively⁷. Few reports have appeared concerning the dimerization of substituted mono-olefins; however the dimerization of methyl acrylate by rhodium chloride in methanol⁵, of acrylonitrile by ruthenium chloride⁸, and the codimerization of ethylene with methyl acrylate and with styrene has been described⁵. With the exception of the dimerization of ethylene by rhodium, of which Cramer has made an elegant study⁹, the details of the mechanism of these reactions are not well understood, indeed, the effective catalyst itself is usually but poorly characterised.

* For Part II see ref. 1.

DISCUSSION

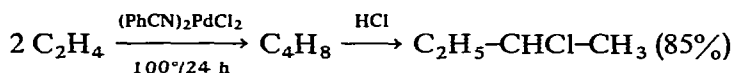
Recently, following a brief mention in 1964¹⁰, reports concerning the dimerization of ethylene^{11,12} and of propene¹² by palladium(II) chloride have appeared. We have also studied these reactions and have extended the study to include the dimerization of n-butenes, methyl acrylate, and styrene, and the codimerization of ethylene with propene, cyclopentene, methyl acrylate, and styrene, of propene with 1-butene, and of methyl acrylate with styrene. With the exception of the ethylene/cyclopentene reaction, remarkably high proportions of linear, rather than branched-chain, dimers are obtained.

Previous studies have utilised palladium dichloride as the catalyst for ethylene and propene dimerization. We have, for the most part, used dichlorobis(benzonitrile)palladium(II) as a readily soluble, non-hygroscopic, catalyst, and dibutyl phthalate as solvent for reactions involving gaseous materials; the ester is a conveniently high-boiling solvent from which volatile products may easily be separated. Ethylene, at an initial pressure of 55 atm, was 95% converted in 24 h at 100° by 0.7 mole % of catalyst to a 90/10 mixture of n-butenes and hexenes, only trace amounts of octene being formed:



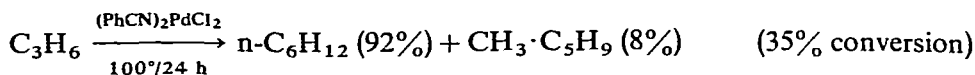
The butenes consisted of 1-butene, *cis*-2-butene, and *trans*-2-butene in the ratio 10/25/65 (the calculated equilibrium ratio¹³ at 100° is 7/26/67) while the hexenes were at least 96% straight-chain isomers, these being present in approximately their equilibrium proportions. Trace amounts of 2-chlorobutane were also formed. It has previously been reported¹¹ that isobutyl chloride is a by-product of this reaction, but we have been unable to confirm this.

The proportion of hexenes formed was increased in the presence of small amounts of triphenylphosphine (3–12 mole % of catalyst), but reaction was completely inhibited in the presence of one equivalent. Stannous chloride had a mild inhibiting effect, while bulk quantities of thiophene had little effect on either the reaction rate, or the formation of isomeric product. It has previously been reported that the reaction is markedly inhibited by the presence of anhydrous hydrogen chloride¹²; in our hands, under somewhat more vigorous conditions, small amounts of hydrogen chloride (Pd/HCl = 1.0) had little effect on the rate, but increased the proportion of hexenes formed to 23%, while in the presence of bulk amounts of hydrogen chloride, the reaction could be operated as a one-step process for the formation of 2-chlorobutane from ethylene:

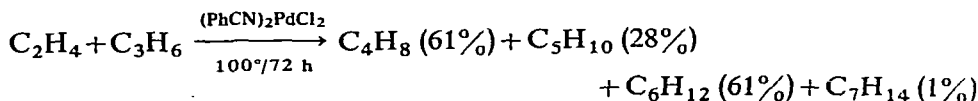


Di- μ -chlorobis(π -allyl)dipalladium(II) was ineffective as a catalyst for ethylene dimerization (it has been suggested that inactivation of catalyst occurs by π -allylic complex formation¹², but if one equivalent of aluminium trichloride was added, a fairly effective system was obtained).

Propene dimerized somewhat less readily than ethylene to give a mixture (92/8) of n-hexenes and methylpentenes:

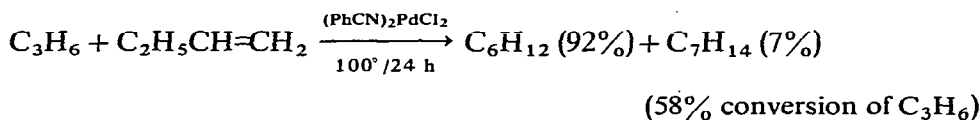


Codimerization of ethylene and propene (1.1/1.0) yielded a mixture of C₄-, C₅-, C₆-, and C₇-olefins in the molar ratio 1.00/0.90/0.62/0.03, respectively:

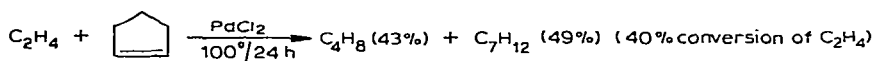


The C₅-fraction consisted of n-pentenes and methylbutenes in the ratio 97/3, the C₆-fraction consisted of n-hexenes and 2-methylpentenes (93/7), while the heptenes were at least 90% straight-chain isomers. In the comparable rhodium catalysed dimerization⁵, it was reported that the pentenes and hexenes contained approximately 50% straight-chain isomers.

Dimerization of 1-butene and of *trans*-2-butene was rather slow, some 3–4% conversion being obtained under conditions where ethylene and propene were converted to the extent of 95% and 35%, respectively, and isomerization occurred at a faster rate. The product octenes, while not completely characterised, were apparently mainly straight-chain isomers. Despite this reluctance of butenes to dimerize, propene and 1-butene could be codimerized, hexenes and heptenes being formed in the molar ratio of 87/13:

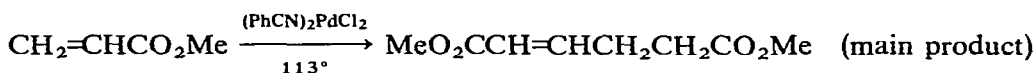


The use of a technique somewhat different from that of the dimerizations described above, in which a solvent was used, enabled cyclopentene and ethylene to be successfully codimerized. When heated alone in the presence of palladium dichloride, they formed a codimer in substantial amounts:



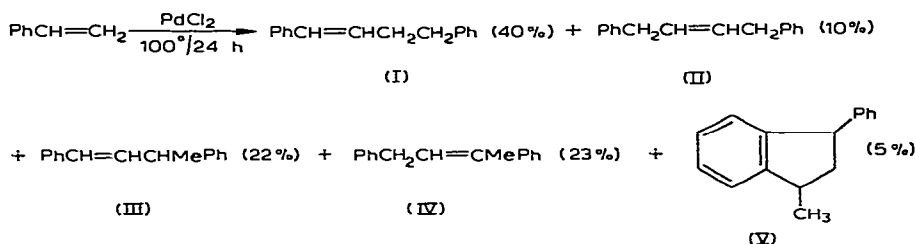
Presumably the cyclopentene was largely in the liquid phase, the more reactive ethylene largely in the vapour phase. The codimer formed consisted of a mixture of ethylenecyclopentane, and 1-, 3-, and 4-ethylcyclopentenes (molar ratio: 3/67/23/7).

A high yield (93%) of dimers was obtained when methyl acrylate was heated with dichlorobis(benzonitrile)palladium(II) at 113° for 23 h:



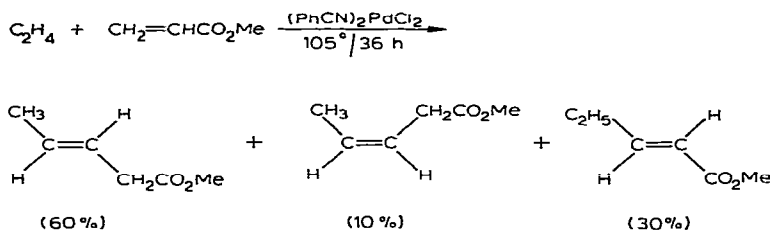
The product contained approximately 90% linear dimers, with dimethyl *trans*-2-hexenedioate (67%) as the major isomer, while the next most prevalent isomer was dimethyl *trans*-3-hexenedioate. The catalytic dimerization of methyl acrylate by rhodium and ruthenium chlorides in methanol, yields exclusively dimethyl 2-hexenedioate⁵, but the conversions are lower than those obtained with our palladium catalyst.

Styrene was dimerized by palladium dichloride only with reluctance to give an 18% conversion, and a 33% yield of dimers, after 24 h at 100°. The dimer product formed was rather complex:



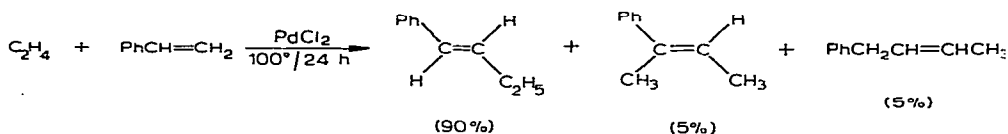
and it was not found possible to separate pure individual components. However the presence of components (I), (III), and (V), was confirmed by synthesis of authentic samples, and that of components (II) and (IV) inferred largely on the basis of spectroscopic evidence. No previous report has apparently appeared of the transition-metal-catalysed dimerization of styrene, or of the formation of straight-chain dimers, (I) and (II), under any conditions. The branched dimer, (III), and cyclic dimer, (V), are the products of dimerization of styrene by acid catalysis¹⁴, and it may be therefore that they are formed in the palladium catalysed reaction, at least in part, owing to the liberation of hydrogen chloride during palladium chloride decomposition. Dimers, (III)–(V), are included among the products of thermal dimerization of styrene¹⁵.

The rhodium and ruthenium chloride catalysed codimerizations of ethylene and methyl acrylate have been reported⁵ to yield only methyl 3-pentenoate as the 1/1 dimer in 47% yield. Dichlorobis(benzonitrile)palladium(II) is also an effective catalyst, and the codimers are formed in 47% yield:



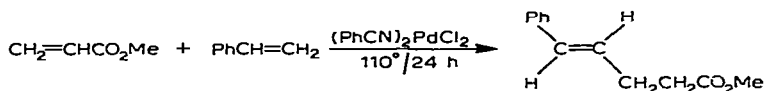
The non-conjugated esters predominate in the mixture of products, but methyl *trans*-2-pentenoate is also present in substantial amounts. No branched-chain isomers are present, since catalytic hydrogenation of the dimer product yields only methyl valerate.

Ethylene and styrene could be successfully codimerized (in 45% yield, and 37% conversion) by palladium dichloride:



The major product was *trans*-1-phenyl-1-butene, some 5% of 2-phenyl-2-butene was present, and NMR spectroscopy inferred the presence of 1-phenyl-2-butene. The corresponding rhodium chloride catalysed codimerization has been reported to yield the branched product, 2-phenyl-2-butene, exclusively⁵.

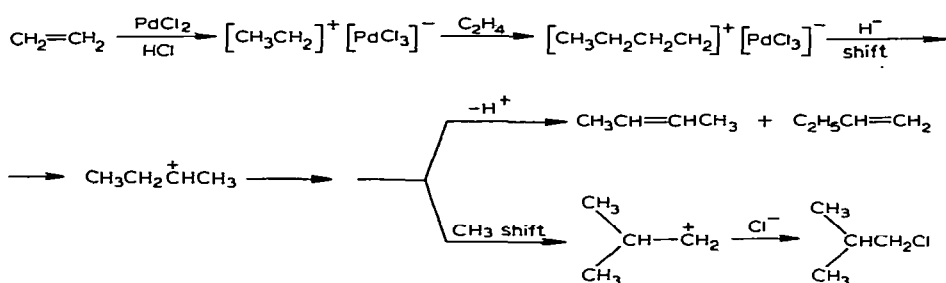
As a final example of successful codimerization, styrene and methyl acrylate, when heated with dichlorobis(benzonitrile)palladium(II), yielded a codimer in 26% yield:



The product was not investigated in great detail, but the codimer fraction contained 85% of the straight-chain isomer, methyl *trans*-5-phenyl-4-pentenoate.

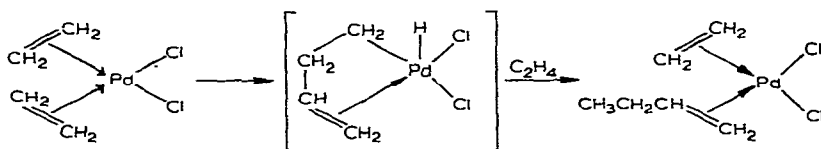
The mechanism of the rhodium catalysed dimerization of ethylene⁹ is well understood, involving the steps: (i) protonation of a bis(ethylene)rhodium(I) complex to form an ethylrhodium(III) complex, possibly via a transient hydridorhodium(III) species; (ii) insertion of ethylene to form a butylrhodium(III) complex; (iii) collapse of the complex to butene and rhodium(I); and (iv) coordination of ethylene to reform the initial complex. The mechanism of the palladium-catalysed olefin dimerizations is less well understood. A satisfactory mechanism must explain the following features: (i) ethylene is much more reactive than other olefins; (ii) there is a high tendency to form linear dimers (this is also true, if to a lesser extent, of rhodium catalysed dimerizations); (iii) unlike the rhodium reaction, no source of proton is apparently necessary; and (iv) olefin isomerization, with the proportions of isomers of any one carbon skeleton approaching the equilibrium proportions¹³, is a closely associated feature of the reaction.

Kusunoki *et al.*¹¹ have suggested a Friedel-Crafts-type reaction, *viz.*:

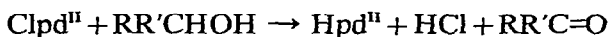


which clearly does not satisfy the requirements, and which includes an unlikely route to isobutyl chloride, which was mistakenly identified instead of 2-chlorobutane.

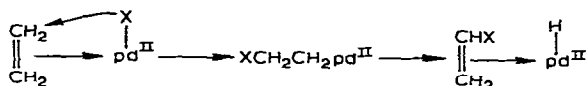
Ketley *et al.*¹² have reported the isolation of dichlorobis(ethylene)palladium(II), and three distinct, but not characterised, di- μ -chlorodichlorobis(butene)dipalladium(II) complexes from the ethylene/palladium chloride system. However, mixtures of π -complexes of isomeric olefins are readily obtained from palladium chloride and olefin¹⁶, and it is not clear what significance, if any, these butene complexes have in the ethylene dimerization reaction. They consider that a palladium hydride species is a reasonable reaction intermediate in the dimerization by palladium dichloride and suggest its formation as a possible transient species:



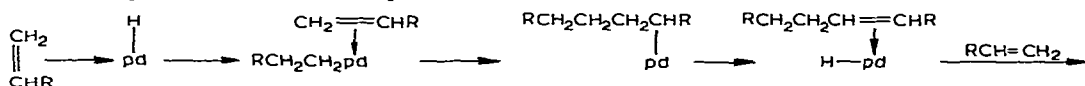
during the formation of butene. However, their transient hydride is effectively a Pd^{IV} species and the oxidation potential required to form it would be so high as to render it unlikely as a reaction intermediate. A Pd^{II} hydride species has been suggested as an intermediate in palladium-catalysed olefin isomerizations¹⁷, and it may be invoked in palladium catalysed dimerizations also. Possible routes to its formation include oxidation of added alcohols (small amounts are reported to catalyse the formation of active species¹²):



attack by added nucleophiles, HX, upon complexed olefin¹⁸:



or direct removal of hydride from olefin. The dimerization of an olefin, RCH=CH₂, may then be formulated as involving formation of an alkyl-palladium(II) complex, insertion of a second olefin molecule (or migration of the alkyl ligand), and reformation of a palladium-hydride species:



To account for the very high proportion of straight-chain dimeric product formed in the palladium catalysed dimerizations, one needs to invoke formation of a primary alkyl-palladium species in the first step, and preferential formation of a secondary alkyl-palladium species in the subsequent olefin insertion step. It may be that, although formation of a primary alkyl complex is favoured, the steric requirements of the alkyl group are such that it prefers to bond to the least hindered end of the complexed olefin in the subsequent insertion.

EXPERIMENTAL

Reactions, unless otherwise stated, were carried out in 300-ml stainless steel autoclaves, fitted with a glass liner, and heated in a rocking furnace. Materials volatile at room temperature were manipulated in a conventional high-vacuum apparatus. Reaction components were separated by distillation or by preparative-scale gas-liquid chromatography (GLC), and were identified by infrared spectroscopy [Perkin-Elmer spectrophotometers, models 21 and 137 (Infracord)], proton magnetic resonance spectroscopy (Perkin-Elmer R10 spectrometer operating at 60 MHz), mass spectrometry (A.E.I. MS/2H instrument), and GLC [Perkin-Elmer Fractometer models 154B and 451 and Varian Aerograph model 1520 (thermistor detectors), or Pye 104 instrument (flame-ionisation detector)]. Simple C₂- to C₈-olefins and C₅- and C₇-cycloolefins were analysed using GLC columns [4 m × 4 mm (i.d.)] packed

with silver nitrate in ethylene glycol (30%) on firebrick^{19,20} and with diisobutyl phthalate (30%) on Celite; analysis on both columns enabled all but the pair of olefins, *trans*-2-hexene and 2-methyl-2-pentene, to be separately identified. Higher boiling products were analysed on a variety of columns.

Dichlorobis(benzonitrile)palladium(II)²¹ (0.2–1.0 mole%), unless otherwise stated, was used as catalyst for the olefin dimerizations here reported.

Dimerization reactions of single olefins

(a). *Ethylene*. The effect of catalyst concentration, solvent, and additives upon the dimerization of ethylene was investigated. In a typical experiment, ethylene (19.7 g, 704 mmoles; initial pressure 55 atm) and catalyst (2.0 g, 5.0 mmoles), heated in dibutyl phthalate (100 ml) at 100° for 24 h, gave recovered ethylene (1.0 g, 35 mmoles; 5% recovery), n-butenes (16.8 g, 300 mmoles; 90% based on ethylene consumed) (containing 1-butene, *cis*-2-butene, and *trans*-2-butene in the proportions 10/25/65), hexenes (1.8 g, 22 mmoles; 10% based on ethylene consumed) (containing 1-hexene, *cis*-2-hexene, *trans*-2-hexene, *cis*-3-hexene, and *trans*-3-hexene in the proportions 2/21/44/9/24, < 4% of 2-methylpentenes being present), and traces (*ca.* 0.05 g) of octenes and 2-chlorobutane. In a similar reaction, 16% ethylene was converted entirely to butenes after 1 h.

At higher pressures, increased conversions of ethylene per unit catalyst were obtained; 1.70 mole of ethylene (initial pressure 125 atm) suffered 98% conversion in 35 h, and 2.80 moles (initial pressure 200 atm) were converted to butenes (92%) and hexenes (8%) to a similar extent. The latter reaction represents a conversion of 526 mole of ethylene per mole of catalyst. Lower ethylene conversions were obtained at lower catalyst concentration; conversion to the extent of 82% in 18 h was obtained when 1.3 mmole of catalyst was used, while conversion fell to 3% when the concentration of catalyst was reduced to 0.25 mmole per 100 ml of solvent. The system still remained catalytically active after removal of volatile product, and a second batch of ethylene was converted to the extent of 82% in 18 h at 100°.

Palladium(II) catalysts other than dichlorobis(benzonitrile)palladium(II) could be used, although they tended to be somewhat more difficult to handle and yield somewhat lower conversions of ethylene. Where dichlorobis(benzonitrile)palladium gave a 95% conversion of ethylene, palladium(II) chloride itself gave an 85% conversion. Di- μ -chlorobis(π -allyl)dipalladium(II) alone was ineffective as a catalyst (< 2% butene formation), but in the presence of 2 equivalents of aluminium trichloride, a 79% conversion of ethylene was obtained; aluminium chloride alone was without effect.

Dimerization of ethylene was completely prevented by one equivalent of triphenylphosphine per mole of catalyst. Smaller amounts (3–12 mole%) reduced the conversion of ethylene somewhat (74% was converted in 18 h at 100° in the presence of 6% Ph₃P) but increased the yield of hexenes to 18–23%. Stannous chloride inhibited reaction slightly, 0.5 equivalents reducing the conversion in 24 h from a typical 95% to 59%; bulk amounts of thiophene (300 mmole) had only a slight inhibiting effect (80% ethylene conversion in 24 h).

Hydrogen chloride had little effect upon ethylene dimerization, even in gross amounts; 1.0 equivalents increased the amount of hexene formation to *ca.* 23% and resulted in the formation of slightly greater amounts of 2-chlorobutane. Hydrogen

chloride (6.57 g, 180 mmoles), ethylene (10.3 g, 370 mmoles), and catalyst (2.0 g, 5.0 mmoles), heated in dibutyl phthalate (100 ml) at 100° for 24 h, gave 2-chlorobutane (14.6 g, 158 mmoles; 85% yield), containing 5% 1-chlorobutane; the remaining product was unreacted hydrogen chloride and n-butenes, no hexenes being detected. 2-Chlorobutane could be obtained (in 95% yield) by heating any or all of the butenes with hydrogen chloride in dibutyl phthalate at 100° for 24 h. Ethylene was unchanged under these conditions.

The following percentage conversions of ethylene (in parentheses) were obtained for a variety of solvents (100 ml), conditions being the same as those of the dibutyl phthalate reaction first described: tetralin (100%); 100–120° petroleum ether (100%); benzonitrile (100%); n-butyl acetate (97.2%); chloroform (95.9%); toluene (94.0%); o-dichlorobenzene (92.7%); dimethyl phthalate (92.3%); anisole (91.1%); nitrobenzene (84.7%); and methyl amyl ketone (50.4%). The amount of hexene formed was significantly greater in tetralin (15% yield), reduced in benzonitrile (2%). In isopropanol, conversion (8%) was much lower, and acetals, rather than butenes, were formed. In the absence of solvent, conversion was much slower (61% in 60 h), the yield of butenes was low (35%), and tarry material was formed.

(b). *Propene*. Propene (30.2 g, 720 mmoles) and catalyst (2.0 g, 5.0 mmoles), heated in dibutyl phthalate (100 ml) at 100° for 24 h, gave unchanged propene (19.7 g, 469 mmoles; 65% recovery) and hexenes (10.5 g, 123 mmoles; 35% conversion), shown by GLC and catalytic hydrogenation (on 10% Pd-C at 20°/1 atm) to consist of n-hexenes and 2-methylpentenes in the ratio 92/8. Both the n-hexenes and 2-methylpentenes were present in approximately the equilibrium proportions^{13,22,23} of isomers with a common carbon-chain.

A similar reaction, in which heating was continued for 172 h, gave a similar conversion (34%) of propene.

(c). *1-Butene*. 1-Butene (16.8 g, 300 mmoles) and catalyst (2.0 g, 5.0 mmoles), heated in dibutyl phthalate (100 ml) at 100° for 24 h, gave recovered n-butenes (16.2 g, 289 mmoles; 96.5%), in equilibrium proportions, and octenes (0.50 g, 4.5 mmoles; 3%) whose chromatographic behaviour was very similar to that of a sample of n-octenes obtained by isomerization of 1-octene (see below).

A sample of butenes, removed from the reaction after 1 h, contained 1-butene, *cis*-2-butene, and *trans*-2-butene in the ratio 62/8/30; at the end of the reaction, the ratio was 10/25/65.

(d). *trans*-2-Butene. *trans*-2-Butene (14.6 g, 261 mmoles) and catalyst (2.0 g, 5.0 mmoles), heated in dibutyl phthalate (100 ml) at 100° for 340 h, gave recovered n-butenes (14.0 g, 250 mmoles, 96%) and octenes (0.60 g, 5.4 mmoles; 4%), both chromatographically similar to those obtained from the 1-butene reaction.

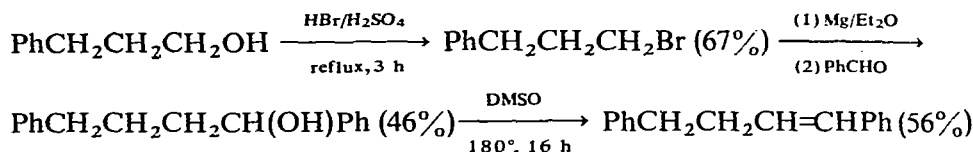
(e). *Methyl acrylate*. Methyl acrylate (85 g, 989 mmoles), containing 0.01% hydroquinone, and catalyst (3.8 g, 9.5 mmoles), heated in a 300-ml Pyrex ampoule at 113° for 23 h, gave, after filtering off precipitated palladium (0.7 g), recovered methyl acrylate (28.3 g, 329 mmoles; 33%) and a dimer fraction (53.1 g, 309 mmoles; 93% yield based on methyl acrylate consumed), b.r. 55–90°/1 mm. A tarry residue (3.9 g) remained after distillation.

Analysis by GLC [2 m × 4 mm (i.d.) polyethylene glycol adipate (30%) on Celite at 193°] of the dimer fraction indicated the presence of three major components, (A), (B), and (C), in the ratio 6/22/67, and at least four minor components

(total 5%). Component (C), present in greatest amount, was isolated by preparative GLC and identified by IR and NMR spectroscopy as dimethyl *trans*-2-hexenedioate (Found: C, 55.8; H, 7.0. $C_8H_{12}O_4$ calcd.: C, 55.8; H, 7.0%). The NMR spectrum of a sample enriched in component (B), indicated it to be dimethyl *trans*-3-hexenedioate, and to be contaminated by dimethyl 2-methyl-2- and 3-pentenedioate; not more than 3% of these were present in the original mixture. Catalytic hydrogenation (5% PdC at 20°/1 atm) of a sample of dimers containing components, (A), (B), and (C), in the ratio 16/32/52, yielded dimethyl adipate (78%) and dimethyl 2-methylglutarate (22%).

(f). *Styrene*. Authentic samples of the following styrene dimers were prepared:

(i) *trans*-1,4-diphenyl-1-butene by a route based on that described by Kuhn and Winterstein²⁴:



(ii) *cis*- and *trans*-1-methyl-3-phenylindane by refluxing styrene with 62% sulphuric acid¹⁴; and (iii) 1,3-diphenyl-1-butene (mainly *trans*) by dimerization of styrene with 53% sulphuric acid¹⁴. 1,3-Diphenyl-1-butene, when heated with palladium chloride (10 mole %) at 100° for 24 h, was partly isomerized to *trans*-1,3-diphenyl-2-butene, spectroscopically identical to that previously reported^{15,25}.

Styrene (104.0 g, 1.00 mole), containing 0.01% *p*-tert-butylcatechol, and palladium chloride (1.80 g, 10.0 mmoles), heated in a 300-ml Pyrex ampoule at 100° for 24 h, gave precipitated palladium (0.7 g), recovered styrene (85.6 g, 0.82 mole; 82% recovery), a dimer fraction (6.0 g, 28.8 mmoles; 33% based on styrene consumed), b.r. 108–134°/0.06–0.09 mm, and a dark polymeric residue (11.0 g, 60% on styrene consumed).

The dimer fraction was shown by GLC [2 m × 4 mm (i.d.) silicone elastomer (30%) on Celite at 204°] to contain at least six major components and three minor components. Although preparative separation of the individual components proved impossible, a combination of analytical GLC and NMR spectroscopy on fractions enriched in various components indicated the original dimer fraction to contain *cis*-1,4-diphenyl-1-butene, *trans*-1,4-diphenyl-1-butene, *cis/trans*-1,4-diphenyl-2-butene (PhCH₂C= at τ ca. 6.60), *cis/trans*-1,3-diphenyl-1-butene, *cis/trans*-1,3-diphenyl-2-butene, and *cis/trans*-1-methyl-3-phenylindanes, in the ratio 17/23/10/22/23/5, respectively, together with other components present to an extent of < 5%.

Codimerization reactions

(a). *Ethylene and propene*. Ethylene (10.6 g, 380 mmoles), propene (14.3 g, 340 mmoles), and catalyst (2.0 g, 5.0 mmoles), heated in dibutyl phthalate (100 ml) at 100° for 24 h, gave unchanged ethylene (0.5 g, 18 mmoles; 5% recovery) and propene (4.8 g, 114 mmoles; 34% recovery), and *n*-butenes (6.2 g, 111 mmoles; 61% based on ethylene consumed) (containing 1-butene, *trans*-2-butene, and *cis*-2-butene in the ratio 10/66/24), pentenes (7.0 g, 100 mmoles; 28% based on ethylene consumed) (containing 1-pentene, *trans*-2-pentene, *cis*-2-pentene, and methylbutenes in the ratio 4/74/19/3), hexenes (5.8 g, 69 mmoles; 61% based on propene consumed)

(containing n-hexenes and 2-methylpentenes in the ratio 93/7), and heptenes (0.3 g, 3 mmoles; 1% based on propene consumed) (>90% n-heptenes).

(b). *Propene and 1-butene*. Propene (15.5 g, 370 mmoles), 1-butene (21.3 g, 380 mmoles), and catalyst (2.9 g, 7.5 mmoles), heated in dibutyl phthalate (100 ml) at 100° for 24 h, gave unreacted propene (6.6 g, 157 mmoles; 42% recovery) and butenes (20.4 g, 364 mmoles; 96% recovery), and hexenes (8.2 g, 98 mmoles; 92% based on propene consumed), heptenes (1.5 g, 15 mmoles; 7% based on propene consumed), and traces of octenes (<0.1 g).

(c). *Ethylene and cyclopentene*. Ethylene (16.8 g, 600 mmoles), cyclopentene (40.0 g, 5.88 mmoles), and palladium dichloride (0.89 g, 5.0 mmoles), heated at 100° for 24 h, gave recovered ethylene (10.1 g, 361 mmoles; 60% recovery) and cyclopentene (32.2 g, 474 mmoles; 80% recovery), and n-butenes (3.4 g, 51 mmoles; 43% based on ethylene consumed) and codimers (11.3 g, 118 mmoles; 49% based on ethylene consumed).

The codimer fraction was shown by GLC analysis [2 m × 4 mm (i.d.) silver nitrate in ethylene glycol on firebrick²⁶, and silicone elastomer on Celite columns] and NMR spectroscopy to consist of ethylenecyclopentane, 1-ethylcyclopentene, 3-ethylcyclopentene, and 4-ethylcyclopentene, in the proportions 3/67/23/7.

(d). *Ethylene and methyl acrylate*. Ethylene (14.0 g, 500 mmoles), methyl acrylate (43.0 g, 500 mmoles), containing 0.01% hydroquinone, and catalyst (3.8 g, 10 mmoles), heated at 105° for 36 h, gave unchanged ethylene (2.4 g, 81 mmoles; 16% recovery), n-butenes (6.1 g, 106 mmoles; 51% based on ethylene reacted), methyl acrylate (20.0 g, 232 mmoles; 47% recovery), a codimer fraction (14.2 g, 125 mmoles; 47% based on methyl acrylate reacted) (Found: C, 63.2; H, 8.45. C₆H₁₀O₂ calcd.: C, 63.2; H, 8.8%), and a still-pot residue, containing mainly methyl acrylate dimers, which was not further examined.

Examination of the codimer fraction by GLC [2 m × 4 mm (i.d.) polyethylene glycol adipate (30%) on Celite at 139°] showed it to contain 3 components in the ratio 10/60/30. The two major components were separated by preparative-scale GLC and shown by IR and NMR spectroscopy to be methyl *trans*-3-pentenoate (28% yield) and methyl *trans*-2-pentenoate (14% yield). Catalytic hydrogenation (5% Pd-C; 20°/1 atm) of a sample of this fraction yielded only methyl valerate.

(e). *Ethylene and styrene*. Ethylene (18.1 g, 646 mmoles), styrene (67.2 g, 650 mmoles), containing 0.01% *p*-tert-butylcatechol, and palladium dichloride (1.5 g, 8.5 mmoles), heated at 100° for 24 h, gave unchanged ethylene (5.7 g, 204 mmoles; 32% recovery) and styrene (44.3 g, 420 mmoles; 63% recovery), and n-butenes (8.9 g, 159 mmoles; 72% based on ethylene consumed), a codimer fraction (13.7 g, 104 mmoles; 45% based on styrene consumed) b.r. 180–200°, and a tarry residue (12.7 g). No fractions corresponding to styrene dimers were observed.

The codimer fraction, GLC analysis (2 m silicone on Celite at 177°) of which showed 2 peaks in the ratio 11/89, was shown by NMR spectroscopy to consist mainly (*ca.* 90%) of *trans*-1-phenyl-1-butene, contaminated by small amounts (*ca.* 5%) of 2-phenyl-2-butenes²⁹, and probably 1-phenyl-2-butene (PhCH₂CH= at τ 6.82).

(f). *Methyl acrylate and styrene*. Methyl acrylate (43.0 g, 500 mmoles), containing 0.01% hydroquinone, styrene (52.0 g, 500 mmoles), containing 0.01% *p*-tert-butylcatechol, and catalyst (3.8 g, 10 mmoles), heated in a 300-ml Pyrex ampoule at 110° for 24 h, gave recovered methyl acrylate and styrene (total 65.6 g), a mixture of

dimers and codimers (16.7 g) b.r. 50–150°/< 1 mm, and a tarry residue (12.7 g). The dimer fraction was redistilled to give a fraction (7.5 g, 39.5 mmoles; *ca.* 26% yield) b.r. 135–138°/7 mm, shown by NMR spectroscopy to be mainly (*ca.* 85%) methyl *trans*-5-phenyl-4-pentenoate, and to contain not more than 10% of branched isomers.

Isomerization of olefins

Samples of the olefins, 2-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, and 1-heptene were isomerized, by heating with dichlorobis(benzonitrile)palladium(II), to provide some comparison of the rate of isomerization and of product formation from olefin dimerizations, and to provide standard mixtures for the calibration of GLC apparatus. In a typical experiment, the olefin (100 mmoles) and catalyst (1 mmole) were heated in a 300-ml Pyrex ampoule at 100° for 18 h: (i) 2-methyl-1-pentene gave 2-methyl-1-pentene, 2-methyl-2-pentene, 4-methyl-1-pentene, *cis*-4-methyl-2-pentene, and *trans*-4-methyl-2-pentene, in the proportions 14/72/0.5/4/9, respectively; (ii) 4-methyl-1-pentene gave the same products in the proportions 13/73/1/4/9; (iii) 1-hexene gave 1-hexene, *cis*-2-hexene, *trans*-2-hexene, *cis*-3-hexene, and *trans*-3-hexene, in the proportions 1.4/16.0/55.6/8.0/19.0, respectively; and (iv) 1-heptene gave *cis*-2-heptene, *trans*-3-heptene, and *cis*-3-heptene and *trans*-2-heptene, in the proportions 16/30/54. The isomeric proportions found are close to the equilibrium values¹³ and to those reported previously for these²² and similar isomerizations^{23,28}.

¹H NMR data

Chemical shift data for five *trans*-1,4-disubstituted 1-butenes of the type, XCH=CHCH₂CH₂Y, are shown in Table 1.

TABLE 1

CHEMICAL SHIFT DATA FOR *trans*-XCH^a=CH^bCH₂^cCH₂^dY

Substituents		τ-values			
X	Y	H ^a	H ^b	H ^c	H ^d
CO ₂ CH ₃	H	4.21	3.06	7.78	8.91
Ph	H	3.72	3.87	7.94	9.01
CO ₂ CH ₃	CO ₂ CH ₃	4.09	3.05	<i>ca.</i> 7.49	
Ph	Ph	3.66	3.83	7.07–7.8	
Ph	CO ₂ CH ₃	3.61	3.79	<i>ca.</i> 7.62	

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