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(54) Title: CATALYST SYSTEM AND PROCESS FOR BENZYL ETHER FRAGMENTATION AND COAL LIQUEFACTION		
(57) Abstract <p>Dibenzyl ether can be readily cleaved to form primarily benzaldehyde and toluene as products, along with minor amounts of bibenzyl and benzyl benzoate, in the presence of a catalyst system comprising a Group 6 metal, preferably molybdenum, a salt, and an organic halide. Although useful synthetically for the cleavage of benzyl ethers, this cleavage also represents a key model reaction for the liquefaction of coal; thus this catalyst system and process should be useful in coal liquefaction with the advantage of operating at significantly lower temperatures and pressures.</p>		

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CATALYST SYSTEM AND PROCESS FOR BENZYL ETHER
FRAGMENTATION AND COAL LIQUEFACTION

5 The present invention is a catalyst system and
process for benzyl ether fragmentation and coal
liquefaction. The catalyst system of the present
invention comprises a Group 6 metal, a salt, and an
organic halide. The process of the present invention
comprises contacting a benzyl ether with the catalyst
10 system of the present invention at a temperature of
100°C to 350°C and pressure of 1 to 200 atm. The
catalyst system and process of the present invention may
also be employed for coal liquefaction.

15 Background of the Invention

Benzyl ethers have long served as models for the
liquefaction of coal since that ether link represents
one of the key bonds that must be broken when
20 fragmenting the coal polymer. If properly controlled,
this reaction may serve as a source of benzaldehydes.
See, for example, Cookson, R. C. and Wallis, S. R.,
"Pyrolysis of Allyl Ethers. Unimolecular Fragmentation
to Propenes and Carbonyl Compounds," J. Chem. Soc. (B),
25 1966, pp 1245-56; and DeChamplain, P. et al., "Flash
Thermolysis: multiple signatropic rearrangements in
ortho-substituted aromatic compounds," Can. J. Chem.,
Vol. 54, 3749-56 (1976). Unfortunately, these reactions
have generally required very high temperatures and/or
30 protracted reaction times.

I have now found that benzyl ether fragmentation
can be conducted under mild conditions by using a
catalyst system composed of a Group 6 metal compound,
preferably molybdenum, and more preferably molybdenum
35 carbonyl, a salt, and an organic halide. Using dibenzyl

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ether in the presence of this catalyst system, the selectivity to benzaldehyde and toluene is increased and the reaction occurs at 160–175°C in a matter of hours. By contrast, earlier work employed temperatures of about 300°C for several days; achieving a more rapid reaction required temperatures approaching 900°C.

As stated above, the benzyl ether linkage has been used a model for coal liquefaction for some time. It has also been known for over thirty years that thermally fragmenting dibenzyl ether, generates toluene, benzaldehyde, bibenzyl ($\text{PhCH}_2\text{CH}_2\text{Ph}$), and, in some cases, 1,2-diphenylethanol and/or stilbene. See, for example, Badr et al., "Molecular Rearrangements: Part IX – Thermolysis of Dibenzyl Ether" *Indian J. Chem.*, Vol. 15B, pp 242–44 (1977). However, these processes require very high temperatures and/or extended reaction times to accomplish the fragmentation. The reaction temperatures required to fragment the benzyl ether link may be dramatically reduced to about 160–175°C and reaction times shortened compared to the earlier processes by applying a catalyst system composed of a chromium group metal compound, most preferably $\text{Mo}(\text{CO})_6$, a salt, and an organic halide.

Since benzyl ether fragmentation serves as a model for the liquefaction of coal, the present catalyst should also serve to lower temperatures and accelerate reaction rates for coal liquefaction to the products oil, asphaltene and preasphaltene. $\text{Mo}(\text{CO})_6$, alone or in combination with sulfur, has been used as a catalyst in coal liquefaction. See, for example, Warzinski, R. P. & Bockrath, B. C. "Molybdenum Hexacarbonyl as a Catalyst Precursor for Solvent-Free Direct Coal Liquefaction," *Energy & Fuels*, Vol. 10, No. 3, pp 612–22 (1996). In addition, $\text{Mo}(\text{CO})_6$ has even been used as a catalyst for cleaving dibenzyl ether models. See, for example,

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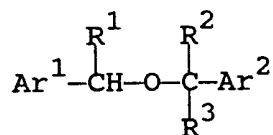
Ikenega, N. et al., "Hydrogen-Transfer Reaction of Coal Model Compounds in Tetralin with Dispersed Catalysts," *Energy Fuels*, 8 (4), pp 947-52 (1994); and
5 Yokokawa C. et al., "Studies on the Catalysts for Coal Liquefaction," *Nenryo Kyokaishi*, 70 (10), pp 978-84 (1991). However, the reaction temperatures were still excessive; the catalyst system of the present invention is expected to substantially reduce these temperatures.

10 Detailed Description of the Invention

As stated above, the present invention comprises a catalyst system and process for benzyl ether fragmentation and coal liquefaction. The catalyst
15 system of the present invention comprises a Group 6 metal, a salt, and an organic halide. Further, the process of the present invention is a process for benzyl ether fragmentation or coal liquefaction which comprises contacting a benzyl ether of the formula

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25



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with a catalyst system comprising a Group 6 metal, a salt, and an organic halide wherein Ar¹ and Ar² are the
35 same or different and each is an aromatic group, and R¹-R³ are the same or different and each is hydrogen, an aliphatic alkyl group, or an aromatic group. The process is carried out at a pressure of 1 atm to 200 atm and a temperature of 100°C to 350°C.

40

The present invention further comprises a catalyst system for cleaving a benzyl ether, such as fragmenting or cleaving dibenzyl ether, to benzaldehyde and toluene. Because benzyl ether cleavage serves as a model for coal

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liquefaction, the process may be used to affect coal liquefaction to oil, asphaltene and preasphaltene. Further, the present invention should be useful for cleaving benzyl ethers as a class of compounds.

5 In an embodiment of the invention, catalytic quantities of $\text{Mo}(\text{CO})_6$, an alkyl halide, and a salt are dissolved in dibenzyl ether and subjected to a pressure of carbon monoxide (34.0 atm) at a temperature of 160–175°C for several hours. Although one may initially
10 expect these conditions to yield benzyl phenylacetate by carbonylation, the major products were found to be toluene and benzaldehyde, along with much smaller amounts of dibenzyl and only small amounts of the expected benzyl phenylacetate.

15 While the carbon monoxide is very useful for maintaining pressure and to maintain a high selectivity to benzaldehyde and toluene, it is not critical to conducting the reaction, which can proceed in the absence of carbon monoxide. In fact, an additional
20 inert gas such as carbon dioxide or nitrogen may be added to maintain pressure and to maintain the reactants in a liquid state; the inert gases do not otherwise affect the reaction. Hydrogen gas may also be added, alone or in addition to carbon monoxide (as synthesis
25 gas), and has no significant impact on the reaction.

 As noted above, the catalyst system of this invention includes a Group 6 metal (Cr, Mo, W), preferably molybdenum. The molybdenum component is more preferably $\text{Mo}(\text{CO})_6$, but any of a host of molybdenum
30 species, particularly those with low valence states (-1 to +2) may be used. $\text{Mo}(\text{CO})_6$ is the lowest cost, low valent molybdenum species readily available. Other complexes, such as those derived from phosphines, amines, or cyclopentadiene would all be useful.
35 Carbonyl compounds of other Group 6 metals, such as

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Cr(CO)₆ and W(CO)₆, are useful, but not as effective as Mo(CO)₆.

The organic halide component, may be added as an alkyl halide, the halide being chloride, bromide or iodide. Further, the alkyl halide of the present invention may be an aliphatic or aromatic halide; ethyl halides and benzyl halides are preferred, with benzyl bromide more preferred. Alternatively, it may be generated *in situ* by adding hydrogen halide to the benzyl ether. The specific choice of halide has a notable effect upon selectivity, with iodides generating higher levels of benzyl phenylacetate than chlorides and bromides. Bromide compounds give the highest conversion rate and highest selectivity to toluene and benzaldehyde, and therefore represent the preferred halide portion of the organic halide catalyst component.

In addition to the organic halide, optimal performance is obtained by adding a salt component that may or may not contain a halide as its anion. An alternative anionic component may be, for example, an acetate; but, a halide anion is preferred. The cationic component of the salt may be selected from a long list of components, which includes alkali metals (e.g., Na, K, or Li) and the Group 15 or 16 elements. Further, the cationic portion may be a quaternary organic compound of Group 15 or 16 with ammonium and phosphonium preferred (e.g., salts of tetraalkyl ammonium or phosphonium), or a trisubstituted organic compound of Group 15 or 16 (again, P or N are preferred). Alternatively, it may be generated *in situ* by adding an alkyl or hydrogen halide to a free phosphine or amine. Examples of such compounds are tetrabutyl ammonium halide or tetrabutyl phosphonium halide.

In describing the relative proportions of each component, combining any two of the components will

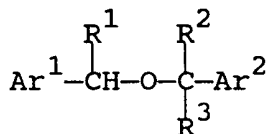
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induce the fragmentation/liquefaction reaction to a very small degree, but only the combination of the three components gives high conversion and good selectivity to benzaldehyde and toluene (i.e., in the case of dibenzyl ether). Therefore, the molar ratios for the catalyst components (organic halide: salt: Group 6 metal) would fall in the range 0.1-100:0.1-100:1. When the Group 6 component is molybdenum, the concentration of Mo may range from 0.001 to 1 moles/L, with a preferred range of 0.01 to 0.1 moles/L.

The process of the present invention may be carried out at temperatures of 100°C to 350°C. A more preferable range of temperatures is 150°C to 250°C. A still more preferable range, such as those employed in the examples that follow, is 160°C to 175°C.

As for the pressure, there is no requirement for an added gas, such as carbon monoxide. However, there is a notable increase in selectivity and reaction rate upon the addition of carbon monoxide. Hydrogen pressure can be added but we have seen neither an advantage or disadvantage to this addition at present. The process of the present invention may be performed at 1 to 200 atm. More preferably, the pressure is 1 to 100 atm. Still more preferably, the process is carried out at 10 to 50 atm.

The present invention as stated above, is a catalyst system and process for fragmenting benzyl ethers, particularly dibenzyl ether, of the general formula:



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wherein Ar¹ and Ar² are the same or different and each is an aromatic group; and R¹-R³ are the same or different and each is hydrogen, an aliphatic alkyl group or an aromatic group. As indicated, an α -hydrogen should be present. The aromatic group in the formula may be polycyclic or heterocyclic and may be optionally substituted or unsubstituted. The benzyl ether link, as noted above, is the key linkage in the coal polymer that researchers seek to break in coal liquefaction. Thus, the present process and catalyst system for fragmenting benzyl ethers, such as dibenzyl ether, should be effective for coal liquefaction.

Examples

Example 1

To a 300 mL Hastelloy[®] B autoclave was added 99 g (0.5 mol) of dibenzyl ether (C₆H₅CH₂OCH₂C₆H₅), 2.64 g (0.01 mol) of Mo(CO)₆, 6.76 g (0.02 mol) of tetrabutylphosphonium bromide, and 3.44 g (0.02 mol) of benzyl bromide. The autoclave was sealed, flushed thoroughly with nitrogen, and pressurized to 10 atm with carbon monoxide. The autoclave was then heated to 160°C and, upon reaching temperature, the pressure was adjusted to 20 atm with CO. The autoclave was held at 160°C and 20 atm for 5 h and then cooled and vented. The anticipated product, benzyl phenylacetate was found to be a minor constituent and GC-MS revealed the major products to be benzaldehyde and toluene, along with minor quantities of bibenzyl (C₆H₅CH₂CH₂C₆H₅).

The quantities of toluene, benzaldehyde, bibenzyl, and benzyl phenylacetate were subsequently determined by gas chromatography (GC) analysis using a Hewlett-Packard 5890 Gas Chromatograph with a Hewlett-Packard 7673

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Autosampler with a J&W 30M long by 0.25mm DB-5 column having a film thickness of 0.25 μ for the separation and helium as a carrier gas flowing at 1.4 mL/min with an FID detector. Weight gains from CO uptake are negligible and there is no lost weight in the transformation. Therefore, the moles of product can be directly estimated from the GC data by the following equation.

$$\text{Moles} = \frac{\text{Weight fraction (from GC)} \cdot \text{Initial Weight}}{\text{Molecular Weight}}$$

Yields are chemical yields and account for recovered starting material. Since each of the products should represent the consumption of one mole of benzyl ether, these are calculated by the following equation:

$$\text{Yield} = \frac{\text{Moles Product}}{\text{Moles of Dibenzyl Ether Added} - \text{Moles of Dibenzyl Ether Recovered}} \cdot 100\%$$

This method revealed the following levels of material to be present.

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	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
5	toluene	17.7	0.215	85
	benzaldehyde	18.6	0.197	78
	bibenzyl	1.4	0.008	3
	benzyl phenylacetate	1.4	0.007	3
10	dibenzyl ether (unreacted)	43.7	0.247	51*

*Conversion

15

This represents a 51% conversion of dibenzyl ether and represents 21.5 turnovers/Mo and 10.8 turnovers/Br (to toluene.)

20 Example 2

The reaction in Example 1 was repeated except the reaction was performed at 175°C and 8.5 g (0.05 mol) of benzyl bromide was used. The conversion was 86% and the results appear below:

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
30	toluene	28.1	0.356	83
	benzaldehyde	29.3	0.320	75
	bibenzyl	1.1	0.007	2
	benzyl phenylacetate	2.9	0.015	3
35	Unreacted dibenzyl ether	12.1	0.071	86*

*Conversion

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Example 3

Example 2 was repeated except that $\text{Cr}(\text{CO})_6$ (0.01 mole, 2.20 g) was used in place of $\text{Mo}(\text{CO})_6$. The conversion if dibenzyl ether was 15% and the results of the GC analysis appear below:

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
10	toluene	4.8	0.061	81
	benzaldehyde	4.1	0.046	60
	bibenzyl	n.d.	0	0
15	benzyl phenylacetate	n.d.	0	0
	Unreacted dibenzyl ether	72.1	0.424	15*

20 * Conversion

n.d. = none detected (below detection limit for analytical procedure.)

25

Example 4

Example 2 was repeated except that $\text{W}(\text{CO})_6$ (0.01 mole, 3.52 g) was used in place of $\text{Mo}(\text{CO})_6$. The conversion if dibenzyl ether was 31% and the results of the GC analysis appear below:

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	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
5	toluene	11.0	0.141	91
	benzaldehyde	10.4	0.116	75
	bibenzyl	0.8	0.005	3
	benzyl phenylacetate	1.2	0.006	4
10	Unreacted dibenzyl ether	57.9	0.345	31*

*Conversion

15

Examples 3 and 4 demonstrate that the other Cr group (Group 6) metals function, but are inferior to Mo.

Example 5

20

Example 2 was repeated except that benzyl chloride (0.05 mole, 6.38 g) was used in place of benzyl bromide and tetrabutylphosphonium chloride (0.02 mole, 5.89 g) was used in place of tetrabutylphosphonium bromide. The conversion of dibenzyl ether was 28% and the results of the GC analysis appear below:

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
30	toluene	8.5	0.106	75
	benzaldehyde	9.1	0.098	70
	bibenzyl	1.2	0.008	5
35	benzyl phenylacetate	1.7	0.008	6
	Unreacted dibenzyl ether	62.2	0.359	28*

40 *Conversion

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Example 6

Example 2 was repeated except that ethyl bromide (0.05 mole, 5.40 g) was used in place of benzyl bromide. The conversion if dibenzyl ether was 54% and the results of the GC analysis appear below:

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
10	toluene	15.6	0.194	72
	benzaldehyde	15.7	0.169	63
	bibenzyl	0.9	0.006	2
15	benzyl phenylacetate	4.1	0.021	8
	Unreacted dibenzyl ether	40.0	0.232	54*

20 * Conversion

Example 7

25 Example 2 was repeated except that ethyl iodide (0.05 mole, 7.80 g) was used in place of benzyl bromide. The conversion if dibenzyl ether was 53% and the results of the GC analysis appear below:

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
30	toluene	10.5	0.136	51
35	benzaldehyde	10.3	0.115	43
	bibenzyl	0.9	0.006	2
	benzyl phenylacetate	10.8	0.057	21
	Unreacted dibenzyl ether	39.0	0.234	53*

40 *Conversion

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Example 8

Example 2 was repeated except that ethyl iodide (0.05 mole, 7.80 g) was used in place of benzyl bromide. The conversion of dibenzyl ether was 36% and the results of the GC analysis appear below:

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
10	toluene	2.4	0.031	17
	benzaldehyde	0.9	0.010	5
	bibenzyl	n.d.	0	0
15	benzyl phenylacetate	14.2	0.075	42
	Unreacted dibenzyl ether	53.2	0.320	36*

20 *Conversion

Example 9

25 Example 8 was repeated except that 10.2 atm of nitrogen was used in place of CO. The conversion of dibenzyl ether was 33% and the results of the GC analysis appear below:

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
30	toluene	7.3	0.089	54
	benzaldehyde	7.9	0.085	51
35	bibenzyl	1.1	0.007	4
	benzyl phenylacetate	4.2	0.021	13
	Unreacted dibenzyl ether	58.7	0.335	33*

40 * Conversion

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This example demonstrates that CO is not necessary for the reaction.

Example 10

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Example 1 was repeated except that a mixture of 5% hydrogen in CO was used as the feed gas. The conversion of dibenzyl ether was 47% and the results of the GC analysis appear below:

10

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
15	toluene	16.4	0.201	85
	benzaldehyde	16.9	0.180	77
	bibenzyl	1.4	0.009	4
	benzyl phenylacetate	4.5	0.022	9
20	Unreacted dibenzyl ether	46.7	0.265	47*

*Conversion

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This example demonstrates that hydrogen can be present but does not demonstrably effect the rates.

Example 11

30

Example 2 was repeated except that tetrabutyl ammonium bromide (0.02 mole, 6.45 g) was used in place of tetrabutyl phosphonium bromide. The conversion of dibenzyl ether was 39% and the results of the GC analysis appear below:

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- 15 -

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
5	toluene	12.0	0.153	79
	benzaldehyde	11.3	0.125	65
	bibenzyl	0.5	0.003	2
	benzyl phenylacetate	6.2	0.032	17
10	Unreacted dibenzyl ether	51.7	0.307	39

* Conversion

15

Example 12

Example 2 was repeated except that NaBr (0.02 mole,
20 2.04 g) was used in place of tetrabutyl phosphonium
bromide. The conversion of dibenzyl ether was 100% and
the results of the GC analysis appear below:

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
25	toluene	15.9	0.195	39
	benzaldehyde	23.2	0.246	49
30	bibenzyl	8.1	0.050	10
	benzyl phenylacetate	0.7	0.003	1
	Unreacted dibenzyl ether	n.d.	0	100

35

* Conversion

n.d. = none detected

40

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Comparative Example 1

Example 10 was repeated except that Mo(CO)₆ was omitted. The conversion of dibenzyl ether was 9% and the results of the GC analysis appear below:

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
10	toluene	2.3	0.028	61
	benzaldehyde	2.5	0.025	56
	bibenzyl	0	0	0
	benzyl phenylacetate	0	0	0
15	Unreacted dibenzyl ether	82.4	0.454	9*

20 * Conversion

Comparative Example 2

25

Example 10 was repeated except that Bu₄PBr was omitted. The conversion of dibenzyl ether was 9% and the results of the GC analysis appear below:

	<u>Product</u>	<u>GC Analysis</u> <u>%</u>	<u>Moles</u>	<u>Yield</u> <u>(%)</u>
30	toluene	1.8	0.021	46
35	benzaldehyde	1.9	0.019	42
	bibenzyl	0	0	0
	benzyl phenylacetate	0	0	0
40	Unreacted dibenzyl ether	85.8	0.455	9*

* Conversion

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Comparative Example 3

Example 10 was repeated except benzyl bromide was omitted. The conversion of dibenzyl ether was only 1% and toluene and benzaldehyde were detected at levels below those established for our GC analysis (<1.5%).

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

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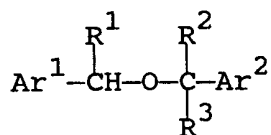
Claims

I Claim:

- 5 1. A process for benzyl ether fragmentation or coal
 liquefaction which comprises contacting a benzyl
 ether compound with a catalyst system comprising a
 Group 6 metal, a halide salt and an organic halide
10 under conditions of temperature and pressure
 sufficient to cause the fragmentation or
 liquefaction.
2. A process as claimed in claim 1 wherein the process
 is carried out at 1 to 200 atm and at 100°C to
15 350°C.
3. A process as claimed in claim 2 wherein the salt is
 an alkali metal salt, a salt of a group 15 or 16
 element, a salt of a quaternary organic compound
20 of an element of Group 15 or generated from a
 trisubstituted organic compound of Group 15.
4. A process as claimed in claim 3 wherein the organic
 halide is an alkyl halide, an aromatic halide or
25 generated from a hydrogen halide.
5. a process as claimed in claim 2 wherein the metal
 is molybdenum, chromium or tungsten.
- 30 6. A process as claimed in claim 5 wherein the metal
 is Mo(CO)₆.
7. A process as claimed in claim 2 wherein the
 pressure is 1 to 100 atm and the temperature is
35 150°C to 250°C.

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8. A process as claimed in claim 7 wherein the pressure is 10 atm to 50 atm and the temperature is 160°C to 175°C.
- 5 9. A process as claimed in claim 4 wherein the salt is tetrabutyl phosphonium halide, tetrabutyl ammonium halide or an alkali metal halide and the organic halide is a benzyl halide or an ethyl halide.
- 10 10. A process according to claim 1 wherein the benzyl ether compound has the formula:



15
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25 and the catalyst system comprises (1) a molybdenum compound, (2) a salt of a quaternary phosphonium or ammonium or an alkali metal salt, and (3) an alkyl halide or an aromatic halide at a pressure of 1 to 100 atm and a temperature of 150°C to 250°C to
30 cause the fragmentation or liquefaction, wherein Ar¹ and Ar² are the same or different and each is an aromatic group, and R¹-R³ are the same or different and each is a hydrogen or an aliphatic alkyl or aromatic group.

- 35
40 11. A process as claimed in claim 10 wherein the molybdenum compound is Mo(CO)₆.
12. A process as claimed in claim 10 wherein the contacting is in the presence of carbon monoxide.

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13. A process as claimed in claim 10 wherein component (2) is a halide of a quarternary phosphonium or ammonium and (3) is a benzyl halide or an ethyl halide.
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14. A process as claimed in claim 10 wherein the pressure is 10-50 atm and the temperature is 160°C to 175°C.
- 10
15. A process as claimed in claim 13 wherein (3) is benzyl bromide.
16. A process as claimed in claim 10 wherein the benzyl ether is dibenzyl ether.
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17. A process according to claim 1 wherein the benzyl ether is dibenzyl ether and the catalyst comprises a catalyst system comprising (1) a molybdenum compound, (2) a salt of a quarternary phosphonium or ammonium or an alkali metal salt, and (3) an alkyl halide or aromatic halide at a pressure of 1 to 100 atm and a temperature of 150°C to 250°C, said contacting being in the presence of carbon monoxide.
- 20
18. A process as claimed in claim 17 wherein the molybdenum compound is $\text{Mo}(\text{CO})_6$, and (3) is benzyl halide or ethyl halide and the pressure is 10 to 50 atm and the temperature is 160°C to 175°C.
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19. A process as claimed in claim 18 wherein (2) is a tetraalkyl ammonium or phosphonium halide and (3) is benzyl bromide.
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/01661

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C07C1/20 C07C45/51 C10G1/08				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) IPC 6 C07C C10G				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	GB 427 275 A (INTERNATIONAL HYDROGENATION PATENTS COMPANY) 18 April 1935 see the whole document -----	1, 5, 10, 17		
<input type="checkbox"/> Further documents are listed in the continuation of box C.				
<input checked="" type="checkbox"/> Patent family members are listed in annex.				
° Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none; vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
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Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">22 April 1998</div>		Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">04/05/1998</div>		
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-size: 1.2em;">Van Geyt, J</div>		

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/01661

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 427275 A		FR 778674 A GB 332246 A GB 422892 A	21-03-35
