(1.5 mol) of cyclohexanol was heated with stirring in an autoclave at 210–220° for 1.5 hr. After cooling, water was added and the oily layer that separated was extracted with ether. The ethereal extract was washed with water and dried ($K_2CO_3$), the ether was removed, and the residue was distilled; 35.5 g (59.5%) of α-cyclohexylphenylacetonitrile[19] resulted which soon solidified to light-yellow prisms. After two recrystallizations from methanol the product melted at 56–58°.

**Registry No.**—**1**, 5558-36-1; **2**, 15601-30-6; **3**, 17178-81-3; **4**, 17179-16-7; **5**, 30889-57-7; **6**, 17179-17-8; **7**, 17179-18-9; **8**, 769-68-6; **9**, 5558-78-1; **10**, 5558-29-2; **11**, 3508-98-3; **12**, 5558-31-6; **13**, 5558-32-7; **14**, 5558-33-8; **15**, 5558-34-9; **16**, 5558-35-0; **17**, 3893-23-0; **18**, 21764-73-8; **19**, 21764-74-9; **20**, 21764-71-6; **21**, 30878-93-4; **22**, 21764-72-7; **28**, 4468-48-8; α-cyclohexylidenephenylacetonitrile, 10461-98-0; phenylacetonitrile, 140-29-4.

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[19] See footnote *k*, Table II.

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# Behavior of Tungsten Hexachloride and Ethylaluminum Dichloride Cocatalyst System in Alkylation and Metathesis Reactions[1]

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We have discovered a novel behavior of the $WCl_6$–$C_2H_5AlCl_2$ when this cocatalyst was preformed in toluene. When this catalyst was treated with 2-pentene, instead of the expected metathesis of 2-pentene, a very rapid Friedel–Crafts alkylation of toluene was encountered. With benzene, the alkylation proceeded at a somewhat slower rate and was accompanied by an even slower 2-pentene metathesis reaction. Thus, in addition to phenylpentane, phenylbutane and phenylhexane were also formed. This is the first observance of metathesis during Friedel–Crafts alkylation. The behavior of the $WCl_6$–$C_2H_5AlCl_2$ catalyst system with pyridine or triphenylphosphine added as the ligand was also briefly studied. When either was added to the preformed $WCl_6$–$C_2H_5AlCl_2$, the alkylation was completely inhibited and a slow metathesis of olefin was observed. Alkylation of benzene with 1-dodecene gave the expected isomeric mixture of phenyldodecanes.

The use of $WCl_6$–$C_2H_5AlCl_2$ or RLi cocatalyst system *in situ* for olefin metathesis, sometimes also designated olefin dismutation or disproportionation, has been investigated by several workers.[2–4] The coordination mechanism for olefin metathesis has been proposed by Kothari[5] in which the reduced tungsten compound is coordinated to two olefin molecules *via* a four-centered "quasicyclobutane" type complex intermediate. This mechanism also applies to the reactions catalyzed by oxides of tungsten, molybdenum, or rhenium and soluble complexes of tungsten and molybdenum.[6,7]

The past investigations on the use of $WCl_6$–$C_2H_5AlCl_2$ cocatalyst were concerned with the fundamental aspects of the metathesis reaction as applied to linear vinylenic olefins[2,3,7] and the ring-opening polymerization of a variety of cyclo olefins.[8] However, these studies did not disclose the behavior of this catalyst when preformed in aromatic solvents. In toluene, this catalyst promoted a rapid Friedel–Crafts alkylation of toluene, whereas, in the case of benzene, both alkylation and metathesis reactions were observed. This behavior of the preformed catalyst system prompted us to carry out a more detailed investigation.

## Results

**Alkylation by 2-Pentene.**—When $WCl_6$–$C_2H_5AlCl_2$ cocatalyst is preformed in toluene and treated with 2-pentene, an almost exclusive and very rapid alkylation of toluene is encountered in contrast to the metathesis of 2-pentene when this cocatalyst is prepared *in situ*. The term *in situ*, as employed in this discussion, pertains to the formation of a cocatalyst in the presence of the olefin. The isomer distribution for pentyltoluenes, based on infrared spectra, is para > ortho > meta. The isomer distribution was determined by comparing their band strengths in 700–800-$cm^{-1}$ region. Due to many inherent differences in Friedel–Crafts catalyst systems, a quantitative comparison between catalysts is difficult. However, the high activity of the $WCl_6$–$C_2H_5AlCl_2$ case is indicated by the alkylation of nearly 1500 mol of toluene per mole of catalyst after 1 hr at 25°.

We have observed that, when $WCl_6$–$C_2H_5AlCl_2$ cocatalyst is preformed in benzene and added to a solution of 2-pentene in benzene, a reaction occurs which gives rise to phenylpentane, phenylbutane, and phenylhexane (I). The latter two products which account for about 10% of the products (Table I) are clearly the result of a 2-pentene metathesis reaction (eq I).

$$\begin{tikzcd}\text{2-pentene} \arrow[r, shift left] \arrow[d, "\text{PhH}"] & \text{2-butene + 3-hexene} \arrow[l, shift left] \arrow[d, "\text{PhH}"] \\ \text{phenylpentane} & \text{phenylbutane + phenylhexane}\end{tikzcd} \qquad \text{(I)}$$

The small amount of these products formed indicates that under these conditions the rate of alkylation is

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[1] (a) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970; (b) abstracted in *Chem. Eng. News*, **48**, 39 (1970).

[2] N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, 3327 (1967).

[3] N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, **90**, 4133 (1968).

[4] J. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).

[5] Reference 4, footnote 6.

[6] C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catal.*, **7**, 269 (1967).

[7] G. C. Bailey, *Catal. Rev.*, **3** (1), 37 (1969), and references cited therein.

[8] N. Calderon, E. A. Ofstead, and W. A. Judy, *J. Polym. Sci., Part A-1*, **5**, 2209 (1967).

TABLE I

$WCl_6$-$C_2H_5AlCl_2$ PREFORMED CATALYZED REACTIONS OF 2-PENTENE AT 25°

| Run | $WCl_6$, mmol | $C_2H_5AlCl_2$, mmol | 2-Pentene, mmol | Solvent | Ratio, Al/W | Reaction time, min | % convn of olefin | Products |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.1 | 0.1 | 43 | Toluene | 1 | 10 | 100 | Pentyltoluenes |
| 2 | 0.05 | 0.1 | 50 | Toluene | 2 | 10 | 100 | |
| 3 | 0.05 | 0.2 | 43 | Toluene | 4 | 10 | 100 | |
| 4 | 0.05 | 0.1 | 45 | Benzene | 2 | 10–15 | 100 | Phenylpentane<br>Phenylbutane<br>Phenylhexane |

much faster than that of metathesis. Although the alkylation of benzene by cyclooctene and cyclooctadiene has been observed in a trace amount during their polymerization with $WCl_6$–$C_2H_5OH$–$C_2H_5AlCl_2$ catalyst system,[9] this is the first example of the observance of metathesis during alkylation giving rise to the disproportionated alkylated products.

The catalysis of both metathesis and alkylation reactions raises certain questions as to the nature of the intermediate responsible for each of these reactions. The simultaneous occurrence may require the formation of two different cocatalyst intermediates. The mechanism of metathesis reaction in which $WCl_6$ reduced by $C_2H_5AlCl_2$ interacts with two olefin molecules to form a "quasicyclobutane" type complex intermediate has been postulated and supported by several investigators.[3,5,7] The inability of the metathesis reaction to compete when the cocatalyst is preformed does suggest that the prior coordination of the reduced tungsten with olefins apparently is necessary for the formation of the active metathesis intermediate. In the benzene case, a small amount of the metathesis catalyst survives and competes with the alkylation catalyst. The inability of metathesis to compete with alkylation is probably due to the coordination of the catalyst to the aromatic ring to give the alkylation intermediate, thus interfering with coordination to the olefin. The alkylation activity of this catalyst produced from the reaction of $C_2H_5AlCl_2$ with $WCl_6$ is quite similar to that of aluminum chloride.

The results of the alkylation reactions of 2-pentene (Table II) further indicate that at higher temperature and higher $C_2H_5AlCl_2$–$WCl_6$ ratio the monoalkylated intermediate reacts faster than the starting compound. The molar ratio of mono- to dialkyl derivatives was established by weighing the distilled fractions.

**Ligand Effects.**—The behavior of $WCl_6$–$C_2H_5AlCl_2$ cocatalyst system upon treatment with ligands pyridine and triphenylphosphine was investigated briefly (Table III).

With the *in situ* catalyst, pyridine inhibited the metathesis reaction while its presence in the preformed system suppressed the Friedel–Crafts alkylation reaction but allowed a 4% conversion to metathesis products. Pyridine has been found to reduce tungsten and form a brown precipitate which is $[WCl_4(pyridine)_2]$.[10] The formation of such an intermediate may explain the suppression of alkylation and greatly reduced metathesis activity.

On the other hand, the triphenylphosphine *in situ* system slowed the metathesis reaction so that about 2–3 hr was required to reach equilibrium which is contrasted with the few minutes needed with the *in situ* catalyst. $P(C_6H_5)_3$ hinders the metathesis of 2-pentene to some extent perhaps by forming a labile complex with reduced tungsten and thus slowing down the rapid interaction of reduced tungsten with olefin. We believe that the competition of phosphine with olefin for reduced tugsten provides an explanation for slower metathesis reaction (eq II). The presence of triphenylphosphine in the preformed catalyst suppressed the alkylation but permitted a slow metathesis process.

TABLE II

DISTRIBUTION OF ALKYLATED AROMATICS IN REACTIONS WITH 2-PENTENE

| Aromatic | Ratio, Al/W | Temp, °C | Products (%) |
|---|---|---|---|
| Benzene | 2 | 50 | Phenylpentane (55)<br>Phenylbutane and phenylhexane (10)<br>Dialkylbenzene (30)<br>Higher alkylated (5) |
| Benzene | 2 | 25 | Phenylpentane (85)<br>Phenylbutane and phenylhexane (10)<br>Dialkylbenzene (5) |
| Benzene | 4 | 30 | Phenylpentane (42)<br>Phenylbutane and phenylhexane (9)<br>Dialkylbenzene (43)<br>Higher alkylated (6) |
| Toluene | 2 | 50 | Monoalkyl/dialkyl = 2.5 |
| Toluene | 2 | 25 | Monoalkyl/dialkyl = 5 |

$$WCl_4 \cdot 2P(Ph)_3 \xrightleftharpoons{\text{olefin}} WCl_4 \cdot P(Ph)_3 \cdot \text{olefin} \xrightleftharpoons{\text{olefin}} WCl_4 \cdot (\text{olefin})_2 \qquad \text{(II)}$$

The inability of the alkylation reaction to proceed when pyridine or triphenylphosphine is added to a preformed catalyst may be due to the neutralization of the active intermediate by ligand which acts more or less as a base. The alternate explanation, for the suppression of alkylation, is the possibility of $(C_6H_5)_3P \rightarrow Al$ interaction and the formation of a pyridine→Al adduct.

**Alkylation by 1-Dodecene.**—The use of the preformed $WCl_6$–$C_2H_5AlCl_2$ catalyst system has been extended to the alkylation of 1-dodecene.

The reaction of 1-dodecene with benzene was investigated in order to obtain an indication of the relative rates of isomerization and alkylation. The results summarized in Table IV show that the isomerization occurs during alkylation and that all the possible phenyldodecanes are obtained except the 1-phenyl isomer. This is similar to the results obtained by others in the Friedel–Crafts alkylation reactions of 1-dodecene and

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[9] K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy, and J. P. Ward, *Advan. Chem. Ser.*, **91**, 399 (1969).

[10] R. E. McCarley and T. M. Brown, *Inorg. Chem.*, **3**, 1232 (1964).

Table III

Ligand Effects in the Preformed and the *in Situ* Catalyst Systems

| Run | $WCl_6$, mmol | $C_2H_5AlCl_2$, mmol | Ligand, mmol | 2-Pentene, mmol | Reaction time | % convn of olefin | Products |
|---|---|---|---|---|---|---|---|
| 1[a] | 0.05 | 0.1 | | 45 | 10 min | 50 | 3-Hexene<br>2-Butene |
| 2 | 0.06 | 0.24 | 0.06 (TPP)[b] | 45 | 10 hr | 47 | 3-Hexene<br>2-Butene |
| 3[a] | 0.06 | 0.24 | 0.06 (TPP) | 45 | 2 hr | 46 | 3-Hexene<br>2-Butene |
| 4[a] | 0.24 | 0.48 | 0.24 (Py)[c] | 90 | 2 hr | None | |
| 5 | 0.24 | 0.48 | 0.24 (Py) | 45 | 5 hr | 4 | 3-Hexene<br>2-Butene |

[a] Run with *in situ* catalyst. [b] TPP, triphenylphosphine. [c] Py, pyridine.

Table IV

Alkylation of Benzene with $WCl_6$–$C_2H_5AlCl_2$ Cocatalyst System

$$\frac{\text{benzene}}{WCl_6} \sim 1000, \frac{C_2H_5AlCl_2}{WCl_6} \sim 2, \frac{\text{olefin}}{WCl_6} \sim 200$$

| | % alkylation by olefin 1-dodecene | | |
|---|---|---|---|
| Compd | 5–10° | 40–45° | 55–60° |
| 2-Phenyl | 38.4 | 29.3 | 26.1 |
| 3-Phenyl | 14.4 | 12.7 | 11.4 |
| 4-Phenyl | 6.8 | 9.3 | 10.3 |
| 5- and 6-phenyl | 11.2 | 16.9 | 18.0 |
| Polyalkylated and polymers | 29.2 | 31.8 | 34.2 |
| Conversion based on olefin | 98.7 | 80.0 | 73.5 |

other olefins[11,12] employing $AlCl_3$. In contrast to $AlCl_3$, the isomerization of pure 3-phenyldodecane was, however, not observed with $WCl_6$–$C_2H_5AlCl_2$ catalyst.

Three common features are found with regard to these results (Table IV) and those reported by Alul[13] using the HCl–$AlCl_3$ catalyst. These are (1) the high formation of 2-phenyldodecane; (2) the increase in this isomer as the reaction temperature is lowered; (3) the high yield of polyalkylated products.

Again, we believe that the active intermediate derived from $WCl_6$–$C_2H_5AlCl_2$ behaves similarly to aluminum chloride. However, unlike aluminum chloride, this catalyst is soluble, can be employed in a low concentration, and does not isomerize phenyldodecane under the alkylating condition.

## Experimental Section

**Materials.**—Benzene, toluene, and pyridine were distilled in nitrogen atmosphere and kept over Drierite. Mixed 2-pentene (99%, trans/cis = 0.85) from Chemical Samples Co., Columbus, Ohio, was distilled from sodium bisulfite under $N_2$. Dodecene-1, from Gulf Oil Co., was distilled in nitrogen atmosphere. Tungsten hexachloride, ethylaluminum dichloride (25% in hexane or heptane), and triphenylphosphine were used as received without further purification. Tungsten hexachloride, when found contaminated with impurities (yellow-orange $WO_2Cl_2$ and $WOCl_4$), was purified by sublimation of the more volatile $WOCl_4$ and $WO_2Cl_2$ under nitrogen at about 200°.

**Alkylation by 2-Pentene.**—The alkylation reactions of benzene and toluene with 2-pentene (Table I, II) were carried out in flask (by the procedure employed in the alkylation of benzene with 1-dodecene) and in 4-oz screwcap bottles flushed with nitrogen and sealed with rubber and teflon gaskets. Injections of chemical reagents were done by means of hypodermic syringes from which air and moisture were carefully excluded. The $WCl_6$–$C_2H_5AlCl_2$ cocatalyst was preformed to give a cherry-red solution in benzene or toluene and 2-pentene was added to it. In some cases, a third component (ligand), triphenylphosphine or pyridine, was added to the preformed catalyst system before adding olefin. In *in situ* systems (Table III), the reagents $WCl_6$, ligand, and $C_2H_5AlCl_2$ were injected into a mixture of benzene and olefin. The reaction mixtures were distilled, where necessary, and analyzed by gas chromatography.

**Alkylation by 1-Dodecene.**—In a three-neck 250-cc flask equipped with a stirrer, thermometer, dropping funnel, condenser, and nitrogen inlet was placed the solution of 0.5 g of $WCl_6$ dissolved in 100 cc of dry benzene (1.25 mmol of $WCl_6$) and 2 cc of 1.55 *M* $C_2H_5AlCl_2$ in heptane (2.90 mmol of $C_2H_5AlCl_2$) in nitrogen atmosphere. To the resultant deep red-brown solution of the cocatalyst was added with stirring over a 20-min period, 38.0 g of 1-dodecene (226 mmol) at 40–45°. The reaction is exothermic and the temperature was maintained in the 40–45° region with ice–water bath. After the addition of 1-dodecene was completed, the reaction mixture was stirred for an additional 0.5 hr. After filtering the solid residue and removing heptane and benzene by distillation, the reaction mixture contained unreacted 1-dodecene, phenyldodecane isomers, and polyalkylated materials. The mixture containing these products then was analyzed by gas chromatography using mesitylene as an internal standard.

Two more alkylation reactions of benzene with 1-dodecene at 5–10 and 55–60° were also carried out employing the same molar quantities of each reagent as described above.

**Vpc Analysis.**—The analyses of alkylated products were done with an Aerograph and Hewlett-Packard F & M 700 thermal conductivity chromatographs using 20 ft × 0.25 in. SE-30 and 12 ft × $^1/_8$ in. Apiezon L columns. The relative retention volumes of phenyldodecanes were determined using 3-phenyldodecane as the standard and were found to compare well with data reported in the literature[14] when recalculated using 3-phenyldodecane as the standard. The identity of the metathesized alkylated products of the 2-pentene reaction with benzene was determined by employing reagent grade 2-phenylbutane, 2- and 3-phenylpentanes, and 3-phenylhexane from Chemical Samples Co.

**Infrared Spectra.**—The infrared spectra on the alkylated products were carried out with a Perkin-Elmer 137 recording spectrophotometer using sodium chloride cells in a neat liquid phase. The assignment of bands for pentyltoluene isomers in 700–800-cm$^{-1}$ region was done by using bands for isopropyltoluenes.[15]

| | Para | Meta | Ortho |
|---|---|---|---|
| Isopropyltoluene | 816, 721 | 783, 703 | 757, 727 |
| Pentyltoluene | 819 vs, 723 sh | 787 m, 702 m | 759 s, 730 ms |

**Registry No.**—Tungsten hexachloride, 13283-01-7; ethylaluminum dichloride, 563-43-9; 2-pentene, 109-68-2; toluene, 108-88-3; benzene, 71-43-2; 1-dodecene, 112-41-4.

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