downfield shift of the bridgehead carbon atom at position 10 would be expected because of the replacement of the nitrogen (bonded to this carbon) with the more strongly deshielding oxygen. If the second explanation is correct, carbon atom 10 would receive an additional γ carbon and therefore experience an upfield shift owing to the γ effect. It was found that introduction of the benzylidene function caused an upfield shift of the C-10 doublet from 63 to 59 ppm, indicating that **5a** is the most probable structure.

It was also observed that the proton and carbon spectra of **5a** were broadened at room temperature. Quantitative work on temperature dependence was not performed, but sharp spectra were obtained at 80–120°. The origin of broadening may be either slow flipping of the seven-membered carbocyclic ring[6] or a slow pyramidal inversion of the bridge nitrogen. Formation of the benzalhydrazone derivative would be expected to flatten the nitrogen by conjugation, but encumber ring flipping somewhat. The fact that sharp spectra on the hydrazones were obtained at room temperature suggests that in their precursors slow pyrimidal inversion rather than slow ring flipping was responsible for broadening.

Experimental Section[7]

Melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected. The infrared spectra were recorded on Perkin-Elmer Model 237 and 457 spectrophotometers. All pure materials were run as Nujol or halocarbon mulls. Nuclear magnetic resonance spectra were determined on Varian A-60 and T-60 spectrophotometers using tetramethylsilane as an internal reference. ^{13}C NMR spectra were determined on a Varian XL-100 spectrophotometer. Mass spectra were recorded on an LKB 9000 spectrometer.

Interpretation of NMR data: δ, chemical shift in parts per million (multiplicity, number of protons, coupling constant, proton assignment); s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

12-Amino-10,11-dihydro-5,10-imino-5*H*-dibenzo[*a,d*]cyclohepten-5-ol (5a). A suspension of 30.0 g of 1 in 150 ml of anhydrous hydrazine was refluxed for 4 hr. The excess hydrazine was removed under reduced pressure and methylene chloride was added to the residue. The resulting solid was filtered, washed twice with ethanol and then with ether to yield 26.8 g (77%) of **5a**, mp 191–194°. An analytical sample was recrystallized from methanol: mp 192–194°; NMR (Me_2SO) δ 7.8–6.5 (m, 8), 4.4 (d, 1, J = 5 Hz, NCH), 3.4 (q, 1, J = 5 Hz, 17, CHH′), 3.5 (s, broad, 3, OH, NH_2), 2.4 (d, 1, J = 17 Hz, CHH′); ^{13}C NMR (Me_2SO) δ 62.8 (CH), 28.1 (CH_2).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.6; H, 5.9; N, 11.8. Found: C, 75.2; H, 6.3; N, 12.0.

12-Benzylideneamino-10,11-dihydro-5,10-imino-5*H*-dibenzo[*a,d*]cyclohepten-5-ol (5b). To a hot solution of 0.5 g of **5a** in 30 ml of methanol was added 1.0 ml of benzaldehyde. The solution was refluxed for 5 min. Upon cooling, a crystalline precipitate formed and was filtered and washed twice with ethanol and then with ether to yield 0.55 g (81%) of **5b:** mp 158–161°; NMR (Me_2SO) δ 8.3 (s, 1, N=CH), 7.9–6.7 (m, 13), 5.4 (d, 1, J = 4 Hz, NCH), 3.5 (m, 1, J = 4, 17 Hz, CHH′), 3.4 (s, 1, OH), 2.5 (d, 1, J = 17 Hz, CHH′); ^{13}C NMR (Me_2SO) δ 59.8 (CH), 27.9 (CH_2).

Anal. Calcd for $C_{22}H_{18}N_2O$: C, 81.0; H, 5.6; N, 8.6. Found: C, 81.1; H, 5.7; N, 8.4.

12-(3,4-Dimethoxybenzylidene)amino-10,11-dihydro-5,10-imino-5*H*-dibenzo[*a,d*] cyclohepten-5-ol (5c). To a hot solution of 10.0 g of **5a** in 400 ml of methanol was added 5.0 g of 3,4-dimethoxybenzaldehyde. The solution was refluxed for 6 hr (after 1 hr a precipitate forms). Upon cooling, the solid was filtered and washed twice with methanol and then with ether to yield 9.0 g (56%) of **5c:** mp 152–155°; NMR (Me_2SO) δ 8.2 (s, 1, N=CH), 7.9–6.8 (m, 11), 5.3 (d, 1, J = 4 Hz, NCH), 3.7 (s, 6, OCH_3), 3.4 (s, 1, OH), 3.35 (q, 1, J = 4, 17 Hz, CHH′), 2.4 (d, 1, J = 17 Hz, CHH′).

Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.6; H, 5.7; N, 7.3. Found: C, 75.0; H, 5.9; N, 7.3.

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Registry No.—**1,** 2222-33-5; **5a,** 55991-62-3; **5b,** 55991-63-4; **5c,** 55991-64-5; hydrazine, 302-01-2; benzaldehyde, 100-52-7; 3,4-dimethoxybenzaldehyde, 120-14-9.

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(7) No attempts were made to optimize yields of the reactions.

Changing the Reaction Paths of a Metathesis Catalyst

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Numerous papers and several reviews have been published on the metathesis of olefins.[1–7] This reaction has also been called olefin "dismutation" or "disproportionation", and involves breaking carbon double bonds and rejoining the fragments: $2RCH{=}CHR' \rightleftharpoons RCH{=}CHR + R'CH{=}CHR'$. We have observed a new phenomenon in catalysis of this kind: the transformation of a metathesizing system into a dimerizing system simply by increasing the amount of aluminum component in the catalyst. Ligands also play an important role in such processes, completely changing the course of the reaction.

Table I shows the importance of the order in which reagents are combined in this metathesizing system.

Table I
Metathesis of Mixed 2-Pentenes
(0.2 m*M* WCl_6, 10 m*M* olefin, 0.3 m*M* $PhNH_2$, 0.3 m*M* $Et_3Al_2Cl_3$)

Injection order[a]	1	2	3	4
Conversion, %	55	51	50	61
Selectivity to 3-hexene, mol %	46	50	53	41
Selectivity to 2-butene, mol %	36	40	44	28
Total selectivity, %	82	90	97	69
2-Pentene, *trans-/cis*[b]	4.9	5.6	5.2	6.1
2-Butene, *trans-/cis-*	2.5	2.0	2.0	2.6

[a] Injection order: 1, W + 2-pentenes (2-P) + aniline ($PhNH_2$) + Al; 2, W + $PhNH_2$ + 2-P + Al; 3, W + $PhNH_2$ + Al + 2-P; 4, W + Al + $PhNH_2$ + 2-P. [b] Initial trans/cis ratio of 2-pentene was 0.59.

Most critical is the interaction of WCl_6 and the aniline ligand: nearest approach to theoretical equilibration was attained when this interaction was most direct, as in injection orders 2 and 3. The poorest selectivity was observed in order 4, where $Et_3Al_2Cl_3$ had reacted with WCl_6 before aniline was added. The importance of the ligand is further illustrated in Table II, where the catalysts with no ligand, or with ethanol, both convert propylene or 2-pentene quantitatively to oligomers or alkylates.

Table II
Metathesis by $Et_3Al_2Cl_3$–WCl_6 and Ligands

Olefin	Ligand	% conversion	% metathesis
2-Pentene[a]	None	100	0
2-Pentene	Aniline	22	100
Propylene[b]	None	99	0
Propylene	Ethanol	99	0
Propylene	Aniline	27	75

[a] 0.2 mM WCl_6 in benzene, 10 mM 2-pentene in n-pentane, 0.4 mM neat ligand, 0.2 mM $Et_3Al_2Cl_3$, in that order. [b] 0.2 mM WCl_6, 0.3 mM ligand, 0.2 mM $Et_3Al_2Cl_3$, 20 mM propylene, in that order, all in chlorobenzene.

In contrast, addition of aniline led exclusively to metathesis. Separate experiments with propylene at Al/W = 10 showed a similar pattern, except that dimerization occurred exclusively, rather than metathesis. The failure of ethanol to modify the catalyst may be due to elimination of ethyl chloride, and the formation of tungsten oxytetrachloride, thus losing any steric or electronic control by the ethoxy group.

A dark brown precipitate was formed upon addition of the aniline. This solid was almost entirely dissolved by the alkylaluminum halide, but complete homogeneity was uncertain.

Figure 1 shows the sharp change from metathesis to dimerization. At Al/W = 1.5, metathesis accounts for almost all the propylene converted (to 2-butenes, ethylene, and some 1-butene). As the amount of $Et_3Al_2Cl_3$ was increased to Al/W = 3.0, both conversion and selectivity toward metathesis fell steeply to zero. From this point on, conversion rose sharply, with dimerization the exclusive reaction. The dimer mixture was composed largely of 2-methyl-1-pentene and 2,3-dimethyl-1-butene.

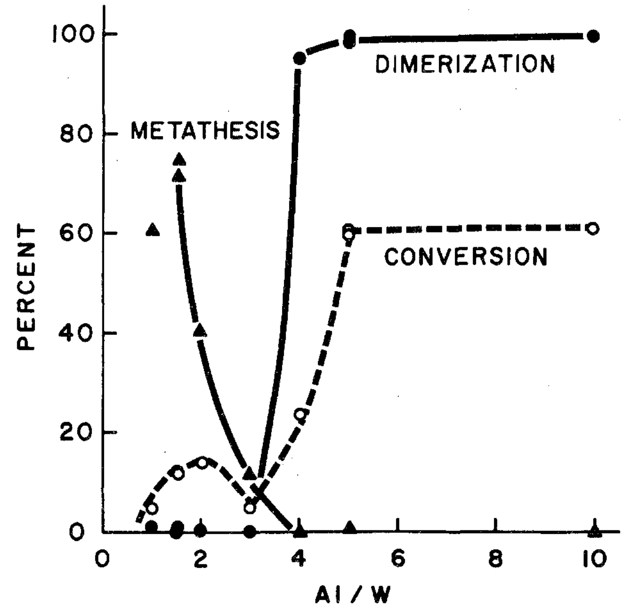


Figure 1. Propylene and $Et_3Al_2Cl_3$.

When $EtAlCl_2$ was employed as cocatalyst, and a chlorinated aniline as ligand, virtually all the ethylene was consumed as fast as it was formed. Figure 2 represents this product mixture, which had the representative composition 22% 1-butene, 17% *trans*-2-butene, 25% *cis*-2-butene, 19% 3-methyl-1-butene, and 15% 2-methyl-1-butene. As Al/W was increased, dimerization again predominated, giving a mixture of branched hexenes.

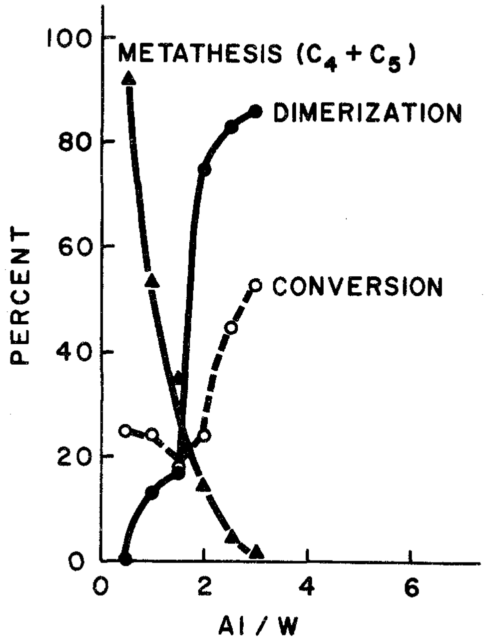
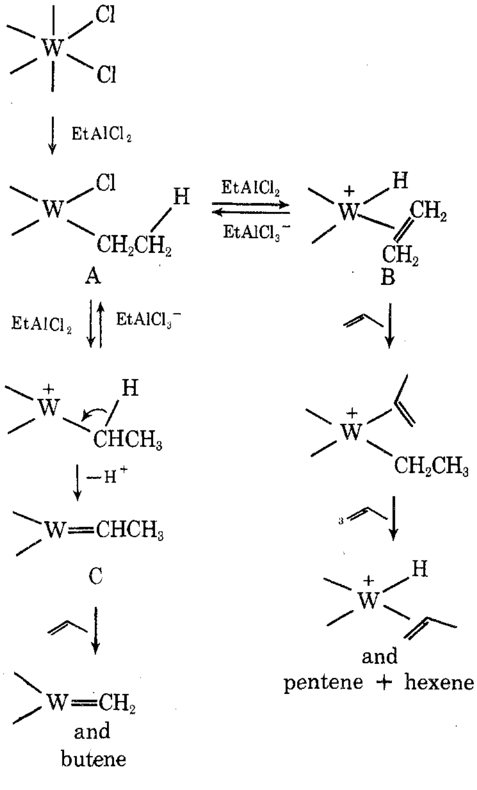


Figure 2. Propylene and $EtAlCl_2$.

Figure 3 shows a similar pattern for 2-pentene, except that essentially no reaction occurred at aluminum/tungsten ratios greater than 5. In earlier work, 2-butene showed the same behavior at such levels of aluminum. For our catalyst, this indicates an intermediate allowing coordination of internal and terminal olefins in the metathesis process, but only terminal olefins in dimerization. This may be explained by the mechanism suggested



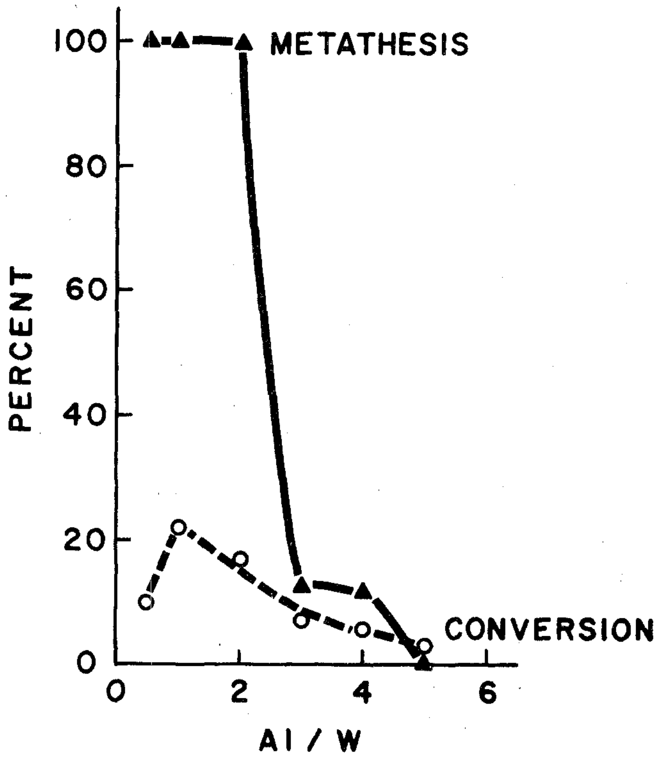


Figure 3. 2-Pentene-2 and $Et_3Al_2Cl_3$.

where intermediate C, with one less ligand, would allow more facile coordination of an internal olefin than B.

Similar results would be observed if the terminal olefin sustained a nonproductive metathesis, such as the exchange of methylene groups only. However, this possibility seems unlikely.

When the tungsten atom of intermediate A is in a relatively high oxidation state (perhaps IV or V), the pathway to the carbene C affords relief to electron-deficient tungsten by expulsion of H^+. When tungsten has been reduced further (perhaps III or IV), the route through intermediate B, where W is relatively electron rich, affords stabilization of the olefin complexes shown. Somewhere in between, A becomes stable and little reaction occurs. Complexes of the type A and B have been reported,[8] and the carbene mechanism for metathesis has been suggested.[9] The route to metathesis should be favored by small amounts of Lewis acid, and we have observed such an effect previously.[5] More basic reductants such as butyllithium may abstract the α proton from A first, followed by ejection of chloride ion.

Experimental Section

2-Pentene was distilled from sodium bisulfite under nitrogen, and propylene was dried through a bed of 3-A molecular sieves. Aniline was vacuum distilled from sodium. Solvents were carefully dried over sodium or silica gel. Tungsten hexachloride was dissolved and used as received, and the ethylaluminum chlorides were diluted to 2 M in benzene or chlorobenzene.

Propane as an internal standard was added to the propylene–chlorobenzene solutions, which were about 0.5 M.

Transfers of olefin solutions and chemical reagents were done by hypodermic syringes. Reactions were carried out for 1 hr in 4-oz glass bottles at room temperature, agitated on a Burrell shaker, and terminated by 1 ml of isopropyl alcohol. Then the reaction mixtures were cooled before VPC analysis.

For 2-pentene, analyses were done on a 42-ft Tergitol column at 60°, using n-pentane as internal standard. For the propylene work, analyses were done on a 60-ft β,β-oxydipropionitrile column at 30° or Tergitol at 30°. Using propane as an internal standard, the weight of propylene converted (expressed in peak area) was calculated and compared to $^3\!/_2$ the observed areas for the 2-butene isomers (since some of the ethylene went on to form 1-butene, etc.). Thus, conversion and total selectivities were simply calculated.

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Registry No.—*trans*-2-Pentene, 646-04-8; *cis*-2-pentene, 627-20-3; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; propylene, 115-07-1; WCl_6, 13283-01-7; $PhNH_2$, 62-53-3; $Et_3Al_2Cl_3$, 12075-68-2; ethanol, 64-17-5; $EtAlCl_2$, 563-43-9.

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Reaction of Diphenylcyclopropenone with Pyridinium *N*-Imine in Protic Media. The Quenching of a Reactive Intermediate

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The reaction of diphenylcyclopropenone (**1**) with N-acyl pyridinium imines (**2a**) has been reported to produce 2,4,5-trisubstituted 6H-1,3-oxazin-6-ones (**3**).[1,2] A pathway involving formation of a ketene[3] intermediate (**4a**) was suggested for the process. However, attempts to quench this intermediate with methanol were unsuccessful, possibly because the intramolecular cyclization process is rapid compared with intermolecular reaction of the ketene with solvent.[1] In this case, absence of the N substituent should permit addition of a protic solvent to the intermediate.

We have, therefore, investigated some reactions of diphenylcyclopropenone with N-aminopyridinium iodide, in protic media, in the presence of a tertiary amine (diisopropylethylamine and triethylamine were found to be equally effective). A methanol solution of these reagents developed a wine-red coloring during several hours at room temperature. After 17 hr, the methanol was evaporated and the residue was purified by extraction and precipitation to give **5** as a crystalline solid in 95% yield. The structure assignment was suggested by the NMR spectrum ($CDCl_3$) which showed a sharp 3 H singlet at δ 3.65 (methyl ester), and by the infrared spectrum ($CHCl_3$), which exhibited prominent absorption at 3490, 3304, and 1660 cm^{-1}. A mild acid hydrolysis of **5** produced the known[4] β-keto ester **6**. Primary enamines analogous to **5** have been reported in the reactions of diphenylcyclopropenone with aziridines[5] and ammonia,[6] the cis configuration being assigned in both cases. Evidence has been presented[6] to suggest that the trans isomer, if formed in the reaction, would be expected to isomerize readily in solution.

The formation of **5** in the present study may be visualized as occurring by way of a 1,2 or 1,4 addition of methanol to an iminoketene intermediate (**4b**), formed by initial conjugate addition of **2b** on **1**. The general applicability of the reaction was demonstrated by considering various protic media. Thus, reaction in aqueous dioxane gave deoxy-