Chloromethylation Reactions. Reaction mixtures were prepared in clean glassware in a fume hood. In competitive studies, 0.05 mol of each aromatic was weighed into a flask and to it was added (calibrated Pasteur pipet) 0.005 mol of the reagent under study. The desired volume of a 0.5 M solution of $SnCl_4$ in cyclohexane (1.00 ml = 0.0005 mol of $SnCl_4$) was added and the flask transferred to the constant-temperature bath. After a predetermined heating period to allow the reactants to come to the bath temperature, the similarly prepared and thermostated solution of the chloromethylating agent was than added with good stirring. The mixtures were either quenched after a specified time or periodically sampled, as described previously.

GLC analysis of products (Aerograph 1200 with flame ionization detector) was carried out using the following columns: 15 ft × 0.125 in. in 5% bentone-34 + 1% DC-200, 60/80 mesh Chromosorb W, acid-washed (for separation of benzyl chloride and isomeric methylbenzyl chlorides) and 5 ft × 0.125 in. 5% SE-30, 80/120 mesh silanized acid-washed Chromosorb W (for separating dimethylbenzyl chlorides). Both columns gave good baseline separation allowing quantitative determination of isomers.

Calculation of product concentration was by the relative response method, and competitive rate ratios were determined from product ratios.

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Registry No.—BCME, 542-88-1; $SnCl_4$, 7646-78-8; bis-1,4-(chloromethoxy)butane, 13483-19-7; 1-chloro-4-chloromethoxybutane, 3970-17-0; mesitylene, 108-67-8; *s*-trioxane, 110-88-3; paraformaldehyde, 30525-89-4.

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Metathesis Catalysts. V. Competitive Character of Metathesis and Alkylation Reactions Catalyzed by Tungsten Hexachloride–Ethylaluminum Dichloride

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The olefin metathesis catalytic system WCl_6–$EtAlCl_2$ in an aromatic solvent promotes both olefin metathesis and solvent alkylation reactions. The yields of these two competitive reactions strongly depend on the relative concentration of the three compounds of the system (olefin, solvent, catalyst), with a marked dependence on the π donor ability of the aromatic solvent; moreover, our catalytic conditions can promote exclusive formation of monosubstituted benzenes at the thermodynamic equilibrium. The mechanism proposed involves competitive coordination equilibria of the solvent and of the olefin as the key step.

The use of WCl_6–$EtAlCl_2$ as a catalytic system for olefin metathesis reactions has been described by several groups.[1] This catalyst, which is also a strong Lewis acid, can consequently promote a variety of cationic reactions such as prototropic isomerizations,[2] oligomerization of olefins,[3] and alkylation of aromatic solvents.[4]

However, neither the specificity nor the optimal conditions for the competition between metathesis and cationic-like reactions have been thoroughly investigated; it is the goal of this paper to study the parameters which govern this competition between metathesis and alkylation processes.

Experimental Section

All solvent and olefins (*trans*-2-pentene, *trans*-4-octene, 1-octene, and 1-dodecene) were dried over $LiAlH_4$ or CaH_2 before distillation and the operations were conducted under an inert atmosphere (argon).

Ethylaluminum dichloride (Fluka), obtained as a 50% solution in hexane, was diluted (after titration) with the appropriate amount of hexane to obtain 0.2 M solutions.

Tungsten hexachloride (Fluka) was purified by sublimation of the volatile impurities ($WOCl_4$, WO_2Cl_2) before dissolution in the aromatic solvents, respectively benzene; *o*-, *m*-, *p*-xylenes; 1,2,4 and 1,3,5-trimethylbenzenes; and finally *o*-dichlorobenzene. The solutions obtained (0.05 M) are intensively colored: benzene, violet blue; toluene, blue; xylenes, green blue; trimethylbenzenes, green; dichlorobenzene, brown.

The different components were injected into the reaction vessel through a septum, together with an internal VPC standard (cyclooctane or undecane).

The solution of olefin in the suitable aromatic solvent was cooled to 5 °C and the appropriate amount of the aromatic solution of WCl_6 was added, immediately followed by the solution of $EtAlCl_2$ in hexane with a molar ratio Al to W kept equal to 4. After 1 min of reaction time, the system was quenched with water.

Quantitative VPC analysis was performed using a silicone column (20% SE-30 on Chromosorb 80/100) (flame ionization detector) and the yields calculated by comparison with the internal standard.

The different olefins and alkylated products have been identified by comparison with standard products which have been obtained from Fluka or by the following classical reaction sequence: addition of the suitable Grignard reagent on the corresponding α-ketoalkylbenzene gives a tertiary alcohol which is dehydrated on *p*-toluenesulfonic acid to a phenylalkene. Subsequent hydrogenation of the olefin on Raney nickel gives the required phenylalkane.

Moreover, some of the alkylated products have been isolated by preparative GLC and analyzed by mass spectrometry which shows a fragmentation pattern characteristic of alkylbenzenes; for in-

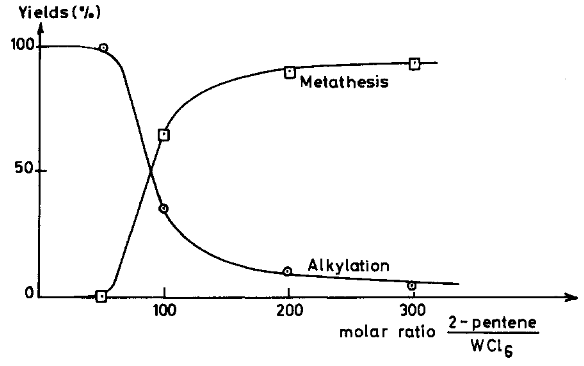

Figure 1. Yields of metathesis and alkylations reactions vs. molar ratio 2-pentene/WCl_6 for a constant molar ratio benzene/WCl_6 = 200.

stance, the 2-, 3- and 4-phenyloctanes have a parent peak at *m/e* 190 ($C_{14}H_{22}$) in addition to groups of peaks differing by 14 (CH_2) mass units.[5]

Results

1. Alkylation–Metathesis Competition in Benzene. We have already observed that the yields of metathesis or alkylated products depend on the ratios benzene to olefin, olefin to catalyst, and benzene to catalyst.[6]

Figure 1 reports the results obtained for a variation of the olefin concentration (with a constant ratio of benzene to catalyst). We have also previously reported[6] the influence of the variations of the concentration of the catalyst (for a constant ratio C_6H_6/olefin) on the relative yields of metathesis and alkylated products. In both cases, S-shaped curves are obtained and Figure 2 sums up the overall situation observed for the C_6H_6–2-pentene system.

It appears that both metathesis and alkylation reactions are competitive over a large range of concentrations, and that alkylation reactions increase with an increase of either the concentration of the catalyst or of the benzene to olefin ratio.

These results are given for a reaction time of 1 min. Longer times slowly increase the yields in alkylated products at the expense of metathesis, as indicated in Table I.

The composition of the mixture remains practically unaltered for several days after quenching with water.

2. Influence of the Nature of the Aromatic Solvent. Besides the relative concentration of the components of the system, the competition between alkylation and metathesis is greatly affected by the π-donor ability of the aromatic molecule used as solvent.[7] Increasing yields in alkylated compounds are observed in going from benzene to toluene, xylenes, and trimethylbenzenes (Table II).

On the other hand, our catalytic system does not alkylate *o*-dichlorobenzene; we then observe the formation of saturated polymers resulting from a cationic polymerization of the olefin, and only traces of alkylated products.

3. Distribution of the Alkylated Products. High concentrations of catalyst and large solvent/olefin ratios thus favor the alkylation of the aromatic solvent. If the latter is large enough, monoalkylated products are exclusively formed, which correspond to a thermodynamic equilibrium as calculated for molar ratio benzene/2-pentene larger than 4.

A similar effect has been noted by Popov[8] with a $NiCl_2$–$EtAlCl_2$ catalytic system although it is not always observed.

(a) $EtAlCl_2$ alone or the mixture WCl_6–$EtAlCl_2$ (the olefin being added to the preformed catalyst in benzene) give mixtures of mono- and polyalkylated benzenes, no change in product with time being observed (Table III, A and B).

(b) With WCl_6 alone at 50 °C or WCl_6–$EtAlCl_2$ (order of addition: benzene, olefin, WCl_6, and finally $EtAlCl_2$) di- and polyalkylated products quickly disappear to give exclusively monoalkylbenzenes (Table III, C, D, and E).

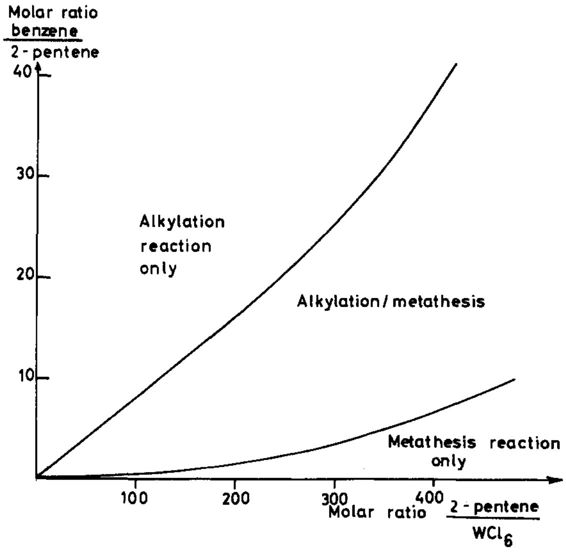

Figure 2. Competitive metathesis and alkylation reactions (after 1 min of reaction time).

Moreover, the thermodynamic distribution between monoalkylated products (in terms of isomers branching) does not depend on the position of the double bond in the original olefin (Table III, D, E).

Under the same catalytic conditions, independently prepared polyalkylbenzenes are quickly transformed to monoalkylbenzenes (Table III, F), but monoalkylbenzenes remain unaffected.

So there is a definite redistribution of polysubstituted benzenes to monoalkylated ones and the kinetics of this transalkylation reaction depend on the molar ratio of aromatic compound to olefin. For a ratio benzene/4-octene = 4, a quantitative formation of monoalkylated products is observed after a few days, but the same result is obtained in a few minutes if the ratio is increased up to 20 (Table III, D, G).

This potentially interesting alkylation redistribution process has been applied to industrial synthesis such as the preparation of monododecylbenzenes (detergent chemistry) and of monoethylbenzene (preparation of styrene). Indeed, 1-dodecene yields monoalkylbenzenes in a few minutes at room temperature (100% yield) when molar ratios benzene/olefin = 20 and olefin/catalyst = 50.

On the other hand, benzene and ethylene (molar ratio = 3, ethylene/catalyst = 50) give polyethylene (25%) and a mixture of mono- and polyethylbenzenes (75%) at room temperature. A few days at 60 °C increase the yield in ethylbenzene up to about 85%, but some diethylbenzenes and polymers remain present.

Discussion

It is well known that the active catalyst resulting from reaction of WCl_6 with $EtAlCl_2$ is a polynuclear species where both tungsten and aluminum atoms are associated via μ-chloride and/or μ-alkyl bonding.[9]

Moreover, the coordination of olefins[10] or of aromatic molecules[11] to tungsten carbonyl complexes or halogenides (WCl_6 and WF_6)[12] has been investigated. It was shown that, at least in the latter case, a rapid exchange process actually takes place.[12b,d]

On the other hand, we have studied the electronic spectra of WCl_6 in aromatic solvents such as, e.g., 1,2,4-trimethylbenzene, which shows three bands: two of these (355 and

Table I. Yields of Metathesis and Alkylation Reactions

$$\frac{\text{2-pentene}}{WCl_6} = 200 \quad \frac{\text{benzene}}{\text{2-pentene}} = 5 \quad \frac{Al}{W} = 4$$

				Alkylation, %			
	Metathesis, %			Monoalkylbenzenes			
Time, min	2-Butene	2-Pentene	3-Hexene	Ph-C_4	Ph-C_5	Ph-C_6	Di- and polyalkylbenzenes
0		100					
5	16	36	16	5	21	4	2
100	15	26	16	6	27	7	4
2400	11	20	12	8	33	11	5

Table II. Relative Yields of Metathesis and Alkylation Reactions in Function of the Aromatic Molecule (Reaction Time 1 min at 5 °C)

		Molar ratios				
Registry no.	Aromatic compd	$\frac{\text{2-Pentene}}{WCl_6}$	$\frac{\text{Aromatic}}{WCl_6}$	$\frac{\text{Aromatic}}{\text{2-pentene}}$	Yields of metathesis, %	Yields of alkylation, %
71-43-2	Benzene	50	200	4	0	100
		100	200	2	65	35
		200	200	1	90	10
		300	200	0.66	94	6
108-88-3	Toluene	100	200	2	0	100
		150	200	1.3	13	87
		200	200	1	67	33
		300	200	0.66	92	8
95-47-6	*o*-Xylene	50	200	4	0	100
		100	200	2	5	95
		200	200	1	42	58
		300	200	0.66	70	30
108-38-3	*m*-Xylene	100	200	2	0	100
		200	200	1	33	67
		400	200	0.5	80	20
		800	200	0.25	94	6
106-42-3	*p*-Xylene	100	200	2	0	100
		200	200	1	52	48
		300	200	0.65	72	28
		400	200	0.5	81	19
		800	200	0.25	96	4
95-63-6	Pseudocumene (1,2,4-trimethylbenzene)	100	200	2	0	100
		200	200	1	1	99
		400	200	0.5	30	70
		800	200	0.25	61	39
108-67-8	Mesitylene (1,3,5-trimethylbenzene)	100	200	2	0	100
		400	200	0.5	24	76
		600	200	0.33	34	66
		1200	200	0.16	67	33

460 nm, ϵ_{355} 6300 and ϵ_{460} 380 l. mol^{-1} cm^{-1}) correspond to electronic transitions of the WCl_6 molecules as observed in an inert solvent[9d,13] and the third one (570 nm, ϵ_{570} 690 l. mol^{-1} cm^{-1}) is assumed to be a charge transfer band from the aromatic molecule to the metal. The formation of such complexes is also supported by the different colors of the aromatic solutions (see Experimental Section).

Moreover, the coordination between the tungsten and the olefinic or aromatic molecules should be strengthened by a lowering of the oxidation state by $EtAlCl_2$[9] [W(VI) is reduced to W(V) or (IV)] owing to an increased back-bonding of the tungsten to the ligands.

The formation of a complex between the tungsten atom and the olefin in an aromatic solution thus involves a competition for the coordination sites of the metal. The relative importance of both tungsten–olefin and tungsten–aromatics complexes depends on the relative stability constants for their formation. This general problem is indeed a very complex one and has been reported by some authors which explains such competition by qualitative HSAB theory.[14]

The evolution of both olefin–tungsten and aromatics–tungsten complexes can respectively give metathesis or alkylation reactions. From a kinetic point of view these two reactions depend on the absolute concentrations and on the partial kinetic orders of the species in solution. Partial kinetic orders for metathesis are difficult to estimate with accuracy but activation energies of 6–8 kcal/mol have been found for this reaction.[15] On the other hand, values of about 10–16 kcal/mol are generally accepted for the alkylation of benzene[16] by secondary carbenium ions; of course, these values are given for quite different experimental conditions and they must be considered only as a crude indication. Nevertheless, a metathesis process should be lower in energy than an alkylation one.

Table III. Alkylation Reactions of Benzene[a]

	Molar ratio benzene/olefin	Molar ratio olefin/catalyst (1)	Time, min	Monooctylbenzenes, %			Dioctylbenzenes, %	Polyoctylbenzenes, %
				$\mathrm{Ph{-}C}{<}^{\mathrm{C}}_{\mathrm{C}_6}$	$\mathrm{Ph{-}C}{<}^{\mathrm{C}_2}_{\mathrm{C}_5}$	$\mathrm{Ph{-}C}{<}^{\mathrm{C}_3}_{\mathrm{C}_4}$		
A	30	20	1-1400	23	16	22	29	10
B	20	60	1	27	22	29	20	2
			15	29	22	34	14	1
			1400	29	23	31	16	1
C	30	30	900	42	28	29	1	
D	20	50	0.5	37	28	33	2	
			1	38	27	32	3	
			10	40	27	33		
			1400	44	27	29		
E	20	50	5	50	27	21	2	
			20	48	26	26		
			1400	43	33	24		
F	20	50	0	18	17	20	33	12
			5	23	14	23	31	9
			20	24	21	25	24	6
			190	42	25	33		
			1400	46	27	27		
G	4	50	3	24	16	21	35	4
			45	25	15	21	39	
			1400	37	23	29	11	
			4300	40	25	33	2	

[a] All reactions are performed at room temperature, except for WCl_6 alone for which a temperature of 50 °C is necessary to promote alkylation. Benzene and 4-octene are respectively used as the aromatic substrate and the olefin (except for experiment E where the olefin is 1-octene). (1) Molar ratio olefin/catalyst is calculated from the concentration of olefin and WCl_6 in the system. Nevertheless, for case A, this molar ratio is based on olefin and $C_2H_5AlCl_2$ concentrations. (A) The catalytic system used is $C_2H_5AlCl_2$ alone. (B) Catalytic system: WCl_6–$C_2H_5AlCl_2$ with addition order aromatic + WCl_6 + $C_2H_5AlCl_2$ + olefin. (C) Catalytic system: WCl_6 alone. (D–G) Catalytic system: WCl_6–$C_2H_5AlCl_2$ with addition order aromatic + olefin + WCl_6 + $C_2H_5AlCl_2$.

The mechanism of olefin metathesis reaction probably involves some tungsten–carbene complexes formed by alkylation of the tungsten atom in interaction with the organoaluminum compound. Such tungsten–carbene complex would react with a probably π-coordinated olefin via a four-atom metallocycle.[9a,17]

On the opposite, the coordination of one aromatic molecule on the tungsten complex prevents metathesis and promotes the alkylation reaction through a completely different pathway which would involve electrophilic substitution of aromatics by a secondary carbenium ion[18] and yields mono- and polyalkylated products for which the thermodynamic equilibrium depends on the initial molar ratio aromatic compound/olefin. When this ratio is greater than 4, monoalkylated products are exclusively formed.

The relative yields of metathesis and alkylation reactions thus depend on two parameters: the relative stability constants of the tungsten–olefin or aromatics π complexes and the relative rates of the alkylation and metathesis reactions.

The importance of the thermodynamic stability of the π complexes is strongly supported by the results quoted in Table II which show that the alkylation yields increase with the donor character of the aromatic ligand (for a constant molar ratio of olefin to aromatics), reflecting so the enhancement of the thermodynamic stability of the π complexes. On the other hand, the alkylation yields do not depend on the relative positions of the methyl substituents; for instance, there is almost no change in the relative reactivity of *o*-, *m*-, and *p*-xylenes. Therefore, in opposition to classical cationic alkylation of aromatics which takes place generally through a σ-type mechanism (characterized by a very large substituent effect),[19] our result is in agreement with the formation of a π tungsten–aromatics complex as the rate-determining step for the alkylation reaction.

The WCl_6–$C_2H_5AlCl_2$ system is therefore a very active and very selective catalyst for both metathesis and alkylation reactions: the relative importance of these two competing problems depends on the relative concentrations of the different components in the reaction mixture. Moreover, under the conditions which lead exclusively to alkylation, the WCl_6–$C_2H_5AlCl_2$ catalytic system is also very efficient for reaching rapidly the thermodynamic equilibrium between the different alkylated isomers.

Registry No.—$C_2H_5AlCl_2$, 563-43-9; WCl_6, 13283-01-7; *trans*-2-pentene, 646-04-8; *trans*-4-octene, 14850-23-8; 1-octene, 111-66-0; 1-dodecene, 112-41-4; ethylene, 74-85-1.

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Homoconjugation Interactions between Occupied and Unoccupied Molecular Orbitals. II

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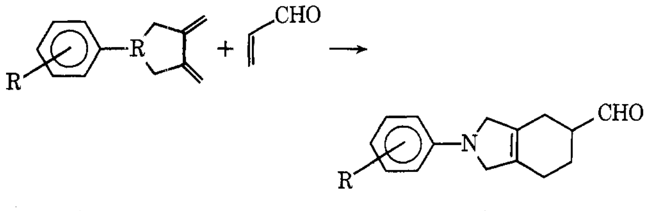
Perturbation molecular orbital theory is used to explain the homoconjugation interactions in systems in which the respective frontier molecular orbitals of the π moieties are of opposite symmetry. The theory predicts a hypsochromic shift in the uv wavelength maximum for such systems from reference compounds. No cases of unambiguous bathochromic λ_{max} shifts were found in the literature to contrast with the theory's prediction. Inductive effects and hyperconjugation were not the origin of the hypsochromic shifts. The prediction of uv data and photoelectron spectroscopy concerning through-space interactions is compared.

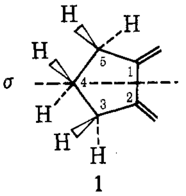
Homoconjugation between nonconjugated π-electron systems has received considerable attention over the last decade.[1] More recently, through-bond and hyperconjugation interactions have been shown to have an important role in certain cases.[1c–e,2] The use of perturbation molecular orbital theory to explain the homoconjugation in systems in which the respective frontier molecular orbitals (MO's) of the π moieties are of the same symmetry was demonstrated by Hofmann et al.[1d,e] Recently, we used the perturbation molecular orbital approach to explain the novel substituent effect in the Diels–Alder reaction between 1-(substituted phenyl)-3,4-dimethylenepyrrolidine, homoconjugated diene, and acrolein.[3] The respective frontier MO's of the π moieties of this exocyclic diene are of opposite symmetry (symmetric or asymmetric) with respect to the plane of symmetry which bisects the molecule. In this paper a general theory for predicting the effect of homoconjugation on the energy separation of the frontier MO's of π moieties whose respective frontier MO's are of opposite symmetry is developed.



Theory

The fundamentals of perturbation molecular orbital theory are as follows. (1) When two molecular orbitals interact (the molecular orbitals must be of the same symmetry), the lower energy molecular orbital is stabilized and the higher energy molecular orbital is destabilized. (2) The smaller the energy separation between the interacting molecular orbitals, the greater the interaction.

The application of this theory to homoconjugation systems with π moieties, whose respective frontier MO's are of opposite symmetry with respect to the plane of symmetry which bisects the molecule, will be first illustrated by the exocyclic dienes 1,2-dimethylenecyclopentane (**1**) and 3,4-dimethylenepyrrolidine (**2**). The relative energies of the frontier MO's of **1** and **2** are determined from orbital interaction diagrams of the CNDO/2 frontier MO's of 2,3-dimethyl-1,3-butadiene with those of methane[4] and ammonia. In **1**, both frontier MO's of methane (4-methylene moiety) interact with the LUMO of the hyperconjugated butadiene (Figure 1). The interaction between the σ^* and the LUMO-butadiene is more important; thus, a small decrease in the LUMO energy of **1** is expected as compared to *cis*-2,3-dimethyl-1,3-butadiene. However, the substitution of a heteroatom as in **2** for the 4-methylene moiety of **1** will replace the above molecular orbital interactions with a single molecular orbital interaction between the nonbonded



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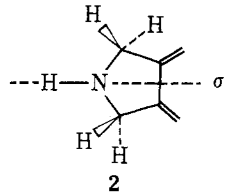

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