

Table VII. Competitive Chloromethylation of Benzene and Toluene with Formaldehyde Derivatives

Reagent/catalyst (mole ratio)	$k_{\text{PhMe}}/k_{\text{PhH}}^a$	Isomer distribution, %		
		Ortho	Meta	Para
Trioxane/SnCl ₄ ^b (5/1)	63	37	2	61
Trioxane/SnCl ₄ ^b (0.9/1)	7.8	55	5	40
Paraform/ZnCl ₂ ^{c,d} (6/1)	28.2	43	4	53
Paraform/ZnCl ₂ ^d (6/1)	40.3	40	3	57
Paraform/ZnCl ₂ ^e (6/1)	112	35	2	64

^a Analysis by GLC. ^b Mole ratio PhMe:PhH:s-trioxane = 12:1 at 65 °C (excess aromatic used as solvent). ^c Paraform = paraformaldehyde. ^d From the same reaction; fourth entry subjected to more extensive workup (both run at 65 °C in glacial acetic acid solvent; see text and note e). ^e Data of H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

products, particularly when considering the necessity of indirect uv spectroscopic analysis, after first converting the chloromethylated products to methylarenes by reduction with LiAlH₄. To this end their procedure for the competitive chloromethylation of benzene and toluene was repeated. For convenience the quantities of materials and the reaction time were reduced by a factor of 20 (while keeping molar ratios identical) and gaseous HCl was used from a lecture bottle (Matheson). The reaction mixture was divided into two parts for analysis. One part was washed with ice water, dried over CaSO₄, and analyzed by the direct GLC analytical method developed in our work for benzyl chlorides and methylbenzyl chlorides (see Experimental Section). The other portion was carried through the identical workup reported by Brown and Nelson: washings with ice water and with 10% aqueous potassium carbonate, extraction of washings with petroleum ether, drying of organic materials over calcium chloride-potassium carbonate, and removal of the petroleum ether and excess hydrocarbon by distillation at atmospheric pressure and at 95 mm. This portion was then analyzed by the same GLC method as used throughout in our work in contrast to Brown and Nelson's method of reducing the benzyl chlorides with LiAlH₄ to the corresponding methylbenzenes followed by uv spectroscopic analysis. It was necessary to dilute samples with carbon tetrachloride prior to GLC analysis, but this in no way affected the product composition.

The results of the chloromethylation reactions with formaldehyde derivatives are summarized in Table VII.

Turning first to the reactions with s-trioxane, it can be seen that the chloromethylations are indeed highly dependent on acidity (catalyst concentration) of the reaction systems. The fact that increased acidity has decreased the relative rate of reactions (cf. $k_{\text{toluene}}/k_{\text{benzene}} = 63$ vs. 7.8, with a 5.5-fold decrease in acid concentration) and also causes significant changes in the isomer distribution clearly indicates that at high acidity the reactivity of the system is higher than that observed at low acidity. This is compatible with an equilibrium-controlled increase in the concentration of the hydroxycarbenium or chloromethyloxonium ion, which would be expected to react more rapidly than a formaldehyde-proton acid complex. There is further evidence of this in the ortho/para ratios of the two reactions. In the low acidity reaction the methyl group plays a greater role in stabilizing the arenium-ion- (or σ -complex)-like transition state by conjugation, and the para isomer predominates ($o/p = 0.63$). This conjugative stabilization is less important in the high-acidity case where in the earlier transition state of arenium ion (or π -complex) nature the electrophile requires less contribution of the aromatic π electrons. As a consequence inductive stabilization predominates and the ortho/para ratio is high (1.38).

While the determination of the isomer distribution in the chloromethylation reactions was accurate (they are considered to be accurate to 1%), it is not possible to exclude some intramolecular isomerization in the arenium type transition states prior to deprotonation. This can be of significance, particularly in reactions with high catalyst concentrations, and affect the results through thermodynamically controlled factors.

Returning to the repetition of the Brown-Nelson experiments, it may be seen that there is less significant difference in the distribution of methylbenzyl chloride isomers from either the simple workup and direct GLC analysis (third entry, Table VII) or the original more elaborate workup (fourth entry, Table VII) or from the results Brown and Nelson reported (fifth entry, Table VII). These differences lie probably within experimental error of the methods used. Clearly, however, the same cannot be said of the relative rates determined from product compositions obtained from the two different workup procedures. The most probable explanation lies in the difficulty of separating chloromethylated products from excess aromatics by distillation without losses of the former, a factor obviously seriously affecting the data of Brown and Nelson. Judging from the difference in $k_{\text{toluene}}/k_{\text{benzene}}$ between these experiments, the removal of solvent causes some loss of the more volatile benzyl chloride. In fact, when the aromatic hydrocarbon forerun obtained from the Brown-Nelson workup procedure was subjected to GLC analysis, a significant amount of benzyl chloride was found in it. The more benzyl chloride lost, the higher the apparent value of $k_{\text{arene}}/k_{\text{benzene}}$.

Conclusions

The paucity of mechanistic information about the chloromethylation reaction led previously to somewhat contradictory results. In our studies we have been able to show that a wide range of selectivity exists for chloromethylations with varying reaction conditions and, therefore, no single set of data can characterize all electrophilic chloromethylation reactions. It is clear from our studies that toluene remains predominantly ortho/para directing in all chloromethylations with the change in meta substitution ranging from 1.5 to 5%, with simultaneous substrate selectivity, i.e., k_T/k_B ratio changes ranging from 15 to 320.

Experimental Section

Reagents. Aromatic hydrocarbons were of the highest purity available and were dried over molecular sieves prior to use. Benzene, toluene, alkylbenzenes, and all solvents used were spectral or highest purity grade, dried over molecular sieves. Stannic chloride was ACS reagent quality. Bis(chloromethyl) ether (Eastman Kodak) was obtained in sealed glass ampules (100 g). These ampules were open in a drybox, and the reagent was stored in and dispensed from Teflon bottles. 1,4-Bis(chloromethoxy)butane and 1-chloro-4-chloromethoxybutane were prepared as reported.⁹

Warning! Bis(chloromethyl) ether¹¹ and 1,4-bis(chloromethoxy)butane are toxic even in small quantities. In addition, bis(chloromethyl) ether has been shown to be a powerful carcinogen.¹² Because of its higher boiling point at atmosphere pressure, 1,4-bis(chloromethoxy)butane is considered a lesser inhalation hazard than bis(chloromethyl) ether, but all chloromethyl ethers (as well as other haloalkyl ethers and difunctional haloalkyl compounds such as haloalkyl tosylates, alcohols, etc) should be stored and dispensed in a fume hood, using rubber gloves and eye protection. Concentrated aqueous NaOH solution was used to hydrolyze material before disposal.

Equipment Used. Flasks and pipets used to contain and dispense the reagents were cleaned with H₂SO₄-K₂Cr₂O₇ solution, rinsed with distilled water, and dried in an oven. Kinetic measurements were carried out in thermostated solutions using a Haake F4291 circulating bath fitted with immersion heater and thermoregulator. This bath was capable of maintaining temperature with a precision of better than ± 0.1 °C.

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 SnCl₄ in cyclohexane (1.00 ml = 0.0005 mol of SnCl₄) 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 then 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 \times 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 \times 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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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 WCl₆-EtAlCl₂ 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 WCl₆-EtAlCl₂ 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 LiAlH₄ or CaH₂ 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 (WOCl₄, WO₂Cl₂) before dissolution in the aromatic solvents, respectively benzene; *o*-, *m*-, *p*-xylenes; 1,2,4-

Registry No.—BCME, 542-88-1; SnCl₄, 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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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 WCl₆ was added, immediately followed by the solution of EtAlCl₂ 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-

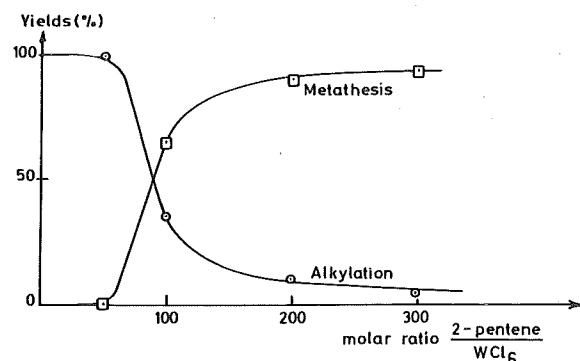


Figure 1. Yields of metathesis and alkylation reactions vs. molar ratio 2-pentene/WCl₆ for a constant molar ratio benzene/WCl₆ = 200.

stance, the 2-, 3- and 4-phenyloctanes have a parent peak at *m/e* 190 (C₁₄H₂₂) in addition to groups of peaks differing by 14 (CH₂) 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 reported⁶ the influence of the variations of the concentration of the catalyst (for a constant ratio C₆H₆/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 C₆H₆-2-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 Popov⁸ with a NiCl₂-EtAlCl₂ catalytic system although it is not always observed.

(a) EtAlCl₂ alone or the mixture WCl₆-EtAlCl₂ (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 WCl₆ alone at 50 °C or WCl₆-EtAlCl₂ (order of

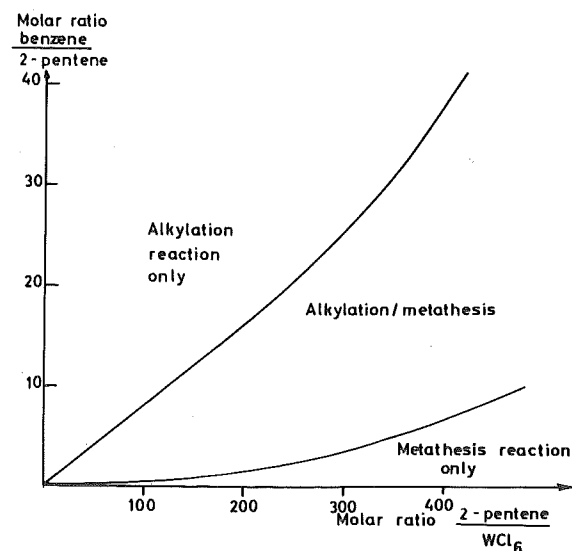


Figure 2. Competitive metathesis and alkylation reactions (after 1 min of reaction time).

addition: benzene, olefin, WCl₆, and finally EtAlCl₂) di- and polyalkylated products quickly disappear to give exclusively monoalkylbenzenes (Table III, C, D, and E).

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 WCl₆ with EtAlCl₂ 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 olefins¹⁰ or of aromatic molecules¹¹ to tungsten carbonyl complexes or halogenides (WCl₆ and WF₆)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 WCl₆ 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

$$\frac{2\text{-pentene}}{\text{WCl}_6} = 200 \quad \frac{\text{benzene}}{2\text{-pentene}} = 5 \quad \frac{\text{Al}}{\text{W}} = 4$$

Time, min	Alkylation, %						
	Metathesis, %			Monoalkylbenzenes			
	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)

Registry no.	Aromatic compd	Molar ratios			Yields of metathesis, %	Yields of alkylation, %
		2-Pentene/WCl ₆	Aromatic/WCl ₆	Aromatic/2-pentene		
71-43-2	Benzene	50	200	4	0	100
		100	200	2	65	35
		200	200	1	90	10
108-88-3	Toluene	300	200	0.66	94	6
		100	200	2	0	100
		150	200	1.3	13	87
95-47-6	<i>o</i> -Xylene	200	200	1	67	33
		300	200	0.66	92	8
		50	200	4	0	100
108-38-3	<i>m</i> -Xylene	100	200	2	5	95
		200	200	1	42	58
		300	200	0.66	70	30
106-42-3	<i>p</i> -Xylene	100	200	2	0	100
		200	200	1	52	48
		300	200	0.65	72	28
95-63-6	Pseudocumene (1,2,4-trimethylbenzene)	400	200	0.5	81	19
		800	200	0.25	96	4
		100	200	2	0	100
108-67-8	Mesitylene (1,3,5-trimethylbenzene)	200	200	1	1	99
		400	200	0.5	30	70
		800	200	0.25	61	39
		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 WCl₆ 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 EtAlCl₂⁹ [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-aromatic 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 benzene¹⁶ 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, %
				Ph-C ₆ H ₄ -C ₈ H ₁₇	Ph-C ₆ H ₃ (CH ₂) ₂ -C ₈ H ₁₇	Ph-C ₆ H ₂ (CH ₂) ₃ -C ₈ H ₁₇		
A	30	20	1-1400	23	16	22	29	10
B	20	60	1	27	22	29	20	2
			15	29	22	34	14	
C	30	30	1400	29	23	31	16	1
			900	42	28	29	1	
D	20	50	0.5	37	28	33	2	
			1	38	27	32	3	
E	20	50	10	40	27	33		
			1400	44	27	29		
F	20	50	5	50	27	21	2	
			20	48	26	26		
G	4	50	1400	43	33	24		
			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		
			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 WCl₆ 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 WCl₆ in the system. Nevertheless, for case A, this molar ratio is based on olefin and C₂H₅AlCl₂ concentrations. (A) The catalytic system used is C₂H₅AlCl₂ alone. (B) Catalytic system: WCl₆-C₂H₅AlCl₂ with addition order aromatic + WCl₆ + C₂H₅AlCl₂ + olefin. (C) Catalytic system: WCl₆ alone. (D-G) Catalytic system: WCl₆-C₂H₅AlCl₂ with addition order aromatic + olefin + WCl₆ + C₂H₅AlCl₂.

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 ion¹⁸ 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 WCl₆-C₂H₅AlCl₂ 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 WCl₆-C₂H₅AlCl₂ catalytic system is also very efficient for reaching rapidly the thermodynamic equilibrium between the different alkylated isomers.

Registry No.—C₂H₅AlCl₂, 563-43-9; WCl₆, 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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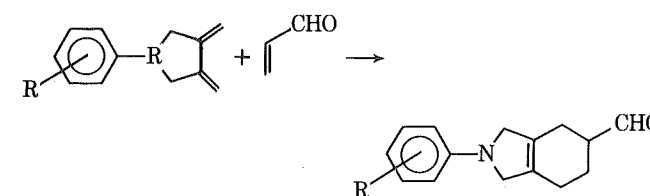
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Perturbation molecular orbital theory is used to explain the homoconjugation interactions in systems in which the respective frontier molecular orbitals of the π moieties are of opposite symmetry. The theory predicts a hypsochromic shift in the uv 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 fron-



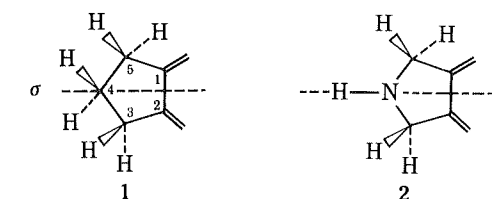
tier MO's of the π moieties of this exocyclic diene are of opposite symmetry (symmetric or asymmetric) with respect to the plane of symmetry which bisects the molecule. In this paper a general theory for predicting the effect of homoconjugation on the energy separation of the frontier MO's of π moieties 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 in-

teract (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 methane⁴ 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