Table IV. Transition Composition and Average Side-Chain Length

poly-soap	transition composn of long-chain alkyl unit, mol %	$\bar{L}^a$	$n\bar{L}^b$
4VP-C_8	40–50	4.4–5.0	35–40
4VP-C_{12}	10–13	3.0–3.3	36–40
4VP-C_{18}	ca. 3	2.5	45

[a] Calculated based on the assumption that all the pyridine units are quaternized by long-chain alkyl or ethyl groups. [b] See text; n is the length of long-chain alkyl groups.

plots of log k_d'' vs. $\bar{L}$ (Figure 5) are approximated by a linear relation (eq 5), although two points deviate to the lower side of the line (see the caption for Figure 5). This

$$\log k_d'' = 0.21L - 4.0 \quad (r = 0.945) \qquad (5)$$

equation reveals several interesting features of the polysoap catalysis. In the first place, the linearity implies that the hydrophobicity of the polysoap can be related to the average length of the alkyl group incorporated by quaternization. For example, the contribution of one docosyl group (C_{22}) is roughly equivalent to that of three octyl groups ($3 \times C_8$). The maximal catalytic efficiency is limited by the solubility of polysoaps. The highest $\bar{L}$ value (5.0) for the water-soluble polysoap (30 °C, no added salt) is achieved by the 4VP-C_8 polymer, whereas that of the 4VP-C_{22} polymer is at most 3.6. Further incorporation of the docosyl group to the 4VP-C_{22} polymer gave water-insoluble polymers. When compared at the same $\bar{L}$ value, the 4VP-C_8 polymer is more water soluble than the 4VP-C_{22} polymer. The octyl side chain produces an optimal balance between the water solubility and the formation of the hydrophobic domain.

Second, the slope of 0.21 in eq 5 implies that the increase in the $\bar{L}$ value by one CH_2 unit lowers the free energy of activation by 0.29 kcal/mol. This value is comparable to the hydrophobic contribution of one methylene unit to the free energy of the Michaelis complex formation (ca. 0.25 kcal/mol) observed in some polymer catalyses.[33,34] On the other hand, the intercept (i.e., $\bar{L} \doteq 0$) may correspond to the rate constant for poly(4-vinylpyridinium), which does not possess the alkyl pendent group. The k_d'' value estimated at $\bar{L} = 0$ from eq 5 (9.5×10^{-5} s^{-1}) is close to the k_d value for 4VP-C_2(84) (3.6×10^{-5} s^{-1}). The latter polymer shows a typical polyelectrolyte behavior.

We consider at this point the transition phenomenon between the polyelectrolyte and polymer micelle in terms of the $\bar{L}$ value. The transition composition and the corresponding $\bar{L}$ value (for the sake of simplicity, it is assumed that all the pyridine units are quaternized) are summarized in Table IV. It is seen that the polysoap with longer alkyl chains undergoes the transition at lower $\bar{L}$ values. The longer alkyl chain along the polymer backbone may interact with each other more easily than the shorter one. This will lead to shrinking of the polymer coil at low $\bar{L}$ values. Interestingly, the product of $\bar{L}$ times n is almost constant (40 ± 5, Table IV) at the transition. If one applies this value ($n\bar{L} = 40$) to the polysoap quaternized by the hexyl group, the transition would occur at the hexyl group content of 110 mol %. This is impossible, and even the completely hexylated poly(vinylpyridine) would not behave as polymer micelle. In fact, the 4VP-C_6(65) polymer (no ethylated unit) we prepared previously[7] behaved as a simple polyelectrolyte. The octyl group is probably the shortest alkyl chain which forms the micellar phase.

The concept of the average side-chain length is applicable only when the polysoap is not greatly perturbed by substrates. Thus, if bound reagents are strongly hydrophobic as in the case of the long-chain hydroxamate anion, the local hydrophobicity, but not the overall polymer hydrophobicity, becomes more influential.

Two-Site Model for Substrate Binding.[35] The substrate binding (and consequently the rate acceleration) is observed for polysoaps at the extent of alkyl substitution above and below the transition composition. Below the transition composition, the side-chain aggregation (i.e., formation of the micellar domain) is not appreciable, but substrate binding is obvious from the data of Figure 2. Substituted but randomly coiled (nonmicellar) polymers such as 4VP-C_6(65) bind 1 and increase the reaction rate about 30-fold, the same enhancement observed for polysoaps 4VP-C_8 and 4VP-C_{12} at a mole percent of alkyl substitution below the transition composition. When the mole percent of alkyl substitution exceeds the transition composition, a new, more condensed polysoap structure (micellar phase) is formed from portions of the polysoap chain, and these more hydrophobic regions also bind 1, producing a further enhancement in rate. The rate increase above the transition composition is gradual rather than discontinuous because the polysoap will have condensed and uncondensed regions that both bind 1 and catalyze its decarboxylation. This supposition is consistent with eq 5 in which log k_d'' is proportional to the average side-chain length. Appearance of the condensed region induces viscosity reduction. The lack of the transition composition for the acyl transfer reaction may also be explained by this model. The hydrophobic nucleophile can induce the transition to the more condensed structure either for the whole polysoap or at least in the vicinity of the substrate binding site.

Concluding Remarks

The poly(4-vinylpyridine) polysoap with systematically varied lengths and contents of the alkyl substituent was prepared for the first time and used as sites of catalysis. Two important conclusions are drawn from the present study: first, the overall hydrophobicity is expressed by the "average side-chain length"; second, the local hydrophobicity is more influential than the overall hydrophobicity when hydrophobic reagents are used. It is interesting that octyl-substituted poly(4-vinylpyridines) provide an optimal balance of water solubility and polymer hydrophobicity. This conclusion gives an important implication for the nature of the amino acid side chain. The interior of enzyme molecules is made to be strongly hydrophobic due to hydrophobic amino acid side chains. These side chains are C_4–C_8 components, and long alkyl chains are not involved in spite of their abundant availability in nature. The globular conformation of enzymes may be formed more conveniently by aggregation of the amino acid side chain of intermediate hydrophobicity, as implied by the superiority of the 4VP-C_8 polymer in the overall hydrophobicity.

Registry No. 1 acid, 28691-50-1; 4VP-C_8, 76010-13-4; 4VP-C_{12}, 76010-14-5; 4VP-C_{18}, 76024-65-2; 4VP-C_{22}, 76010-15-6; 4VP-C_2, 57033-24-6.

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Transition-Metal-Catalyzed Reactions of Diazo Compounds. 2.[1] Addition to Aromatic Molecules: Catalysis of Buchner's Synthesis of Cycloheptatrienes

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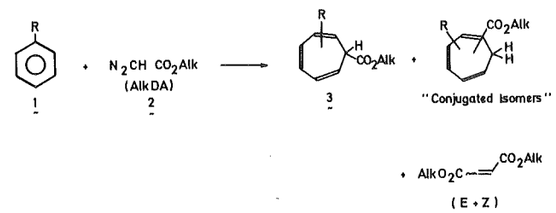
The addition of carbenes (generated from diazo esters) to aromatic molecules is efficiently catalyzed at room temperature by electron-poor Rh(II) carboxylates [tetrakis(perfluorocarboxylato)dirhodium(II)]. The reaction gives ready access to 1-carbalkoxycyclohepta-2,4,6-trienes (the kinetic *non*conjugated isomer) in very good yield. The observed regioselectivities are rationalized in terms of an attack of a highly electrophilic carbenoid species on the aromatic molecule. A competitive reduction of the catalyst simultaneously occurs and is responsible for a slow deactivation of the system.

Since Buchner's classical work, the chemistry of cycloheptatrienes has been adequately discussed in the literature. However, the problem of efficient and selective synthesis of substituted cycloheptatrienes is still unsolved. Indeed, because of the lability of the triene system, except for intramolecular reactions, a direct addition of carbenes to aromatic molecules produces hard-to-purify mixtures of isomers[2] (Scheme I). Our general investigations of transition-metal catalysis in carbene chemistry led to the discovery of the high efficiency of rhodium(II) carboxylates for promoting the insertion of carbenes into activated hydrogen bonds[3] and the cycloaddition to olefins,[4] acetylenes,[5] acrylonitriles,[6a] and carbodiimides.[6b] We now report that some Rh(II) complexes also catalyze carbene additions to aromatic substrates under mild conditions, allowing easy, resonably regioselective access to substituted cycloheptatrienes.

Scheme I



Results and Discussion

Rhodium(II) carboxylate catalyzed decomposition of alkyl diazoacetates (**2**, AlkDA) in a large excess of an aromatic substrate **1** produces cycloheptatrienes at room temperature. Yields are good, and the selectivity for the nonconjugated isomers **3** (Scheme I) is very high (>90%; see Tables I and II). The relative ratios of isomers (Table III), their yields, and their structures were determined by VPC and NMR (LIS) and are described in the Experimental Section. With benzene or toluene, **3** is formed practically quantitatively when the ratio of substrate to diazo ester is kept above 10 (typically 20).

The most efficient catalysts are specifically tetrakis(carboxylato)dirhodium(II) complexes of very strong organic acids such as trifluoroacetic and perfluorobenzoic acids. Indeed, a correlation is observed between the acidity of the metal counterions and the yields in **3** (R = H); e.g.: CF_3COOH, $pK_a = 0$, 100% of **3**; C_6F_5COOH, $pK_a = 1.5$, 89%; CH_3OCH_2COOH, $pK_a = 3.6$, 30%; CH_3COOH, $pK_a = 4.7$, 7%; $(CH_3)_3CCOOH$, $pK_a = 5$, 5%. Substitution of the aromatic nucleus somewhat decreases the overall yield of **3**, although the yield is also related to some extent to the bulkiness of the diazo ester alkoxy group, especially with substituted benzenes (Tables II and III). For example, with toluene a higher regioselectivity is clearly obtained with the more bulky diazo ester (Table III; with *t*-BuDA, the more sterically crowded 2-isomer is no longer formed). However, *tert*-butyl diazoacetate regularly gives

Table I. Formation of 1-Carbalkoxy-2,4,6-cycloheptatrienes (3) from 1 (100 mmol), Methyl Diazoacetate (MeDA, 5 mmol), and Rhodium(II) Trifluoroacetate (0.02 mmol) at 22 °C

substrate[a]	yield,[b,c] %	substrate[a]	yield,[b,c] %
benzene	100 (87)	anisole	73 (79)
toluene	95 (77)	chloro-benzene	72
o-xylene	80	fluoro-benzene	46
m-xylene	90	ethyl-benzoate	10
p-xylene	90	hexafluoro-benzene	~5
1,3,5-trimethyl-benzene	60	pyridine	0
indan	53 (59)		

[a] For the isomeric distribution, see Table III. [b] Relative to MeDA. [c] Values in parentheses refer to rhodium(II) perfluorobenzoate catalysis.

Table II. Effects of the Diazoacetate (AlkDA) and of the Catalyst on the Yields and Selectivities in Alkyl Cyclohepta-2,4,6-triene-1-carboxylates (3)[a]

substrates	diazo esters	catalysts: $Rh_2(O_2CCF_3)_4$	$Rh_2(O_2CC_6F_5)_4$	$Rh_2(O_2CR)_4$[b]
benzene	MeDA	100	87	85
	EtDA	98	89	76
	t-BuDA	80	84	51
toluene	MeDA	95	77	88
	EtDA	89	73	55
	t-BuDA	45	78	50

[a] Same reaction conditions as in Table I. [b] R stands for the 2,4-dichloro-3,5-dinitrophenyl group.

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0022-3263/81/1946-0873$01.00/0

Table III. Isomeric Distribution in Methyl Cycloheptatrienecarboxylates 3[a]

substrate	isomers[d]	isomeric distribution, %
benzene		100
toluene	4-methyl	56, 70,[b] 32[c]
	3-methyl	23, 15,[b] 13[c]
	2-methyl	17, 10,[b] 0[c]
o-xylene	2,3-dimethyl	18
	3,4-dimethyl	39
	4,5-dimethyl	43
m-xylene	2,4-dimethyl	12
	2,6-dimethyl	43
	3,5-dimethyl	43
p-xylene	2,5-dimethyl	85
	3,6-dimethyl	10
	others	5
anisole	3-methoxy	8
	4-methoxy	56
chlorobenzene	4-chloro	80
	3-chloro	15
	2-chloro	5
fluorobenzene	4-fluoro	80
	3-fluoro	12
	2-fluoro	8

[a] For the overall reaction yields and experimental conditions, see Table I. [b] Isomeric distribution observed with EtDA. [c] Isomeric distribution observed with *t*-BuDA. [d] All for 1-ester except entry for "others".

Table IV. Relative Reactivities of Substituted Aromatic Compounds in Competition against C_6H_6[a]

substrate	Rh(II)[b]	thermal[c]
chlorobenzene	0.1	0.84
fluorobenzene	0.46	0.80
benzene	1	1
toluene	1.10	1.06
anisole	1.16	1.15
o-xylene	1.6	
m-xylene	1.20	1.2
p-xylene	1.0	1.2

[a] Reaction conditions were the same as in Table I but with 100 mmol of each aromatic compound. [b] Rhodium(II) trifluoroacetate catalyzed competitions. [c] From ref 15, thermal decomposition of EtDA.

lower yields than methyl diazoacetate in rhodium(II) trifluoroacetate and rhodium(II) 2,4-dichloro-3,5-dinitrobenzoate catalyzed reactions. Strangely enough, the catalytic efficiency of rhodium(II) perfluorobenzoate seems unaffected by the nature of the diazo ester alkoxy group (Table III).

The synthetic interest of the method is further widened by the possibility of a direct and controlled functionalization of polymers. For example, polystyrene was readily converted into a polymer containing ester-substituted cycloheptatriene units in one single step (see Experimental Section).

The dimeric nature of rhodium(II) carboxylates is well established.[7] These diamagnetic complexes have only one coordination site per metal.[8] In fact, formation of highly electrophilic carbenoid species is expected with electron-poor carboxylates (carbenes are good σ donors, and poor

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(9) Mechanistically, the rhodium(II) acetate cyclopropanation of olefins was proposed to occur through a bimolecular attack of a Rh carbenoid on a noncomplexed olefin (see ref 4).

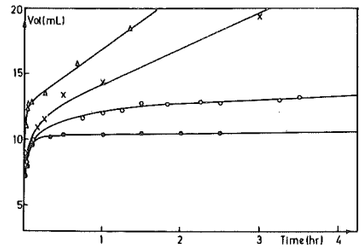

Figure 1. Evolution of N_2 against time in rhodium(II) trifluoroacetate catalyzed decompositions of *n*-BuDA (●), EtDA (○), and MeDA, X and Δ, respectively, 1.15×10^{-3} and 2.47×10^{-3} mol L^{-1} at − 12 °C in toluene.

metal retrodonation into the carbene empty p orbital is expected with strongly electron-withdrawing ligands). Indeed, the electrophilic character of the attacking species is evidenced by the results of the competitive experiments summarized in Table IV. There is always a preferential addition to the electron-rich molecule, although the reactive species is rather indiscriminate in its selection of substrates. Increasing alkyl substitution of the benzene nucleus does not necessarily further increase the selection of the electron-rich molecule (for competition between toluene and *p*-xylene, the relative reactivity is 1.06), revealing, in that case, dominance of steric over electronic effects. Fluorobenzene and especially chlorobenzene are notable exceptions, the catalytic system generating in those particular cases much more discriminating species than in its thermal counterpart.

The much lower yields observed in thermal and photochemical reactions relative to the catalyzed reactions (e.g., with EtDA thermal decomposition in C_6H_6 is 22% and photochemical decomposition is 39%; photochemical decomposition in toluene is 43%) might also be an indication against the generation of free carbenes in the presence of rhodium catalysts. Eventually the results of intermolecular competitions between benzene and cyclohexane also support the hypothesis of reacting carbenoids. In the latter case, while thermally or photochemically generated carbenes (from EtDA) do not discriminate between the substrates (overall yield <50%), the Rh-catalyzed decomposition shows a large selectivity for the addition to benzene (ratio of reacted C_6H_6 to C_6H_{12} of 6.5, overall yield >70%).

Whether the addition of the carbenoid to the aromatic molecule is concerted or takes place via a stepwise ionic mechanism as proposed by Müller and co-workers for the CuCl-catalyzed addition of methylene to aromates[10] remains to be answered. Since the reactions are observed to be much less sensitive to substituent effects than electrophilic aromatic substitution reactions, they might be classified as "concerted". This conclusion would imply that carbenoids undergo cycloadditions in a concerted fashion, a fact that has never been convincingly proved.[11]

We simply note that products expected to be formed in multistep mechanisms (e.g., phenyl acetate or molecules resulting from 1,3-dipolar addition of carbalkoxycarbene on an hypothetic arenium intermediate) are not observed.

The fate of the catalyst was next investigated. The original green rhodium(II) carboxylate is not recovered after reaction. Actually, all of the catalysts described in this study are slowly transformed into inactive species

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during the course of the reaction. TLC or column chromatography of the nonvolatile fraction of rhodium(II) trifluoroacetate catalyzed reaction only allowed isolation of noncrystalline fractions.[12] Modification of the catalyst was also evidenced by the kinetics of the reaction in toluene at −12 °C (measure of N_2 evolution, catalyst rhodium(II) trifluoroacetate). The fast initial N_2 evolution was followed by a slow step (Figure 1, break in the curve) corresponding to the formation of byproducts, mostly maleates, fumarates, and polyketocarbenes. In fact, the reaction completely stopped with *tert*-butyl diazoacetate. Moreover, the yield of **3** was directly related to the first part of the curve, and that approximately corresponded to 20 turnovers of the catalyst. The above system remained inactive for the formation of **3** even when warmed up to 25 °C. On the contrary, when the reaction was directly performed at 25 °C, carbene addition to toluene was kinetically sufficiently favored so as to perform the ring-enlargment reaction in good yield, a process requiring over 100 catalytic cycles. Deactivation of the catalyst is probably related to the formation of reduced rhodium species. Indeed, the reducing ability of diazo esters has been amply demonstrated.[13] Moreover, the electrochemical reduction of rhodium(II) trifluoroacetate is easy, and it was shown to be favored by 500 mV compared to the corresponding rhodium(II) acetate[14] and irreversibly led to stable yellow Rh(I) species.

Experimental Section

Analysis and purification of the cycloheptatrienes were carried out on Varian 3700 and 2800 gas–liquid chromatographs using, respectively, capillary (50 m × 0.25 mm, FFAP) and analytical (1.2 m × 5 mm) FFAP, 15% on Chromosorb W, 45-60 DMCS columns. The preparative separations were run on a 3 m × 9.5 mm, FFAP, 20% Chromosorb A 45-60 column: carrier gas He, 40 mL/min; temperature program from 70 to 230 °C at 15 °C/min. Aromatic solvents were distilled under nitrogen. Most reactions were carried out under N_2 at room temperature, but identical results were obtained when the reactions were run in the atmosphere. The catalysts were prepared according to Wilkinson's[16] or Johnson's[7] procedure. Rhodium(II) trifluoroacetate was further crystallized from benzene prior to use.

Tetrakis(pentafluorobenzoato)dirhodium(II). A 4.5-g sample of pentafluorobenzoic acid and 1 g of hydrated $RhCl_3$ were dissolved in 80 mL of ethanol. After dissolution, 0.8 g of NaOH was added and the mixture heated for 3 h under nitrogen. After the mixture was cooled and filtered, the insoluble fraction was further refluxed for 1 h in 80 mL of fresh ethanol. The liquid fractions were added and the solvent was evaporated under vaccum. The solid green residue was extracted with ether until colorless and chromatographed on SiO_2 (toluene–ether 9:1). A 1-g sample of complex was collected and dried in vacuo for 3 h [150 °C (10^{-2} mm)]: IR (KBr) 1655 (m), 1597 (s), 1525 (m), 1500 (s), 1433 (s), 1405 (s), 1297 (w), 1118 (m), 997 (s), 942 (w), 768 (m) cm^{-1}. Anal. Calcd for C, H (±0.5%).

Tetrakis(2,4-dichloro-3,5-dinitrobenzoato)dirhodium(II). A 250-mg sample of hydrated $RhCl_3$ and 3 g of 2,4-dichloro-3,5-dinitrobenzoic acid were dissolved in 100 mL of ethanol. After solubilization, 220 mg of sodium bicarbonate was added and the mixture refluxed under nitrogen for 2 h. After the mixture cooled, the deep green precipitate was filtered off. After a slow evaporation, the ethanol solution yielded a second crop of the same complex, which was washed twice with acetone and ether (yield 69%). Analytical samples were obtained by crystallization from chloroform (slow solubility): IR (KBr) 1617 (s), 1600 (s), 1555 (s), 1393 (s), 1335 (s), 1350 (s), 1110 (m), 425 (m) cm^{-1}. Anal. Calcd for C, N, H (±0.3%).

Preparation of Alkyl Cyclohepta-2,4,6-triene-1-carboxylates. General Procedure. The diazo ester (5 mmol) was added with an automatic syringe (Sage Model 352) to the aromatic substrate (0.1 mol) containing the catalyst (2×10^{-2} mmol) within approximatively 2 h while the mixture was stirred magnetically at room temperature. After absence of any residual absorption of the diazo group (2175 cm^{-1}) had been confirmed, the reaction mixture was analyzed by VPC using an internal standard (dimethyl fumarate or diethyl phthalate). In preparative experiments, the mixture was distilled under vacuum (10^{-2}–10^{-3} mm) at a relatively low temperature so as to minimize isomerization.

The isomeric mixture was then analyzed by VPC and IR and NMR spectroscopy. Typically, all the isolated cycloheptatrienes showed a nonconjugated ester absorption at 1740–1750 cm^{-1} in the IR (cf. 1720 cm^{-1} for an ester-conjugated isomer[18]) and C=C stretching in the range of 1630–1615 cm^{-1}. All the products gave satisfactory elemental analyses (C, H, ±0.5%).

Analysis of the Isomeric Distribution of the Cycloheptatrienes. The LIS technique was used for identifying the various isomers of substituted cycloheptatrienes. Variations of the H chemical shifts were recorded for various concentrations of the europium complex (ratios of Eu to substrates of 0.05, 0.1, 0.2, and 0.5). The paramagnetic complex used was $Eu(DPM)_3$ [(2,2,6,6-tetramethylheptane-3,5-dionato]europium(III). The results of the analysis are summarized hereafter for the methyl esters.

For toluene as substrate:[17] ^1H NMR ($CDCl_3$, Me_4Si) δ 6.6–4.4 (5 H, olefinic H); 3.77, 3.76, and 3.74 (three s, 3 H, 3 different OCH_3), 2.87 (d, 1 H, ^3J = 7 Hz), 2.56 (t, 1 H, ^3J = 6 Hz), 2.24 (t, 1 H, ^3J = 6 Hz, three different C**H**COOCH_3). The doublet at δ 2.87 is attributed to the H on the sp^3 C of the 2-CH_3-substituted isomer (17%; see Table III). The triplet at δ 2.24 is attributed to the corresponding 3-CH_3 isomer (23%) and the triplet at δ 2.56 to the same H of the 4-CH_3 isomer (56%), a chemical shift very close to that of the unsubstituted 1-(carbomethoxy)cycloheptatriene **3**. Moreover, the relative areas also correspond to those of the ester group (OCH_3; see below). The CH_3 groups absorbs at δ 2.06 (4-isomer) and 1.96 (2- and 3-isomers). The above assignments have been checked by the use of $Eu(DMP)_3$. Resolution of the previously ill-resolved CH_3 and OCH_3 signals then became distinct and allowed us to conclude that (1) a CH_3 at the 2-position is more deshielded than the other ones; (2) the H-1 and OCH_3 chemical shifts of both the 4- and 7-methyl-substituted isomers are identical; (3) the influence of the paramagnetic ion is smaller on the 2-CH_3 isomer than on the 3- and 4-isomers, and steric hindrance by a methyl on carbon 2 destabilizes the complex; and (4) the deshielding of the olefinic proton also allowed some attributions: 6.1 and 6.38, H-4, H-5 or H-3, H-6; 5.28, H-2 and H-7 of the 4-Me-substituted cycloheptatriene; 4.69 and 4.97, H-2 and H-7 of the 3-Me isomer. The remaining signals could not be assigned.

For *p*-Xylene as Substrate.[18a,b] **Methyl 2,5-dimethylcyclohepta-2,4,6-triene-1-carboxylate:** yield 85%; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.89 (s, 3 H, 2-CH_3), 2.01 (s, 3 H, 5-CH_3) 2.86 (s, ^3J = 7 Hz, 1 H, CHCOOMe), 3.65 (s, 3 H, $COOCH_3$), 6.5–5.5 (m, 4 H, olefinic H). For the **3,6-dimethyl isomer:** yield 10%; ^1H NMR δ 1.92 (s, 6 H, 2 CH_3), 2.26 (t, ^3J = 6 Hz, 1 H, C**H**COOCH_3), 3.71 (s, 3 H, OCH_3).

For *m*-Xylene as Substrate.[18a,b] **Methyl 2,4-dimethylcyclohepta-2,4,6-triene-1-carboxylate:** yield 12%; ^1H NMR

(12) The elemental analysis of those fractions was close to $Rh_2(O_2C-CF_3)_4N_2(CHCO_2CH_3)_{12}$. A product corresponding to $N_2(CHCO_2Et)_{12}$ has been isolated by Forbes after decomposition of EtDA in an alkane: Forbes, A. D.; Wood, J. *J. Chem. Soc. B* **1971**, 646.
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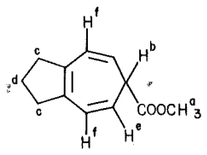
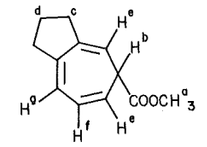
($CDCl_3$, Me_4Si) δ 1.92 (s, 3 H, 2-CH_3), 2.02 (s, 3 H, 4-CH_3), 3.71 (s, 3 H, OCH_3), 2.86 (d, ^3J = 7 Hz, 1 H, $CHCOOCH_3$). For the **2,6-dimethyl isomer:** yield 43%; 1.92 (s, 6 H, 2- and 6-CH_3), 2.89 (d, 1 H, ^3J = 7 Hz, $CHCOOCH_3$), 3.71 (s, 3 H, $COOCH_3$). For the **3,5-dimethyl isomer:** yield 43%; 1.92 (s, 3 H, 3-CH_3), 1.96 (s, 3 H, 5-CH_3), 2.08 (t, 1 H, ^3J = 7 Hz, $CHCOOCH_3$), 3.72 (s, 3 H, $COOCH_3$). **For *o*-Xylene as Substrate. Methyl 4,5-dimethylcyclohepta-2,4,6-triene-1-carboxylate:** yield 43%; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.93 (large s, 6 H, 4- and 5-CH_3), 2.23 (t, 1 H, $CHCOOCH_3$), 3.74 (s, 3 H, $COOCH_3$), 4.73 (dd, 2 H, ^3J = 5, 8 Hz, H-2 and H-7), 5.99 (d, ^3J = 8 Hz, 2 H, H-3 and H-6). For the **3,4-dimethyl isomer:** yield 39%; ^1H NMR ($CDCl_3$, Me_4Si) 1.93 (s, 3 H, 3-CH_3), 1.99 (s, 3 H, 4-CH_3), 2.15 t, 1 H, $=CHCOOCH_3$), 3.74 (s, 3 H, CO_2CH_3), 4.57–5.13 (m, 2 H, H-2 and H-7), 5.95–6.61 (m, 2 H, H-5 and H-6). For the **2,3-dimethyl isomer:** yield 18%; ^1H NMR ($CDCl_3$, Me_4Si) 1.82 (s, 3 H, 2-CH_3), 1.86 (s, 3 H, 3-CH_3), 2.69 (d, 1 H, $=CHCOOCH_3$), 3.68 (s, 3 H, $COOCH_3$), 5.65–6.65 (m, 4 H, olefinic H).

For Anisole as Substrate.[18a,c] **Methyl 4-methoxycyclohepta-2,4,6-triene-1-carboxylate:** yield 56%; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.58 (t, 1 H, ^3J = 6 Hz, $=CHCOOCH_3$), 3.56 (s, 3 H, OCH_3), 3.68 (s, 3 H, $COOCH_3$), 5.05–5.64 (dd, ^3J = 6, 10 Hz, H-2 and H-7), 5.64–6.36 (m, other olefinic H). For the **2-methoxy isomer:** yield 29%; ^1H NMR ($CDCl_3$, Me_4Si) δ 3.08 (d, 1 H, $CHCOOCH_3$), 3.53 (s, 3 H, OMe), 3.61 (s, 3 H, $COOCH_3$), 5.40–5.93 (m, 2 H), 6.20–6.60 (m, 2 H), 6.63–7.20 (m, 1 H). For the **3-methoxy isomer:** yield 8%; 1.58 (t, 1 H, $=CHCOOCH_3$), 3.56 (s, 3 H, OMe), 3.67 (s, 3 H, COOMe). **For Chlorobenzene as Substrate. Methyl 4-chlorocyclohepta-2,4,6-triene-1-carboxylate** yield 80%; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.70 (t, 1 H, ^3J = 6 Hz, $=CHCOOCH_3$), 3.77 (s, 3 H, $COOCH_3$), 6.80 (d, ^3J = 7 Hz, H-5). For the **3-chloro isomer:** yield 15%; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.49 (t, 1 H, ^3J = 6 Hz, $=CHCOOCH_3$), 3.76 (s, 3 H, $COOCH_3$), 5.16 (d, 1 H, H-2). For the **2-chloro isomer:** yield 5%; ^1H NMR ($CDCl_3$, Me_4Si) δ 3.47 (d, 1 H, ^3J = 7 Hz, $=CHCOOCH_3$), 3.70 (s, 3 H, $COOCH_3$). **For Indan as Substrate. Isomer A:** yield 40%; ^1H NMR ($CDCl_3$, Me_4Si) δ 3.74 (s, 3 H, CH^a_3), 5.34 (dd, 2 H, ^3J = 6, 10 Hz, H^e), 6.17 (d, 2 H, ^3J = 10 Hz, H^f), H^b was visible at high Eu concentration and appeared as a triplet, 1.68–2.14 (m, 2 H, CH^d_2), 2.26–3.35 (m, 4 H, CH^c_2).



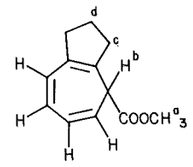
A

Isomer B: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.72 (s, 3 H, $COOCH_3$), the protons b, c, and d have the same attribution as those for isomer A, 4.94 (m, 2 H, H^e), 6.52–6.0 (m, 2 H, H^f and H^g).



B

Isomer C: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.22 (d, 1 H, ^3J = 7 Hz, H^b) 3.67 (s, 3 H, $COOCH_3$). The CH^c_2 and CH^d_2 signals were same as above; the remaining olefinic H could not be assigned.



C

Application to Polystyrene. (a) Solution in C_6H_6. A 0.610-g sample of EtDA was slowly added at room temperature to a solution of 1 g of polystyrene (mol wt 40 000, $M_w/M_n < 1.1$), in 10 mL of C_6H_6 containing 10 mg of rhodium trifluoroacetate. The resulting polymer (0.84 g), twice reprecipitated from methanol and dried in vacuo, shows an IR absorption at 1745 cm^{-1}. Its elemental analysis (C, 90.6; H, 8.0) indicates a 10% incorporation of the carbalkoxycarbene.

(b) Solution in $CHCl_3$. The same procedure was used as in part a, but the solvent was $CHCl_3$. The analysis of the reprecipitated polymer (C, 91.7; H, 8.3) corresponds to a 3.7% functionalization.

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Registry No. 3 (R = 4-methyl; Alk = Me), 75862-71-4; **3** (R = 4-methyl; Alk = Et), 75862-72-5; **3** (R = 4-methyl; Alk = *t*-Bu), 75862-73-6; **3** (R = 3-methyl; Alk = Me), 75862-74-7; **3** (R = 3-methyl; Alk = Et), 75862-75-8; **3** (R = 3-methyl; Alk = *t*-Bu), 75862-76-9; **3** (R = 2-methyl; Alk = Me), 75862-77-0; **3** (R = 2-methyl; Alk = Et), 75862-78-1; **3** (R = 2,3-dimethyl; Alk = Me), 75862-79-2; **3** (R = 3,4-dimethyl; Alk = Me), 75862-80-5; **3** (R = 4,5-dimethyl; Alk = Me), 75862-81-6; **3** (R = 2,4-dimethyl; Alk = Me), 75862-82-7; **3** (R = 2,6-dimethyl; Alk = Me), 75862-83-8; **3** (R = 3,5-dimethyl; Alk = Me), 75862-84-9; **3** (R = 2,5-dimethyl; Alk = Me), 75862-85-0; **3** (R = 3,6-dimethyl; Alk = Me), 75862-86-1; **3** (R = 3-methoxy; Alk = Me), 75862-87-2; **3** (R = 4-methoxy; Alk = Me), 75862-88-3; **3** (R = 4-chloro; Alk = Me), 75862-89-4; **3** (R = 3-chloro; Alk = Me), 75862-90-7; **3** (R = 2-chloro; Alk = Me), 75862-91-8; **3** (R = 4-fluoro; Alk = Me), 75862-92-9; **3** (R = 3-fluoro; Alk = Me), 75862-93-0; **3** (R = 2-fluoro; Alk = Me), 75862-94-1; benzene, 71-43-2; toluene, 108-88-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; anisole, 100-66-3; chlorobenzene, 108-90-7; fluorobenzene, 462-06-6; tetrakis(trifluoroacetato)dirhodium(II), 31126-95-1; tetrakis(pentafluorobenzoato)dirhodium(II), 75863-37-5; tetrakis(2,4-dichloro-3,5-dinitrobenzoato)dirhodium(II), 75863-38-6; methyl diazoacetate, 6832-16-2; ethyl diazoacetate, 623-73-4; (1,1-dimethylethyl) diazoacetate, 35059-50-8; **3** (R = H; Alk = Me), 32399-46-5; **3** (R = H; Alk = Et), 27332-37-2; **3** (R = H; Alk = *t*-Bu), 75862-95-2; pentafluorobenzoic acid, 602-94-8; trichlororhodium, 10049-07-7; 2,4-dichloro-3,5-dinitrobenzoic acid, 52729-03-0; polystyrene, 9003-53-6; indan, 496-11-7; methyl 1,2,3,6-tetrahydro-6-azulenecarboxylate, 75862-96-3; methyl 1,2,3,5-tetrahydro-5-azulenecarboxylate, 75862-97-4; methyl 1,2,3,4-tetrahydro-4-azulenecarboxylate, 75862-98-5; 1,3,5-trimethylbenzene, 108-67-8; **3** (R = 2,4,6-trimethyl; Alk = Me), 75862-99-6; ethyl benzoate, 93-89-0; hexafluorobenzene, 392-56-3; **3** (R = hexafluoro; Alk = Me), 75863-00-2; **3** (R = 4-carbethoxy; Alk = Me), 75863-01-3; **3** (R = 3-carbethoxy; Alk = Me), 75863-02-4; **3** (R = 2-carbethoxy; Alk = Me), 75863-03-5.

Rearrangement of 1-Azidoadamantane to 3-Aryl-4-azahomoadamantane in the Presence of Aluminum Chloride and Aromatic Substrates[1]

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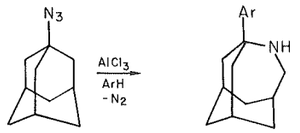
Reaction of 1-azidoadamantane (**1**) with aromatic substrates in the presence of aluminum chloride at 80 °C for 1.25 h gave the corresponding 3-aryl-4-azahomoadamantane (**2**) in >90% yield. The reaction of **1** to **2** represents the first report of intermolecular aminoalkylation of aromatics in the benzene series, presumably from an imine intermediate. At 18 °C, only 3-hydroxy-4-azahomoadamantane is obtained. Addition of water to the reaction system at 80 °C yielded 1-phenyladamantane (**4**) as the major product. Mechanistic features are treated.

The literature contains relatively few reports on the reactions of organic azides in the presence of Lewis acids and aromatic substrates. Whereas aryl,[3-5] acyl,[5,6] sulfonyl,[5] α-carbonyl,[7] and alkoxycarbonyl[8,9] azides are reported to react primarily with evolution of nitrogen gas, yielding N-substituted anilines, alkyl azides may also undergo elimination of azide ion.[5,10] The resulting products from reactions of the alkyl azides with aluminum chloride in benzene were *N*-alkylanilines, imines from rearrangement, or alkylbenzenes.[10] The imines apparently did not participate in Friedel–Crafts alkylation. In fact, intermolecular aminoalkylation of aromatic substrates with imines is extremely rare.[11]

In the present study, we report the first reaction of an alkyl azide with aromatic compounds catalyzed by aluminum chloride, resulting in rearrangement followed by aminoalkylation of the aromatic reagents. In addition, we explore the crucial effect of temperature and catalyst on the nature of the product. Mechanistic features are treated.

Results and Discussion

1-Azidoadamantane (**1**) was prepared by a modified published procedure.[12] Exposure of **1** at 80 °C for 1.25 h to aluminum chloride in the presence of an aromatic substrate (Table I) resulted in formation of the corresponding 3-aryl-4-azahomoadamantane (**2**) in >90% yield (eq 1). When the reaction of **1** is carried out in the absence



(1)

1 **2a**, Ar = C_6H_5; **b**, Ar = $C_6H_4CH_3$

Table I. Reaction of **1** with $AlCl_3$ and C_6H_5Y[a]

C_6H_5Y		**1**		$AlCl_3$,	
Y	mol × 10^3	mol × 10^3	mol/L × 10^2	FW × 10^3	product %[b]
H	281	1.70	6.81	15.0	**2a**, 98
H	281	1.70	6.81	15.0	**2a**, 99[c]
H	518	2.27	4.93	22.5	**2a**, 97
H	844	5.67	7.56	45.0	**2a**, 92
CH_3	235	1.70	6.81	15.0	**2b**, 90[e]
CH_3	235	1.70	6.81	15.0	**2b**, 92[c]
CH_3	442	2.27	4.83	22.5	**2b**, 91
CH_3	706	5.67	7.56	45.7	**2b**, 94
CH_3	1442	2.27	1.51	7.5	**2b**, 94[d]

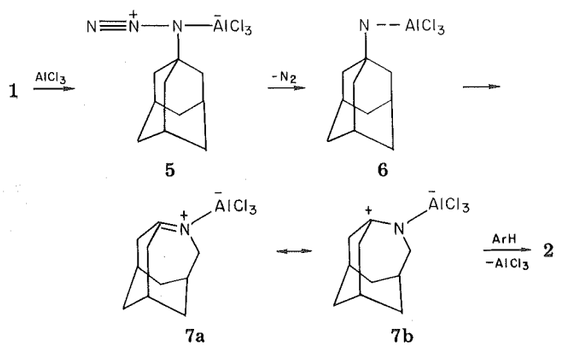
[a] General procedures A, nonhomogeneous. [b] Isolated yield of pure product. [c] Under N_2. [d] Homogeneous.

Table II. Effect of Temperature on the Reaction of **1** with $AlCl_3$ and C_6H_6[a-d]

temp, °C	% yield		temp, °C	% yield	
	2[e]	**3**[f]		**2**[e]	**3**[f]
18		94	60	23	74
50	10	79	70	80	16

[a] General procedures A (nonhomogeneous). [b] **1**, 2.27 × 10^{-3} mol (6.35 × 10^{-2} mol/L) for all runs. [c] $AlCl_3$, 2.25 × 10^{-2} mol. [d] C_6H_6, 450 × 10^3 mol; 1.25 h. [e] Isolated yield of pure products. [f] Isolated yield of crude product.

Scheme I



of the Lewis acid catalyst (24 h at 80 °C), approximately 86% **1** is recovered with no **2** present. At room temperature (1.25 h) in the presence of the catalyst, only 3-hydroxy-4-azahomoadamantane (**3**) was isolated. Table II contains data on the effect of temperature. Alkyl azides are generally considered to be thermally stable at room temperature, but at temperatures in excess of 100 °C nitrogen gas is eliminated in a first-order, homogeneous

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