was evaporated to dryness and the residue was washed with ether to give the pure adduct **20** (0.022 g, 72%), mp 295–296° dec (lit.[3] mp 296–297°).

Reaction of 1,2-Diphenylanthra[*b*]cyclobutadiene (4) with 1,3-Diphenylisobenzofuran (19). A solution of **4** (0.0354 g, 0.1 mmol) and furan **19** (0.027 g, 0.1 mmol) in dichloromethane (1.5 ml) was allowed to stand at room temperature for 30 hr. The resulting mixture was chromatographed (neutral I alumina, benzene eluent) to give 0.025 g (70%) of hydrocarbon **4**, identical with an authentic sample.

Acknowledgment. We thank the National Science Foundation for a grant (GP 24057X) in support of this research.

Registry No. **2**, 4023-74-9; **4**, 49626-41-7; **5**, 7149-49-7; **6**, 36229-72-8; **7**, 49626-44-0; **8**, 49626-45-1; **12**, 24234-76-2; **13**, 49626-46-2; **16**, 49626-47-3; **17**, 49626-48-4; **18**, 42189-19-5; **23**, 49626-50-8; **24**, 49626-51-9; *o*-xylylenebis(triphenylphosphonium bromide), 1519-46-6; [2,3-naphthalenediylbis(methylene)]bis(triphenylphosphonium bromide), 39013-98-4; tetracyanoethylene, 670-54-2; 4-phenyltriazoline-3,5-dione, 4233-33-4; phenylacetylene, 536-74-3.

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Cyclopropanols. XI. Acid-Catalyzed Ring Opening of Arylcyclopropanols

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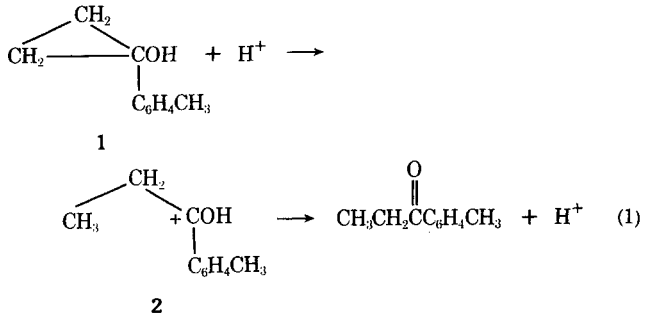
Rates of acid-catalyzed ring opening of a series of 1-arylcyclopropanols and of 1-phenyl-2-arylcyclopropanols and their acetates have been measured in several solvents. The effect of substituents on the rate for the former series is moderately large ($\rho = -1.5$) but substituents in the 2-aryl group have almost no effect on the acid-catalyzed cleavage of the 1,2 bond. Substituents in the 1-aryl ring have little effect on the rates of base-catalyzed cleavage of 1-arylcyclopropanols. The implication of these results on the mechanism of cyclopropane ring cleavage by acids and bases is briefly discussed.

The cleavage of the carbon–carbon single bond of a cyclopropane by electrophiles is a reaction of some mechanistic interest.[1] Stereochemical studies have shown that the ring-opening reaction with a proton can occur with either retention[2] or inversion[3] of configuration, and, while Markovnikov's rule is followed in a broad sense,[4] the tendency for a proton to add to the least substituted carbon atom of the ring is not great.[1] Even an example of complete anti-Markovnikov cleavage has been reported.[5]

Only a very few actual kinetic studies on electrophile ring openings of cyclopropanes have been reported,[6-8] and these have not been especially revealing about the nature of the transition state for the reaction. In this paper we report some studies on the rates and direction of ring opening of a series of aryl-substituted 1-phenyl- and 1,2-diphenylcyclopropanols.

Results and Discussion

Our initial studies were with 1-(*p*-tolyl)cyclopropanol (**1**), since this molecule is crystalline and undergoes ring opening (eq 1) at a convenient rate for study over a large range of acid concentrations. The reaction rate is easily followed by ultraviolet spectroscopy, since the propiophenone product absorbs strongly and the cyclopropanol does not.



1

(1)

2

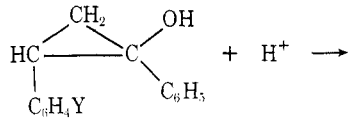
The rate constants for the ring opening of **1** of 60:40 vol. % dioxane–water as a function of perchloric acid concentration are given in Table I. The most important conclusion is that the reaction is first order in both cyclopropanol and in acid. Bunton and coworkers[9] have determined values for the Hammett acidity function in this solvent system; a plot of log k *vs.* H_0 gives a slightly better straight line than a similar plot *vs.* pH. However, in view of the difficulties of drawing mechanistic conclusions from such plots, we will not comment further.

To determine something about the amount of charge which develops on the benzylic carbon in the transition state, the rate of ring opening of a series of 1-arylcyclopropanols was determined in 60:40 dioxane–water and 1.45 *M* $HClO_4$. The results are given in Table II. These rate data indicate that a positive charge is present in the transition state, although not a particularly large one. The correlation of rate with σ is better than with σ^+; ρ for the former is -1.46 and ρ^+ for the latter is -0.755. Stewart and Yates[10] have measured the pK_a's of 20 substituted acetophenones in H_2SO_4. The protonated forms of these ketones resemble **2**, which might have been suggested as a reasonable model for the transition state of the ring-opening reaction. Plotted against σ^+ these pK_a data gave $\rho^+ = -2.17$ and, slightly less satisfactorily, against σ, $\rho = -2.22$. Both values are significantly larger than those measured for the ring opening.

Table I
Rate of the Acid-Catalyzed Ring Opening of 1-(*p*-Methylphenyl)cyclopropanol in 60:40 Vol. % Dioxane–Water at 50°

$[HClO_4]$, mol/l.	pH	H_0	$k \times 10^5$	Log k
0.552	+0.276	1.31	1.01 ± 0.05	−4.914
1.005	−0.002	0.67	2.75 ± 0.11	−4.561
1.019	−0.005	0.67	2.69 ± 0.07	−4.570
1.801	−0.256	−0.05	9.44 ± 0.30	−4.025
1.819	−0.260	−0.07	10.3 ± 0.4	−3.987
2.483	−0.395	−0.70	26.4 ± 0.4	−3.578
2.483	−0.395	−0.70	26.7 ± 1.1	−3.573
3.455	−0.538	−1.45	81.0 ± 2.7	−3.092
3.455	−0.538	−1.45	87.0 ± 1.9	−3.061
3.990	−0.601	−1.84	172.0 ± 5.0	−2.764
3.990	−0.601	−1.84	167.0 ± 4.0	−2.772

In an attempt to gain insight into events occurring at the carbon to which the electrophile becomes attached, studies were made on the rates and direction of ring opening of 2-aryl-1-phenylcyclopropanols and their acetates (eq 2). The acetates were chosen for the most extensive study



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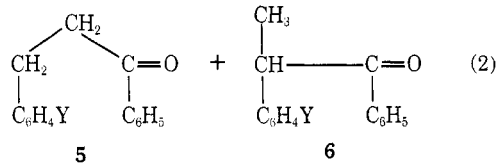

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rather than the alcohols when it was found that the latter are exceedingly difficult to purify because they undergo base-catalyzed ring opening so readily, especially when the 2-aryl group is substituted by electron-withdrawing groups, and because both give identical product ratios on opening. The cyclopropanols themselves, however, undergo acid-catalyzed ring opening at a slightly slower rate than do the acetates, under the conditions studied, so that the acetates are not hydrolyzing to alcohols under the reaction conditions. Landgrebe[11] has also noted the greater rate of ring opening for a 1-arylcyclopropyl acetate than for the corresponding alcohol.

Table III shows the rates and direction of ring opening in compounds **4**. The first thing to be noted is the great predominance of cleavage between the two aromatic rings. In earlier work[2] we showed that 2-phenyl-1-methylcyclopropanol opens mostly (60%) away from the phenyl group. The greater reactivity of the bond between two phenyls is apparently a general phenomenon and has not as yet been given a satisfactory explanation. Since both the cis and trans isomers give essentially the same product distribution on ring opening, it is hard to ascribe the results to steric factors.

The most striking conclusion from these data is that substitution on the 2-aryl group has practically no effect on the rate of cleavage of the C_1–C_2 bond. This shows up qualitatively in the direction of ring cleavage; the amount of C_1–C_2 bond breaking only changes from 88 to 98% over the range of substituents studied. Even this small change of product composition is due more to a substituent effect on the C_1–C_3 than the C_1–C_2 bond-breaking reaction. Although the number of substituents studied was not great, approximate ρ values for C_1–C_2 cleavage for *cis*-1-phenyl-2-arylcyclopropyl acetates (four points), *trans*-1-phenyl-2-arylcyclopropyl acetates (three points), and *trans*-1-phenyl-2-arylcyclopropanols (two points) can be calculated,

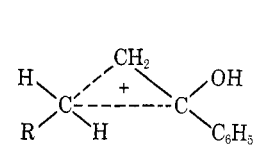
Table II
Rates of the Acid-Catalyzed Ring Opening of 1-Arylcyclopropanols in 1.45 *M* $HClO_4$ in 60:40 Dioxane–Water at 50°

Registry no.	Substituent	$k \times 10^5$, sec^{-1} [a]
15973-65-6	*p*-OCH_3	11.0 ± 0.5
40122-37-0	*p*-CH_3	6.67 ± 0.15
29526-96-3	H	3.18 ± 0.22
43187-67-3	*m*-Cl	1.06 ± 0.05
43187-68-4	*m*-CF_3	0.97 ± 0.03

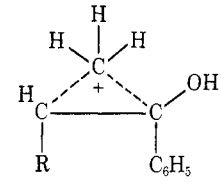
[a] Each result is the average of four or more runs with average deviation.

and all are near −0.5. Similar, limited Hammett correlation can be made for C_1–C_3 cleavage; the same three series of compounds all give ρ values near −1.6. Here the possible error in the ρ value is even larger because of the larger relative uncertainty in the analysis of the minor component in the product mixture. Nevertheless, the general trend for a larger ρ value for C_1–C_3 than for C_1–C_2 bond cleavage seems secure.

The kinetic and product studies for ring opening of both the 1-arylcyclopropanols and the 1-phenyl-2-arylcyclopropyl acetates and alcohols are in good accord with a transition state for the reaction which resembles a corner-protonated cyclopropane (**7a, 7b**). The very small ρ value ob-



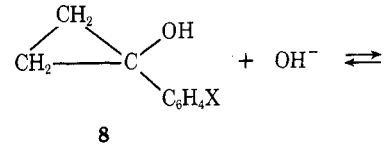
7a



7b

served for **7a** (R = aryl) might be expected, since little or no charge resides on the benzylic, pentavalent carbon. The larger ρ for **7b** (R = aryl) is accounted for if both benzylic carbons can help stabilize the charge. In the case of opening of 1-arylcyclopropanols (**7a, 7b**, R = H) presumably most of the charge is concentrated at the benzylic carbon. However, the lower ρ value compared with that observed in the protonation of acetophenones, and the better fit for σ rather than σ^*, suggests that the transition state is still some distance from the structure of the product **2**.

Cyclopropanols also undergo ring opening to ketones in the presence of base (eq 3). Opening occurs in the direc-



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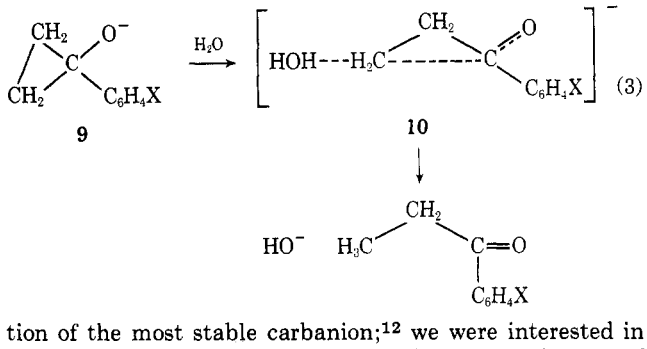

9 10 (3)

tion of the most stable carbanion;[12] we were interested in the effect of substituents in the 1-aryl group on the rate of reaction. The results are given in Table IV.

There is a very small substituent effect operative here, and a composite one. A substituent may stabilize the neg-

Table III
Rates and Direction of Cleavage in the Acid-Catalyzed Cleavage of 1,2-Diarylcyclopropyl Acetates[a]

Registry no.	Compd	$k \times 10^5$, sec^{-1}	% C_1–C_2 cleavage	% C_1–C_3 cleavage	$k_{1,2} \times 10^5$, sec^{-1}	$k_{1,3} \times 10^5$, sec^{-1}
	1-Phenylcyclopropanol	1.16 ±0.01	50	50	5.80 ±0.05	5.80 ±0.05
43187-69-5	*trans*-1,2-Diphenylcyclopropanol	1.70 ±0.15	93.4 ±0.5	6.6 ±0.5	16.6 ±1.4	1.12 ±0.09
43187-70-8	*trans*-1-Phenyl-2-(4-methylphenyl)cyclopropanol	2.13 ±0.10	90.9 ±0.5	9.1 ±0.5	19.3 ±0.9	1.94 ±0.09
43187-71-9	*trans*-1-Phenyl-2-(4-methylphenyl)cyclopropyl acetate	2.97 ±0.02	90.7 ±0.7	9.3 ±0.7	26.9 ±0.2	2.76 ±0.20
43187-72-0	*trans*-1-Phenyl-2-(4-methoxyphenyl)cyclopropyl acetate	3.45 ±0.18	88.1 ±0.5	11.9 ±0.5	30.4 ±1.6	4.05 ±0.21
27067-53-4	*trans*-1,2-Diphenylcyclopropyl acetate	2.30 ±0.10	93.3 ±0.5	6.7 ±0.5	21.4 ±0.9	1.54 ±0.11
43187-74-2	*cis*-1,2-Diphenylcyclopropyl acetate	3.87 ±0.03	95.1 ±0.5	4.9 ±0.5	36.8 ±0.3	1.89 ±0.21
43187-75-3	*cis*-1-Phenyl-2-(4-methoxyphenyl)cyclopropyl acetate	5.50 ±0.17	91.7 ±0.7	8.3 ±0.7	50.4 ±1.6	4.57 ±0.46
43187-76-4	*cis*-1-Phenyl-2-(4-chlorophenyl)cyclopropyl acetate	3.15 ±0.08	97.6 ±0.3	2.4 ±0.3	30.7 ±0.8	0.756 ±0.094
43187-77-5	*cis*-1-Phenyl-2-(4-methylphenyl)cyclopropyl acetate	4.73 ±0.17	93.2 ±0.4	6.8 ±0.4	44.1 ±1.6	3.22 ±0.19

[a] In 60:40 vol. % dioxane–water, 2.50 *N* H_2SO_4, and 49.85°.

Table IV
Base-Catalyzed Ring Opening of 1-Arylcyclopropanols[a]

Substituent	$k \times 10^4$, sec^{-1}
p-OCH_3	0.91
p-CH_3	0.75
H	0.70
m-Cl	1.10
m-CF_3	1.31

[a] In 95% ethanol, 0.011 *N* NaOH at 50°.

ative charge in a transition state resembling **10**, it will have an effect on the preequilibrium, and it may also interact conjugatively with the developing carbonyl group. These effects seem nearly to cancel each other out, leading to a shallow, slightly curved ρ–σ plot, with the unsubstituted 1-phenylcyclopropanol reaction slower than either positively or negatively substituted derivatives.

Experimental Section

All melting points are uncorrected. Ir spectra were determined on a Perkin-Elmer Model 21 or Beckman IR-10 spectrometer. Nmr spectra were recorded on a Varian HR-60 or A-60 spectrometer. Kinetics were followed spectrophotometrically on a Cary 14 spectrophotometer. Elemental analyses were performed by Elek Microanalytical Laboratories, Torrance, Calif.

1-Arylcyclopropanols. The synthesis of these alcohols has been reported earlier.[13] Their purity was determined spectroscopically, and their identity was confirmed by the preparation of their *p*-toluenesulfonate esters.

2-Aryl-1-phenylcyclopropyl Acetates. The method used for the synthesis of these compounds is essentially that of Freeman.[14] Chalcone (75 g, 0.36 mol) was prepared from the condensation of acetophenone and benzaldehyde[15] and 12.5 g (0.39 mol) of 97% hydrazine were condensed to yield, in quantitative yield, 3,5-diphenyl-2-pyrazoline. The pyrazoline was treated with 230 g (0.5 mol) of lead tetraacetate to yield 98 g of the 3-acetoxypyrazoline. Pyrolysis gave a mixture of *cis*- and *trans*-1,2-diphenylcyclopropyl acetate in a 27:73 ratio. Fractional distillation through a Nester-Faust 24-in. spinning band distillation column separated the two isomers into fractions which were 79% pure, and crystallization from hexane gave pure material. The stereochemistry was assigned on the basis of relative yields, nmr chemical shifts, and relative boiling points. *cis*-1,2-Diphenylcyclopropyl acetate had mp 74.5–75°; nmr ($CDCl_3$) δ 1.78 (m, 5 H), 2.65 (dd, 1 H), 6.29 (s, 5 H), 6.36 (s, 5 H).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.94; H, 6.39. Found: C, 81.05; H, 6.61.

***trans*-1,2-Diphenylcyclopropyl acetate** had mp 53–54°; nmr ($CDCl_3$) δ 1.83 (m, 2 H), 2.0 (s, 3 H), 2.80 (dd, 1 H), 7.05, 7.17 (m, 10 H). *Anal.* Calcd for $C_{17}H_{16}O_2$: C, 80.94; H, 6.39. Found: C, 80.76; H, 6.35.

***cis*-1-Phenyl-2-(4-methylphenyl)cyclopropyl acetate** had mp 74.5–75°; nmr ($CDCl_3$) δ 1.69 (m), 1.81 (s), 2.32 (s), 2.60 (t), 7.12 (s), 7.31 (m). *Anal.* Calcd for $C_{18}H_{18}O_2$: C, 81.19; H, 6.81. Found: C, 81.15; H, 6.85.

***trans*-1-Phenyl-2-(4-methylphenyl)cyclopropyl acetate** had mp 73.5–75°; nmr ($CDCl_3$) δ 1.80 (m), 1.93 (s), 2.15 (s), 2.75 (q), 6.87 (s), 7.13 (m). *Anal.* Calcd for $C_{18}H_{18}O_2$: C, 81.19; H, 6.81. Found: C, 80.95; H, 6.92.

***cis*-1-Phenyl-2-(4-methoxyphenyl)cyclopropyl acetate,** mp 90–92°, was separated by preparative scale thin layer chromatography after fractional distillation and crystallization failed, nmr ($CDCl_3$) δ 1.58 (m), 1.78 (s), 2.52 (m), 3.72 (s), 8.02 (m). *Anal.* Calcd for $C_{18}H_{18}O_3$: C, 76.60; H, 6.42. Found: C, 76.43; H, 6.38.

***trans*-1-Phenyl-2-(4-methoxyphenyl)cyclopropyl acetate** had mp 66.5–67°; nmr ($CDCl_3$) δ 1.71 (m), 2.00 (s), 2.72 (m), 3.67 (s), 6.82 (m), 7.09 (m). *Anal.* Calcd for $C_{18}H_{18}O_3$: C, 76.60; H, 6.42. Found: C, 76.44; H, 6.43.

***cis*-1-Phenyl-2-(4-chlorophenyl)cyclopropyl acetate,** mp 81.5–82°, crystallized directly from a hexane mixture of the cis-trans mixture upon cooling to −20°, nmr ($CDCl_3$) δ 1.69 (m), 1.80

(s), 2.59 (t), 7.27 (m). *Anal.* Calcd for $C_{17}H_{15}O_2Cl$: C, 71.19; H, 5.27; O, 11.16. Found: C, 71.16; H, 5.37; O, 11.28.

1-Phenyl-2-arylcyclopropanols. These compounds were prepared from the corresponding acetates by reaction with methyllithium and work-up in boric acid solution as previously described.[16]

The alcohols are air and base sensitive, and must be stored in polyethylene bottles in the freezer. Their melting points tended to vary depending upon their method of recrystallization, and were broad in range.

cis-**1,2-Diphenycyclopropanol** had mp 79–82.5° (hexane–ether), nmr ($CDCl_3$) δ 1.65 (m, 2 H), 2.21 (s, 1 H, OH), 2.49 (dd, 1 H), 7.33 (d, 10 H).

trans-**1-2-Diphenylcyclopropanol** had mp 96.5–99° (hexane–ether), nmr ($CDCl_3$) δ 1.65 (m, 2 H), 2.53 (s, 1 H), 2.77 (dd, 1 H), 7.03, 7.18 (m, 10 H).

trans-**1-Phenyl-2-(4-methylphenyl)cyclopropanol** had mp 75–77°.

Kinetic Procedures. Kinetics were run in 60:40 v/v dioxane–water with either perchloric acid or sulfuric acid as catalyst, or in 95% ethanol with NaOH as catalyst. For the acid-catalyzed reactions an appropriate amount of the alcohol or acetate (0.01–0.03 g) was accurately weighted into a 100-ml volumetric flask and the flask was allowed to equilibrate with the constant-temperature bath for 2 min. The flask was then filled to the mark with the acid solution, which was already at thermal equilibrium with the bath.

Acknowledgment. Support of this research by National Science Foundation Grant GP-13783X is gratefully acknowledged.

Registry No. *trans*-1-Phenyl-2-(4-chlorophenyl)cyclopropyl acetate, 43187-78-6; *cis*-1,2-diphenylcyclopropanol, 43187-79-7.

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Claisen Rearrangement of Some (Substituted allyl)indoles

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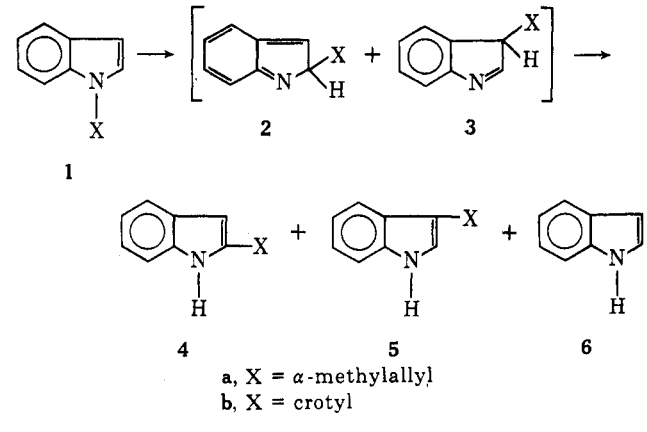
The pyrolysis of *N*-crotylindole over the temperature range of 450–470° produces 3α-methylallylindole (reversibly) and indole as major primary reaction products. The possible N to 2 sigmatropic shift with noninversion of the allyl substituent does not compete with the Claisen migration. However, at the longer residence times at 470° 2α-methylallylindole appears as a secondary product from 3α-methylallylindole. Under the same reaction conditions, 3α-methylallylindole rearranges by competitive paths to *N*-crotylindole (inversion of the allyl group) and to 2α-methylallylindole (noninversion of the allyl group). Cleavage to indole is also observed. The irradiation of *N*-crotylindole in ether solution at either 254 nm or 313–366 nm does not result in the group migration reaction.

The majority of previously reported Claisen rearrangements in heterocyclic systems have involved the migration of the allylic group from an exocyclic heteroatom to a ring position in the heterocyclic system.[1-3] Recently, we reported examples (allylpyrroles) of thermally[4] and photochemically induced[5] Claisen rearrangements in which the allylic substituent migrated from an endocyclic heteroatom to a new ring position. These Claisen migrations competed with the 1,5 shifts (N to 2 position) usually observed in N-substituted pyrrole systems.

In our search for additional examples of this kind of Claisen migration, the thermolysis of the closely related substituted allyl indoles was investigated. In this latter system, it might be expected that the N to 3 Claisen shift would compete with the N to 2 sigmatropic migration even more effectively than was observed in the pyrrole series because of the greater stability differences of the 2*H*- and 3*H*-indole intermediates **2** and **3**. The results of representative product composition–residence time studies at selected temperatures for *N*-crotylindole (**1b**) and 3α-methylallylindole (**5a**) are reported in Table I.

The starting materials and pyrolysis reaction products were synthesized by the alkenylation of indolylmagnesium halides. The reaction of crotyl bromide with indolylmagnesium bromide in hexamethylphosphoramide (HMPT)



produced *N*-crotylindole almost exclusively, a result which is consistent with the observation previously reported[6] that the reaction of allyl bromide with indolylmagnesium bromide in HMPT resulted in the formation of the N isomer only. Extension of this procedure to the synthesis of *N*-α-methylallylindole was unsuccessful. When α-methylallyl chloride was used as alkylating agent (HMPT solvent), the predominant product as determined by glpc retention time was *N*-crotylindole.