(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.

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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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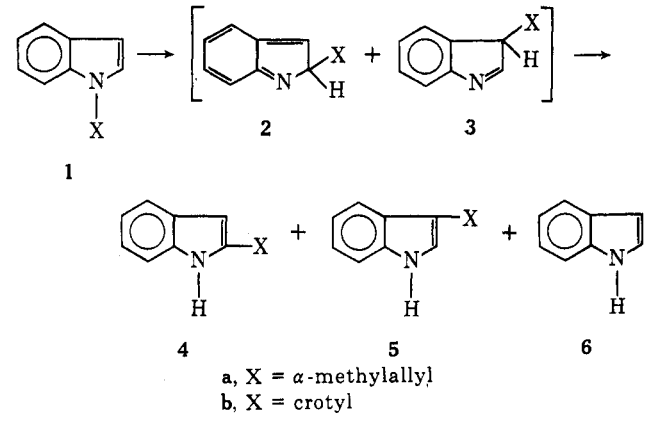
The pyrolysis of *N*-crotylindole over the temperature range of 450–470° produces 3α-methylallylindole (reversibly) and indole as major primary reaction products. The possible N to 2 sigmatropic shift with noninversion of the allyl substituent does not compete with the Claisen migration. However, at 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.

Table I
Pyrolysis of *N*-Crotylindole (1b) and 3α-Methylallylindole (5a)

Substance pyrolyzed	Residence time, sec	Temp, °C	Product composition, % 1b	4a	5a	6
1b	17.8	460	83.3	0	8.4	7.8
5a	17.8	460	7.2	1.5	88.5	2.8
1b	21.4	460	81.0	0	10.3	7.9
5a	21.4	460	9.6	2.0	84.7	3.7
1b	26.8	460	80.3	0	11.5	7.7
5a	26.7	460	14.7	3.5	74.6	5.4
1b	35.7	460	75.5	0	14.5	9.4
5a	35.7	460	18.9	4.5	66.6	10.2
1b	53.5	460	68.1	0	15.8	15.0
1b	17.6	470	78.9	0	10.8	9.9
5a	17.6	470	16.1	2.6	76.1	3.7
1b	21.1	470	74.9	0	14.5	9.8
1b	26.4	470	66.2	0.8	19.4	13.3
1b	35.2	470	60.3	1.5	22.2	14.9
5a	35.2	470	25.3	4.9	48.7	6.7
1b	52.8	470	53.6	1.8	24.1	19.1
5a	55.0	470	46.9	5.6	28.5	13.0

Alkenylation of indolylmagnesium iodide with crotyl bromide in an ether medium produced a mixture of isomeric 3-substituted indoles[7] consisting of *ca.* 30% 3α-methylallylindole and 70% 3-crotylindole.

Structural assignments for these alkylation products were based upon elemental analyses and spectral properties (mass, ir, and nmr). Each substance exhibited the appropriate substituted allyl pattern in the nmr spectrum. That these substances were 3 isomers was established by the C-2 proton resonance observed at *ca.* 6.60–6.70 ppm.

Pyrolysis products were identified by product isolation from preparative-scale pyrolyses and by comparisons of glpc retention times and spectral properties with those obtained in the alkenylation experiments. In the large-scale pyrolyses, 3-crotylindole was identified but was not present to a significant extent in the residence time–composition studies carried out subsequently. The structure of the pyrolysis product, 2α-methylallylindole, was assigned on the basis of its spectral properties. The mass and infrared spectra indicated a C-substituted indole and the nmr spectrum was identical with that obtained from 3α-methylallylindole except for the multiplet attributed to the heterocyclic ring proton. The 2α-methylallylindole exhibited this multiplet at 6.18 ppm while 3α-methylallylindole exhibited the multiplet at 6.70 ppm.

An examination of the data obtained from the residence time–product composition studies indicates that the primary pyrolysis products from *N*-crotylindole are 3α-methylallylindole, which arises from a Claisen-type migration, and indole, which arises by a competitive cleavage process. The facts that only 3α-methylallylindole is produced in the isomerization rather than a mixture of isomeric (substituted allyl)indoles and that high molecular weight substances, such as disubstituted indoles or dimers, are not observed indicate that the isomerization reaction is probably intramolecular. At the longer residence times in the 470° pyrolyses, 2α-methylallylindole begins to appear as a minor product in the reaction mixture. Since the pyrolysis of 3α-methylallylindole under identical conditions with those used for *N*-crotylindole produces 2α-methylallylindole, some of the 2α-methylallylindole observed in the *N*-crotylindole experiments arises as a secondary product. While the data for the formation of 2α-methylallylindole from 3α-indole **5a** largely accounts for the production of 2α-methylallylindole as a secondary product in the *N*-crotylindole pyrolyses, the variation in the concentrations of products produced in small amounts does not permit the exclusion of other minor paths.

Furthermore, the major primary product arising in the 3α-methylallylindole pyrolysis is *N*-crotylindole, indicating that the Claisen migration of *N*-crotylindole is reversible. By contrast, N to C shifts (involving both inversion or noninversion of the allyl group) in the pyrrole series were found to occur irreversibly.[4]

3-Crotylindole appeared only in trace amounts when the pyrolyses were carried out at higher temperatures and longer residence times. Independent experiments using the same conditions described above showed that 3-crotylindole did not undergo isomerization.

Information about the relative orders of reactivity of *trans*- and *cis*-crotyl groups in *N*-crotylindole can be obtained from a comparison of the trans–cis ratios prior to and after pyrolysis. Since the ratio changed from 3 to *ca.* 1 over the temperature range studied, the *trans*-crotyl group migrates with greater facility than the *cis*-crotyl group. A similar reactivity order was observed in the pyrrole series.[4] In addition more *N*-*trans*-crotyl product (than *cis*-crotyl) was produced in the pyrolysis of 3α-methylallylindole. Presumably, the transition states involved in the Claisen isomerization of indoles are similar to those proposed for the pyrrole isomerization.[4]

Experimental Section

Boiling points are uncorrected. Solvent or product purifications when used were carried out on a Nester-Faust auto annular Teflon spinning band distillation column. Infrared spectra were measured on a Beckman IR-8 spectrophotometer; ultraviolet spectra were measured on a Perkin-Elmer Model 202 spectrophotometer; nmr spectra were measured on a Varian HA-60-IL spectrometer or a Varian T-60 spectrometer in carbon tetrachloride solutions (*ca.* 10%) using tetramethylsilane (TMS) or hexamethyldisiloxane (HMDS) as internal standards; and mass spectra were taken on a Hitachi RMU-7 mass spectrometer. Gas chromatographic analyses were made on a Hewlett-Packard Model 5750 or F & M Model 810 gas chromatograph using a 6 ft × 0.125 in. Carbowax 20M Hewlett-Packard high-efficiency packed column at 210°. Preparative-scale separations of the pyrolyzates were carried out using a 6 ft × 0.375 in. 2 Carbowax 20M column at 210°.

Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

***N*-Crotylindole.** The procedure utilized was adapted from the procedures reported by Reinecke[8] and Cardillo.[6] To an ether solution (110 ml) of indolylmagnesium bromide prepared from 11.0 g (0.10 mol) of ethyl bromide, 2.4 g (0.11 mol) of magnesium, and 10.0 g (0.09 mol) of indole, there was added 125 ml of dry hexamethylphosphoramide (HMPT). After removal of the ether by heating to 90° under reduced pressure, 13.5 g (0.10 mol) of crotyl bromide in 20 ml of HMPT was added dropwise during 15 min and the mixture was heated at 90° for 1.5 hr. After cooling to room temperature, the mixture was treated with saturated ammonium chloride solution (250 ml) and extracted with ether. The ether extract was washed with saturated NaCl solution (3 × 50 ml), then with water (2 × 75 ml) and dried over Na_2SO_4. After removal of the ether, the residue was distilled *in vacuo* to give 12.5 g (73%) of *N*-crotylindole (98.5% pure, glpc): bp 127° (5 mm); $n^{25}D$ 1.5854; uv max (cyclohexane) 224, 278, 284, 290, 296 nm; ir (CCl_4) 970, 690 cm^{-1}; nmr (CCl_4) δ 1.60 (m, 3), 4.40 (m, 2), 5.53 (m, 2), 6.76 (q, 2), 7.50 ppm (m, 4); mass spectrum *m/e* 171 (parent peak).

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.13; H, 7.58; N, 8.24.

In a second experiment in which larger quantities were employed, an 80% yield of *N*-crotylindole was obtained.

The *N*-crotylindole (glpc analysis) consisted of *ca.* 75% trans isomer and 25% cis isomer. The trans configuration was assigned to the major component (which had the shorter retention time) on the basis of the infrared spectrum taken on a sample isolated by preparative glpc. The isomer showed strong absorption at 970 cm^{-1} and none at 690 cm^{-1}.

Reaction of Indolylmagnesium Iodide with Crotyl Bromide. The procedure of Brown, Henbest, and Jones was adapted.[7] To indolylmagnesium iodide in 2:1 ether–benzene solvent, prepared from 39.8 g (0.28 mol) of methyl iodide, 6.5 g (0.27 mol) of magnesium, and 25 g (0.21 mol) of indole, 32.3 g (0.24 mol) of crotyl bro-

mide in 20 ml of benzene was added slowly. After stirring at room temperature overnight, the reaction mixture was diluted with 100 ml of ether and the ether solution was extracted with 1 *M* ammonium chloride solution. After drying with $MgSO_4$ and removal of the ether on a rotary evaporator (steam bath), there was obtained 63 g of crude product consisting of (glpc analysis) 41% indole, 35% 3-crotylindole, 15% 3α-methylallylindole, and 9% unidentified constituents. The 3-crotyl- and 3α-methylallylindoles were isolated from the reaction mixture by preparative glpc.

3-Crotylindole. The indole was 99.9% pure (glpc analysis): uv max (cyclohexane) 228, 268, 273, 279, 290 nm; ir (CCl_4) 3400 cm^{-1} (NH); nmr (CCl_4) δ 1.65 (d, 3), 3.35 (d, 2), 5.50 (m, 2), 6.60 (m, 1), 7.05 (m, 4), and 7.50 ppm (m, 1); mass spectrum *m/e* 171 (parent peak).

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.14; H, 7.70; N, 8.08.

3α-Methylallylindole. The indole was 99.3% pure (glpc analysis): uv max (cyclohexane) 225 nm (ε 2.87 × 10^4), 280 (0.60 × 10^4), 290 (0.56 × 10^4); ir (CCl_4) 3400 cm^{-1} (NH); nmr (CCl_4) δ 1.50 (d, 3), 3.70 (m, 1), 5.10 (t, 2), 6.00 (m, 1), 6.70 (m, 1), 7.10 (m, 3), and 7.50 ppm (m, 2); mass spectrum *m/e* 171 (parent peak).

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N. 8.18. Found: C, 84.40; H, 7.49; N, 7.97.

Pyrolyses of the Indoles. Large-scale pyrolyses were carried out using the procedure and apparatus previously described[9] for the purpose of product identification.

Pyrolysis of *N*-Crotylindole. In a typical pyrolysis, 0.55 g of *N*-crotylindole was introduced into the pyrolysis apparatus (550°, nitrogen flow 60 ml/min) at a rate of 4.20 ml/hr. The pyrolyzate (0.4 g, 72% recovery) contained (glpc area %) unidentified component, 8%; *N*-crotylindole, 47%; indole, 9%; 2α-methylallylindole, 9%; 3α-methylallylindole, 27%; and 3-crotylindole, *ca.* 1%. The pyrolyzates from several runs were combined and components were separated by preparative glpc. *N*-Crotylindole and indole were identified by comparisons of spectral properties (uv, ir, nmr) and glpc retention times with those obtained from authentic samples. The trans-cis ratio of recovered *N*-crotylindole was 1.3. 3-α-Methylallylindole was identified by comparisons of spectral properties (ir, nmr) and glpc retention time with those obtained from α-methylallyl product produced in the reaction of indolylmagnesium bromide with crotyl bromide. 3-Crotylindole was identified by comparison of spectral properties (ir) and glpc retention times with those of the crotyl product obtained in the Grignard alkylation reaction.

2α-Methylallylindole was identified by comparison of its spectral properties with those of isomeric indoles: uv max (cyclohexane) 222, 268, 279, 283, and 289 nm; ir (CCl_4) 3400 cm^{-1} (NH); nmr (CCl_4) δ 1.50 (d, 3), 3.70 (m, 1), 5.10 (t, 2), 6.00 (m, 1), 6.18 (m, 1), 7.10 (m, 3), and 7.50 ppm (m, 2); mass spectrum *m/e* 171 (parent peak).

Pyrolysis of 3α-Methylallylindole. The indole (99.3% pure, glpc) was introduced (rate, 0.67 ml/hr) into the pyrolysis apparatus using a nitrogen flow of 30 ml/min. From the pyrolysis of 0.86 g of the indole at 500°, there was obtained 0.57 g (66% recovery) of pyrolyzate which contained (glpc analysis) *N*-crotylindole, 5%; indole, 4%; 2α-methylallylindole, 2%; and 3α-methylallylindole, 87%. The components of the pyrolyzate were separated by preparative glpc and identified as follows: *N*-crotylindole by comparison of spectral properties (uv, ir, mass spectrum) and glpc retention times with those of an authentic sample; indole and 3α-methylallylindole by comparisons of ir spectra and glpc retention times with those obtained from authentic samples; and 2α-methylallylindole by comparisons of ir spectra and glpc retention times with those obtained from 2α-methylallylindole produced in the pyrolysis of *N*-crotylindole.

Pyrolysis of 3-Crotylindole. The pyrolysis of the 3-crotylindole at 500° using the conditions described for the pyrolysis of 3α-methylallylindole did not produce rearrangement products.

Product Composition–Residence Time Studies. The effect of temperature and residence time on the gas-phase isomerizations was investigated by using the previously described[10] system of a capillary flow reactor joined to a gas chromatograph. The tubular reactor consisted of a 3 ft × 0.09 in. i.d. gold tube wrapped around a nickel heat sink. Reactor temperatures were measured with an iron–constantan thermocouple connected to a Leeds and Northrup millivolt potentiometer and were controlled to ±1° with a Chemical Data Systems Model 200 temperature controller. The residence times were obtained from flow-rate measurements and were corrected for thermal expansion of the carrier gas, reactants, and products. Analyses of the isomerization products were carried out on a 6 ft × 0.125 in. Carbowax 20M column at 210° and concentration values were obtained from the chromatograms by the electronic integration of peaks. The experiments were carried out with the reactor and the glpc system in parallel. The results, which are averages of three runs, are reported in Table I. The standard deviations of concentrations of constituents produced in low yields (less than 5%) were within ±20% of the value reported.

Irradiation of *N*-Crotylindole. Ether (50 ml) solutions of *N*-crotylindole (5 g) were irradiated in quartz tubes with a Rayonet reactor, Model 100 (254 nm), and with a Hanovia Model 654A lamp for 12 and 20 hr, respectively. Analysis of the ether solutions by glpc showed no evidence of reaction.

Registry No. *cis*-**1b**, 49650-75-1; *trans*-**1b**, 49650-76-2; **4a**, 49650-77-3; **5a**, 49650-78-4; **5b**, 49650-79-5.

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