Nonbenzenoid Aromatic Systems. I. Synthesis of 1-Vinylazulene and Certain Substituted 1-Vinylazulenes

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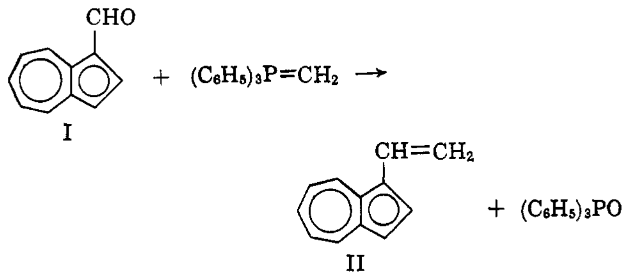
The synthesis of 1-vinylazulene, *cis*- and *trans*-β-phenyl-1-vinylazulene, and *trans*-β-phenyl-3-vinylguaiazulene by the Wittig reaction are reported. Their physical and spectral properties, and their reactivities (or lack thereof) are discussed.

One of our principal goals in these studies has been to determine the effects of an azulene ring system on a carbonium ion center. It would be of interest to determine whether the effect of changing the site of the α-carbinyl carbonium ion is directly related to the calculated π-electron densities[1,2] for this nonbenzenoid aromatic system.

One approach to such studies is to follow the rates of addition of some acid, HA, to the five vinylazulenes, as has been done with certain vinylmetallocenes.[3] We wish to report in this paper the synthesis of 1-vinylazulene (II) and certain substituted 1-vinylazulenes.

Our first approach to the preparation of 1-vinylazulene (II) was to allow methyl Grignard reagent to react with 1-azulenecarboxaldehyde (I)[4] following the method reported for 3-vinylguaiazulene.[5] The resulting blue solids appeared to be polymers of the desired 1-vinylazulene and no efforts were made to identify the extent of polymerization.

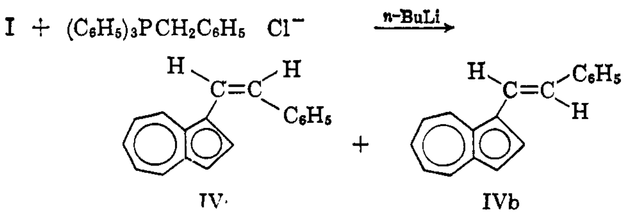
We then turned our attention to application of the Wittig reaction to produce the desired unsaturated compound II. The resulting dark blue oil was extremely sensitive to air and upon standing in a neat condition readily polymerized. A number of reactions were attempted in order to fully characterize the compound. Reactions with 2,4-dinitrobenzenesulfenyl chloride and tetracyanoethylene gave in each case polymeric products whose melting points were greater than 350°. Solubilities of these materials in polar and nonpolar organic solvents were so small that even recrystallizations were impractical. A *sym*-trinitrobenzene derivative of II could be isolated, but recrystallization of this derivative was unsuccessful owing to decomposition of the material upon heating. As a result the elemental analysis indicated that the derivative was contaminated with impurities. Therefore, owing to the extreme reactivity of II we were unable to study the rates of addition of weak acids to the vinyl group.



To establish the identity of this blue oil as II we carried out a quantitative hydrogenation using Adams catalyst. Approximately 99% of the theoretical quantity of hydrogen was absorbed. The resulting blue oil was identified as 1-ethylazulene by its ultraviolet and visible absorption spectra, and the preparation of its *sym*-trinitrobenzene derivative.

We next attempted the preparation of 3-vinylguaiazulene (III) by an analogous Wittig procedure. The product of this reaction, believed to be III, was observed to be even less stable than the azulene analog II. Polymerization was apparently induced even by absolute ethanol, considered to be very weakly acidic, thereby, preventing catalytic hydrogenation and spectral identification in that solvent. While standing in cyclohexane the material thought to be III deposited a blue polymer on the walls of the containing glass vessel, and reactions with *sym*-trinitrobenzene,[6] 2,4-dinitrobenzenesulfenyl chloride, and tetracyanoethylene in each case gave materials of a polymeric nature. These products would not melt below 350° and were only very slightly soluble in polar and nonpolar organic solvents.

In an effort to reduce the tendency to polymerize, the β-phenyl derivatives of II, *cis*- and *trans*-β-phenyl-1-vinylazulene (IVa, and IVb, respectively), were prepared by reaction of carboxaldehyde I with triphenylphosphinephenylmethylene. The assignment of structures of the *cis* (IVa) and *trans* isomers (IVb) are based on their visible spectra (see Table I) and the fact that IVa is isomerized to IVb by heating in benzene containing a trace of iodine. The melting points of these two compounds are also in line with the assignments.



When 3-guaiazulenecarboxaldehyde was treated under analogous Wittig conditions only a single isomer of β-phenyl-3-vinylguaiazulene (V) was obtained along with a small amount of guaiazulene. We have assigned the *trans* geometry to this isomer since it is not isomerized by refluxing in benzene containing a trace of iodine. However, guaiazulene was isolated from this attempted isomerization in approximately 33% yield.

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[1] E. Heilbronner, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p. 186.

[2] T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

[3] G. R. Buell, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, **84**, 40 (1962).

[4] K. Hafner, *Angew. Chem.*, **70**, 419 (1958).

[5] M. Miyazaki, M. Hashi, and T. Ukita, *Chem. Pharm. Bull.* (Tokyo), **8**, 140 (1960).

[6] We were unable to duplicate the synthesis of a stable *sym*-trinitrobenzene derivative as previously reported.[5]

TABLE I

Compd.	λ_{max}, mμ	$\Delta\lambda_{max}$, mμ^a	M.p., °C.
Azulene	579		99–100
1-Vinylazulene (II)	628	49	Liquid
1-Ethylazulene	608	29	Liquid
cis-β-Phenyl-1-vinylazulene (IVa)	625	46	91–92
trans-β-Phenyl-1-vinylazulene (IVb)	647	68	181–182
Guaiazulene	603		31–32
trans-β-Phenyl-3-vinylguaiazulene (V)	645	42	88–89

[a] $\Delta\lambda_{max}$ is the difference in the visible maximum absorbance of the parent compound and its respective derivative.

Of significance was the change in reactivity of these three β-phenylvinyl derivatives compared with 1-vinylazulene (II). Compounds IVa, IVb, and V resisted catalytic hydrogenation in a variety of solvents under conditions used for reduction of II. Some isomerization of IVa to IVb was noted. Under increased hydrogen pressure and temperature complete hydrogenation of the azulene nucleus took place as evidenced by the rapid loss of color of the reduction mixture.

Reaction of IVa and IVb with tetracyanoethylene gave in each case brown solids whose melting points were greater than 350°. The infrared spectra of these materials, however, indicated the absence of the vinylic double bond. Attempts to further purify these products by column chromatography and recrystallizations were futile, and it is suspected that a complex mixture of substitution,[7] addition, and a combination of substitution and addition products were present. Similar substances were observed in the reaction of IVa and IVb with 2,4-dinitrobenzenesulfenyl chloride.[8] Again the infrared spectra of these materials showed the absence of the vinyl group absorptions; however, the derivatives resisted purification.

Attempted peroxidation of IVa, IVb, and V with *m*-chloroperbenzoic acid and trifluoroperacetic acid, with anhydrous sodium carbonate as an insoluble base with the latter peracid, were unsuccessful. The former reagent gave back starting material with IVb and V, while IVa yielded 50–60% isomerization to IVb. The latter oxidant resulted in total destruction of the molecule.

A solution of IVb in absolute acetic acid was treated with a catalytic amount of *p*-toluenesulfonic acid[9] in an effort to add acetic acid to the double bond and produce the α-carbinyl acetate. The infrared spectrum of the product showed neither carbonyl nor hydroxyl absorptions thus eliminating the possibility of the desired addition to give rise to the acetate, or its hydrolysis product, an alcohol. Elemental analysis and a molecular weight determination (Rast method) indicated the compound was polymeric, most likely a tetramer of IVb. This explains the high melting point of the material (280–281° dec.) and its insolubility in organic solvents.

Table I summarizes the long-wave bands of maximum intensity in the visible spectra of the compounds prepared. This absorption band has been described as the most intense subband of the $^1A \rightarrow {}^1L_b$ long-wave transition[10,11] and has proven to be the extremely useful band in the visible spectrum of this nonalternate ring system for determining the positions of attached groups.[10] It is shifted by substitution on the azulene ring and the shift may be either bathochromic or hypsochromic depending on the site of substitution and the nature of the substituent. These shifts are also very dependent on steric hindrance.[11]

In IVb it would appear likely that the carbon skeleton would be coplanar, or approximately so. This is definitely not the case of V where the interference radii[12] of the 8-methyl group strongly overlap the α-hydrogen interference radii of the vinyl group. This forces the group from coplanarity, and the result is a much reduced $\Delta\lambda_{max}$ for V (42 mμ) compared with that for IVb (68 mμ). The smaller $\Delta\lambda_{max}$ for IVa over that of IVb is readily explained by the partial overlap of the ortho hydrogens interference radii of the benzene ring with that of the 2-hydrogen on the azulene ring causing a twist through the β-phenyl-1-vinylazulene system, probably in much the same way as observed for hindered stilbenes.[13]

Our results of a hypsochromic effect with increased steric hindrance to coplanarity in IVb, IVa, and V are those normally found the long-wave band in stilbenes[13] and certain other systems.[14] They do, however, differ from those of Heilbronner and Gerdil[11] who found that; with increasing steric hindrance to coplanarity between the azulene ring and the carbonyl group for several azulyl ketones, there is an increasing bathochromic effect. As expected in comparing IVb and IVa, we find that the usual observance of a decrease in intensity is associated with increased hindrance.

Several workers have reported on the n.m.r. spectra of the conjugate acids of azulenes[15–18] with 98% sulfuric acid and trifluoroacetic acid mainly employed as solvents and proton donors. We have found that n.m.r. spectra of up to 20 wt. % of azulene in 98% sulfuric acid duplicates that reported[18] as does up to 14 wt. % of azulene in trifluoroacetic acid.[16] However, at 15 wt. % (about 11 mole %) of azulene in trifluoroacetic acid the spectrum changes. This change is quite abrupt, but most pronounced at 20 wt. % of azulene in trifluoroacetic acid and is recorded in Figure 1.

In b of Figure 1 we find a similar broad multiplet (five hydrogens) centered at τ 1.4 for the seven-membered ring protons. The multiplet at τ 2.4 integrates for a single proton, while the methylene multiplet centered at 6.15 shows the presence of four protons. No satisfactory explanation for this remarkable effect has as yet been found.

trans isomer IVb was too insoluble in either 98% sulfuric acid or trifluoroacetic acid to allow us to study its conjugate acid in the n.m.r. The *cis* isomer IVa

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(7) K. Hafner and K. L. Moritz, *Angew. Chem.*, **72**, 918 (1960).

(8) For substitution of this reagent into the azulene nucleus, see A. G. Anderson, Jr., and R. N. McDonald, *J. Am. Chem. Soc.*, **81**, 5669 (1959).

(9) No reaction took place in the absence of this acid.

(10) See ref. 1, pp. 218–245.

(11) E. Heilbronner and R. Gerdil, *Helv. Chim. Acta*, **39**, 1996 (1956).

(12) E. A. Braude, *Experientia*, **11**, 457 (1955), discussed by E. Heilbronner, ref. 1, pp. 239–242.

(13) H. H. Jaffe and M. Orchin, *J. Chem. Soc.*, 1078 (1960).

(14) See H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., Chapter 15, for further discussions.

(15) S. S. Danyluk and W. G. Schneider, *J. Am. Chem. Soc.*, **82**, 997 (1960).

(16) J. Schulze and F. A. Long, *ibid.*, **86**, 322 (1964).

(17) D. Meuche, B. B. Molloy, D. H. Reid, and E. Heilbronner, *Helv. Chim. Acta*, **46**, 2483 (1963).

(18) A. G. Anderson, Jr., and W. F. Harrison, *J. Am. Chem. Soc.*, **86**, 708 (1964).

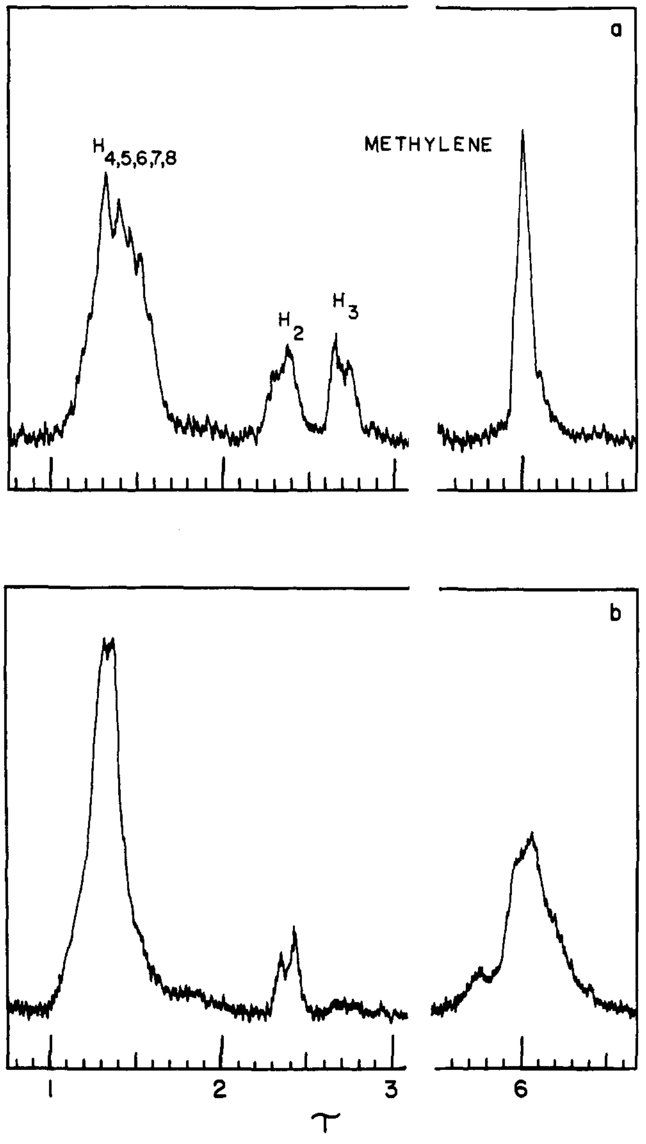
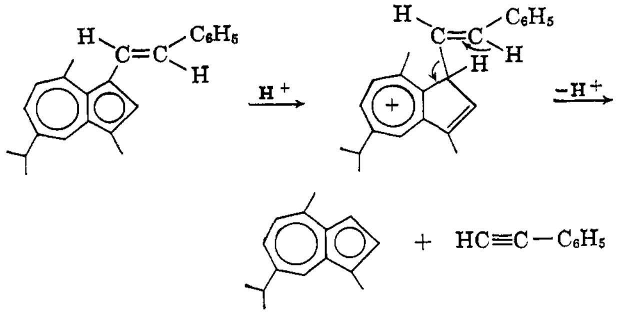


Figure 1.—N.m.r. of 10 wt. % (a) and 20 wt. % (b) of azulene in CF_3CO_2H. The τ-values are relative to an external TMS standard.

readily became insoluble in both acids probably due to isomerization to IVb. *trans* V also was found to be of no value in either acid for determining the site of protonation, however, for a different reason. It was found to decompose to guaiazulene plus some other unidentified fragment.

Since guaiazulene was identified in the attempted isomerization of V with iodine, in the above n.m.r spectral determination in acid, and from certain other reactions, we suggest that the other molecular fragment is phenylacetylene which possibly arises in the following acid-catalyzed manner.



Experimental[19]

1-Azulenecarboxaldehyde.—This liquid aldehyde was prepared according to the procedure of K. Hafner[4] in 91% yield (lit.[4] 90% yield).

3-Guaiazulenecarboxaldehyde.—This reaction was carried out as described previously for 1-azulenecarboxaldehyde, m.p. 84°, 83% yield (lit.[4] m.p. 85°, 90% yield).

1-Vinylazulene.—To a stirred suspension of 2.85 g. (8.0 mmoles) of triphenylmethylphosphonium bromide and 250 ml. of anhydrous ether in a dry nitrogen atmosphere was added 0.5 g. (8.0 mmoles) of *n*-butyllithium in *n*-hexane. The reaction mixture immediately turned a dark yellow and stirring was continued for 1 hr. under a nitrogen atmosphere. Then 1.24 g. (7.9 mmoles) of 1-azulenecarboxaldehyde in 25 ml. of anhydrous ether was added dropwise. The resulting dark green solution was stirred at reflux for an additional 3 hr. This solution was filtered twice with the use of Filter Cell, and then concentrated under reduced pressure. The residue was dissolved in Skelly B and chromatographed on an activated alumina column. Elution with Skelly B gave 0.543 g. (46%) of a blue oil. The infrared spectrum (neat) showed the following bands that can be attributed to the vinyl grouping: 3.3 (m), 6.2 (m), 7.2 (s), 7.6 (m), 10.1 (m), and 11.2 (m) μ. Also bands appeared at 3.5 (m), 6.4 (m), 6.8 (w), 7.0 (w), 8.2 (w), 10.5 (w), 11.7 (w), 12.7 (m), and 13.2 (m) μ. A *sym*-trinitrobenzene derivative was prepared, m.p. 97–98°.

Anal. Calcd. for $C_{18}H_{13}N_3O_6$: C, 58.85; H, 3.54. Found: C, 59.94; H, 4.36.

Ultraviolet and visible spectral analysis of 1-vinylazulene in cyclohexane showed the following data: λ_{max} 735 mμ (log ε 3.40), 691 (3.76), 660 (3.80), 628 (3.87), 603 (3.84), 580 (3.78), 292 (5.98), and 234 (5.61).

1-Ethylazulene.—To a solution of finely divided platinum in 10 ml. of absolute ethanol, obtained by previously reducing 10 mg. of platinum oxide (Adams catalyst), was added 210 mg. (2.01 mmoles) of 1-vinylazulene in 20 ml. of absolute ethanol. An uptake of 98.8% of the theoretical amount of hydrogen was observed. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in Skelly B and chromatographed on a column of activated alumina. A blue band was eluted with Skelly B which gave 197 mg. (98%) of a blue oil. Visible spectral analysis of 1-ethylazulene in cyclohexane showed the following data: λ_{max} 737 mμ (O.D. 0.40), 697 (0.62), 664 (1.33), 632 (1.36), 608 (1.51), and 583 (1.25) mμ [lit.[20] λ_{max} 740 mμ (log ε 1.89), 668 (2.35), and 610 (2.45) with no solvent mentioned]. A *sym*-trinitrobenzene derivative was prepared, m.p. 109–110° (lit.[20] m.p. 112–113.5°).

The Reaction of 3-Guaiazulenecarboxaldehyde with Triphenylmethylphosphonium Bromide.—The procedure for the preparation of 1-vinylazulene was used. Elution of the alumina column gave 1.080 g. (75%) of a blue-green oil whose infrared spectrum (neat) showed the following bands which can be attributed to the vinyl group: 3.2 (m), 6.2 (s), 7.1 (m), 7.7 (w), 10.1 (m), and 11.2 (s) μ. Also bands appeared at 3.5 (vs), 6.5 (m), 6.9 (m), 7.2 (m), 7.5 (w), 8.3 (w), 8.5 (m), 8.9 (vw), 9.1 (w), 9.5 (m), 9.7 (w), 10.5 (w), 10.9 (w), and 12.2 (m) μ. The ultraviolet and visible spectral data of this material in cyclohexane was obtained: λ_{max} 692 mμ (O.D. 0.96), 632 (1.22), 303 (2.13), and 251 (1.19).

The Reduction of 3-Vinylguaizulene.—The procedure for the preparation of 1-ethylazulene substituting freshly distilled glyme for absolute ethanol was used. An uptake of 91.3% of the theoretical amount of hydrogen was observed. Elution of the chromatographed product on activated alumina with Skelly B gave 0.328 g. (99%) of a blue-green oil. The infrared spectrum (neat) of this material showed the absence of bands due to vinyl absorptions. Absorption bands were observed at 3.5 (vs), 6.1 (vw), 6.5 (m), 6.9 (m), 7.3 (m), 7.5 (vw), 7.7 (vw), 7.9 (vw), 8.3 (vw), 8.5 (w), 9.5 (w), 9.7 (w), 10.9 (w), 11.5 (w), and 12.8 (m) μ. Ultraviolet and visible spectral analysis in cyclohexane gave the following data: λ_{max} 692 mμ (O.D. 0.98), 626 (1.33), 307 (0.53), 291 (1.09), and 248 (0.68).

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[19] All melting points were taken on a Kofler hot stage and are corrected. Infrared absorption spectra were determined on a Perkin-Elmer Model 137 double beam recording spectrophotometer. Ultraviolet and visible absorption spectra were determined on a Cary Model 11 recording spectrophotometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

[20] A. S. Rao and M. S. Muthana, *J. Indian Inst. Sci.*, **37**, 79 (1955); *Chem. Abstr.*, **50**, 3377*b* (1956).

Attempts to prepare a *sym*-trinitrobenzene derivative of the reaction product were unsuccessful.

cis- **and** *trans*-β-**Phenyl-1-vinylazulene.**—This reaction was carried out as previously discussed in the preparation of 1-vinylazulene, using 0.447 g. (2.9 mmoles of 1-azulenecarboxaldehyde, 1.9 g. (5.0 mmoles) of benzyltriphenylphosphonium chloride, 0.29 g. (4.5 mmoles) of *n*-butyllithium in *n*-hexane, and 250 ml. of anhydrous diethyl ether. Initial elution of an activated alumina column of the chromatographed product with Skelly B gave 0.16 g. (23%) of *cis*-β-phenyl-1-vinylazulene. Recrystallization from Skelly B gave dark green plates, m.p. 91–92°. The infrared spectrum (KBr pellet) showed the following absorption bands that can be attributed to the vinyl group: 3.2 (w), 6.2 (w), 7.1 (m), 7.7 (m), 10.4 (m), and 11.2 (w) μ. Also bands appeared at 13.9 (m) and 14.4 (s) μ due to the monosubstituted benzene ring. In addition there were bands at 6.4 (m), 6.7 (w), 7.0 (w), 8.0 (m), 9.1 (m), 9.7 (m), 10.5 (w), 11.7 (w), 12.6 (s), and 13.2 (s) μ.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.91; H, 6.09. Found: C, 93.63; H, 6.38.

The ultraviolet and visible spectral analyses in cyclohexane gave the following data: λ_{max} 625 mμ (log ε 2.46), 313 (5.47), and 259 (5.25).

Further elution of the chromatographic column with Skelly B gave 0.35 g. (51%) of *trans*-β-phenyl-1-vinylazulene which was readily recrystallized from Skelly B to give dark green needles, m.p. 181–182°. The infrared spectrum showed the following absorption bands that can be attributed to the vinyl group: 3.3 (w), 6.2 (w), 7.2 (m), 7.7 (m), 10.3 (m), and 10.5 (vs) μ (*trans* hydrogens of a double bond). Bands appeared at 13.5 (vs) and 14.4 (s) μ due to absorptions of a monosubstituted benzene ring. There were also bands at 6.4 (m), 6.7 (w), 6.9 (w), 11.7 (w), 11.9 (w), 12.7 (vs), and 13.1 (m) μ.

Anal. Found: C, 93.83; H, 6.17.

The ultraviolet and visible spectral analyses in cyclohexane gave the following data: λ_{max} 717 (log ε 2.34), 647 (2.52), 318 (4.48), and 255 (4.18). Attempts to reduce both *cis* and *trans* isomers catalytically, using Adams catalyst, in a variety of solvent systems (glyme, ethanol, tetrahydrofuran, dioxane, and an ethanol–glyme mixture) were unsuccessful.

Isomerization of *cis*- **to** *trans*-β-**Phenyl-1-vinylazulene.**—A solution of 20 mg. (0.086 mmoles) of pure *cis*-β-phenyl-1-vinylazulene in 10 ml. of anhydrous benzene with a trace of iodine was heated under reflux for 24 hr. After removing the benzene under reduced pressure, the residue was taken up in Skelly B and chromatographed on activated alumina. One green band developed and when eluted with Skelly B gave 20 mg. (100%) of dark green needles, m.p. 181–182°. Mixture melting point with an authentic sample of *trans*-β-phenyl-1-vinylazulene showed no depression. The above procedure was repeated, substituting Skelly B for benzene resulting in only a 33.3% conversion of *cis* to *trans* isomer.

The Reaction of *trans*-β-**Phenyl-1-vinylazulene with Acetic Acid.**—A solution of 50 mg. (0.217 mmole) of *trans*-β-phenyl-1-vinylazulene in 15 ml. of "dry"[21] acetic acid was added dropwise to a solution of 10 mg. of *p*-toluenesulfonic acid in 15 ml. of "dry" acetic acid. The reaction mixture was allowed to stand at room temperature for two days, concentrated under reduced pressure, dissolved in a 4:1 mixture of Skelly B–methylene chloride, and chromatographed on an activated alumina column. Elution with the above 4:1 solvent mixture gave 35 mg. of a dark blue crystalline material (m.p. 280–281°) whose infrared spectrum showed no carbonyl or hydroxyl absorption. Elemental analysis gave the following data.

Anal. Found: C, 92.20 H, 6.08.

Assuming the remaining percentage (1.72%) to be oxygen, an empirical formula was calculated to be $C_{72}H_{56}O$ (formula wt. 936). A molecular weight determination (Rast method) gave an average value of 928.

trans-β-**Phenyl-3-vinylguaiazulene.**—The reaction was carried out in the manner described previously for 1-vinylazulene using 1.0 g. (4.42 mmoles) of 3-guaiazulenecarboxaldehyde, 2.9 g. (7.5 mmoles) of benzyltriphenylphosphonium chloride, 0.45 g. (7.0 mmoles), of *n*-butyllithium in *n*-hexane, and 300 ml. of anhydrous ether. The reaction mixture after work-up was chromatographed on a column of Florisil. Elution with Skelly B gave 0.1 g. of a blue oil whose infrared, ultraviolet, and visible spectrum was identical with that of guaiazulene. A *sym*-trinitrobenzene derivative was prepared, m.p. 151–152° (lit.[4] m.p. 151–152°). Mixture melting point with a *sym*-trinitrobenzene derivative prepared from an authentic sample of guaiazulene was not depressed.

Further elution of the column gave 0.735 g. (56%) of a green solid which was readily recrystallized from petroleum ether, m.p. 87–88°. The infrared spectrum showed the following absorption bands that can be attributed to the vinyl group: 3.2 (w), 6.2 (m), 7.1 (m), 7.8 (w), 10.5 (s) (*trans* hydrogens of a double bond), and 11.5 (w) μ. Bands appeared at 13.8 (m) and 14.5 (s) μ due to absorptions of a monosubstituted benzene ring. In addition there were absorption bands at 3.5 (w), 6.0 (w), 6.9 (w), 8.5 (w), 11.0 (w), 11.9 (w), 12.4 (w), and 13.4 (m) μ.

Anal. Calcd. for $C_{23}H_{24}$: C, 92.06; H, 7.94. Found: C, 91.83; H, 8.04.

The ultraviolet and visible spectral analysis in cyclohexane gives the folllwing data: λ_{max} 645 (log ε 2.62), 328 (4.43), and 268 (4.33); in ethanol, λ_{max} 647 mμ (log ε 2.65), 329 (4.46), 269 (3.43), and 231 (4.20) mμ. A 20% conversion of the *trans*-β-phenyl-3-vinylguaiazulene to guaiazulene was obtained by refluxing the former in benzene for 24 hr. with a trace of iodine.

Acknowledgment.—The authors wish to thank the National Science Foundation (NSF G-17430) and the Directorate of Chemical Sciences, Air Force Office of Scientific Research (AF-AFOSR-145-63), for support of this research.

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[21] N. R. Slobodkin and N. Kharasch, *J. Am. Chem. Soc.*, **82**, 5837 (1960).