The Reaction of Azulenes with Aliphatic Diazo Compounds[1,2]

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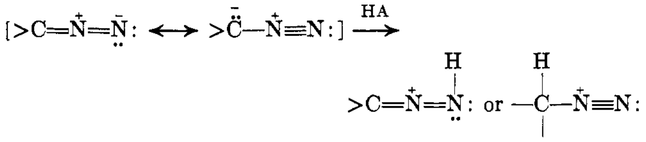
The acid-catalyzed and photocatalyzed reactions of azulene with certain diazoalkanes and diazo ketones, and with ethyl diazoacetate have been found to give varying yields of the corresponding 1-substituted azulenes. Both types of reaction were also carried out with ethyl diazoacetate on guaiazulene and 4,6,8-trimethylazulene. The acid-catalyzed reaction of *p*-diazoquinone with azulene gave 1-(4-hydroxyphenylazo)azulene in high yield.

Among the first successful electrophilic substitution reactions of azulene was that with benzenediazonium ions to form 1-azuleneazobenzene compounds.[4] Later it was found that the reaction of azulene with N-nitrosoacetanilide also gave 1-azuleneazobenzene as the principal product , and most probably not *via* a radical mechanism.[5] It was therefore of interest to consider alkyldiazonium ions. These can be formed by protonation of the neutral diazo compounds and, further, the proton can be bonded to either the terminal nitrogen or the α-carbon. The latter possibility leads to a reagent which could react with a nucleophile directly or



$$[>C{=}\overset{+}{N}{=}\underset{\cdot\cdot}{\overset{-}{N}}{:} \longleftrightarrow >\overset{-}{C}{-}\overset{+}{N}{\equiv}N{:}] \xrightarrow{HA} >C{=}\overset{+}{N}{=}\underset{\cdot\cdot}{\overset{H}{N}}{:} \text{ or } -\overset{H}{\underset{|}{C}}-\overset{+}{N}{\equiv}N{:}$$

with prior dissociation to a carbonium ion. This type of reactivity has been known for some time and the effect of substituent groups[6] as well as the nature of the acid catalysis[7] has been studied. Useful applications have included the methylation of alcoholic hydroxyl groups[8] and the N-phenacylation of pyridine and related aromatic heterocyclic compounds.[9] These results prompted us to examine the utility of the method for the alkylation of azulene.

In that carbenes are electron deficient, and thus electrophilic species, the formation of these by photo- or thermal decomposition of aliphatic diazo compounds was potentially an additional means of achieving the substitution of azulene with the diazo reagents. The aromatic character of azulene made it probable that a substitution rather than an addition process would occur. Several examples of this type of substitution of aromatic systems have been reported. Among these are the irradiation of diazomethane in pyridine to give 2-picoline[10] and the formation of ethyl pyrrole-2-acetate[11] and ethyl 1-methylindole-3-acetate[12] upon thermolysis of the parent heterocyclic compounds with ethyl diazoacetate.

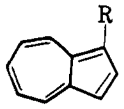
As previous alkylation methods have not been very satisfactory, it was hoped that the reactions with diazoalkanes would provide a better means of attaching a saturated carbon to the azulene ring.

The Acid-Catalyzed Reactions.—Fluoroboric acid (100%), aluminum chloride, and stannic chloride were investigated as acid catalysts. Only the first proved to be useful and the yields with this were not uniformly good.

Diphenyldiazomethane, diazobutane, and vinyldiazomethane were selected as examples of diazoalkanes.[13] The first was obtained from the oxidation of benzophenone hydrazone with mercuric oxide by the method of Smith and Howard.[14] Diazobutane and vinyldiazomethane were prepared by the addition of the appropriate amine to mesityl oxide, nitrosation, and then cleavage of the N-nitroso product.[15]

Treatment of a solution of diphenyldiazomethane and azulene with 100% fluoroboric acid afforded 1-benzhydrylazulene (**1**) in 75% yield and the same reaction with diazobutane gave 61% of 1-butylazulene (**2**). No attempt was made to determine whether or not isomerization of the butyl group had occurred. In contrast to these promising results, the reaction with vinyldiazomethane produced colored, tarry material from which no simple products could be isolated. Thus any allylazulene which may have formed was no longer present as the monomer.

It was found that the acid-catalyzed reaction of azulene with ethyl diazoacetate yielded ethyl 1-azulylacetate (**3**, 32%) which was identified by conversion to the known acid.[16] Comparable yields were obtained of ethyl 1-(4,6,8-trimethylazulyl)acetate and ethyl 3-guaiazulylacetate from the corresponding azulene hydrocarbons. Although these yields are only fair, the directness and simpleness of the procedure plus the re-



1, R = $CH(C_6H_5)_2$
2, R = C_4H_9
3, R = $CH_2CO_2C_2H_5$
4, R = CH_2COCH_3
5, R = $CH_2COC_6H_5$
6, R = $CH(C_6H_5)COC_6H_5$

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[3] National Institutes of Health Predoctoral Fellow, 1961–1963.

[4] P. A. Plattner, *Chimia*, **4**, 260 (1950); A. G. Anderson, J. A. Nelson, and J. J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953).

[5] A. G. Anderson and G. M-C. Chang, *J. Org. Chem.*, **23**, 151 (1958).

[6] H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916).

[7] J. N. Brønsted and R. P. Bell, *J. Am. Chem. Soc.*, **64**, 199 (1942); J. D. Roberts, E. A. McElhill, and R. Armstrong, *ibid.*, **71**, 2923 (1949); J. D. Roberts and W. T. Moreland, *ibid.*, **75**, 3615 (1953); H. Zollinger, "Diazo and Azo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961, p. 103.

[8] M. Neeman, M. Caserio, J. D. Roberts, and W. S. Johnson, *Tetrahedron*, **6**, 36 (1959); J. D. Roberts, C. M. Regan, and I. Allen, *J. Am. Chem. Soc.*, **74**, 3679 (1952).

[9] C. C. King and F. M. Miller, *ibid.*, **70**, 4154 (1948).

[10] R. Daniels and O. Salerni, *Proc. Chem. Soc.*, 286 (1960).

[11] C. D. Nenitzescu and E. Solomonica, *Ber.*, **64**, 1924 (1931).

[12] G. M. Badger, B. J. Christie, H. J. Rodda, and J. M. Pryke, *J. Chem. Soc.*, 1179 (1958).

[13] Diazoalkanes with smaller alkyl groups were not used as the expected 1-alkylazulene products are difficult to separate from azulene.

[14] L. I. Smith and K. L. Howard, *Org. Syn.*, **24**, 53 (1944).

[15] D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 286 (1935); E. C. S. Jones and J. Kenner, *ibid.*, 363 (1938).

[16] A. G. Anderson, R. G. Anderson, and T. Fujita, *J. Org. Chem.*, **27**, 4535 (1962).

covery of most of the unreacted azulene reagent make this a useful route to 1-azulylacetic acid and derivatives.

Diazoacetone, diazoacetophenone, and phenylbenzoyldiazomethane were investigated as examples of diazo ketones. The first two were prepared from the corresponding acyl halides and diazomethane.[17] Phenylbenzoyldiazomethane was prepared from benzil *via* the hydrazone.[18] The actual yields of products realized from the acid-catalyzed reactions of the diazo ketones were low, but the net yields were somewhat better. The data for these are included in the summary of results of Table I. Although the diazo ketones and ethyl diazoacetate can also undergo protonation on an oxygen atom and thus form a potentially reactive species, no products corresponding to substitution of this type were isolated. Also, the initial product from such reactions would probably undergo further reactions and thus would not have been found even if they had been formed.

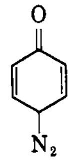
TABLE I

ACID-CATALYZED REACTION OF AZULENES WITH DIAZO COMPOUNDS

Azulene compd.	$R_1R_2CN_2$	% yield of 1-(R_1R_2CH)-azulene (net yield[a])	λ_{max}, mμ
Azulene	$(C_6H_5)_2CN$	75 (81)	596[b]
Azulene	$C_3H_7CHN_2$	61 (95)	606[c]
Azulene	$C_2H_5O_2CCHN_2$	32 (93)	597[c]
Azulene	CH_3COCHN_2	10 (27)	595[b]
Azulene	$C_6H_5COCHN_2$	6 (52)	593[b]
Azulene	$C_6H_5CN_2COC_6H_5$	7 (25)	590[b]
4,6,8-Trimethylazulene	$C_2H_5O_2CCHN_2$	38 (91)	561[c]
4,6,8-Trimethylazulene	$C_6H_5COCHN_2$	7 (25)	590[b]
Guaiazulene	$C_2H_5O_2CCHN_2$	31 (62)	616[d]

[a] Net yields are based on unrecovered azulene. [b] Dichloromethane solution. [c] Cyclohexane solution. [d] *n*-Pentane solution.

A conjugate unsaturated diazo compound, *p*-diazoquinone (**7**) was also studied. This compound, which was quite sensitive to light and heat, was synthesized from *p*-aminophenol.[19] The reaction of **7** with azulene in the presence of fluoroboric acid gave an 87% yield of 1-(4-hydroxyphenylazo)azulene (**8**). Thus the presence of the basic oxygen in conjugation with the diazo group resulted in the formation of the oxygen-protonated conjugate acid (the *p*-hydroxybenzenediazonium ion). Compound **8** was found to be a deep purple in acid media and orange in basic media, and this change was reversible. The same product was obtained in high yield when azulene and **7** were heated together, and also from the reaction of *p*-hydroxybenzenediazonium chloride with azulene.



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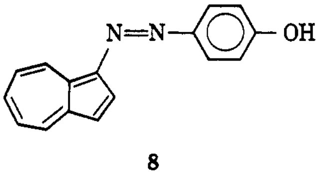

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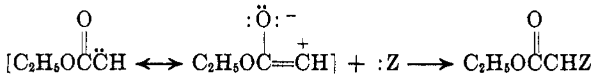
The observed order of magnitude of the yields with the different types of diazoalkanes was the same as that of the rates of decomposition with acids.[20] Attempts to bring about the acid-catalyzed substitution of the less reactive 1-nitroazulene and ethyl 1-azulylacetate were not successful and the azulenic reagents were recovered unchanged.

The Photocatalyzed Reactions.—Thermal decomposition of ethyl diazoacetate in the presence of guaiazulene has been reported to yield an ethyl guaiazulylacetate.[21] The reaction was presumed to involve free radicals and the reported hypsochromic shift (604 to 590 mμ) was interpreted to indicate substitution on an even-numbered carbon (probably 2 or 6). In that the visible absorption band was described as broad, the spectral shift is perhaps subject to question, as is the evidence of the degradation of the product to a supposed methyl derivative which was not characterized.

A study of the selectivity of carbenes in reactions with primary, secondary, and tertiary carbon–hydrogen bonds by Doering and Knox[22] points to the existence of the photogenerated carboethoxycarbene in the singlet state. This structure could act as an electrophile in the usual manner.



$$[C_2H_5O\overset{O}{\overset{\|}{C}}\ddot{C}H \longleftrightarrow C_2H_5O\overset{:\ddot{O}:^-}{\overset{|}{C}}{=}\overset{+}{C}H] + :Z \longrightarrow C_2H_5O\overset{O}{\overset{\|}{C}}CHZ$$

In the present work the irradiation of a solution of guaiazulene and ethyl diazoacetate gave a blue oil (11%) which showed a λ_{max} at 616 mμ and was identical in all other respects with ethyl 3-guaiazulylacetate. The net yield of the reaction was 50% but no product corresponding to that described by Treibs was found. The same reaction with azulene and with 4,6,8-trimethylazulene formed ethyl 1-azulylacetate (**3**) and ethyl 1-(4,6,8-trimethylazulyl)acetate, respectively, in higher yields (Table II).

TABLE II

PHOTOCATALYZED REACTION OF AZULENES WITH DIAZO COMPOUNDS

Azulene compd.	$R_1R_2CN_2$	% yield of 1-(R_1R_2CH)-azulene (net yield[a])
Azulene	$(C_6H_5)_2CN_2$	67 (75)
Azulene	$C_6H_4COCHN_2$	17 (85)
Azulene	CH_3COCHN_2	21 (80)
Azulene	$C_6H_5CN_2COC_6H_5$	26 (88)
Azulene	$C_2H_5O_2CCHN_2$	31 (99)
Guaiazulene	$C_2H_5O_2CCHN_2$	11 (50)
4,6,8-Trimethylazulene	$C_6H_5O_2CCHN_2$	17 (68)
4,6,8-Trimethylazulene	$C_6H_5COCHN_2$	17 (24)

[a] Net yields are based on unrecovered azulene.

The photocatalyzed reaction of azulene with the diazo ketones studied gave appreciably better yields of the 1-substituted azulenes (Table II) than did the acid-catalyzed reactions. The photolysis of diphenyldiazomethane in the presence of azulene gave a good yield of 1-benzhydrylazulene (**1**). The relatively high yield and the specificity of this reaction is of interest in that

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[17] W. Bradley and R. Robinson, *J. Chem. Soc.*, 1310 (1920); P. Yates, *J. Am. Chem. Soc.*, **81**, 212 (1959).

[18] C. D. Nenitzescu and E. Solomonica, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 309.

[19] L. C. Anderson and M. J. Roedel, *J. Am. Chem. Soc.*, **67**, 955 (1945).

[20] R. Huisgen, *Angew. Chem.*, **67**, 439 (1955).

[21] W. Treibs, *Ann.*, **603**, 149 (1957); *Angew. Chem.*, **67**, 76 (1955).

[22] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **83**, 1989 (1961).

there is evidence[23] that the species formed by the photodecomposition of diphenyldiazomethane has the unpaired electron structure. Also, the reaction of azulene with benzyl radicals gives low yields of predominantly 1- and 2-benzylazulene,[24] and azulene has been found to be quite unreactive toward certain other radical reagents.[25]

Experimental[26]

1-Benzhydrylazulene (1). A. **By Acid Catalysis.**—To a magnetically stirred solution of diphenyldiazomethane (0.4 g., 1.36 mmoles), prepared as described by Smith and Howard,[14] and azulene (0.2 g., 1.56 mmoles) in 10 ml. of dichloromethane cooled in a Dry Ice–acetone bath was added 2 drops of 100% fluoroboric acid. The mixture was stirred for 1 hr. and then allowed to come to room temperature. Ten milliliters of 5% sodium bicarbonate, 40 ml. of water, and 50 ml. of dichloromethane were added, the whole was shaken, and the separated organic phase was washed twice with water and then dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was chromatographed over alumina. *n*-Pentane eluted a blue-violet fraction which contained 35 mg. (18%) of unchanged azulene. A 20% solution of dichloromethane in *n*-pentane removed a blue fraction and slow evaporation of the solvent from this gave 305 mg. (75%, 81% net) of 1 as blue needles, m.p. 123.5–125°. Dichloromethane solutions showed λ_{max} in mμ (O.D.) at 228 (1.75), 282 (1.50), 287 (1.47), 293 (1.47), 337 (0.13), 347 (0.17), and 363 (0.12) in the ultraviolet, and at 596 (0.71), 645 (0.58), and 715 mμ (0.17) in the visible. The infrared spectrum was recorded.

Anal. Calcd. for $C_{23}H_{18}$: C, 93.84; H,6. 16. Found: C, 93.76; H, 5.92.

B. **By Photolysis.**—A solution of azulene (0.256 g., 2 mmoles) and diphenyldiazomethane[14] (1.0 g., 5 mmoles) in 25 ml. of dry ether was irradiated for 68 hr. at room temperature by a 450-w. Hanovia quartz immersion mercury vapor lamp. The solvent was then removed under reduced pressure and the residue was placed on an alumina column. Petroleum ether (b.p. 40–60°) eluted 31 mg. (12%) of unchanged azulene, and a 25% solution of dichloromethane in petroleum ether removed a blue fraction, which afforded 392 mg. (67%, 75% net) of blue needles which were identical (mixture melting point; ultraviolet, visible, and infrared spectra) with the product obtained by method A.

1-Butylazulene (2).—A solution of azulene (0.12 g., 0.94 mmole) and diazobutane (26 mg., 0.25 mmole), prepared as reported by Kenner and co-workers,[15] in 50 ml. of anhydrous ether was treated with fluoroboric acid and then the crude product was isolated as described for the analogous preparation of 1-benzhydrylazulene. The crude material was chromatographed on alumina. Elution with *n*-pentane removed 95 mg. (79%) of unchanged azulene, and then a blue fraction which gave 32 mg. (61%, 95% net) of 2 as a blue oil was eluted with a 50% solution of dichloromethane in *n*-pentane. Cyclohexane solutions showed λ_{max} in mμ (O.D.) at 262 (1.25), 274 (1.35), 348 (0.11), and 3.66 (0.08) in the ultraviolet, and at 560 (0.48), 584 (0.56), 606 (0.65), 630 (0.58), 663 (0.52), and 696 (0.27) in the visible. The infrared spectrum was recorded.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.50; H, 8.69.

Ethyl 1-Azulylacetate (3). A. **By Acid Catalysis.**—A solution of azulene (0.1 g., 0.78 mmole) and ethyl diazoacetate[27] (0.5 ml., 4.8 mmoles) in 5 ml. of dry dichloromethane was treated with fluoroboric acid and the crude product was isolated as described for the preparation of 1-benzhydrylazulene. The material so obtained was chromatographed on acid-washed alumina. Unchanged azulene (65 mg., 65%) was removed with petroleum ether and a 50% solution of dichloromethane in petroleum ether was then used to elute a light blue fraction. The latter afforded 54 mg. (32%, 93% net) of 3 as a blue oil which showed absorption at 5.78 μ (ester carbonyl). Cyclohexane solutions showed λ_{max} in mμ (O.D.$_{max}$) at 238 (1.48), 278 (1.18), 329 (0.15), 344 (0.13), and 362 (0.09) in the ultraviolet, and at 597 (1.08), 615 (0.96), 650 (0.93), and 718 (0.36) in the visible. The identity of the product as 3 was further shown by heating a sample (100 mg., 0.45 mmole) with 25 ml. of a 10% potassium hydroxide solution under reflux for 2 hr. The basic solution was extracted with three 30-ml. portions of ether. The dried (sodium sulfate) ether extract yielded 61 mg. (72%) of blue needles, m.p. 90–92°, which were identical (absorption spectra and mixture melting point) with an authentic sample of 1-azulylacetic acid.[16]

B. **By Photolysis.**—A solution of azulene (0.3 g., 2.34 mmoles) and ethyl diazoacetate[27] (0.87 g., 7.60 mmoles) in 50 ml. of 1,2-dimethoxymethane was irradiated for 84 hr. as described for the preparation of 1-benzhydrylazulene. After removal of the solvent under reduced pressure, the residue was chromatographed on acid-washed alumina. Petroleum ether removed 204 mg. (68%) of unchanged azulene, and then a 1:1 mixture of dichloromethane and petroleum ether eluted a blue fraction from which was obtained 157 mg. (31%, 99% net) of 3 which was identical (infrared, ultraviolet, and visible spectra) with the product obtained by method A.

Ethyl 1-(4,6,8-Trimethylazulyl)acetate. A. **By Acid Catalysis.**—A solution of 4,6,8-trimethylazulene (0.17 g., 1 mmole) and ethyl diazoacetate[27] (0.5 ml., 4.8 mmoles) in 7 ml. of dry dichloromethane was treated with fluoroboric acid and the crude product was isolated as described for the analogous preparation of ethyl 1-azulylacetate. The material so obtained was chromatographed over acid-washed alumina. Unchanged trimethylazulene (97 mg., 58%) was removed with a 20% solution of dichloromethane in petroleum ether. A 1:1 mixture of dichloromethane in petroleum ether eluted a violet fraction which yielded 97 mg. (38%, 91% net) of a violet oil. The product showed absorption at 5.77 μ (ester carbonyl). Cyclohexane solutions showed λ_{max} in mμ (O.D.) at 247 (0.55), 289 (0.92), 294 (0.90), 300 (0.88), 339 (0.8), 353 (0.11), and 364 (0.04) in the ultraviolet, and at 561 (1.9) with shoulders at 605 (1.5) and 660 (0.5) in the visible region.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.51; H, 7.88.

B. **By Photolysis.**—A solution of 4,6,8-trimethylazulene (0.17 g., 1 mmole) and ethyl diazoacetate (0.7 g., 6.14 mmoles) in 10 ml. of dry ether was irradiated for 48 hr. as described for the preparation of 1-benzhydrylazulene. The solvent was removed (reduced pressure) and the residue was chromatographed over acid-washed alumina. A 1:20 solution of dichloromethane in petroleum ether removed 128 mg. (75%) of unchanged trimethylazulene. Then a 1:3 mixture of the same solvents eluted a purple fraction which afforded 43 mg. (17%, 68% net) of product identified by its absorption spectra as the same as that from A.

Ethyl 3-Guaiazulylacetate. A. **By Acid Catalysis.**—A solution of guaiazulene (0.4 g., 2.22 mmoles) and ethyl diazoacetate[27] (0.75 g., 6.6 mmoles) in 15 ml. of dry dichloromethane was treated with fluoroboric acid and the crude product was isolated as described for the preparation of 1-benzhydrylazulene. The material so obtained was chromatographed over acid-washed alumina and unchanged guaiazulene (0.185 g., 46%) was removed with petroleum ether. A 30% solution of dichloromethane in petroleum ether eluted a blue fraction from which was obtained 0.194 g. (31%, 62% net) of blue oil. The product showed absorption at 5.77 μ (ester carbonyl). *n*-Pentane solutions exhibited λ_{max} in mμ (O.D.) at 246 (0.35), 287 (0.65), 306 (0.22), 353 (0.08), and 369 (0.08) in the ultraviolet, and at 616 (0.58) with a shoulder at 664 (0.28) in the visible region.

Anal. Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 79.93; H, 8.27.

B. **By Photolysis.**—A solution of guaiazulene (0.21 g., 1.06 mmoles) and ethyl diazoacetate (0.98 g., 8.7 mmoles) in 25 ml. of dry ether was irradiated for 72 hr. as described for the preparation of 1-benzhydrylazulene. The solvent was removed (reduced pressure) and the residue was chromatographed on acid-washed alumina. Petroleum ether eluted 161 mg. (76%) of unchanged guaiazulene. A 1:1 dichloromethane–petroleum ether solvent removed a blue fraction which yielded 33 mg. (11%, 50% net) of a blue oil identified by its absorption spectra as the same as the product from A.

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(23) R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959); W. Kirmse, L. Horner, and H. Hoffman, *Ann.*, **614**, 19 (1958).

(24) J. F. Tilney-Bassett and W. A. Waters, *J. Chem. Soc.*, 3123 (1959).

(25) A. G. Anderson and G. M-C. Chang, *J. Org. Chem.*, **23**, 151 (1958); A. G. Anderson and L. L. Replogle, unpublished results.

(26) Melting points are uncorrected and were taken on a Fisher-Johns apparatus. Ultraviolet and visible spectra were taken with a Model 14 Cary spectrophotometer. Infrared spectra were taken with a Model 21 Perkin-Elmer spectrophotometer. Analyses were performed by one of the authors (R. C. R.) or by Dr. Alfred Bernhardt, Microanalytical Laboratory, Mulheim (Ruhr), Germany.

(27) E. B. Womack and A. B. Nelson, *Org. Syn.*, **24**, 56 (1944).

1-Azulylacetone (4). A. By Acid Catalysis.—A solution of azulene (0.12 g., 0.84 mmole) and diazoacetone[17] (0.5 g., 5.9 mmoles) in 5 ml. of dry dichloromethane was treated with fluoroboric acid and the crude product was isolated as described for the preparation of 1-benzhydrylazulene. The material thus obtained was chromatographed on acid-washed alumina. Unchanged azulene (90 mg., 75%) was removed with *n*-pentane and a blue fraction was then eluted with 1:1 dichloromethane–petroleum ether and yielded 17 mg. (10%, 38% net) of a blue oil. The infrared spectrum of this product (dichloromethane solvent) showed a peak at 5.96 μ (ketone carbonyl), and dichloromethane solutions displayed λ_{max} in mμ (O.D.) at 239 (0.58), 280 (1.13), 348 (0.15), and 3.64 (0.12) in the ultraviolet, and at 599 with shoulders at 650 and 720 in the visible region.

Anal. Calcd. for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.86; H, 6.50.

B. By Photolysis.—A solution of azulene (0.256 g., 2 mmoles) and diazoacetone (0.7 g., 8.3 mmoles) in 25 ml. of dry ether was irradiated for 72 hr. as described for the preparation of 1-benzhydrylazulene. The solvent was removed (reduced pressure) and the residue was chromatographed over basic alumina. Petroleum ether eluted 189 mg. (74%) of unchanged azulene, and a blue fraction was then removed with 1:1 dichloromethane–petroleum ether. From this fraction was obtained 76 mg. (21%, 80% net) of blue oil which was identical (ultraviolet, visible, and infrared spectra) with the product from A.

2-(1′-Azulyl)acetophenone (5). A. By Acid Catalysis.—A solution of azulene (0.1 g., 0.78 mmole) and diazoacetophenone[17] (0.125 g., 0.86 mmole) in 6 ml. of dry dichloromethane was treated with fluoroboric acid and the crude product was isolated as described for the preparation of 1-benzhydrylazulene. The material so obtained was chromatographed on basic alumina and 85 mg. (85%) of unchanged azulene was recovered from the fraction eluted by *n*-pentane. Dichloromethane then removed a blue fraction which yielded 15 mg. (6%, 52% net) of a blue oil. The product (dichloromethane solvent) showed absorption at 5.95 μ (ketone carbonyl) and dichloromethane solutions exhibited λ_{max} in mμ (O.D.) at 237 (1.28), 280 (1.55), 283 (1.47), 333 (0.13), 346 (0.14), and 363 (0.09) in the ultraviolet, and at 594 (0.96), 640 (0.81), and 710 (0.28) in the visible region.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.72. Found: C, 87.53; H, 5.58.

B. By Photolysis.—A solution of azulene (0.3 g., 2.34 mmoles) and diazoacetophenone (0.4 g., 1.63 mmoles) in 25 ml. of dry ether was irradiated for 72 hr. as described for the preparation of 1-benzhydrylazulene. The solvent was removed (reduced pressure) and the residue was chromatographed on basic alumina. Unchanged azulene (0.24 g., 80%) was removed by petroleum ether and then 1:1 dichloromethane–petroleum ether eluted a blue fraction which yielded 93 mg. (17%, 85% net) of blue oil, identical (ultraviolet, visible, and infrared spectra) with the product from A.

2-[1′-(4,6,8-Trimethylazulyl)]acetophenone. A. By Acid Catalysis.—A solution of 4,6,8-trimethylazulene (0.12 g., 0.7 mmole) and diazoacetophenone[17] (0.25 g., 1.7 mmoles) in 10 ml. of dry diazomethane was treated with fluoroboric acid and the crude product was isolated as described for the preparation of 1-benzhydrylazulene. The material so obtained was chromatographed on alumina. A violet fraction which contained 105 mg. (89%) of unchanged trimethylazulene was eluted with petroleum ether and a purple fraction was then removed with 1:1 dichloromethane–petroleum ether. Removal of the solvent gave 13 mg. (7%, 75% net) of product as a purple solid. The infrared spectrum (chloroform solvent) showed absorption at 5.93 μ (ketone carbonyl). Dichloromethane solutions showed λ_{max} in mμ (log ϵ) at 248 (4.54), 290 (4.60), 293 (4.58), 300 (4.47), and 353 (3.72) in the ultraviolet, and at 559 (ϵ 363) in the visible.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.46; H, 7.18.

B. By Photolysis.—A solution of 4,6,8-trimethylazulene (0.2 g., 1.17 mmoles) and diazoacetophenone (0.25 g., 1.71 mmoles) in 25 ml. of dry ether was irradiated for 38 hr. as described for the preparation of 1-benzhydrylazulene. The crude product was chromatographed on acid-washed alumina and unchanged trimethylazulene (77 mg., 39%) was removed with petroleum ether. A 1:1 solution of dichloromethane and petroleum ether eluted a purple fraction which gave 58 mg. (17%, 24% net) of material which was identical (ultraviolet, visible, and infrared spectra) with the product from method A.

Phenylbenzoyl-1-azulylmethane (6). A. By Acid Catalysis.—A solution of azulene (0.228 g., 1.78 mmoles) and phenylbenzoyldiazomethane[18] (0.67 g., 3 mmoles) in 10 ml. of dry dichloromethane was treated with fluoroboric acid and the crude product was isolated as described for the preparation of 1-benzhydrylazulene. The material thus obtained was chromatographed on alumina and 0.165 g. (72%) of unchanged azulene was removed as the first fraction with petroleum ether. A blue fraction was then eluted with a 1:1 dichloromethane–petroleum ether mixture and removal of the solvent (nitrogen stream) gave 38 mg. (7%, 25% net) of a blue oil. The product (chloroform solvent) showed absorption at 5.88 μ (ketone carbonyl), and dichloromethane solutions of it exhibited λ_{max} in mμ (O.D.) at 240 (0.85), 281 (1.06), 293 (0.94), 346 (0.11), and 365 (0.09) in the ultraviolet, and at 590 (1.11), 672 (0.88), and 700 (0.33) in the visible.

Anal. Calcd. for $C_{24}H_{18}O$: C, 89.41; H, 5.63. Found: C, 89.13; H, 5.39.

B. By Photolysis.—A solution of azulene (0.277 g., 2.17 mmoles) and phenylbenzoyldiazomethane (0.576 g., 2.6 mmoles) in 30 ml. of dry ether was irradiated for 48 hr. as described for the preparation of 1-benzhydrylazulene. The solvent was removed (reduced pressure) and the residue was chromatographed on basic alumina. Unchanged azulene (0.195 g., 75%) was removed with petroleum ether and then a 1:1 dichloromethane–petroleum ether mixture eluted a blue fraction which gave 182 mg. (26%, 88% net) of a blue oil which was identical (ultraviolet, visible, and infrared spectra) with the product from A.

1-(4′-Hydroxyphenylazo)azulene (8). A. By Acid Catalysis.—A solution of azulene (0.256 g., 2 mmoles) and *p*-diazoquinone[19] (0.12 g., 1 mmole) in 10 ml. of anhydrous 1,2-dimethoxyethane (or dichloromethane) was treated with fluoroboric acid and the crude product was isolated as described for the preparation of 1-benzhydrylazulene. The material so obtained was chromatographed on neutral alumina. Unchanged azulene (117 mg., 46%) was removed with *n*-pentane and a yellow-brown fraction was then eluted with ether. Removal of the solvent afforded 220 mg. (88%, 93% net) of 8 as a viscous brown oil. The infrared spectrum of the product (chloroform solvent) showed peaks at 6.82 and 7.55 μ (azo group). Dichloromethane solutions showed λ_{max} in mμ (O.D.) at 226 (0.53), 283 (0.38), and 334 (0.12) in the ultraviolet, and at 427 in the visible. A trace of acid changed the color of the compound to a deep purple, while base changed it to orange. The changes were reversible.

Anal. Calcd. for $C_{16}H_{12}N_2O$: C, 77.41; H, 4.88. Found: C, 76.99; H, 5.29.

B. By Thermal Catalysis.—A solution of azulene (0.36 g., 2.81 mmoles) and *p*-diazoquinone in 15 ml. of 1,2-dimethoxyethane was heated under reflux for 2 hr. The solvent was removed under reduced pressure and the residue was chromatographed on alumina. Unchanged azulene (0.21 g., 58%) was eluted with *n*-pentane and then a yellow-brown fraction was removed with ether. Removal of the solvent from the latter gave 0.285 g. (92%) of brown oil which was identical (ultraviolet, visible, and infrared spectra) with the product from A.

C. From *p*-Hydroxybenzenediazonium Chloride.—To a cooled (ice bath) solution of *p*-hydroxybenzenediazonium chloride (prepared by the diazotization of 0.25 g. (1.72 mmoles) of *p*-hydroxyanilinium chloride) in 25 ml. of absolute ethanol was added a solution of absolute ethanol. The mixture was allowed to stand at 0° for 1 hr. and the black solid which had precipitated was then separated by filtration. This material was extracted with three 50-ml. portions of ether and the solvent was then removed from the combined, yellow, dried (sodium sulfate) organic extracts. The yellow-brown oil which remained (100 mg., 50%) was identical (ultraviolet, visible, and infrared spectra) with the product obtained in A.