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Tropylation of Azulene, 1-Oxaazulan-2-one, and Their Derivatives, and Electrophilic Reactions of the Tropylazulene Derivatives*[1]

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The tropylation of azulene, oxaazulan-2-one, and their derivatives was investigated, and various 1 and/or 3-tropylazulenes and 3-tropyloxaazulan-2-ones were obtained. The NMR, UV, and visible spectra of these tropylazulenes were then discussed. Some electrophilic reactions, such as azo-coupling and the acid treatment of four kinds of tropylazulenes, were studied, and it was found that exchanges of the tropyl group and the attacking electrophilies occurred.

The tropylium ion, one of the most stable carbonium ions, is known to react with various bases (anionoid reagents) resulting in the tropylation of nucleophiles, and in hydride abstraction in some cases.[1,2] The reaction can also be carried out conveniently using tropyl ethers,[2] sometimes with the addition of catalytic amounts of the tropylium ion or acids, in place of tropylium salts because of the facile ionization of the former to the latter under these conditions. In our laboratory, a continuous effeort has been made to tropylate various phenols[3,4] and tropolone[5] with these reagents, as well as to abstract the hydride ion from the tropylated products by means of the tropylium ion or other oxidizing reagents.[3,4]

Since sodium salts of cyclopentadiene[1,6] and indene[6] are also known to undergo tropylation by

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1) W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956); W. von E. Doering, "Theoretical Organic Chemistry" (The Kekule Symposium), Butterworth, London (1959), p. 35; T. Nozoe, "Progress in Organic Chemistry," Ed. by J. W. Cook, Vol. 5, Butterworth, London (1961), p. 132; D. M. G. Ll'oyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier (1966), pp. 98—114.

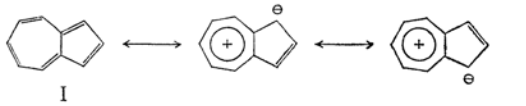
2) M. E. Vol'pin, I. S. Akhrem and D. N. Kursanov, *Izvest. Acad. Nauk USSR, Otdel, Khim. Nauk*, **1957**, 1501.

3) T. Nozoe, S. Ito, and T. Tezuka, *Chem. & Ind.*, **1960**, 1088.

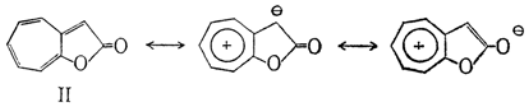
4) T. Nozoe and K. Kitahara, *ibid.*, **1962**, 1192, K. Takahashi, This Bulletin, **40**, 1462 (1967); T. Nozoe and K. Takahashi, *ibid.*, **40**, 1473, 1480 (1967).

5) T Nozoe, T. Tezuka and Y. Mukai, *ibid.*, **36**, 1470 (1963).

the tropylium ion, the 1 and 3 positions of azulene, being of the highest electron density in the ring system and having properties similar to those of these carbanions,[7a] may have sufficient anionic property to undergo tropylation. This anticipation led us to investigate the reaction of tropyl ethers with azulene (I) as well as 1-oxaazulan-2-one (II), the 3-position of which was also expected to be capable of electrophilic substitution.[7b] However, apart from our studies, Hafner *et al.*[8] and Anderson and Replogle[9] have reported the synthesis of some tropylazulenes by the reaction of of azulenes with tropylium perchlorate or tropylium fluoroborate.

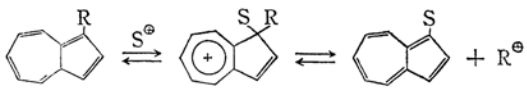


I



II

The intermediate of the electrophilic substitution reactions of azulenes may be represented as Formula A; it gives a final procuct such as B.[7b]



A B

It is a well-known phenomenon that when azulenes are dissolved in concentrated acids, the color of the azulenes disappears,[7a,10] while when R and S are hydrogen atoms, it has actually been proved by NMR[11] and UV[12] spectral techniques that azulenes exist in Formula A. When R is a group or atom can be eliminated easily, R will be replaced by other reagents, S. In fact, when R is acetyl, carboxyl, or sulfonyl, those groups are replaced by arylazo or halogens.[13,14] Since the tropyl groups readily forms the tropylium ion, the 1-tropylazulenes obtained above may be expected to cause an exchange reaction with other electrophilic reagents.

No reaction took place in benzene or cyclohexane between azulene and tropyl ethyl ether or ditropyl ether, even when the mixture was heated. However, the addition of a catalytic amount of tropylium bromide or mineral acids to the above mixture caused a smooth reaction, one which gave 1,3-ditropylazulene (III). In a similar manner, 5-isopropylazulene and 2-acetamidoazulene yielded the corresponding 1,3-ditropyl derivatives, (IV) and (V) respectively. Although it was difficult to control the reaction at the stage of monotropylation in the above reactions, this was achieved with 2-chloroazulene (VI); 2-chloro-1-tropylazulene (VIII) and 2-chloro-1,3-ditropylazulene (VII) were obtained using a half-molar equivalent of the reagent.

1-Methylazulene and guaiazulene (IX) which are substituted at the 1-position, gave monotropyl derivatives, (X) and (XI) respectively; diethyl azulene-1,3-dicarboxylate did not undergo tropylation, even when the reaction mixture was heated. Hence, it may be considered that the tropyl groups in the tropylazulenes are located at the 1 and/or 3-positions of azulene nuclei; this is clear from the studies of their NMR spectra and visible absorption spectra, which will be described later.

A formyl or ethoxycarbonyl group at the C 1-position diminishes the reactivity of azulene to tropylation; however, 1-formylazulene, ethyl azulene-1-carboxylate (XII), and their 2-chloro derivatives gave, in the reaction with ditropyl ether in the presence of tropylium bromide or hydrochloric acid, the corresponding monotropyl derivatives (XIII-XVI) in high yields at an elevated temperature. Ethyl 2-aminoazulene-1-carboxylate also gave the 3-tropyl derivative (XVII). XV was also obtained by the formylation of 2-chloro-1-tropylazulene (VIII) by Vilsmeyer's method.

1-Tropylazulene (XVIII) was obtained from ethyl 1-tropyl-azulene-3-carboxylate (XIV) by alkaline hydrolysis and subsequent decarboxylation. The heating of the oxime of XV with acetic anhydride furnished 2-chloro-1-cyano-3-tropylazulene (XIX).

It has been known[15] that the thermal isomerization of double bonds in a tropyl group occurs readily. Therefore, the tropyl group in XVIII or XIX obtained through thermal process might undergo isomerization.*3

6) H. Prinzbach, *Angew, Chem.*, **73**, 167 (1961); H. Prinzbach and D. Seip, *ibid.*, **73**, 169 (1961); H. Prinzbach and W. Rosswog, *ibid.*, **73**, 543 (1961).

7) a) T. Nozoe and T. Asao, "Dai-Yuki Kagaku" (Comprehensive Organic Chemistry), Vol. 13, Asakura Shoten, Tokyo (1960), p. 439, and the references cited therein; b) T. Nozoe and K. Kikuchi, *ibid.*, p. 455.

8) K. Hafner, A. Stephan and C. Bernhard, *Ann.*, **650**, 42 (1961).

9) A. G. Anderson, Jr., and L. L. Replogle, *J. Org. Chem.*, **28**, 262 (1963).

10) A. E. Sherndal, *J. Am. Chem. Soc.*, **37**, 167, 1537 (1915).

11) W. G. Schneider, J. H. Bernstein and J. A. Pople, *J. Am. Chem. Soc.*, **80**, 3497 (1958); H. W. Frey, *J. Chem. Phys.*, **25**, 600 (1956).

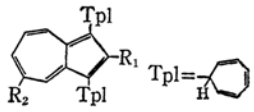
12) Pl. Plattner, E. Heilbronner and S. Weber, *Helv. Chim. Acta*, **35**, 1036 (1952).

13) A. G. Anderson, J. A. Nelson and J. J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953).

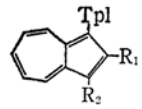
14) W. Treibs and W. Schroth, *Ann.*, **586**, 202 (1954).

15) A. P. ter Borg. H. Kloosterzield and N. van Meurs, *Proc. Chem. Soc.*, **1962**, 359; *Rec. trav. chim.*, **82**, 717 (1963); A. P. ter Borg and H. Kloosterziel, *ibid.*, **82**, 741 (1963); T. Nozoe and K. Takahashi, This Bulletin, **38**, 665 (1965).

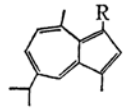
*3 Anderson *et al.*[9] reported that 1-tropylazulene has a mp of 60.5°C, however, the substance obtained in this experiment did not crystallize, perhaps because of the contamination of the thermal isomerization products.



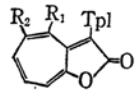
III $R_1=R_2=H$
IV $R_1=H$, $R_2=$isopro.
V $R_1=NHCOCH_3$, $R_2=H$
VII $R_1=Cl$, $R_2=H$



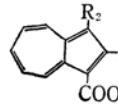
VIII $R_1=Cl$, $R_2=H$
X $R_1=H$, $R_2=CH_3$
XIII $R_1=H$, $R_2=CHO$
XIV $R_1=H$, $R_2=COOC_2H_5$
XV $R_1=Cl$, $R_2=CHO$
XVI $R_1=Cl$, $R_2=COOC_2H_5$
XVII $R_1=NH_2$, $R_2=COOC_2H_5$
XVIII $R_1=R_2=H$
XIX $R_1=Cl$, $R_2=CN$



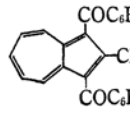
IX R=H
XI R=Tpl
XXIV $R=N=N-C_6H_4(CH_3)p$
XXVI $R=COC_6H_5$



XX $R_1=R_2=H$
XXI $R_1=CH_3$, $R_2=H$
XXII $R_1=H$, $R_2=$isopro.



XXV $R_1=NH_2$, $R_2=N=N-C_6H_4(CH_3)p$
XXVIII $R_1=H$, $R_2=COC_6H_5$
XXIX $R_1=NH_2$, $R_2=NO$



XXVII

Fig. 1

Since it has been found[16] that diethyl 2-amino- or 2-hydroxy-azulene-1,3-dicarboxylate was brominated on its 6-position, the tropylation of diethyl 2-amino or 2-hydroxyazulene-1,3-dicarboxylate was attempted. However, even at an elevated temperature, the azulenes failed to undergo tropylation, and the starting azulenes were recovered.

As in the case of azulene, the tropylation of 1-oxaazulan-2-one (II) with tropyl ethyl ether in the presence of tropylium bromide or hydrochloric acid yielded the 3-tropyl derivative (XX). In a similar manner, the 4-methyl and 5-isopropyl derivatives of II gave the corresponding 3-tropyl derivatives, (XXI) and (XXII).

In order to determine the position of the extra hydrogen in the tropyl group attached to azulene, the NMR spectra were studied. The peaks due to the extra hydrogen (C_7-H) in the tropyl group appear as a triplet at τ 6.68 (J=5.3 cps) in III, 6.42 (J=5.3 cps) in VII, and 7.38 (J=5.4 cps) in XX, and the peaks due to olefinic protons of the 1- and 6-positions in the tropyl group appear as a double doublet (d, d) at τ 4.46 (J=5.3 and 9.0 cps) in III, 4.48 (J=5.3 and 9.4 cps) in VII, and 4.59 (J=5.4 and 9.6 cps) in XX. The ratio of the areas of above two kinds of proton signals is about 1 : 2, showing clearly that the bonds are formed between the 7-position of tropilidene and the azulene nuclei.

The facts that the signal of the C_2-H of the azulene nucleus of III appears at τ 1.90 as a singlet, and that no signals of C_1-H and C_3-H are observed in the spectra of III and VII, clearly show tropyl groups are located at the and 3-positions of azulenes. The large down-field shifts of the C_7-H of the tropyl groups in these compounds compared with that of tropilidene[17] (7.806 τ) may be ascribed to the paramagnetic deshielding effects of the azulene or oxaazulanone nucleus.

The absorption maxima in the visible spectra of tropylazulenes are recorded in Table 1. From this table, it is clear that the introduction of one tropyl group causes a bathochromic shift of 16—24 mμ in the maxima of the highest intensity, this effect being almost equal to that of alkyl groups.[7a,18]

In order to clarify the electronic and steric effects of the electrophilic substitution reactions of substituted tropylazulenes, 2-chloro-1-tropylazulene (VIII), 3-tropylguaiazulene (XI), ethyl 3-tropylazulene-1-carboxylate (XVII) were submitted to electrophilic substitution reactions.

The treatment of XI and XVII with *p*-toluenediazonium chloride (XXIII) under mild conditions readily afforded the corresponding azo compounds, 3-(*p*-tolylazo)guaiazulene (XXIV) and ethyl 2 - amino - 3 - (*p* - tolylazo)azulene - 1 - carboxylate

16) T. Nozoe, S. Seto and S. Matsumura, This Bullethin, **35**, 1990 (1962); T. Nozoe, T. Asao and M. Oda, to be published.

17) G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richard, *J. Am. Chem., Soc.* **82**, 5846 (1960).

18) Cf. E. Heilbronner, "Non-Benzenoid Aromatic Compounds," ed. by D. Ginsburg, Interscience, New York (1959), p. 171.

Table 1. Visible spectra of tropylazulenes

Compounds*	λ_{max}: mμ (ε)	λ'_{max}**	$\Delta\lambda$***
III	742(130), 674(333), 640s(341), 618(391), 590s(326), 570s(280)	580	19
IV	730s(133), 656(320), 628(362), 575s(292)	590	19
V	704s(138), 634(350), 594(393), 550s(289)	540	27
VII	690(136), 630(346), 584(392), 545s(282)	552	16
VIII	674(119), 662(128), 615(323), 605(321), 567(368), 530s(265)	552	15
X	730(139), 684(282), 663(311), 628(354), 610(340), 588s(297)	608	20
XI	750s(106), 677s(229), 624(369), 600s(347), 575s(303)	603	21
XIII	670(108), 607(299), 560(368), 525s(300)	542	18
XIV	673(105), 648s(142), 612(324), 588(348), 565(392)	544	21
XV	620s(144), 566(351), 534(398)		
XVI	624s(180), 575(423), 540(464)	521	19
XVIII	720(101), 650(244), 604(286), 560s(226)	580	24
XIX	655s(153), 596(377), 558(427)		

* Solvent: cyclohexane except V (benzene).
** Maxima having the highest intensity of the corresponding compounds without tropyl group.
*** $\Delta\lambda=(\lambda_{max}$ of the highest intensity$-\lambda'_{max})$/number of tropyl group in a molecule.

Table 2. The results of the acid treatment of tropylazulene derivatives

Tropylazulene / Condition	VIII	XI	XIV	XVII
Conc. H_2SO_4	VI and VIII	IX (74%)	Recovery (94%)	Recovery (61%)
Dil. H_2SO_4	VI and VIII	IX (90%)	Recovery (100%)	Recovery (90%)

(XXV).[19] However, VIII and XIV were recovered when treated under the same reaction conditions. Also, ethyl azulene-1-carboxylate was recovered by the same treatment. Although the azo-coupling reaction of VIII was carried out at an elevated temperature, 80% of the starting material was recovered, plus a small amount of a black resinous substance, which has so far not been identified.

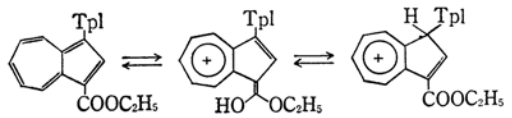
The Friedel-Crafts reaction of XI with an equimole of benzoyl chloride afforded 32% of guaizulene and 23% of 3-benzoylguaiazulene (XXVI).[20] The yield of XXVI from guaiazulene (IX) under the same reaction conditions was also not good, 16%. The treatment of XVII under the same reaction conditions resulted in an entire recovery of the starting material. This may be explained as follows: the formation of the complex of the 2-amino-group of XVII with aluminum chloride decreases the electron density of the azulene nucleus, and, at the same time the bulkiness of the complex causes serious steric hindrance. On the other hand, the reaction of VIII and XIV with 2 equimoles of benzoyl chloride afforded 1,3-dibenzoyl-2-chloro-azulene (XXVII), together with a small amount of the recovered starting substances, and ethyl 3-benzoylazulene-1-carboxylate (XXVIII), respectively. Although the C-3 position of VIII is not substituted, 3-benzoyl-2-chloro-1-tropylazulene could not be isolated even when an equimole of benzoyl chloride was used. It was also found that the reaction of 2-chloroazulene and one mole of benzoyl chloride resulted in the formation of XXVII and the recovery of 2-chloroazulene.

It is expected that the reaction of tropylazulene with acids regenerates azulenes and the tropylium ion. The results of the treatment of tropylazulenes with concentrated and diluted sulfuric acid are shown in Table 2.

Although a small amount of VI was separated from the reaction mixture of VIII and acid, the complete separation of VI and VIII was unsuccessful. The mixture was identified with a mixture of authentic samples of VI and VIII by means of their IR spectra. However, the exact ratio of VI and VIII was not clear.

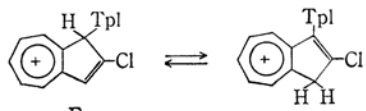
The recovery of XIV can be explained as follows: the protonation of XIV took place not only at C-3, as has been shown before, to form a D intermediate, but also at the carbonyl group to form a C intermediate. In fact, the NMR spectrum of XIV shows at τ 8.3 and the methylene quartet at τ 5.6 in carbon tetrachloride, but the signal is changed to a complex multipet in a trifluoroacetic acid solution. It can resonably be understood that XIV is protonated to form and equilibrium mixture of substances such as C, D, and XIV in the acidic solution, and presumably the equilibrium

19) T. Nozoe, T. Asao and M. Kobayashi, to be published.
20) W. Treibs, *Chem. Ber.*, **90**, 761 (1957); D. H. Reid, W. H. Stafford and W. L. Stafford, *J. Chem. Soc.*, **1958**, 1118.



XIV C D

tends to the C form; because XIV was recovered quantitatively. An analogous phenomenon was observed when 1-nitroazulene was dissolved in strong acid and protonation was favorable at the oxygen atoms of the nitro group, but not at the C-3 position.[21] In the case of XVII, the protonation takes place not only at the carbonyl group, but also at the amino group, this makes protonation at C-3 harder and no proton-tropylium cation exchange reaction occurs. In the case of VIII, E- and F-type intermediates may form, 2-chloroazulene should be obtained from the E-type intermediate. Therefore, the prolonged treatment of VIII with acid would give VI in a good yield.



E F

However, because of the unstability of the tropyl group in relation to acid, the prolonged treatment of VIII increases the amount of intractable resinous products and does not give any clear-cut results.

The treatment of XVII with isoamyl nitrite and sulfuric acid afforded brown micro needles (XXIX) which were identical with ethyl 2-amino-3-nitrosoazulene-1-carboxylate.[22] As has been mentioned above, XVII did not eliminate the tropylium cation to form ethyl 2-aminoazulene-1-carboxylate upon acid treatment. Therefore, the nitrosation of XVII must happen by the direct exchange reaction of the tropylium cation and the nitrosonium ion. It is interesting and noteworthy that even though the C-1 and C-3 positions of azulene nuclei of XVII are substituted, the diazotization of amino group does not take place and an exchange reaction occurs.

Experimental*4

General Procedure for the Tropylation of Azulenes and 1-Oxaazulanones. To a stirred solution of azulenes (or 1-oxaazulanones) in cyclohexane (or benzene), ditropyl ether (or tropyl ethyl ether) and a catalytic amount of tropylium bromide (or concentrated hydrochloric acid) were added at room temperature. After the solution has been stirred at room temperature for 2 hr—one day, it was washed with water and dried over anhydrous sodium sulfate, and the products purified by passing them through an alumina column and then recrystallizing them.

1,3-Ditropylazulene (III). The reaction of azulene and 2 molar equivalents of tropyl ether afforded III as blue needles (62%), mp 137—138°C (from cyclohexane).

Found: C, 93.23; H, 6.46%. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54%.

1,3-Ditropyl-5-isopropylazulene (IV). The reaction of 5-isopropylazulene and 2-molar equivalents of tropyl ether gave IV as a blue oil (90%). IV did not give a trinitrobenzene complex and changed to a dark yellow substance upon standing in air.

Found: C, 92.30; H, 7.79%. Calcd for $C_{27}H_{26}$: C, 92.52; H, 7.48%.

2-Acetamido-1,3-ditropylazulene (V). The reaction of 2-acetamidoazulene and 2 molar equivalents of tropyl ether gave V as blue crystals (45%), mp 206.5—207°C (from benzene-cyclohexane).

Found: C, 85.58; H, 6.65; N, 3.42%. Calcd for $C_{26}H_{23}ON$:C, 85.45; H, 6.34; N, 3.83%.

2-Chloro-1,3-ditropylazulene (VII). The reaction of 2-chloroazulene and 2-molar equivalents of tropyl ether afforded VII as blue needles (85%), mp 164—165°C (from cyclohexane).

Found: C, 83.79; H, 6.01%. Calcd for $C_{24}H_{19}Cl$: C, 84.08; H, 5.59%.

2-Chloro-1-tropylazulene (VIII). The reaction of 2-chloroazulen with one molar equivalent of tropyl ether afforded VII (27%) and VIII (62%) as violet needles, mp 87—88°C (from petroleum ether), besides the recovered 2-chloroazulene.

Found: C, 80.60; H, 5.56%. Calcd for $C_{17}H_{13}Cl$: C, 80.60; H, 5.17%.

1-Methyl-3-tropylazulene (X). X was obtained from 1-methylazulene as a blue oil (75%).

Trinitrobenzene complex: mp 155.5—156°C.

Found: C, 64.98; H, 4.19; N, 9.07%. Calcd for $C_{21}H_{19}O_6N_3$: C, 64.71; H, 4.30; N, 9.43%.

3-Tropylguaiazulene (XI). XI was obtained from guaiazulene as blue crystals (86%), mp 74—75°C.

Found: C, 91.56; H, 8.50%. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39%.

Trinitrobenzene complex: black needles, mp 96—97°C.

Found: C, 67.12; H, 5.24; N, 8.23%. Calcd for $C_{28}H_{27}O_6N_3$: C, 67.05; H, 5.43; N, 8.38%.

1-Formyl-3-tropylazulene (XIII). XIII was obtained from 1-formylazulene as a reddish-violet oil.

Trinitrobenzene complex: brown needles, mp 108—109°C.

Found: C, 63.02; H, 3.92; N, 8.60%. Calcd for $C_{24}H_{17}O_6N_3$: C, 62.74; H, 3.73; N, 9.15%.

Ethyl 3-Tropylazulene-1-carboxylate (XIV). XIV was obtained from ethyl azulene-1-carboxylate as a reddish-violet oil (98%).

Trinitrobenzene complex: brown needles, mp 80°C.

Found: C, 61.97; H. 4.18; N, 8.11%. Calcd for $C_{26}H_{21}O_8N_3$: C, 62.02; H, 4.20; N, 8.35%.

2-Chloro-1-formyl-3-tropylazulene (XV). a) A solution of 65 mg of VIII, 3 m*l* of dimethylformamide, and 50 mg of phosphoryl chloride was allowed to stand overnight. Water (30 m*l*) was then added, and the mixture was neutralized with sodium hydrogen carbonate and extracted with benzene. The extract was

21) D. Menche and E. Heilbronner, *Helv. Chim. Acta*, **45**, 1965 (1962).
22) T. Nozoe, P. W. Yang, H. Ogawa and T. Toda, This Bulletin, **41**, 2095 (1968).
*4 All melting points are uncorrected.

dried and passed through an alumina column. VIII (52 mg) was recovered from the first eluate, and 14 mg of XV, from the next eluate. Recrystallization from benzene-petrolum ether afforded XV as reddish-violet needles, mp 192.5—193.5°C.

Found: C, 77.13; H, 4.91%. Calcd for $C_{18}H_{13}OCl$: C, 77.01; H, 4.67%. b) The tropylation of 2-chloro-1-formylazulene afforded XV (68%), mp 191—192°C, which showed no depression of melting point on admixture with the sample obtained by Procedure a).

Ethyl 2-Chloro-3-tropylazulene-1-carboxylate (XVI). The tropylation of ethyl 2-chloroazulene-1-carboxylate afforded XVI as reddish-violet crystals (quantitative yield), mp 115°C.

Found: C, 74.30; H, 5.23%. Calcd for $C_{20}H_{17}O_2Cl$: C, 73.95; H, 5.28%.

Ethyl 2-Amino-3-tropylazulene-2-carboxylate (XVII). The tropylation of ethyl 2-aminoazulene-1-carboxylate afforded XVII as a reddish-brown oil (quantitative yield).

Picrate, mp 133—134°C.

Found: C, 58.45; H, 3.89; N, 10.03%. Calcd for $C_{26}H_{22}O_9N_4$: C, 58.42; H, 4.15; N, 10.43%.

1-Tropylazulene (XVIII). A solution of 390 mg of XIV and 230 mg of potassium hydroxide in 20 m*l* of ethanol and 6 m*l* of water was refluxed for 4.5 hr. After the ethanol had then been removed, the solution was acidified with hydrochloric acid. A reddish-violet precipitate was collected, dried, and heated in a sublimation apparatus under reduced pressure to give a blue oil. This oil was purified by chromatography to afford 1-tropylazulene as a greenish-blue oil.

Found: C, 93.30; H, 6.39%. Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.47%.

Trinitrobenzene complex: mp 97.5°C.

Found: C, 64.50; H, 4.02; N, 9.83%. Calcd for $C_{23}H_{17}O_6N_3$: C, 64.03; H, 3.97; N, 9.74%.

2-Chloro-1-cyano-3-tropylazulene (XIX). A solution of 130 mg of XV, 200 mg of hydroxylamine hydrochloride, and 2 m*l* of a 0.5 N sodium hydroxide solution in 3 m*l* of ethanol was refluxed for 20 min. The ethanol was removed, water was added and then extracted with chloroform, and the extract was evaporated to leave a green solid. When a solution of the solid in 2 m*l* of acetic anhydride was refluxed for 30 min, 20 mg of reddish-violet crystals (XIX) were obtained, mp 155°C.

Found: C, 64.57; H, 3.80; N, 5.35%. Calcd for $C_{14}H_{10}O_2NCl$: C, 64.77; H, 3.88; N, 5.40%.

3-Tropyl-1-oxaazulan-2-one (XX). The tropylation of 1-oxaazulan-2-one afforded XX (85%), as yellowish-orange plates, mp 108-110°C (from ethanol).

Found: C, 81.65; H, 5.48%. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12%.

4-Methyl-3-tropyl-1-oxaazulan-2-one (XXI). The tropylation of 4-methyl-1-oxaazulan-2-one gave XXI (80%), as orange prisms, mp 170—171°C (from acetone).

Found: C, 81.44; H, 5.63%. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%.

5-Isopropyl-3-tropyl-1-oxaazulan-3-one (XXII). The tropylation of 5-isopropyl-1-oxaazulan-2-one gave XXII (73%), as orange needles, mp 87—89°C (from ethanol).

Found: C, 82.08; H, 6.74%. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52%.

3-(*p*-Tolylazo)guaiazulene (XXIV). a) Into a solution of 100 mg of IX in 1 m*l* of pyridine cooled in an ice bath, aqueous *p*-toluidine diazonium chloride (XXIII) prepared from 54 mg of *p*-toluidine, 50 mg of sodium nitrite, 0.5 m*l* of 6 N hydrochloric acid, and 0.3 m*l* of water, was stirred, drop by drop. The solution turned from blue to a brownish yellow. After the solution had been stirred for one hour at room temperature, 2 m*l* of water were added and then extracted with chloroform. The combined chloroform layers were dried over sodium sulfate, filtered off, and concentrated to give a dark green, crystalline substance. Recrystallization from ethanol afforded 144 mg of XXIV, mp 138°C.

Found: C, 83.46; H, 7.50; N, 8.45%. Calcd for $C_{22}H_{24}N_2$: C, 83.50; H, 7.64; N, 8.85%.

b) To a solution of 100 mg of XI in 1 m*l* of pyridine cooled in an ice bath, a solution of XXIII prepared from 75 mg of *p*-toluidine was added, drop by drop. The reaction was carried out for 4 hr at room temperature, and then the results were treated as above to give 50 mg of XXIV, mp 136°C, which was identical with the XXIV obtained above.

Ethyl 2-Amino-3-(*p*-tolylazo)azulene-1-carboxylate (XXV). From 100 mg of XVII in 1 m*l* of pyridine and XXIII prepared from 53 mg of *p*-toluidine, 160 mg of an oily substance was obtained. The oil was chromatographed on alumina; the cyclohexane eluate afforded 107 mg of reddish-brown micro-needles whose melting point was 119.5°C after having been recrystallized from ethanol and which was identical with authentic XXV.[15]

Azo-coupling Reaction of VIII. Into a solution of 100 mg of VIII in 1.5 m*l* of pyridine in an ice bath, aqueous XXIII (from 43 mg of *p*-toluidine) was stirred. A precipitate formed immediately, but the reaction was continued for 2 hr. The precipitate was then filtered off and dried in a desiccator. The mother layer was extracted with chloroform, and the combined extracts were washed with water, dried over sodium sulfate, and concentrated to give a residue. The residue and the precipitate were dissolved in petroleum ether and chromatographed on alumina to give 86 mg of recovered VIII.

Ethyl 3-Benzoylazulene-1-carboxylate (XXVIII). a) To 30 m*l* of dry carbon disulfide, 200 mg of XIV, 195 mg of benzoyl chloride, and 183 mg of anhydrous aluminum chloride were added, and the resulting solution was refluxed for 15 hr. The organic layer was separated, washed with water and N sodium hydroxide, dried over sodium sulfate, and then concentrated to give a residue. The residue was dissolved in petroleum chromatographed on alumina. The petroleum ether eluate afforded 125 mg of XIV while the benzene-petroleum ether eluate gave 70 mg of a dark red residue, which in turn afforded 64 mg of dark red prisms of XXVIII, mp 107°C, after recrystallization from ethanol.

Found: C, 79.26; H, 5.39%. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30%.

b) A solution of 200 mg of ethyl azulene-1-carboxylate, 282 mg of benzoyl chloride, and 266 mg of aluminum chloride in 30 m*l* of carbon disulfide was heated to reflux for 13 hr and then worked up as above to give 170 mg of XXVII, mp 108°C, after recrystallization from ethanol.

3-Benzoylguaiazulene (XXVI). A solution of 400 mg of XI, 215 mg of aluminum chloride, and 202 mg of benzoyl chloride in 20 m*l* of carbon disulfide was heated to reflux for 14 hr. After the reaction had been

completed, the mixture was worked up as above and chromatographed on alumina. The first benzene effluent afforded 87 mg of a blue oil which was identical with guaiazulene (31.6%), while the second effluent gave 41 mg of a dark green semisolid which in turn afforded 10 mg of XXVI, mp 119°C, after recrystallization from ethanol and which was identical with the 3-benzoylguaiazulene prepared by the reported method.[20]

2-Chloro-1,3-dibenzoylazulene (XXVII). a) solution of 150 mg of VIII, 168 mg of benzoyl chloride, and 160 mg of aluminum chloride in 25 m*l* of carbon disulfide was refluxed for 14 hr, and then worked up in the usual manner. The first petroleum ether effluent gave 22 mg of VI, while the second gave 124 mg of a dark red oil. The latter was rechromatographed, and the benzene effluent gave 25 mg of red prisms of XXVII, mp 179—180°C; recrystallization from benzene raised its melting point to 185°C.

Found: C, 77.85; H, 4.28%. Calcd for $C_{24}H_{15}O_2Cl$: C, 77.73; H, 4.35%.

b) A solution of 200 mg of VI, 260 mg of benzoyl chloride, and 245 mg of aluminum chloride in 30 m*l* of carbon disulfide was refluxed for 13 hr; a subsequent work-up in the usual manner afforded 32 mg of VI and 143 mg of XXVII.

Ethyl 2-Amino-3-nitrosoazulene-1-carboxylate (XXIX). a) To a solution of 450 mg of XVII in 20 m*l* of ethanol in an ice bath, 1 m*l* of concentrated sulfuric acid was added, and then 342 mg of isoamyl nitrite were added. After the mixture had been allowed to stand overnight at room temperature, the precipitate thus formed was filtered off, washed with aqueous sodium hydrogen carbonate and water, and dried in a desiccator. Recrystallization from chloroform afforded 190 mg of dark brown scales of XXIX, mp 174—174.5°C.

Found: C, 63.61; H, 4.73; N, 11.25%. Calcd for $C_{13}H_{12}O_3N_2$: C, 63.92; H, 4.95; N, 11.47%.

b) A solution of 300 mg of XVII in 12 m*l* of ethanol cooled in an ice bath was saturated with dry hydrogen chloride, and then 230 mg of isoamyl nitrite were added, drop by drop. After 4 hr, the solution was poured into 50 m*l* of water, and the separated water layer was neutralized with sodium hydrogen carbonate to form a precipitate. The precipitate was washed with water, dried in a desiccator, and recrystallized from chloroform to afford 90 mg of XXIX, mp 174°C.

The Exchange Reactions of the Tropyl Group with the Proton on the Tropylazulenes. *i) 3-Tropylguaiazulene.* a) A solution of XI in 4 m*l* of concentrated sulfuric acid was allowed to stand at room temperature for 1 hr; then it was poured into 20 m*l* of ice water and extracted with benzene. The combined extract was washed with aqueous sodium hydrogen carbonate and water, dried over sodium sulfate, and chromatographed on alumina to afford 50 mg of a blue oil. The IR, UV, and visible spectra of the oil were identical with those of guaiazulene.

b) To a solution of 100 mg of XI in 4 m*l* of dioxane, 2 m*l* of 1 N sulfuric acid were added, after which the mixture was heated on a water bath for 30 min. After cooling, the solution was neutralized with aqueous sodium hydrogen carbonate, and extracted with benzene. The combined extracts were washed with water, dried over sodium sulfate, and chromatographed on alumina to give 60 mg of IX.

ii) Ethyl 2-Amino-3-tropylazulene-1-carboxylate. a) A solution of 100 mg of XVII in 5 m*l* of concentrated sulfuric acid was treated as above; the ethyl acetate effluent yielded 61 mg of the starting material.

b) To a solution of 100 mg of XVII in 4 m*l* of dioxane, 2 m*l* of 1 N sulfuric acid were added, after which the mixture was heated on a water bath for 2 hr. A subsequent work-up in the usual method gave 92 mg of the unchanged, recovered substance.

iii) Ethyl 3-Tropylazulene-1-carboxylate. a) To a solution of 100 mg of XIV in 4 m*l* of dioxane, 1 m*l* of dioxane, 1 m*l* of concentrated sulfuric acid was added, after which the solution was allowed to stand for 1 hr at room temperature. The reaction mixture was then worked up in the usual manner: the benzene effluent of the chromatography of the crude substance gave 94 mg of the starting substance.

b) A mixture of 100 mg of XIV, 4 m*l* of dioxane, and 2 m*l* of 1 N sulfuric acid was heated on a water bath for 2 hr; then it was worked up as above to give 100 mg of the recovered starting substance.

iv) 2-Chloro-1-tropylazulene. a) To a solution of VIII in 3 m*l* of dioxane, 1 m*l* of concentrated sulfuric acid was added, after which the solution was allowed to stand at room temperature for 30 min and then worked up as above. The petroleum ether effluent of the chromatography afforded 76 mg of a blue oil substance whose IR spectrum showed that the oil was a mixture of VIII and 2-chloroazulene.

b) A mixture of 100 mg of VIII, 4 m*l* of dioxane, and 2 m*l* of 1 N sulfuric acid was heated on a water bath for 2 hr, and then worked up as above. The first petroleum ether effluent gave 10 mg of 2-chloroazulene, mp 91°C, while the second effluent afforded 70 mg of a blue oil which was a mixture of VI and VIII.

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