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The Reactions of 1-Tropylazulenes with Phosphorus Pentachloride

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The reactions of three 1-tropylazulenes——ethyl 2-acetamido-3-(cycloheptatrien-7-yl)azulen-1-carboxylate (I), 2-chloro-1-(cycloheptatrien-7-yl)azulene (II) and ethyl 3-(cycloheptatrien-7-yl)-azulen-1-carboxylate (III)——with phosphorus pentachloride were investigated. The reactions of I and II gave ethyl 2-acetamidoazulen-1-carboxylate and 1,2,3-trichloroazulene respectively. On the other hand, III afforded ethyl 3-chloroazulen-1-carboxylate (IV) and (3-ethoxycarbonylazulen-1-yl)tropylium perchlorate (V). The thermal isomerization of III formed *ca.* 2:3 mixtures of ethyl 3-(cycloheptatrien-3-yl)azulen-1-carboxylate (IV) and ethyl 3-(cycloheptatrien-1-yl)azulen-1-carboxylate (VII), but not ethyl 3-(cycloheptatrien-2-yl)azulen-1-carboxylate. The treatment of the above mixtures with phosphorus pentachloride raised the yield of V; however, IV was also obtained. The sodium borohydride reduction of V gave *ca.* 2:3 mixtures of VI and VII.

Syntheses of 1-tropylazulenes have been reported by Hafner and his coworkers,[2] by Anderson and Replogle,[3] and by the present authors.[4] Although attempts to synthesise azulenyltropylium ions by means of the hydride abstraction of tropylazulenes have been carried out,[2,3] there are no reports in the literature that azulenyltropylium ions have been successfully isolated in a pure state. Azulenyltropylium ions are of interest because of their possible canonical formulae, *e.g.*, the azulenyltropylium-ion type (A) and the condensed fulvalene-tropylium-ion type (B), as is shown in Fig. 1. The contribution of which canonical formula is more important is the first question. Secondly, if those types of ions are synthesized, they should be useful potential key intermediates for synthesizing non-benzenoid polycondensed aromatics, corresponding to benzanthracene, pentacene, *etc.*, in benzenoid polycondensed aromatics. Also, it is interesting to compare their properties with those of 1-azulenylfulvenes (C),[5]

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

[3] A. G. Anderson and L. L. Replogle, *J. Org. Chem.*, **28**, 262 (1963).

[4] T. Nozoe, T. Toda, T. Asao and A. Yamanouchi, This Bulletin, **41**, 2935 (1968).

[5] K. Hafner and C. Bernhard, *Ann.*, **625**, 108 (1959); T. Toda, P. W. Yang and T. Mukai, *Sci. Repts. Tohoku Univ. I*, **50**, 208 (1967).

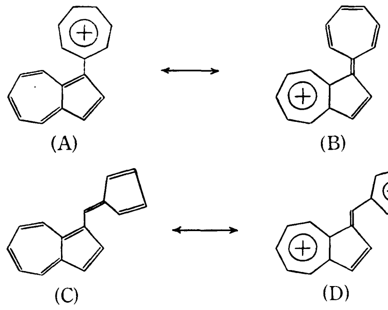

Fig. 1

which possess a (D)-type canonical formula.

In order to study the influence of substituents on azulene nuclei for hydride abstraction reactions and the stability of the formed azulenyltropylium ions, hydride abstraction reactions of three different kinds of tropylazulenes4)——ethyl 2-acetamido-3-(cycloheptatrien-7-yl)azulen-1-carboxylate (I), 2-chloro-1-(cycloheptatrin-7-yl)azulene (II), and ethyl 3-(cycloheptatrin-7-yl)azulen-1-carboxylate (III)——were investigated. Bromination-dehydrobromination,6) triphenylmethyl ions,7) and phosphorus pentachloride8) have been previously used for hydride abstraction reactions of tropylidenes. In this report, phosphorus pentachloride will be employed.

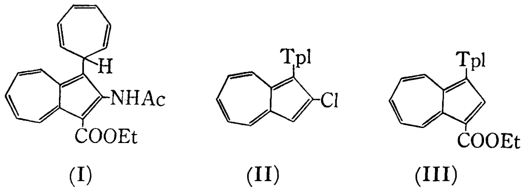

Fig. 2

The reaction of I with phosphorus pentachloride in anhydrous carbon tetrachloride afforded ethyl 2-acetamidoazulen-1-carboxylate9) besides some intractable resinous substances. However, an attempt to isolate the removed tropylium ion as perchlorate was unsuccessful. Also, when II was treated as above, 1,2,3-trichloroazulene9) was obtained in a 35% yield, but no other clear resultants could be identified.

The action of phosphorus pentachloride on III gave two substances, (IV) and (V). The elemental analysis ($C_{13}H_{11}O_2Cl$) and the IR spectrum (1655 cm^{-1}) of IV indicated that its structure is ethyl 3-chloroazulen-1-carboxylate. The hydrolysis and subsequent decarboxylation of IV gave 1-chloroazulene.10) V was isolated as perchlorate salt from the water layer. The results of the elemental analysis of V are consistent with the molecular formula of ($C_{20}H_{17}O_6Cl$), and a new strong absorption band at 763 cm^{-1}, with a weakening of the 748 cm^{-1} band of III (which possesses the characteristic, very strong bands at 780, 748, and 708 cm^{-1}), is observed in the IR spectrum of V.11) V also shows a broad strong band at 1080 cm^{-1}; presumably, this band is due to the Cl–O vibrations of the perchlorate anion.12) Therefore, hydride abstraction must have occurred and the structure of V is (3-ethoxycarbonylazulen-1-yl)tropylium perchlorate. V is stable in air at room temperature and can be recrystallized from alcohol, but it burns explosively when heated.

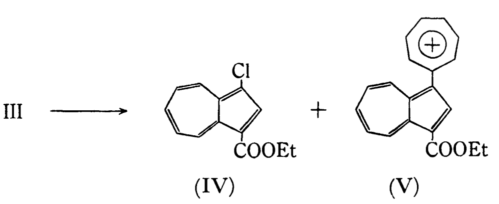

Fig. 3

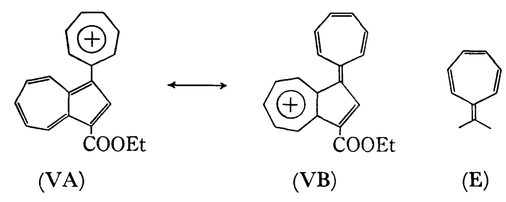

Fig. 4

As has been mentioned above, V possesses VA- and VB-type canonical formulae. If VB is the important canonical formula, the UV and a visible spectra of V should show spectra analogous to those of heptafulvenes (E). However, the spectra of V, although lacking the fine structure in the visible region, are similar to those of III, but not to those of heptafulvenes,13) as is shown in Fig. 4. Thus,

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6) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954).

7) H. J. Dauben, F. A. Gadecki, K. M. Harmon and D. L. Pearson, *ibid.*, **79**, 4557 (1957).

8) D. N. Kursanov and M. E. Vol'pin, *Doklady Akad. Nauk S. S. S. R.*, **113**, 339 (1957); *Chem. Abstr.*, **51**, 1457 (1957).

9) Unpublished results obtained in the authors' laboratory.

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

11) All the tropylazulenes (more than thirty) which were synthesized in the authors' laboratory show characteristic, very strong bands in this region of their IR spectra.

12) P. A. Giguère and R. Savoie, *Can. J. Chem.*, **40**, 495 (1962).

13) a) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960). b) T. Nozoe, T. Mukai, K. Osaka and N. Shishido, This Bulletin, **34**, 1384 (1961). c) Y. Kitahara, K. Doi and T. Kato, *ibid.*, **37**, 1747 (1964).

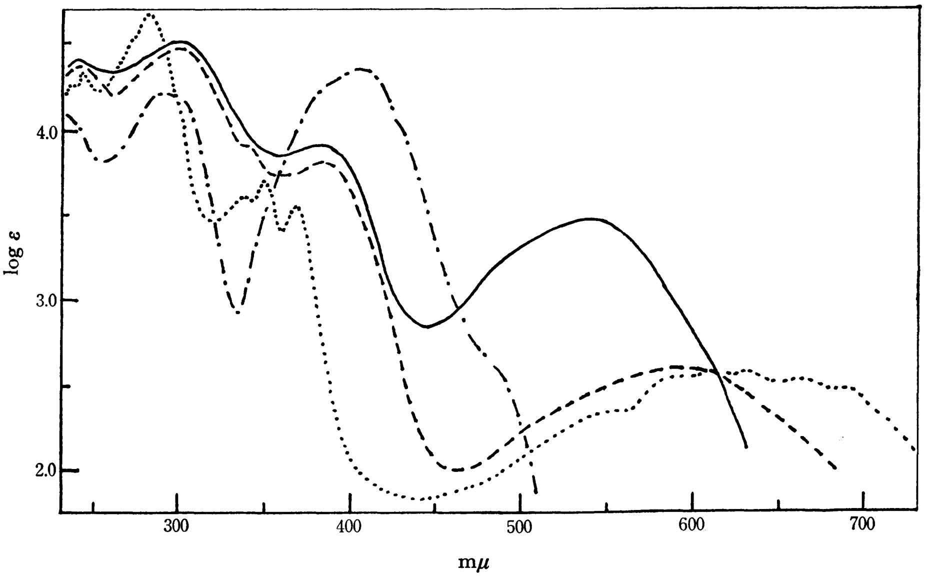

Fig. 5

-------- III —— V ---- VI

–·–·– 8,8-Dicyano-2,3-dimethoxyheptafulvene[13c]

the contribution of the VB-type canonical formula is not important. Also, from the stereochemical point of view, this is rather reasonable, for if V takes a VB-type structure, the interference between the C_4-hydrogen of the azulene nucleus and the C_2-hydrogen of the tropylium moiety is fairly large.

The above reaction sometimes afforded a neutral substance (mp 181°C) which showed, in its IR spectrum, a strong absorption band at 1640 cm^{-1} beside the ester carbonyl band. This is presumably ethyl 3-(troponyl)azulen-1-carboxylate, which is formed from V by the attack of water and the following disproportionation reaction.[14] However, we did not obtain this in a quantity sufficient to investigate it further.

The reaction of III with chlorine was carried out for the purpose of obtaining V by chlorination-dehydrochlorination reaction. The results were the formation of IV and the recorvery of the starting substance, plus some resinous substances. Therefore, only the exchange reaction of the chlorine cation with the tropyl group occurred. Analogous types of reactions were observed when several 1-tropylazulenes were treated with cationoid reagents.[4]

The formation of 1,2,3-trichloroazulene from II and that of IV from III with phosphorus pentachloride can also be explained as exchange reactions of the chlorine cation with the tropyl groups of the above compounds, for phosphorus pentachloride is said to exist as a PCl_4^+-PCl_6^- complex[15] and it seems possible that the PCl_4^+ moiety dissociates to Cl^+ and PCl_3. The tetrachlorophosphonium cation or the formed chlorine cation then attacks the C_1- and C_3-positions of the azulene nucleus to form 1,2,3-trichloroazulene and IV respectively.[16]

Although 1-azulenyltropylium ion was obtained in the pure state, the yield of the ion was unsatisfactory because of the formation of IV as a by-product. The formation of IV can be explained as follows; if a tropyl group is attached to azulene by its C_7-position (allylic carbon), the exchange reaction takes place more readily than the hydride abstraction reaction. Therefore, if a tropyl group is attached to azulene by a carbon atom (vinyl carbon) other than C_7, the cleavage of the vinyl-carbon bond should not so easy. For this purpose, the thermal isomerization reactions of III was studied, as were the hydride abstraction reactions of the obtained isomers of III.

The thermal isomerization reactions of several different types of tropylidenes have been investigated by ter Borg *et al.*,[17] by the present au-

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[14] T. Ikemi, T. Nozoe and H. Sugiyama, *Chem. Ind.*, (London), **1960**, 932; A. P. ter Borg, R. van Helden, A. F. Bickel, W. Renold and A. S. Dreiding, *Helv. Chim. Acta*, **43**, 457 (1960).

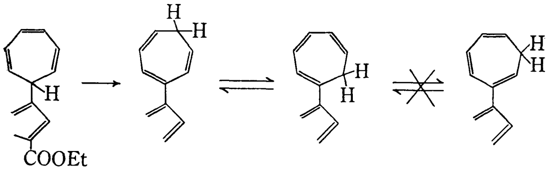
[15] D. Clark, H. M. Powell and A. F. Wells, *J. Chem. Soc.*, **1942** 642; E. S. Gould, "Inorganic Reactions and Structure," 2nd Ed., Holt, Rinehart and Winston, New York (1962), p. 259.

[16] It is also possible that phosphorus pentachloride dissociates in small amounts to chlorine and phosphorus trichloride, and that this chlorine behaves as a cation; T. Chitani, "Inorganic Chemistry," New Ed., Sangyo Tosho KK, Tokyo (1963), p. 737.

[17] A. P. ter Borg, H.K. Kloosterziel and N. van Meus, *Rec. Trav. Chim. Pays-Bas*, **82**, 717 (1963); A. P. ter Borg and H. K.Kloosterziel, *ibid.*, **82**, 741 (1963).

thors,[18] and by Murry and Kaplan;[19] the results have shown that a 1,5-hydrogen shift occurs in all cases. III was heated under a nitrogen atmosphere, and the reactions were followed by NMR spectroscopy. The methyne hydrogen of the tropyl group of III appears as a triplet ($J=5.5$ Hz) at 3.20 ppm in its NMR spectrum. When III was heated at 150°C, the triplet disappeared gradually and a new triplet ($J=7.0$ Hz) appeared at 2.38 ppm. After the disappearance of the triplet at 3.20 ppm, another new peak (doublet, $J=7.5$ Hz) appeared, at 2.80 ppm while the triplet at 2.38 ppm reached a maximum intensity and then decreased in intensity. The ratio of the intensities of the triplet at 2.38 ppm and the doublet at 2.80 ppm reached equilibrium (about 2:3) after *ca.* 20 hr, and no change was observed. The above peaks could be assigned to the methylene hydrogens of the tropyl groups of ethyl 3-(cycloheptatrien-3-yl)azulen-1-carboxylate (VI) and ethyl 3-(cycloheptatrien-1-yl)azulen-1-carboxylate (VII) respectively. The assignement can also be explained reasonably as follows. VI is formed from III by a 1,5-thermal hydrogen shift of the tropyl group, and then VII is formed from VI by the same procedure. The coupling constants and patterns of the above compounds are also reasonable in view of the assigned structures. Prolonged heating or heating at elevated temperature caused the formation of resinous substances, but no formation of (cycloheptatrien-2-yl)-azulene (VIII)-type isomers could be observed. Some examples of the obtained results are listed in the table.

Although the IR spectrum of III shows characteristic absorption bands at 708, 748, and 780 cm^{-1}, the band at 708 cm^{-1} becomes very weak as the isomerization proceeds and a new, strong band appears at 730 cm^{-1}.



(III) (VI) (VII) (VIII)

Fig. 6

TABLE 1

Conditions	130°/ 1 hr	130°/ 2 hr	150°/ 3 hr	170°/ 10 hr	190°/ 18 hr
III	60%	30%	2%		
VI	40%	70%	90%	40%	56%
VII			5%	55%	
Polymers				5%	40%

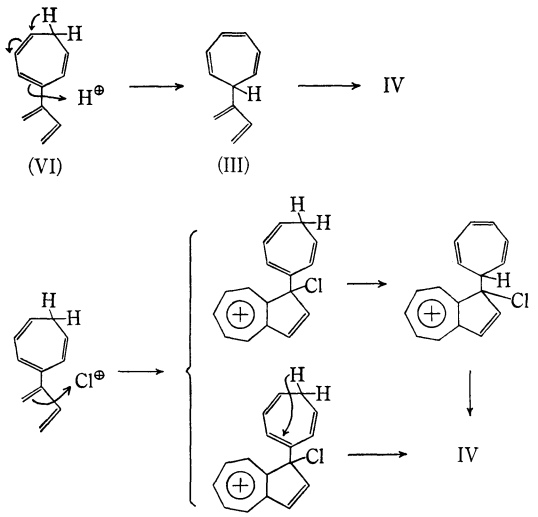


Fig. 7

When the mixtures of VI and VII were treated with phosphorus pentachloride under the same conditions as in the case of III, the yield of V was raised to 50—55%. However, IV was surprisingly obtained in a 20—25% yield. These are very interesting results. The explanation was first thought to be as follows: the protons which are formed as the reaction proceeds react with VI and VII to form III, as is shown in Fig. 6, and then the exchange reaction of the tropyl group of the formed III takes place, thus giving IV. However, the treatment of the mixtures of VI and VII with hydrogen chloride under the present reaction conditions did not provide any evidence of the formation of III or ethyl azulen-1-carboxylate. The second possible mechanism of this reaction is that the attack of the chlorine cation takes place at the C_3-position of the azulene nucleus, and then the isomerization and elimination of the tropyl group occurs, either step by step or simultaneously, to give IV. Further investigation of the reaction mechanism is in progress.

The metal - hydride reductions of tropylium ions have been reported to give mixtures of several different kinds of tropylidenes by Vol'pin *et al.*,[20] and by Conrow.[21] Also, Anderson and Replogle[3] reported the formation of 1-chloro-3-(cyclohepta-trien-7-yl)azulene by the reduction of the 1-(3-chloroazulen-1-yl)tropylium ion with sodium borohydride. However, they did not isolate the chloroazulenetropylium ion which was used for reduction, and the reduction product was identified only by means of its UV and visible spectra.

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18) T. Nozoe and K. Takahashi, This Bulletin, **38**, 665 (1965). T. Mukai, H. Kubota and T. Toda, *Tetrahedron Lett.*, **1967**, 3581.

19) R. W. Murry and H. L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 3527 (1966).

20) Z. N. Parness, M. E. Vol'pin and D. N. Krusanov, *Tetrahedron Lett.*, **1960**, 20.

The sodium borohydride reduction of V gave only 2 : 3 mixtures of VI and VII, as shown by an investigation of the IR and NMR spectra of the reduction products, but the formation of III was not observed. According to Conrow,[21] the hydride reduction of the methyltropylium ion gave mixtures of 1-methyl-, 2-methyl-, and 3-methyl-tropylidenes in more than a 95% yield and the yield of 7-methyltropylidene was about 2%. The formation of a large amount of a 7-tropyl-type compound does not seem reasonable either from the point of view of the thermodynamical stability of the resultants and the steric requirements of the reaction.

The results of the reduction of V, together with the consideration of the spectroscopic properties of V mentioned above, support the idea that the structure of V is (3-ethoxycarbonylazulen-1-yl)-tropylium perchlorate.

Experimental[22]

Hydride Abstraction Reaction of I. Into a suspension of 0.60 g of phosphorus pentachloride in 20 m*l* of anhydrous carbon tetrachloride, a solution of 0.50 g of I in 5 m*l* of anhydrous carbon tetrachloride was stirred, and then stirring was continued for 6 hr. The reaction mixture was poured into 30 m*l* of cold water, and the water layer was extracted with benzene. After separation, the combined organic layers were dried over sodium sulfate, separated from the drying reagent, and concentrated *in vacuo*; the residue was dissolved in benzene and submitted to chromatography. The first eluate gave 89 mg of dark red prisms (mp 141—142°C, which did not show any mixed-melting-point depression with ethyl 2-acetamidoazulen-1-carboxylate[9]); the second eluate gave 9 mg of violet crystalline substances (mp 111—112°C), and the third gave 23 mg of violet, crystalline substances (mp 146—182°C), the rest was composed of 156 mg of resinous, oily substances. The second crystalline substances show a positive Beilstein test: however, further purification of the second and the third eluates failed to provide pure substances.

The addition of 60% perchloric acid to the water layer did not give any crystalline substances.

Hydride Abstraction Reaction of II. A solution of II in 5 m*l* of anhydrous carbon tetrachloride and 1.0 g of phosphorus pentachloride in 20 m*l* of carbon tetrachloride was treated as above. Cyclohexane eluates of the chromatography gave 173 mg of dark blue, crystalline substances (mp 120—124°C). Recrystallization from ethyl acetate raised its melting point to 137°C; yield, 140 mg. A mixed-melting-point determination of this and 1,2,3-trichloroazulene[9] failed to show any depression.

Found: C, 51.70; H, 2.20%. Calcd for $C_{10}H_5Cl_3$: C, 51.88; H, 2.18%.

The water layer did not give any crystalline substances after the addition of 60% perchloric acid.

Hydride Abstraction Reaction of III. Into a suspension of 1.13 g of phosphorus pentachloride in 25 m*l* of anhydrous carbon tetrachloride, a solution of 0.78 g of III in 5 m*l* of carbon tetrachloride was stirred, and then the stirring was continued for 1.5 hrs. After the reaction, the reaction mixture was treated as above. The organic layer gave blue black needles (mp 62°C), after chromatography and recrystallization from cyclohexane; yield, 133 mg.

Found: C, 66.27; H, 4.30%. Calcd for $C_{13}H_{11}O_2Cl$: C, 66.30; H, 4.75%.

The addition of 60% perchloric acid to the water layer formed dark brown precipitates. The precipitates were then separated by filtration and dried in a desiccator to give 0.40 g of a dark brown powder (mp 180—182°C (dec.)). Recrystallization from alcohol raised its melting point to 205°C (dec.), and this crystalline substance vigorously burned when heated in air.

Found: C, 61.71; H, 4.30%. Calcd for $C_{20}H_{17}O_6Cl$: C, 61.79; H, 4.41%.

$\lambda_{\text{max}}^{\text{MeOH}}$, m$\mu$ (log ε); 238 (4.43), 305 (4.54), 382 (3.94), and 536 (3.49).

Hydride Abstraction Reaction of the Mixtures of VI and VII. From 0.50 g of the mixtures of VI and VII, 0.34 g of V was obtained when the reaction was carried out as above. From the organic layer, 85 mg of IV were obtained; the rest was composed of resinous, oily substances which did not give any pure substances upon further purification. The average yields of IV and V from the mixture were 20—25% and 50—55% respectively, and no remarkable change was observed when the ratio of VI and VII in the starting mixtures was changed.

Sometimes a few mg of dark blue, crystalline substances (mp 181°C) were obtained from the organic layer; these substances showed a strong absorption band at 1640 cm^{-1} (KBr pellet) besides the ester carbonyl band at 1675 cm^{-1}.

Hydrolysis and Decarboxylation of IV, 1-Chloroazolene. A solution of 50 mg of IV and 38 mg of potassium hydroxide in 3 m*l* of alcohol and 1 m*l* of water was heated under reflux for 4 hr, and then 5 m*l* of cold water were added. The pH of the solution was adjusted to *ca.* 3.0 with 6N hydrochloric acid to give 32 mg of dark violet precipitates (mp 225°C (dec.)) after having been dried *in vacuo*. The precipitates were heated in a sublimation apparatus for decarboxylation at 190°C (3 mmHg), and the blue oil thus formed was chromatographed on alumina. The cyclohexane eluate gave 21 mg of a blue oil, and its IR spectrum was superimposable upon that of 1-chloroazulene prepared by the authentic method.[10] The treatment of the oil with trinitrobenzene gave dark brown needles (mp 132—133°C) from benzene (reported, mp *ca.* 105°C).[10]

Found: C,51.26; H, 2.58; N, 10.66%. Calcd for $C_{16}H_{10}O_6N_3Cl$: C, 51.14; H, 2.68; N, 11.19%.

Reaction of III with Chlorine. To a solution of 116 mg of III in 10 m*l* of anhydrous carbon tetrachloride, 30 mg of chlorine in 0.25 m*l* of anhydrous carbon tetrachloride were added, then the mixture was allowed to stand overnight. After the solvent has then been removed, 142 mg of an oily substance were obtained; the oil was submitted to chromatography. The benzene eluate gave 88 mg of a dark blue oil, and the ethyl acetate eluate gave 24 mg of a black tar. Rechromatography of the first eluate by petroleum ether - cyclohexane (4 : 1) gave 35 mg of dark blue, crystalline substances (mp 61°C) from cyclohexane as the first eluate, and, as the second eluate, 25 mg of

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[21] K. Conrow, *J. Amer. Chem. Soc.*, **83**, 2343 (1961).

[22] All melting points are uncorrected.

a violet oil. The former was identical with ethyl 3-chloroazulene-1-carboxylate (IV), and the latter was the recovered starting materials, as determined by a comparison of their IR spectra with those of the respective authentic samples.

Thermal Isomerization of III. III (0.51 g) was heated under a nitrogen stream at 130°C for 2 hr without any solvent; after heating, the resultant substance was chromatographed on alumina. The benzene eluate gave 0.51 g of dark blue-violet oil. The results of the elemental analysis of the resultant are as follows:

Found: C, 82.56; H, 6.38%. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%.

The ratio of the isomers was determined by measuring the areas of the methine and methylene hydrogens of mixtures of the isomers. The NMR spectra were measured with *ca.* 10% solutions of each resultant in carbon tetrachloride, with TMS as the internal standard, using a Varian A-60-type spectrometer. Some examples of the obtained results are listed in the table.

About 2 : 3 mixtures of VI and VII were obtained when the isomerization was carried out at 150°C for *ca.* 20 hr. However, when heating was continued for more than 15 hr at 190°C, VI and VII amounted to *ca.* 56%, with the rest being a polymer which could be separated from VI and VII by means of alumina chromatography.

Sodium Borohydride Reduction of V. Into a solution of 0.20 g of V in 5 m*l* of acetonitrile, a solution of 40 mg of sodium borohydride in 2 m*l* of acetonitrile was stirred in small portions. The color of the solution changed from a dark reddish violet to brown; then 40 more mg of borohydride were added, thus causing the color of the solution to change from brown to a greenish violet. The solution was then allowed to stand at room temperature for 30 min with stirring, and water was added. The water layer was extracted with petroleum ether; the combined organic layers were then washed with water and dried over sodium sulfate, and the drying reagent was separated by filtration. The petroleum ether was removed to give 155 mg of a greenish-brown oil; the obtained oil was chromatographed on alumina. A light petroleum - benzene (9 : 1) eluate afforded 109 mg of a greenish-violet oil the IR and NMR spectra of which were identical with those of the 2 : 3 mixtures of VI and VII.

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