BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2095—2101 (1968)

Synthesis and Properties of Nitrosoazulenes[1)]

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(Received January 27, 1968)

Ethyl 2-amino-3-nitrosoazulene-1-carboxylate (II) was synthesized from ethyl 2-aminoazulene-1-carboxylate by treatment with isoamyl nitrite. The structure of the amino-nitrosoazulene was proved by the reductive acetylation of the azulene to give ethyl 2,3-diacetylaminoazulene-1-carboxylate. This nitrosation method was then applied to several azulenes possessing different substituents; it yielded some stable nitrosoazulene derivatives. The spectral properties of the nitrosoazulenes will be discussed. The condensation reactions of II with aromatic amines failed to give azo-dyes, but with diethyl malonate and malononitril they gave the corresponding pyrazinoazulene derivatives.

Although Hafner and his co-workers reported the formation of 1-nitrosoazulene in 1961,[3)] they could not succeed in isolating the pure substance. Kitahara and Kato obtained 2-amino-1-cyano-3-nitroso-7-isopropylazulene in a poor yield;[4)] however, its chemical and physical properties have not been investigated. The present authors have observed the formation of ethyl 2-amino-3-nitrosoazulene-1-carboxylate (II) in a fairly good yield[5)] accompanied

1) Presented at the Local General Meeting of the Tohoku District of the Chemical Society of Japan, Morioka, October, 1964.

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

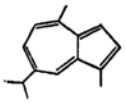
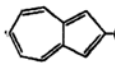
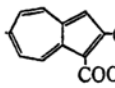
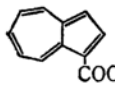
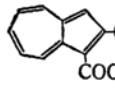
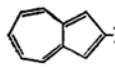
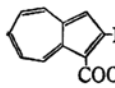
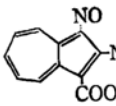
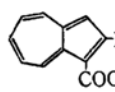
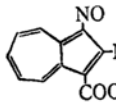
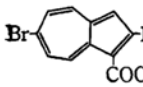
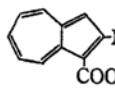
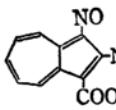
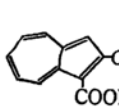
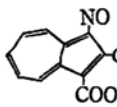
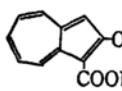
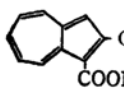
4) Y. Kitahara and T. Kato, *Bulletin of the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University*, **14**, 53 (1964).

5) T. Nozoe, T. Toda, T. Asao and A. Yamanouchi, This Bulletin, **41**, No. 12 (1968), in press.

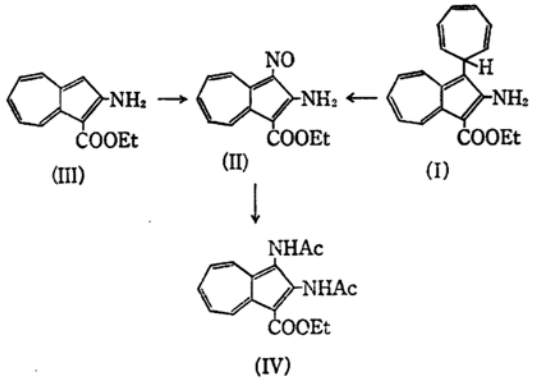
by the exchange of the tropyl group and the nitroso group when ethyl 2-amino-3-tropylazulene-1-carboxylate (I) was treated with isoamyl nitrite (IAN) in alcohol or benzene. It is very interesting that the deamination reaction of I did not take place and that II was obtained in a good yield even though the reaction was carried out in the presence of a reducing reagent such as alcohol. We applied this method to several azulenes and investigated the properties of the nitrosoazulenes thus obtained.

Although 1-nitrosoazulene has been reported to be very unstable and could not be isolated,[3] II is a

Table 1

Starting substances	No.		Products No.	mp °C	Yield %	Recovery %	N analysis as mononitrosoazulene Calcd	Found
	(V)	reddish brown powder	(XVIII)	>300	72	9	6.16	7.20
	(VI)	reddish brown powder	(XIX)	>200	30		7.31	7.81
	(VII)	black powder		>200	7	80		
	(VIII)	black powder	(XX)	152—160	20	75	6.11	6.53
	(IX)	black powder	(XXI)	>300	39	36	5.76	7.05
	(X)	dark brown powder			10			
	(XI)		(XXII)	156	100		10.85	10.45
	(XII)		(XXIII)	oil 244 as picrate	58	25	13.97 as picrate	13.65
	(XIII)	dark brown powder		138—145	77			
	(XIV)		(XXIV)	>300	4	95	9.79	9.38
	(XV)		(XXV)	156	77		5.51	5.27
	(XVI)	black powder	(XXVI)		65		5.40	4.74
	(XVII)	black powder	(XXVII)	>200	20	36	4.88	4.92

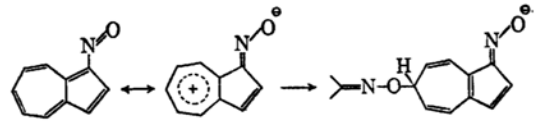
very stable entity. Therefore, ethyl 2-aminoazulene-1-carboxylate (III), which does not possess a tropyl group at the C-3 position, was treated with IAN in alcohol or benzene; II was thus obtained in a 95% yield. The addition of a trace amount of hydrogen chloride or concentrated sulfuric acid to the reaction mixture did not affected the yield of II. However, when III was treated with sodium nitrite together with a mineral acid in alcohol, II could not be isolated and intractable resinous substances were formed. Since I and III afforded the same product, II, the position of the introduced nitroso group should be C-3 position of the azulene ring. This was confirmed by the reductive acetylation of II, which yielded ethyl 2,3-diacetylaminoazulene-1-carboxylate (IV).[6]



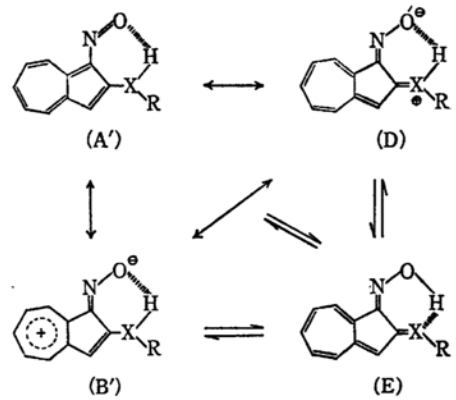
In order to investigate the effect of substituents on the nitrosation reaction, the reactions of several azulenes (V—XVII),[7] possessing different substituents, such as alkyl, alkylamino, ethoxycarbonyl, or hydroxyl groups, have been carried out under the same reaction conditions; the results obtained are shown in Table 1.

II and ethyl 2-methylamino-3-nitrosoazulene-1-carboxylate (XXII) are very stable, but 2-dimethylamino-, 2-acetylamino-, and 2-hydroxy-3-nitrosoazulene derivatives (XXIII, XIV, and XXV respectively) are not very stable and change to black, resinous substances when heated for a long time during the purification process or when stored for a long period. The products in other cases should be nitrosation products, according to their analytical data; however, they are very unstable and are obtained only as amorphous powders, accompanied by large amounts of tarry substances, and they could not be purified. The reductive acetylation of those substances (XVIII, XX, XXI, XXVI and XXVII) was then attempted. Although almost two equivalent moles of hydrogen were taken up in each case, only resinous products were obtained. On the other hand, XXV afforded ethyl 3-acetylamino-2-hydroxyazulene-1-carboxylate (XXVIII) in a good yield under the same conditions. XXVIII was also obtained by the same reductive acetylation of ethyl 3-(*p*-tolyl)azo-2-hydroxyazulene (XXIX), which had been obtained from XV.

The results presented above suggested that the nitrosation reaction of the azulenes takes place first, but the nitrosoazulenes formed are unstable, except for II, XXII XXV, *etc.*, and the polymerization and/or other reactions occur to give resinous materials. The molecular weights of XVIII, XIX, *etc.*, could not be measured because of their insolubility. It can reasonably be understood that 1-nitrosoazulenes can possess A- and B-type canonical formulae and that the self-condensation reactions occur to form C- and other-type polymers.



The nitrosoazulenes which have an amino or hydroxyl group at the C-2 position are stable entities. Therefore, one of the canonical formulae of those nitrosoazulenes is a D-type formula (and also A′ and B′); this plays an important role in the stability of those nitrosoazulenes. D-type entities are able to tautomerize with E-type entities with an exchange of hydrogen atoms; this tautomerization may contribute to the stabilization of those nitrosoazulenes.



The nitrosation of azulenes with IAN may proceed by a radical mechanism. However, it is well-known that the cationoid substitution reactions of azulenes readily occur at C-1 and C-3 positions.[7a] The results shown in Table 1 indicate that azulenes which possess electron-releasing groups readily afford

6) M. Kobayashi, Master's thesis submitted to Tohoku University, March, 1961.

7) The methods of synthesizing known azulenes are described in the following articles and in the litratures cited therein: a) T. Nozoe and T. Asao, "Dai Yuki Kagaku, (Comprehensive Organic Chemistry)," Vol. 13, ed. by M. Kotake, Asakura Shoten, Tokyo (1960), pp. 439—534. b) T. Nozoe, S. Seto, K. Takase, S. Matsumura and T. Nakazawa, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 346 (1965).

nitroso derivatives, whereas azulenes which have electron-withdrowing groups do not give the corresponding nitrosoazulenes easily, but rather resulted in the recovery of the original azulenes under the same reaction conditions. Furthermore, I readily yielded II with the exchange of the tropyl group. In view of the above facts, it seems rather reasonable to say that the reaction proceeds through an ionic process.

Generally, the UV and visible spectra of azulenes show fine structures; however, the spectrum of II shows a fairly broad structure compared with that of III, as is shown in Fig. 1. The spectrum of azulene in concentrated sulfuric acid[8] and the spectrum of 1-ethoxycarbonylazulene-3-tropylium perchlorate[9] do not show such fine structures either. These facts suggest that the contribution of B- and D-type canonical formulae to II is fairly important.

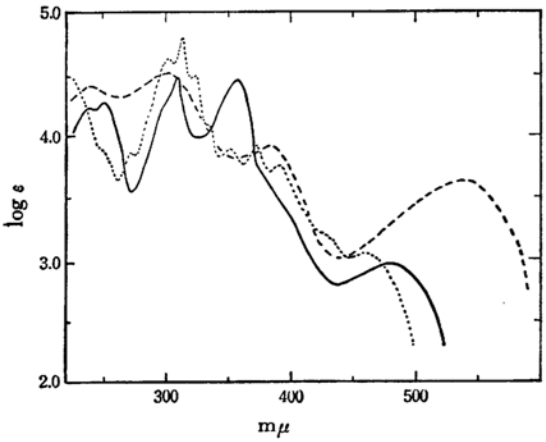


Fig. 1

—— II
---- III
— — 1-Ethoxycarbonylazulene-3-tropylium perchlorate

The IR spectrum of 5-nitrosotropolone, which is said to exist as a tropo-quinone oxime form,[10] shows strong bands at 1603 and 1325 cm^{-1}, a weak band at 1522 cm^{-1}, and a very weak band at 1439 cm^{-1}. On the other hand, the IR spectra of the nitrosoazulenes show several bands between 1530—1480 cm^{-1} as follows II, 1600 (s), 1570 (m), 1540 (m), 1515 (s), 1450 (m) and 1430 (s) cm^{-1}; XXII, 1605 (S), 1570 (m), 1525 (s), 1480 (w) and 1440 (s) cm^{-1}; XXIII, 1600 (s), 1570 (w), 1520 (s), 1480 (w) and 1430 (s) cm^{-1}; XXV, 1620 (m), 1580 (w), 1495 (v.s.), 1450 (v.s) and 1405 (w) cm^{-1}; XXVI, 1600 (m), 1545 (s), 1520 (s), 1475 (w), 1440 (s) and 1404 (s) cm^{-1}; and an ester carbonyl band near 1670 cm^{-1} in all the nitrosoazulenes above.[11] Although XXIII and XXVI do not have oxime-type tautomeric forms, they possess a strong band between 1525—1520 cm^{-1}. Therefore, the absorptions of the nitrosoazulenes are assigned to N=O stretching vibrations of the nitroso group this is in agreement with those of the nitroso group of aromatic compounds.[12] However, XXV does not show such a band in this region, but shows a very strong band at 1490 cm^{-1}. Presumably this is due to the contribution of the E-type canonical form; the band at 1700 cm^{-1} of XXV may be assigned to a C=O or C=N stretching vibration of the five-membered ring of D- or E-type entities of XXV, because no band is observed near 1700 cm^{-1} in other nitrosoazulenes.

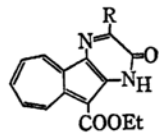
Azulenes which possess a condensed imidazole ring fused to the C-1 and C-2 of the azulene nucleus have been synthesized.[6] The synthesis of the same type azulenes which possess an oxazole ring fused to C-1 and C-2 was attempted. XXV and XXIX were reduced over palladized charcoal in formic acid, providing ethyl 3-formamide-2-hydroxyazulene 1-carboxylate (XXX). However, the treatment of XXVIII and XXX in anhydrous formic acid and in acetic anhydride resulted in only the recovery of the starting substances and 3-diacetylamino-2-acetoxyazulene-1-carboxylate (XXXI) respectively. When the reactions were carried out with a small amount of concentrated sulfuric acid or under more drastic conditions, only tarry materials were formed. The treatment of XXXI with sodium hydroxide in alcohol regenerated XXVIII readily.

It is well known that the aromatic nitroso compounds afford azo-dyes and Shiff bases upon treatment with the corresponding amines and active methylene compounds respectively. The reaction of II with *p*-toluidine, *p*-nitroaniline, 2,4-dichloroaniline in benzene, pyridine or xylene resulted in the recovery of II under mild conditions; under more drastic conditions, only black, intractable, resinous substances were obtained. When the reaction was carried out in boiling aniline, red-violet needles were obtained. However, they were not identical with ethyl 2-amino-3-(phenylazo)azulene-1-carboxylate. The amount of this substances was insufficient for further investigation.

The treatment of II with diethyl malonate and malononitril gave diethyl 3(4*H*)-oxoazuleno[1,2-*b*]pyrazine-2,5-dicarboxylate (XXXII) and ethyl 2-cyano-3(4*H*)-oxoazuleno[1,2-*b*]pyrazine-5-carboxylate (XXXIII) respectively. They are hardly soluble in most organic solvents, and XXXIII could not be

8) Pl. A. Plattner, E. Heilbronner and S. Weber, *Helv. Chim. Acta*, **35**, 1036 (1952).
9) A. Yamanouchi, M.Sc. thesis submitted to Tohoku University, March, 1964; T. Nozoe, A. Yamanouchi and T. Toda, to be published.
10) T. Nozoe, K. Takase and H. Matsumura, "Dai Yuki Kagaku, (Comprehensive Organic Chemistry)," Vol. 13, ed. by M. Kotake, Asakura Shoten, Tokyo (1960), p. 274.
11) The IR spectra of the nitrosoazulenes were measured in the solid state by the KBr pellet method.
12) J. L. Bellamy, "the Infra-red Spectra of Complex Molecules," Methuen, London (1958), p. 305.

obtained in an analytically-pure state. However, the spectral and analytical data indicate that a pyrazine ring is formed during the condensation



XXXII: R=COOEt
XXXIII: R=CN

reactions. Their UV spectra are very similar to that of 2,3-dimethylazuleno-[1,2-*b*]pyrazine,[6] as is shown in Fig. 2.

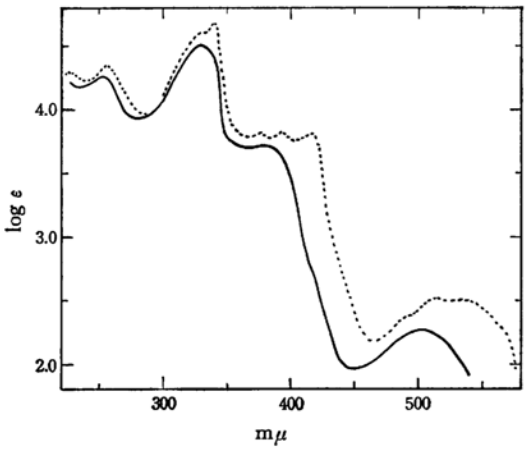


Fig. 2.
—— XXXII
---- 2,3-dimethylazuleno[1,2-*b*]pyrazine

Experimental[13]

Ethyl 2-Methylaminoazulene-1-carboxylate (XI). To a solution of 0.36 g of VII in 2 m*l* of dioxane, 0.50 g of 30% aqueous methylamine was added, and then the mixture was heated under reflux for 12 hr. The solvent was removed under reduced pressure, and the residue was dissolved in benzene. The benzene layer was washed with water, dried over sodium sulfate, filtered, and concentrated to give 0.365 g of a reddish-brown oil. The oil was chromatographed on alumina, and the cyclohexane eluate gave 50 mg of the recovered starting material, while the ether eluate gave 0.285 g of yellow needles of XI, mp 66—67°C. The recrystallisation of this from light petroleum raised its mp to 67.5—68°C; orange plates.

Found: C, 73.32; H, 6.52; N, 6.04%. Calcd for $C_{14}H_{15}O_2N$: C, 73.34; H, 6.59; N, 6.11%.

Ethyl 2-Diethylaminoazulene-1-carboxylate (XII). A solution of 0.80 g of VII and 0.83 g of 40% aqueous dimethylamine in 5 m*l* of alcohol was heated under reflux for 3 hr, and then the reaction mixture was treated as above. A brown oil, 0.835 g, was obtained and gave trinitrobenzoate (mp 159.5°C from alcohol) as reddish-brown needles.

Found: C, 55.79; H, 4.46; N, 11.89%. Calcd for $C_{21}H_{20}O_8N_4$: C, 55.26; H, 4.42; N, 12.28%.

Ethyl 2-Amino-6-bromoazulene-1-carboxylate (XIV). A solution of 0.427 g of diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate[14] and 0.28 g of potassium hydroxide in 10 m*l* of alcohol was heated under reflux for 3 hr. The alcohol was then removed, and 8 m*l* of water was added to the reaction mixture to give 8.5 mg of the recovered starting material, which was separated by filtration. The water layer was acidified with N hydrochloric acid to form yellow precipitate. The separated precipitate was dried in a desiccator to give 0.38 g of a yellow-green powder. The powder was heated under reflux for 2.5 hr in 3 m*l* of pyridine and then concentrated. The residue was submitted to chromatography after having been dissolved in benzene, and then washed with water and dried over sodium sulfate. The benzene-ether (1: 1) eluate afforded 32 mg of 2-amino-6-bromoazulene, and the same mixed solvent (1: 4) gave 66 mg of brown micro needles of XIV, which did not show any clear melting point.

Found: C, 54.47; H, 3.80; N, 5.79%. Calcd for $C_{13}H_{12}O_2NBr$: C, 54.20; H, 3.48; N, 6.32%.

Ethyl 2-Acetoxyazulene-1-carboxylate (XVII). A solution of 0.454 g of XV in 3 m*l* of acetic anhydride was heated on a water bath for 5 min, and then the excess acetic anhydride was removed under reduced pressure to give 0.462 g of deep red needles of XVII, mp 62—63°C from alcohol.

Found: C, 69.50; H, 5.59%. Calcd for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46%.

Ethyl 2-Amino-3-nitrosoazulene-1-carboxylate (II). a) Into an ice-cold solution of 0.30 g of III in 9 m*l* of benzene, 0.216 g of IAN was stirred drop by drop; the solution was then allowed to stand overnight at room temperature. The solution was washed with water, dried over sodium sulfate, and concentrated to give 0.324 g of dark brown needles of II. The recrystallisation of crude II from benzene raised its mp to 177—178°C; brown needles.

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%.

When alcohol was used instead of benzene, the same results were obtained.

b) When benzene which had been saturated with dry hydrogen chloride or which contained a drop of conc. sulfuric acid was used and treated as above, 0.304 g of II was obtained from 0.30 g of III.

c) Into an ice-cold solution of 0.30 g of III in 10 m*l* of alcohol containning 0.4 m*l* of N hydrochloric acid, a solution of 0.22 g of sodium nitrite in 2 m*l* of water was stirred. After having been allowed to stand overnight at room temperature, the solution was neutralized with aqueous sodium bicarbonate, and then concentrated under reduced pressure to give a black residue, which failed to give a pure substance by means of column- or thinlayer-chromatography or other methods. When III was treated for a shorter period under the same conditions, the recovered III and some intractable gummy substances were obtained.

Ethyl 2-Methylamino-3-nitrosoazulene-1-carboxylate (XXII). By the same treatment as in the case of III, 50 mg of XI and 34 mg of IAN gave 59 mg of XXII as brown plates, mp 157°C from benzene.

13) All melting points are uncorrected.

14) T. Nozoe, S. Seto and S. Matsumura, This Bulletin, **35**, 1990 (1962).

Found: C, 65.47; H, 5.14; N, 10.45%. Calcd for $C_{14}H_{14}O_3N_2$: C, 65.10; H, 5.46; N, 10.85%.

Ethyl 2-Dimethylamino-3-nitrosoazulene-1-carboxylate (XXIII). From 0.30 g of XII and 0.30 g of IAN, 0.37 g of crude products was obtained; this was then submitted to chromatography. The benzene-ethyl acetate (1:1) eluate afforded 71 mg of the recovered substance, and the ethyl acetate eluate gave 0.193 g of a brown oil which did not give trinitrobenzolate, but a picrate as yellow-brown prism, mp 240—244°C from alcohol.

Found: N, 10.38%. Calcd for $C_{15}H_{16}O_3N_2$: N, 10.29%.

Found: C, 50.62; H, 4.07; N, 13.51%. Calcd for $C_{21}H_{19}O_{10}N_5$: C, 50.30; H, 3.82; N, 13.97%.

Ethyl 2-Hydroxy-3-nitrosoazulene-1-carboxylate (XXV). A solution of 0.60 g of XV in 18 m*l* of benzene and 0.36 g of IAN was treated as before. After the solution had been allowed overnight at room temperature, the formed precipitate was separated by filtration, and from the benzene layer a black powder was obtained. When the powder was recrystallized from benzene, acetone, or alcohol, this changed to an intractable gummy substance. The powder was washed with alcohol to give 0.522 g of XXV, mp 156°C (dec.).

Found: C, 61.85; H, 4.73; N, 5.27%. Calcd for $C_{13}H_{11}O_4N \cdot \frac{1}{2}H_2O$: C, 61.41; H, 4.76; N, 5.51%.

The ir spectrum of this shows a broad band at 3510 cm^{-1}.

Nitrosation of Other Azulenes. The other azulenes listed in Table 1 (V—XVII) were treated with IAN as above or with modified methods. However, the nitrosoazulenes formed were very unstable, and during the recrystallisation process they turned to intractable tarry or resinous substances. Some of them became resinified even when allowed to stand at room temperature or stored in an ice box. Therefore, the nitrosoazulenes obtained were washed with suitable organic solvents and submitted to analysis.

Reduction of II; Ethyl 2,3-Diacetylaminoazulene-1-carboxylate (IV). II (0.10 g) in 5 m*l* of acetic anhydride was reduced over 0.10 g of 10% palladised charcoal, and two equivalent moles of hydrogen was taken up. After the catalyst had been removed by filtration, the solution was concentrated and the residue was chromatographed on alumina. From the ethyl acetate eluate, pale violet crystals were obtained; the recrystallization of this from benzene afforded 43 mg of IV, mp 218—219°C, which failed to show any depression when mixed with an authentic sample of ethyl 2,3-diacetylaminoazulene-1-carboxylate.[6]

Ethyl 3-Acetylamino-2-hydroxyazulene-1-carboxylate (XXVIII). A solution of 0.12 g of XXV in 10 m*l* of acetic anhydride was treated as above over 0.12 g of 10% palladised charcoal. The residue obtained was recrystallized from alcohol to give 70 mg of XXVIII as reddish-brown micro needles, mp 220—220.5°C.

Found: C, 65.58; H, 5.62; N, 5.11%. Calcd for $C_{15}H_{15}O_4N$: C, 65.92; H, 5.53; N, 5.13%.

By the same method, 0.10 g of ethyl 3-(*p*-tolyl)azo-2-hydroxyazulene-1-carboxylate afforded 50 mg of XXVIII, and the mixed-melting-point measurement of XXVIII obtained from different starting substances did not show any depression.

Ethyl 3-(*p*-Tolyl)azo-2-hydroxyazulene-1-carboxylate (XXIX). A solution of 4.0 g of XV in 40 m*l* of pyridine was cooled in an ice bath, and into this *p*-tolyldiazonium chloride, prepared from 2.16 g *p*-toluidine in the usual way, was stirred drop by drop. After the mixture had been allowed to stand for a couple hours at room temperature, the precipitate formed was separated by filtration and recrystallized from alcohol to give 5.88 g of reddish-brown needles of XXIX, mp 146—147°C.

Found: C, 71.79; H, 5.64; N, 8.18%. Calcd for $C_{20}H_{18}O_3N_2$: C, 71.84; H, 5.43; N, 8.38%.

Ethyl 3-Formamide-2-hydroxyazulene-1-carboxylate (XXX). The catalytic reduction of 1.2 g of XXV over 0.20 g of 10% palladised charcoal in 15 m*l* of anhydrous formic acid caused the absorption of two moles of hydrogen. After the catalyst had been separated by filtration and the formic acid was removed, the residue was washed with water and dried in a desiccator; recrystallization from benzene then gave 1.05 g of reddish-brown micro needles of XXX, mp 187°C.

Found: C, 65.18; H, 5.34; N, 4.88%. Calcd for $C_{14}H_{13}O_4N$: C, 64.86; H, 5.05; N, 5.40%.

XXX was also obtained in a good yield by the catalytic reduction of XXIX in formic acid.

Cataltyic Reduction of Other Nitrosoazulenes. The catalytic reduction of XX,XXI, XXVI, and others over palladised charcoal was attempted. Although about two equivalent moles of hydrogen were taken up in every case, no pure substances could be obtained. Example: after reduction, 97 mg of brown powder were obtained from 0.15 g of crude XXVI and was submitted to chromatography. The benzene eluate was recrystallized from light petroleum-benzene to give 32 mg of a brown powder, mp 186°C, which did not give a correct analysis.

λ_{max}^{MeOH}, mμ; 238, 294, 305 and 275. IR in $CHCl_3$; 3450, 3000, 2950, 1680, 1430, 1370 and 1200 cm^{-1}.

Attempted Isooxazole-ring Formation. *a*) A solution of 0.10 g of XXX in 5 m*l* of anhydrous formic acid was heated under reflux for one hour; the formic acid was then removed under reduced pressure. The residue was washed with water and recrystallized from alcohol to give 85 mg of the recovered starting material. The addition of concentrated sulfuric acid or prolonged heating at an elevated temperature gave a black, intractable resinous substance.

b) Ethyl 3-Diacetylamine-2-acetoxyazulene-1-carboxylate (XXXI). A solution of 0.15 g of XXVIII in 10 m*l* of acetic anhydride was dissolved in benzene, washed with water, and dried over sodium sulfate, and the benzene was removed. The recrystallisation of the residue from alcohol-light petroleum afforded 0.14 g of pure XXXI as dark red prisms, mp 137.5—138.5°C.

Found: C, 63.41; H, 5.42; N, 3.88%. Calcd for $C_{19}H_{19}O_6N$: C, 63.86; H, 5.36; N, 3.92%.

Hydrolysis of XXXI. To a solution of 66 mg of XXXI in 2 m*l* of alcohol, 0.17 m*l* of N sodium hydroxide was added, and then the resulting solution was heated on a water bath for 2 hr. After the ethanol had been removed, water was added to the solution and the pH of the solution was adjusted to about 4 with N hydrochloric acid. The recrystallisation of the precipitate obtained above from alcohol gave 47 mg of micro needles, mp 219—220°C, which did not show any depression on admixture with the authentic sample of XXVIII.

Reaction of II with Aromatic Amines. A solution of 0.50 g of II in 10 m*l* of aniline was heated under

reflux for 2 hr, and then the excess aniline was removed under reduced pressure. The residue was dissolved in benzene, washed with water, dried over sodium sulfate, and chromatographed on alumina. The light petroleum eluate gave 88 mg of violet-brown needles, mp 232—234°C.

Found: C, 72.67; H, 5.49; N, 12.55%. λ_{max}^{MeOH}, mμ; 255, 320, 370 and 535; this is analogous to that of ethyl 2-amino-3-(phenylazo)azulene-1-carboxylate.

The condensation reactions of II with *p*-toluidine, *p*-nitroaniline, and 2,4-dichloroaniline in benzene, alcohol, xylene, or pyridine resulted in the recovery of II under milder conditions or in the formation of intractable tar under drastic conditions.

Ethyl 2-Amino-3-(phenylazo)azulene-1-carboxylate. Into a cold solution of 0.215 g of II in 5 m*l* of alcohol, 1 m*l* of phenyl diazonium chloride prepared from 0.15 g of aniline in an ordinary way was stirred drop by drop. The solution was then allowed to stand for 1 hr at room temperature. The precipitate formed was then separated by filtration and recrystallized from alcohol to give 0.275 g of violet needles, mp 136—137°C.

Found: N, 13.27%. Calcd for $C_{19}H_{17}O_2N_3$: N, 13.16%.

Diethyl 3(4*H*)-Oxoazuleno[1,2-*b*]pyrazine-2,5-dicarboxylate (XXXII). A solution of 0.25 g of II and 0.24 g of diethyl malonate in 3 m*l* of acetic anhydride was allowed to stand at room temperature for 4 hr with stirring, and then the excess acetic anhydride was removed under reduced pressure. The residue was dissolved in chloroform, washed with water, and dried over sodium sulfate; the concentration of the solution left a brown resinous substance which was submitted to chromatography. The ether - ethyl acetate (1 : 3) eluate afforded 28 mg of a violet-brown powder; the recrystallisation of this from light petroleum - benzene gave pale violet micro prisms of XXXII, mp 204—207°C.

Found: C, 62.43; H, 5.41; N, 8.09%. Calcd for $C_{18}H_{16}O_5N_2{\cdot}\frac{1}{2}H_2O$: C, 61.90; H, 4.90; N, 8.02%.

Ethyl 2-Cyano-3(4*H*)-oxoazuleno[1, 2-*b*]pyrazine-5-carboxylate (XXXIII). Into a solution of 0.25 g of II in 6 m*l* of anhydrous alcohol cooled in an ice bath, a solution prepared from 30 mg of sodium and 0.10 g of malononitril in 1 m*l* of anhydrous alcohol was stirred drop by drop; the reaction mixture was then stored in ice box overnight. The solvent was then removed under reduced pressure, and the residue was washed with water and dried in a desccator to give 0.16 g of a brown solid. The recrystallisation of this from methanol gave a dark violet powder of XXXIII, mp <250°C. Although the UV spectrum of XXXIII is very similar to that of XXXII, and although the IR spectrum of XXXIII agrees with the proposed structure (3300, 2180, 1670, 1600, 1540, 1470, 1440, 1430, 1255, 1110 and 860 cm^{-1}, KBr pellet), we failed to obtain analytically-pure substances.