alumina should more closely resemble reaction in acetic acid solution, in which solvent has been shown to have a stabilizing effect on the ions, than will bromination at activated carbon.

Thus, two independent considerations predict that reaction on the inorganic adsorbents will more closely resemble that in solution than will reaction on activated carbon. Such has been shown to be the case; the *ortho/para* ratios for bromination of toluene at the surfaces of activated carbon, silica gel, and alumina are 1.1, 0.59, and 0.37, respectively, compared with 0.49 in 85% acetic acid[8] and 0.71 in excess toluene.[9] Bromination at the surface of alumina actually gives a lower *ortho/para* ratio than does bromination in 85% acetic acid.

The effect of interaction between bromine and the surface on isomer distributions must also be considered.

In chlorination of toluene in various solvents the *ortho/para* ratios varied from 2.2 in trifluoroacetic acid to 0.52 in nitromethane. The *ortho/para* ratio decreased as the complexing of chlorine with solvent increased.[10]

The differential heat of adsorption of bromine is 7719 cal/mol on silica gel and 11,430 cal/mol on activated carbon; the former value is only a few hundred calories above the heat of condensation of bromine.[20] If being held more tightly on the surface would increase the selectivity of bromine for the *para* position of toluene over the *ortho* positions, than the lowest *ortho/para* ratios should be obtained on activated carbon. Since the opposite was observed, the combination of steric and electronic effects of the surface on the aromatic hydrocarbon is probably more important in determining the course of attack than are the effects of the surface on the bromine.

Registry No.—Cyclohexene, 110-83-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; cumene, 98-82-8; butylbenzene, 98-06-6; ethylene, 74-85-1.

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(20) L. H. Reyerson and A. E. Cameron, *J. Phys. Chem.*, **39**, 181 (1935).

The Synthesis of Azulene-1-alkanoic Acids, Azulene-1,3-dialkanoic Acids, and Related Compounds. A 1,3-Bridged Azulene[1]

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Received October 31, 1968

1,3-Bis(2′,2′-dicarboxyethyl)azulene (**2**), azulyl-1,3-bis(propanoic acid) (**3**), 1,3-bis(2′-carbethoxy-3′-oxobutyl)azulene (**4**), 1,3-bis(3′-oxobutyl)azulene (**5**), diethyl azulene-1,3-dipropanoate (**6**), and 1,3-bis(3′-hydroxypropyl)azulene (**7**) have been synthesized *via* nucleophilic displacement reactions on azulyl-1,3-bis(methyltrimethylammonium) diiodide (**1**). Vilsmeier acylation reactions and reduction of the carbonyl groups in the 1-acylazulene products to methylenes by either the hydride reduction–alkylideneazulenium salt–hydride reduction method or, in one step, by diborane have been used to prepare 1-ethylazulene, ethyl 5-(1-azulyl)-5-oxopentanoate (**8a**), ethyl 5-(1-azulyl)pentanoate (**10a**), 1-(1′-oxo-4′-carbethoxybutyl)-3-(5′-chloropentyl)-azulene (**11a**), azulene-1,3-bis(hexanenitrile) (**14a**), ethyl 4-(1-azulyl)-4-oxobutanoate (**8b**), 1-(4′-chlorobutyl)-3-(1′-oxo-3′-carbethoxypropyl)azulene (**11b**), azulene-1,3-bis(pentanenitrile) (**14b**), 1,3-bis(1′-oxo-3′-carbomethoxypropyl)azulene (**16**), N,N-diethyl-10-(1-azulyl)decanamide (**21**), pentylazulene (**22**), 1,3-dipentylazulene (**23**), 1,3-dipropionylazulene (**24**), and 1,3-dipropylazulene (**25**). The principal maxima in the visible absorption spectra for the 1-alkyl- and 1,3-dialkylazulenes are compared. The diborane reduction of the acylazulenes is discussed. A high-dilution Thorpe–Ziegler ring closure of **14a** gave 1,3-(5′-cyano-6′-oxoundecamethylene)azulene (**26**), the first example of a 1,3-bridged azulene. Attempts to form 1,3-bridged products from **14b**, **21**, and **6** were unsuccessful.

In the course of studies on azulene[3] it was desired to prepare the derivatives given in the title, in part because certain of these might lead to 1,3 bridging of the nonbenzenoid azulene structure and thus provide a novel example of this type of structure. The syntheses required the formation of a saturated methylene carbon attached to the ring and a suitable functional group at the other end of the chain. This paper describes the methods found to accomplish these objectives and the preparation of the first example of a 1,3-bridged azulene.

The direct introduction of a methylene carbon onto the 1 position of azulene had been found practical as a synthetic method only for aminomethylation[4–6] and, for certain cases, the reaction with aliphatic diazo compounds.[7] The former had provided the first step in pathways to azulene-1-ethanoic acid and azulene-1-propanoic acid,[4] and the latter afforded a direct route to ethyl azulene-1-ethanoate. Since the results of an attempt to form an azulene-1,3-dialkanoic acid ester by the acid-catalyzed decomposition of an ω-diazo ester in the presence of azulene were not promising, the displacement reactions of azulyl-1,3-bis(methyltrimethylammonium) diiodide (**1**) with the anions of active methylene compounds were tried (Scheme I). From **1** and diethyl sodiomalonate was obtained, after hydroly-

(1) Supported in part by a grant from the National Science Foundation. From the Ph.D. Thesis of R. D. Breazeale, University of Washington, 1964.

(2) Weyerhaeuser Fellow, 1962–1963.

(3) *Cf.* A. G. Anderson, Jr., and R. C. Rhodes, *J. Org. Chem.*, **30**, 1616 (1965), and preceding papers.

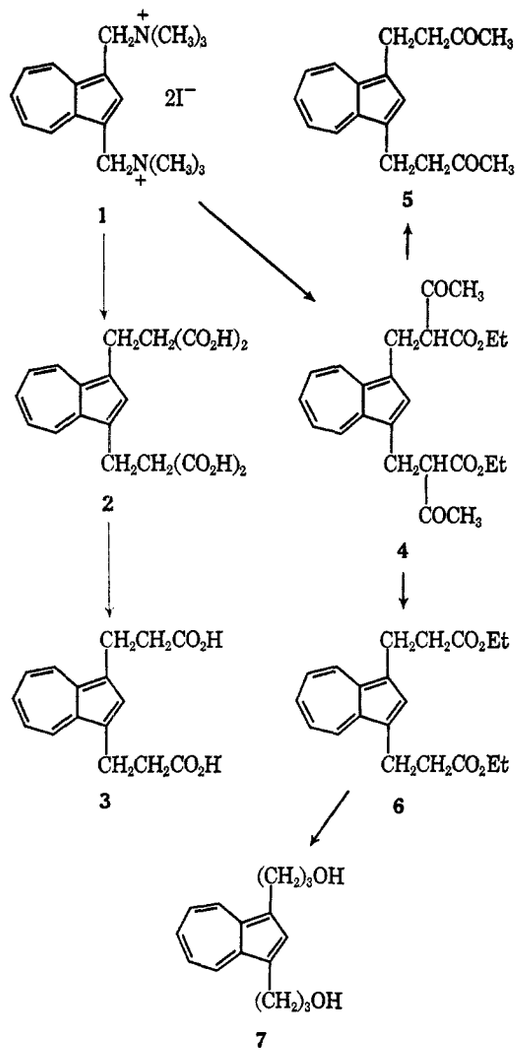
(4) A. G. Anderson, Jr., R. G. Anderson, and T. S. Fujita, *ibid.*, **27**, 4535 (1962).

(5) K. Hafner, *Angew. Chem.*, **70**, 419 (1958).

(6) M. Mühlstadt, W. Treibs, and J. Mohr, *Chem. Ber.*, **94**, 808 (1961).

(7) (a) A. G. Anderson, Jr., and R. C. Rhodes, *J. Org. Chem.*, **30**, 1616 (1965); (b) S. Hauptmann and K. Hirschberg, *J. Prakt. Chem.*, **34**, 272 (1966).

SCHEME I



sis, 1,3-bis(2′,2′-dicarboxyethyl)azulene (**2**, 86% yield). The decarboxylation of **2**, however, gave only 21% azulyl-1,3-bis(propanoic acid) (**3**). The direct displacement on **1** with sodium α-sodioacetate would circumvent the low yield decarboxylation, and precedent for the action of this anion as a nucleophile at a benzylic position was found in the formation of phenylpropanoic acid in good yield from benzyl chloride.[8] Although a variety of conditions was tried, the displacement by sodium α-sodioacetate on **1** did not occur. A possible reason is that the disodium salt was acting as a base on the diquaternary salt.[9]

Another anion investigated as a nucleophile was ethyl sodioacetoacetate, which had been used previously on the corresponding monoquaternary salt.[4] From the reaction with **1** followed by hydrolysis and acidification (decarboxylation occurred spontaneously) was obtained 1,3-bis(3′-oxobutyl)azulene (**5**) in 53% yield. An iodoform reaction with **5**, which had been used with success on 1-acetyl- and 1,3-diacetylazulene,[10] did not give **3**[11] and a different degradation of **4** was sought. The deacetylation of substituted acetoacetic esters in good yield had been reported by Ritter and Kaniecki[12] and the application of this method to 1,3-bis(2′-carbethoxy-3′-oxobutyl)azulene (**4**), formed in 80% yield, afforded a 69% yield of diethyl azulene-1,3-dipropanoate (**6**). Hydride reduction of **6** produced 1,3-bis(3′-hydroxypropyl)azulene (**7**) in high yield. As had been found earlier with 1-methylazulene, these 1,3-dialkylazulenes were unstable to atmospheric oxygen and good analyses were not obtained for some, although the spectral data were clearly consistent with the proposed structures.

The introduction of an unsaturated carbon with subsequent reduction to a methylene was the alternative possibility and a variety of reactions for the first step were available. The Vilsmeier reaction of N,N-dialkylamides and phosphorus oxychloride with activated aromatic compounds to give aryl aldehydes or ketones had been used effectively by Hafner[13] and Treibs[14] and coworkers, although the preparation of 1,3-diformylazulene was the only case of disubstitution reported.[13,14] This method and that of the more common acylation reactions offered potential means of forming azulyl alkyl ketones having the desired functional groups on the ω carbon.

Vilsmeier substitution with ω-carbethoxy-N,N-dialkylamides[15] was chosen for the synthesis of 1-(α-oxo-ω-carbethoxyalkyl)azulenes[7b] (Scheme II). Reaction of azulene with ethyl N,N-diethylglutaramate, prepared in 52% yield by the reaction of glutaric anhydride and diethylamine followed by esterification, gave an 86% yield of ethyl 5-(1-azulyl)-5-oxopentanoate (**8a**), and there remained the reduction step. Consideration of previous findings on the reduction of 1-acyl- and 1,3-diacylazulenes indicated that Wolff–Kishner,[13,14,16,17] Clemmensen,[16,17] or Raney nickel desulfurization[16,17] methods would not be satisfactory. Attention was therefore turned to other methods. Hafner, *et al.*,[18] had found that the alcohol formed by hydride reduction of an acylazulene was converted by 70% perchloric acid or anhydrous fluoroboric acid into an alkylideneazulenium salt, and this, in turn, was reduced by lithium aluminum hydride to an alkylazulene. In a model experiment 1-(α-hydroxyethyl)azulene, obtained by sodium borohydride reduction of 1-acetylazulene, was converted into 1-ethylazulene *via* a modification of the Hafner method (perchlorate salt) in 27% yield. The rather low yield realized led to the trial of boron trifluoride etherate and sodium borohydride which Pettit, *et al.*,[19] had used for the reduction of β-propionylnaphthalene and β-(1-hydroxypropyl)naphthalene to

(8) Technical brochure kindly provided by the Ethyl Corp. We also thank this company for a sample of the sodium α-sodioacetate.

(9) The sodium α-sodioacetate is a stronger base than amide ion and the latter had been found to give only polymeric material with **1**.

(10) A. G. Anderson, Jr., R. Scotoni, Jr., E. J. Cowles, and C. G. Fritz, *J. Org. Chem.*, **22**, 1193 (1957).

(11) The amount of acidic azulenic product was very small and other products were not identified.

(12) J. J. Ritter and T. J. Kaniecki, *ibid.*, **27**, 622 (1962).

(13) K. Hafner and C. Bernhard, *Ann.*, **625**, 108 (1959).

(14) W. Treibs, H. Neupert, and J. Hiebsch, *Chem. Ber.*, **92**, 141 (1959).

(15) A. W. D. Avison, *J. Appl. Chem.*, **1**, 469 (1951).

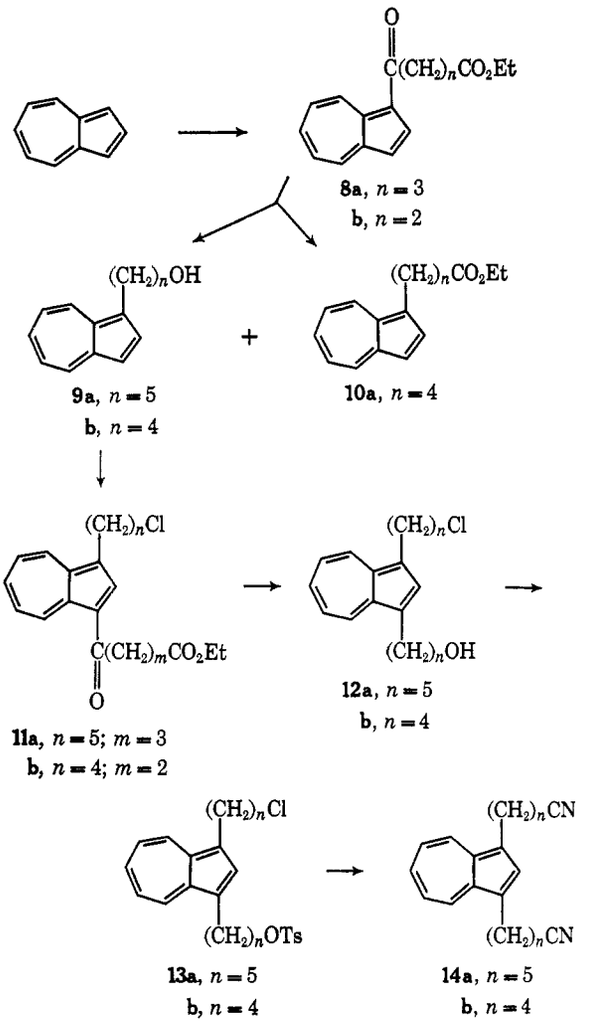
(16) E. J. Cowles, Ph.D. Thesis, University of Washington, 1953, pp 146–149; J. A. Nelson, Ph.D. Thesis, University of Washington, 1950, pp 121–125.

(17) K. Hafner and D. L. Dreyer, unpublished results. Private communication from Dr. Dreyer. Trial Wolff–Kishner, modified Wolff–Kishner [D. J. Cram. M. R. V. Sayhun, and G. R. Knox, *J. Amer. Chem. Soc.*, **84**, 1734 (1962)], and Clemmensen reductions on **15**, **16**, and 1,3-diformylazulene, and nickel desulfurization reactions on the bis ethylthio ketals of **18** and 1,3-diacetylazulene were run in the present investigation. All gave negative results.

(18) K. Hafner, H. Pelster, and J. Schneider, *Ann.*, **650**, 62 (1961).

(19) G. R. Pettit, B. Green, P. Hofer, D. C. Ayres, and P. J. S. Pauwels, *Proc. Chem. Soc.*, 357 (1962); G. R. Pettit and D. M. Piatek, *J. Org. Chem.*, **27**, 2127 (1962).

Scheme II

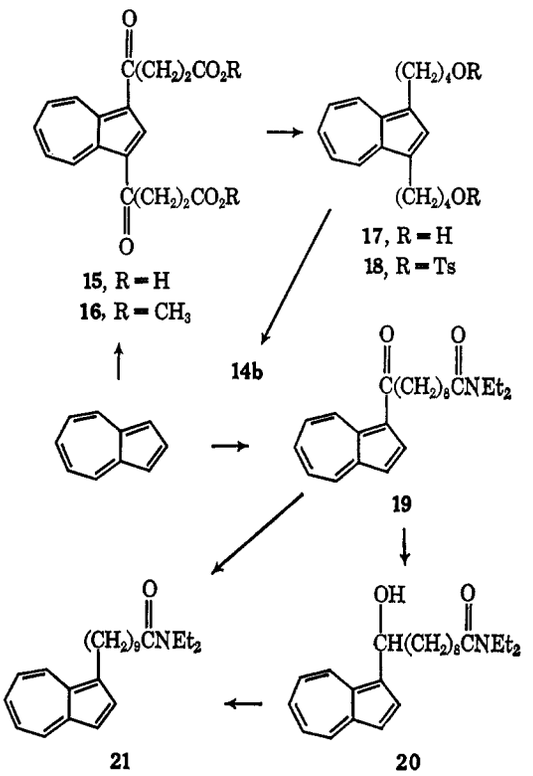


β-propylnaphthalene. A modification of this procedure gave an approximately quantitative reduction of the keto ester (**8a**) to a mixture (*ca.* 9:1) of 5-(1-azulyl)-1-pentanol (**9a**) and ethyl 5-(1-azulyl)pentanoate (**10a**). Under different reaction conditions, a higher yield (52%) of **10a** was obtained. The alcohol (**9a**) was then treated with ethyl N,N-diethylglutaramate under Vilsmeier conditions and a 48% yield of 1-(1′-oxo-4′-carbethoxybutyl)-3-(5′-chloropentyl)azulene (**11a**) resulted. Sodium borohydride–boron trifluoride reduction of **11a**, treatment of the product (presumed to be **12a**) with *p*-toluenesulfonyl chloride, and then reaction of the derivative product (formulated as **13a**) with potassium cyanide in dimethyl sulfoxide gave azulene-1,3-bis(hexanenitrile) (**14a**) in 44% yield from **11a**.

The achievement of this synthesis of **14a** led to the repetition of this scheme using ethyl N,N-diethylsuccinamate in the Vilsmeier steps. In this manner the corresponding compounds **8b** (44%), **11b** (34% from **8b**), and **14b** (36% from **11b**) having one less carbon in the side chains were isolated and characterized.

The success of the Vilsmeier reaction for the preparation of **8** and the fact that Friedel–Crafts acylation conditions which gave disubstitution directly had been readily found[20] led to an attempt to achieve the disubstitution of azulene using an excess of N,N-dimethylacetamide and phosphorus oxychloride. An 87% yield of 1-acetylazulene, but no diacetylazulene, was obtained. Despite this result a second route to azulene-1,3-bis(pentanenitrile) (**14b**) involving diacylation was found (Scheme III). Azulene was treated with an excess of succinic anhydride under Friedel–Crafts conditions. The bis keto acid disubstitution product (**15**) was difficult to purify and clean separation from succinic acid was obtained only after esterification to form the bis keto ester (**16**). Despite the trial of many different reaction conditions, the best yield of **16** obtained was 15%. Curiously, the optimum conditions found for disubstitution resulted in the recovery of more than half of the azulene, but no monosubstitution product was observed.[21] In carrying out the synthesis of **14b** the crude bis keto acid (**15**) was reduced directly to the diol (**17**) by the sodium borohydride–boron trifluoride reagent. The diol was then converted into the tosylate (**18**) and finally to **14b** in the same manner as before.

Scheme III



The Vilsmeier reaction of azulene with N,N,N′,N′-tetraethyldecanediamide (Scheme III) gave the monosubstitution product (**19**) which could not be completely separated from starting materials and so the crude product was reduced with sodium borohydride to N,N-diethyl-10-(1-azulyl)-10-hydroxydecanamide (**20**). Further reduction of **20** by sequential treatment with perchloric acid and sodium borohydride, or the treatment of **19** with sodium borohydride–boron trifluoride gave N,N-diethyl-10-(1-azulyl)decanamide (**21**). The latter method was the better in this case and gave an over-all yield from azulene of 31%. A minor by-product of the several steps was tentatively identified as 1,10-bis(1-azulyl)decane, which could have been formed

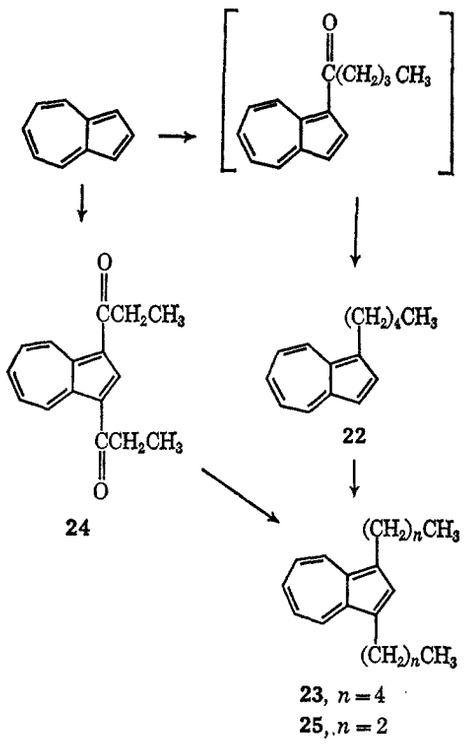
(20) A. G. Anderson, Jr., J. A. Nelson, and J. J. Tazuma, *J. Amer. Chem. Soc.*, **75**, 4980 (1953).

(21) This phenomenon had been observed earlier with the aluminum chloride catalyzed acetylation of azulene.[20]

by further Vilsmeier substitution of azulene by **19** and subsequent reduction.

As no 1,3-polymethylene-substituted azulenes had been characterized previously, it was desirable to have a model compound of this type as a spectral standard. For this purpose 1,3-dipentylazulene (**23**) was synthesized (Scheme IV), again using the Vilsmeier method

SCHEME IV



with N,N-diethylvaleramide as the reagent. The crude ketonic product was subjected to the sodium borohydride–boron trifluoride reduction and 1-pentylazulene (**22**) was obtained in 78% yield. Reduction of the crude keto compound by externally generated diborane gave a somewhat lower yield (59%) of **22**. Repetition of the Vilsmeier acylation and then reduction afforded **23** in 74% yield (55.5% from azulene). Application of the sodium borohydride–boron trifluoride reduction to 1,3-dipropionylazulene (**24**) provided an additional spectral reference compound, 1,3-dipropylazulene (**25**).

A compilation of the principal maxima in the visible spectra of 1-alkyl- and 1,3-dialkylazulenes is given in Table I. If the relatively small deviations are real, it is curious that the *n*-propyl group causes the largest bathochromic shift for the monoalkyl compounds, whereas the methyl group does this for the dialkyl derivatives.

The successful application of the above hydride reductions to azulene species concerned merits further comment. Wechter[22] had found that diborane in tetrahydrofuran reduced xanthone to xanthene but, under similar conditions, benzophenone, *o*-methoxybenzophenone, *p,p'*-dimethoxybenzophenone, and fluorenone were converted only into the alcohols. Also,

(22) W. F. Wechter, *J. Org. Chem.*, **28**, 2935 (1963).

TABLE I

PRINCIPAL VISIBLE MAXIMA OF 1-ALKYL AND 1,3-DIALKYLAZULENES[a]

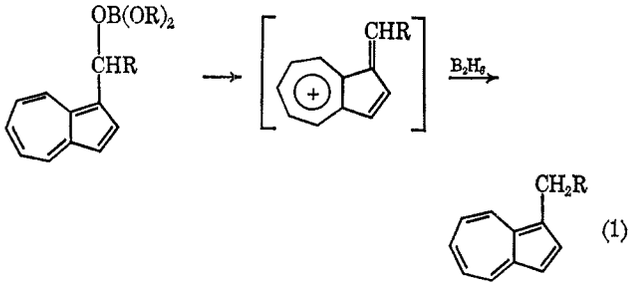
1-Alkyl or 1,3-dialkyl	λ_{max}, mμ	Ref
Methyl	608	*b*
Ethyl	610, 608	*b, c*
n-Propyl	613	*b*
Isopropyl	604, 607	*d, b*
n-Butyl	606	*e*
s-Butyl	610	*b*
t-Butyl	607	*d*
n-Pentyl	608	*c*
Dimethyl	638, 635	*b, f*
Diisopropyl	632	*d*
Di-*n*-propyl	631	*c*
Di-*n*-pentyl	632	*c*

[a] In solvents of low polarity (*e.g.*, alkanes). [b] E. Heilbronner, "Non-Benzenoid Aromatic Hydrocarbons," D. Ginsberg, Ed., Interscience, New York, N. Y., 1959, p 226. [c] Present work. [d] K. Hafner, H. Pelster, and J. Schneider, *Ann.*, **650**, 62 (1961). [e] R. C. Rhodes, Ph.D. Thesis, University of Washington, 1963, p 40. [f] K. Hafner and W. Senf, *Ann.*, **656**, 34 (1962).

sodium borohydride reduced xanthone to xanthol. Wechter concluded that the reduction of xanthone involved the participation of an unshared electron pair of the ether oxygen. One might, *a priori*, have considered that diborane was therefore not solely responsible for the reduction of β-propionylnaphthalene to β-propylnaphthalene.[19] A further observation of pertinence is that indole-3-aldehydes, ketones, -carboxylic acids, esters, -carbinols, and -carbinyl ethers are readily transformed by lithium aluminum hydride in ether into the corresponding methylene compounds if the indole nitrogen bears a hydrogen,[23] but the N-alkyl analogs are reduced only to the alcohol stage.[24] If aluminum chloride is added, however, 3-acetyl-N-methylindole is reduced by lithium aluminum hydride to 3-ethyl-N-methylindole in 74% yield and this method has been applied with general success[25] for the conversion of the carbonyl in diaryl and arylalkyl ketones into a methylene. It would appear, therefore, that the hydride donors in these reactions can effect the hydrogenolysis step only if a sufficiently stabilized intermediate, as with xanthone and N-hydrogen indoles, or reactive species (aluminum chloride complexed arylcarbinyloxyaluminum species) is involved. The pK_R^+ values for the xanthyl system (−0.84)[26] and for the di-*p*-anisylmethyl system (−5.71),[27] for example, are in agreement with this line of reasoning. No quantitative data on the stability of the 1-azulylmethyl cation are available but studies by Long and Schulze[28] led to approximate pK values of −1.7 and −0.83 for azulene and 1-methylazulene, respectively. These pK values are not strictly comparable with pK_R^+ values but provide a good indication that the 1-azulylmethyl cation has a considerably greater stability than does the di-*p*-anisylmethyl cation, relative to their respective

(23) E. Leete and L. Marion, *Can. J. Chem.*, **31**, 775 (1953).
(24) K. T. Potts and D. R. Liljegren, *J. Org. Chem.*, **28**, 3202 (1963).
(25) R. F. Nystrom and C. R. A. Berger, *J. Amer. Chem. Soc.*, **80**, 2896 (1961); J. Blackwell and W. J. Hickenbottom, *J. Chem. Soc.*, 1405 (1961); B. R. Brown and A. M. S. White, *ibid.*, 3755 (1957).
(26) N. C. Deno and W. L. Evans, *J. Amer. Chem. Soc.*, **79**, 5804 (1957).
(27) N. C. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955).
(28) F. A. Long and J. Schulze, *ibid.*, **86**, 327 (1964).

alcohols, and this could account for the reduction of the 1-acylazulenes by diborane (eq 1).

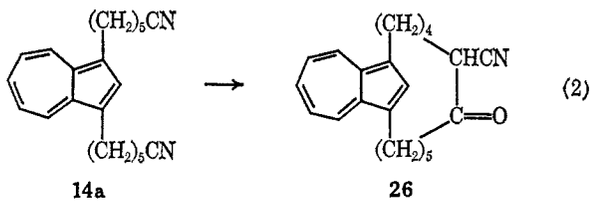


(1)

Diborane is reported to react quite slowly with esters[29] and the use of diborane in the absence of a Lewis acid catalyst would thus be predicted to be the reagent of choice for the selective reduction of keto esters **8**, **11**, and **16** to the saturated esters, whereas sodium borohydride–boron trifluoride reduced both groups readily even at 0°.

Phenol has been reported to react with acrylonitrile in the presence of aluminum chloride to give β-(*p*-hydroxyphenyl)propionitrile in good yield.[30] Attempts to apply this reaction to azulene were not successful.

For the formation of a 1,3-bridged azulene structure the Thorpe–Ziegler ring-closure reaction was run on the dinitriles **14a** and **14b** using a procedure adapted from the work of Allinger, *et al.*[31] From **14a** a 31% yield (5.4% from azulene) of 1,3-(5′-cyano-6′-oxoundecamethylene)azulene (**26**) was obtained (eq 2). The observed maximum of 629 mμ in the visible indicated that the azulene ring was probably not distorted by the 11-carbon bridged ring. Repetition of the Thorpe–Ziegler reaction with **14b**, however, did not give a product which could be identified as the desired bridged structure.



(2)

14a **26**

A high-dilution Vilsmeier procedure was carried out with the azulyldecanamide (**21**) in the hope that some 1,3-cyclized product would be formed, but the small and impure quantities of nonpolymeric materials obtained showed hydroxyl as well as carbonyl absorption and maxima in the region 628–632 mμ, and no product could be identified as the cyclic ketone expected.

Cram, *et al.*, found the acyloin condensation to be the preferred method of ring closure for the preparation of [12]-, [10]-, and [9]paracyclophanes.[32] It was found that azulene reacted with sodium under the conditions of the acyloin reaction to give a dark red-brown solution from which, after 90 min, only 12% of the azulene could be recovered.[33] Therefore a large excess of sodium was to be avoided. A reaction using an ester/sodium mole ratio of 1:4.7 was run with diethyl azulene-1,3-dipropanoate (**6**) but the only azulenic material recovered was the original ester (75%).

An X-ray structural analysis of the azulene-1,3-dipropanoic acid prepared in this work has been carried out by Ammon and Sundaralingam.[34]

Experimental Section

General.—Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Ultraviolet and visible spectra were recorded with either a Model 115 or 14 Cary recording spectrophotometer and, unless otherwise specified, were recorded using the same solvent. Infrared spectra were taken on a Perkin-Elmer Model 21 recording spectrophotometer. A Mechrolab Model 301A osmometer was used to determine molecular weights. Microanalyses were performed by Dr. A. Bernhardt, Microanalytical Laboratory, Max Planck Institute, Mülheim (Ruhr), Germany.

Dimethyl sulfoxide was distilled under vacuum and dried over 4-Å molecular sieves just prior to use. Boron trifluoride etherate was distilled and kept protected from moisture and light. Diglyme was dried over 4-Å molecular sieves. Tetrahydrofuran was distilled from potassium. Nitrogen was passed through sulfuric acid, over Drierite, and finally over hot copper wire.[35] Unless otherwise noted anhydrous sodium sulfate was used to dry solutions of compounds purified by distillation or chromatography. The latter were then concentrated to near dryness on a water bath with a rotary evaporator under aspirator pressure. The petroleum ether had bp 30–60°. Purified solvents were used for the purification and spectra of azulene derivatives. Crystalline compounds were obtained from the final eluent solvent unless otherwise specified. Analytical samples of unstable compounds were handled under nitrogen, and repeated attempts were made to achieve analytical purity for those not so obtained.

Azulyl-1,3-bis(methyltrimethylammonium) Diiodide (1).—This compound was obtained as fine, violet crystals in 98% yield by the treatment of 1,3-bis(dimethylaminomethyl)azulene[4] with an excess of CH_3I in ethanol. The salt decomposed on heating such that no characteristic temperature range could be recorded.[5] An ethanol solution showed λ_{max} (OD_{max}) at 537 (1.06), 567 (0.97, sh), and 624 mμ (0.36, sh) as reported.[36]

1,3-Bis(2′,2′-dicarboxyethyl)azulene (2).—To the solution formed from the reaction of 920 mg (40 mmol) of Na and 100 ml of absolute ethanol was added 8 ml (53 mmol) of distilled diethyl malonate under anhydrous conditions. The mixture was stirred for 10 min and 1.052 g (2 mmol) of **1** was then added in one portion. The solution was heated under reflux for 2 hr, cooled, diluted with 500 ml of water, made slightly acidic with 6 *N* hydrochloric acid, and finally extracted with ether. The residue from the concentration of the ether solution was dissolved in 20 ml of 20% methanolic KOH and the solution was heated under reflux for 105 min. The cooled solution was diluted with 100 ml of water, made slightly acidic with 6 *N* hydrochloric acid, and then continuously extracted with ether for 40 hr. Evaporation of the ether left a solid which was triturated with pentane and dried in a vacuum desiccator. The crude product (3.08 g) contained malonic acid which was removed by sublimation at 125–130° (2 mm). The residue of **2** amounted to 617 mg (86%): mp 171–172°; uv (OD_{max}) (95% ethanol) 236 (0.46), 282 (1.13), 292 (0.82, sh), 349 (0.11), and 367 mμ (0.09); visible (OD_{max}) 615 (0.72), 650 (0.63, sh), and 735 mμ (0.22, sh).

Anal. Calcd for $C_{18}H_{16}O_8$: C, 60.00; H, 4.47. Found: C, 59.60; H, 4.88.

Azulyl-1,3-bis(propanoic Acid) (3).—A 100-mg (0.28 mmol) sample of the tetraacid (**2**) was heated in a small glass sublimation

(29) H. C. Brown, "Hydroboration," W. A. Benjamin, Ed., New York, N. Y., 1962, p 249.

(30) H. W. Johnston and F. J. Gross, *J. Org. Chem.*, **22**, 1264 (1957).

(31) N. L. Allinger and S. Greenberg, *J. Amer. Chem. Soc.*, **84**, 2394 (1962); *ibid.*, **81**, 5733 (1959); N. L. Allinger, M. Nakazaki, and V. Zalkow, *ibid.*, **81**, 4074 (1959).

(32) D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954); D. J. Cram and H. Daenkier, *ibid.*, **76**, 2743 (1954); D. J. Cram and M. F. Antar, *ibid.*, **80**, 3109 (1958).

(33) The formation of a similar red-brown solution with sodium in tetrahydrofuran from which only *ca.* 8% 1-azuloic ester products could be obtained had also been observed: A. G. Anderson, Jr., D. J. Gale, R. N. McDonald, R. G. Anderson, and R. C. Rhodes, *J. Org. Chem.*, **29**, 1373 (1964).

(34) H. L. Ammon and M. Sundaralingam, *J. Amer. Chem. Soc.*, **88**, 4794 (1966).

(35) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 219.

(36) T. S. Fujita, M. S. Thesis, University of Washington, 1959.

apparatus[37] at 160° (2 mm) for 8 hr giving 36 mg (21%) of **3** as long needles: mp 183–184°; uv (OD_{max}) (95% ethanol) 238 (0.17), 282 (0.64), 349 (0.06), and 367 mμ (0.04); visible (OD_{max}) 618 (0.53), 673 (0.43, sh), and 750 mμ (0.15, sh).

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.78; H, 6.05.

1,3-Bis(3′-oxobutyl)azulene (5).—To the solution formed from 460 mg (20 mg-atoms) of Na and 40 ml of absolute ethanol was added 4 ml (30 mmol) of distilled ethyl acetoacetate under anhydrous conditions. The mixture was stirred for 10 min and 526 mg (1 mmol) of the bis quaternary salt (**1**) was added in one portion. The solution was heated under reflux for 2 hr, cooled to room temperature, diluted with 200 ml of water, and then extracted with ether. The extract was washed twice with water and once with saturated NaCl solution. The product from the concentration of the dried (Na_2SO_4) solution was dissolved in 30 ml of 10% methanolic KOH and the solution was heated under reflux for 1 hr. The heating bath was removed and 7 ml of 12 *N* sulfuric acid was added carefully to the hot, stirred solution. Carbon dioxide evolution ceased after *ca.* 10 min. and the solution was cooled (ice bath), diluted with 200 ml of water, and extracted with ether. The extract was washed with water and NaCl solution, and then dried. Chromatography over acidic alumina (CH_2Cl_2) gave 216 mg of blue solid which afforded 143 mg (53%) of **5** after recrystallization from cyclohexane: mp 64–66°; ir (CCl_4) 5.80 μ (carbonyl); uv (OD_{max}) (cyclohexane) 233 (0.78), 282 (1.37), 350 (0.12), and 3.68 mμ (0.10); visible (ε) 625 (331), 683 (271), and 760 mμ (89).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.55; H, 7.45.

1,3-Bis(2′-carbethoxy-3′-oxobutyl)azulene (4).—A solution of ethyl sodioacetoacetate was prepared in the manner described from 920 mg (40 mg-atoms) of Na, 100 ml of absolute ethanol, and 8 ml (61 mmol) of ethyl acetoacetate and to this was added 1.052 g (2 mmol) of the bis quaternary salt (**1**). The solution was heated under reflux for 2 hr and then allowed to stand at room temperature for 7 hr before dilution with 700 ml of water and then extraction with ether until the aqueous layer was colorless. The material from the concentration of the dried extract was heated at 50° (0.5 mm) for 4 hr and then chromatographed over acidic alumina. Elution with CH_2Cl_2 gave 660 mg (80%) of **4** as a blue oil: ir (CCl_4) 5.75, 5.80 μ; uv (log ε) (ethanol) 234 (4.00), 282 (4.61), 285 (4.58, sh), 348 (3.65), and 365 mμ (3.57); visible (ε) 610 (293), 650 (246), and 830 mμ (87).

Anal. Calcd for $C_{24}H_{28}O_6$: C, 69.88; H, 6.84. Found: C, 70.01; H, 6.86.

Diethyl Azulene-1,3-dipropanoate (6).—To 20 ml of absolute ethanol in a dry flask equipped with a 20-cm column packed with metal helices was added 5 mg (0.2 mg-atom) of Na. When the Na had reacted, 308 mg (0.75 mmol) of the above diacetoacetate compound (**5**) in 5 ml of absolute ethanol was added and the mixture was heated to reflux. The temperature at the top of the column rose to 78°, dropped to 77° after 3.5 hr, and remained there for 12 hr. Distillation of the solvent was begun and after 45 min 10 ml of distillate had been collected and the vapor temperature was 79°. Distillation was stopped and reflux continued with the vapor temperature at 79° for 5 hr. An odor of ethyl acetate was noted from the distillate. The cooled reaction mixture was diluted with 200 ml of water and extracted with ether until the aqueous layer was colorless. The washed (water) extract was dried and the concentrate from this was chromatographed over acidic alumina. Elution with 7:3 petroleum ether–methylene chloride gave 170 mg (69%) of **6** as a blue oil: ir (CCl_4) 5.75 μ; uv (log ε) (ethanol) 244 (3.98), 282 (4.63), 350 (3.66), and 367 mμ (2.56); visible (ε) 618 (280), 670 (230), and 745 mμ (75).

Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 73.59; H, 7.90.

1,3-Bis(3′-hydroxypropyl)azulene (7).—A solution of 122 mg (0.37 mmol) of the above diester (**6**) in 5 ml of ether (distilled from NaH) was added over 5 min to 76 mg (2 mmol) of $LiAlH_4$ and 10 ml of the dry ether stirred under nitrogen at 0° and the mixture was then stirred for 1 hr. The excess hydride was destroyed by the addition of 5 ml of water and the mixture was then poured into 0.5 ml of cold 10% sulfuric acid, vigorously shaken until the complex had decomposed, and then extracted with ether. The washed (20 ml of 5% $NaHCO_3$), dried, concentrated organic fraction was chromatographed over silica gel (ether) giving 82 mg (91%) of **7** as a blue oil: ir ($HCCl_3$) 2.71 and 2.89 μ.

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 77.91; H, 8.31.

Ethyl N,N-Diethylglutaramate.—To a solution of 17.1 g (0.15 mol) of glutaric anhydride[38] in 30 ml of benzene was added 34 ml (0.32 mol) of diethylamine over a 10-min period and the mixture was then heated under reflux for 1 hr. After removal of most of the solvent, a solution of 15 ml of absolute ethanol, 30 ml of benzene, and 2 ml of concentrated sulfuric acid was added and the reaction mixture was then heated under reflux overnight using a Dean–Stark trap. The cooled solution was diluted with 100 ml of water and extracted with ether, and the ether extract was washed with water and then with saturated NaCl solution. Distillation of the dried solution yielded a forerun, bp 81–83° (1.5 mm), of about 2 g which was discarded. The product was collected at bp 121–123° (1.5 mm) [lit.[15] bp 115–118° (0.5 mm) and weighed 16.8 g (52%).

Ethyl 5-(1-Azulyl)-5-oxopentanoate (8a).—To a stirred solution of 560 mg (4.38 mmol) of azulene and 2 ml (9.3 mmol) of ethyl N,N-diethylglutaramate in 5 ml of dry tetrahydrofuran at 0° was added 2 ml (15.5 mmol) of $POCl_3$ under anhydrous conditions. The mixture was stirred for 15 min at 0° and for 30 min at room temperature and finally was heated under reflux for 6 hr. The cooled solution was diluted with 100 ml of water, made slightly basic with 10% KOH, and then extracted with ether. The extract was washed twice with 50 ml of saturated NaCl, dried, concentrated, and chromatographed over acidic alumina. Elution with 9:1 petroleum ether–methylene chloride afforded 50 mg of azulene, and then 4:1 petroleum ether–methylene chloride removed a yellow oil, which was discarded, followed by 1.029 g (86%, 95% net) of keto ester **8a**, mp 38–41°. Two additional chromatographic purifications provided the analytical sample as a maroon solid: mp 45–46°; ir (CCl_4) 5.75 and 6.05 μ; uv (OD_{max}) (cyclohexane) 230 (0.56), 283 (0.59), 305 (0.69), 368 (0.12), and 382 mμ (0.13); visible (OD_{max}) 530 (0.67, sh), 548 (0.77), 565 (0.68, sh), 593 (0.65), and 652 mμ (0.25). The corresponding methyl ester and acid have been reported.[7b]

Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.64; H, 6.80.

1-Acetylazulene.[39]—Under anhydrous conditions 3 ml (22.5 mmol) of $POCl_3$ was added dropwise to a stirred solution of 630 mg (5 mmol) of azulene in 5 ml of dry (molecular sieves) N,N-dimethylacetamide. The mixture was stirred for 5 min at room temperature and at 80° for 2 hr, then cooled, and diluted with 100 ml of water. The red solution was made slightly alkaline with 10% KOH and extracted with ether. The extracts were washed with five 50-ml portions of water and once with saturated NaCl solution, dried, concentrated, and chromatographed over acidic alumina. Petroleum ether–methylene chloride (9:1) eluted a trace of azulene and petroleum ether–methylene chloride (3:1) removed 737 mg (87%) of 1-acetylazulene having the spectra reported.[20]

1-Ethylazulene. Method A.—To a solution of 141 mg (0.83 mmol) of 1-acetylazulene in 5 ml of 95% ethanol containing 5 drops of 10% KOH was added 200 mg (5.1 mmol) of $NaBH_4$ and the reaction mixture was stirred for 5.5 hr at room temperature. Ice water (50 ml) was added, the mixture was extracted with ether, and the extract was washed three times with water and once with saturated NaCl solution. The concentrate from the dried solution was chromatographed over basic alumina and elution with 1:1 methylene chloride–ether afforded a blue oil (*ca.* 74 mg, 52%) presumed to be 1-(α-hydroxyethyl)azulene: uv (OD_{max}) (CH_2Cl_2) 240 (0.32), 279 (0.99), 285 (0.90), 34 (0.09), and 359 mμ (0.06); visible (OD_{max}) 590 (1.22), 625 (1.10, sh), and 700 mμ (0.42, sh); ir 2.79 and 2.91 μ. This product was quite unstable, as reported,[13] and was used immediately in the next step.

A flask with a sintered-glass bottom attached to a filter bell was equipped with a pressure-equalized dropping funnel and a stirrer. It was dried, flushed with nitrogen, and cooled to 0° before 10 ml of anhydrous ether, 1 ml of acetic anhydride, and then 0.3 ml of 70% perchloric acid were introduced. The solution was stirred for 5 min at 0°, the ice bath was replaced by one containing Dry Ice–methanol, and the above blue oil was dis-

(37) Reference 35, p 115.

(38) We are grateful to the Textile Fibers Department, E. I. du Pont de Nemours and Co., for a generous sample of this compound.

(39) This procedure is a modification of the method of Hafner and Bernhard[13] which gave a 70% yield.

solved in 10 ml of methylene chloride–ether (1:1) and added over a period of 10 min. The solvent was removed (filtration) and the precipitate was washed with two 10-ml portions of dry ether. The temperature was increased to 0° and 5 ml of CH_3NO_2 (dried over acidic alumina) was added. To the stirred yellow-brown solution was added 100 mg (2.5 mmol) of $NaBH_4$, which turned the solution blue. After 15 min the contents of the flask were removed, taken up in ether, and washed three times with water. The concentrate from the dried organic fraction was chromatographed over basic alumina. Petroleum ether–methylene chloride (5:1) eluted 35 mg (27%) of 1-ethylazulene as a blue oil: uv (OD_{max}) (cyclohexane) 238 (0.63), 280 (1.48), 345 (0.14), and 362 mμ (0.10); visible (OD_{max}) 584 (1.37). 608 (1.62), 633 (1.56), 665 (1.43), 698 (0.90), 738 (0.525), and 773 mμ (0.14) in agreement with the reported spectra.[40] The ir spectrum showed no absorption for hydroxyl or carbonyl functions.

Method B.—To a solution of 15 mg (0.09 mmol) of 1-acetylazulene in 0.5 ml of anhydrous ether was added 0.5 ml (4 mmol) of boron trifluoride etherate. The orange solution was added over 30 min to 100 mg (2.6 mmol) of $NaBH_4$ in 1 ml of diglyme at 0° with stirring. The mixture was stirred 1 hr longer, poured into 50 ml of ice water, and extracted with petroleum ether. Chromatography (basic alumina and petroleum ether) of the concentrate from the washed (water), dried extract gave 9 mg (64%) of 1-ethylazulene identical (ir, uv, and visible spectra) with the product from method A.

Ethyl 5-(1-Azulyl)pentanoate (10a).—To a solution of 135 mg (0.5 mmol) of the above keto ester (**8a**) and 100 mg (2.6 mmol) of $NaBH_4$ in 2 ml of dry diglyme stirred at 0° was added 0.5 ml (4 mmol) of boron trifluoride etherate over a period of 10 sec. The mixture was stirred for 3 min and then poured into 50 ml of ice water. The aqueous product was extracted with ether and the concentrate from the washed (water and saturated NaCl) and dried extract was chromatographed over basic alumina. Elution with 1:1 petroleum ether–methylene chloride gave 68 mg (52%) of **10a** as a blue oil: ir (CCl_4) 5.75 μ; uv (OD_{max}) (cyclohexane) 238 (0.31), 275 (0.81), 279(0.82), 285 (0.85), 345 (0.09), and 362 mμ (0.06); visible (OD_{max}) 562 (0.56 sh), 582 (0.66), 606 (0.80), 632 (0.68), 663 (0.70), 698 (0.32, sh), and 736 mμ (0.29).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.43; H, 8.03.

1-(1′-Oxo-4′-carbethoxybutyl)-3-(5′-chloropentyl)azulene (11a).—To a solution of 270 mg (1 mmol) of the above keto ester (**8a**) in 2 ml of anhydrous ether was added 1.5 ml (12 mmol) of boron trifluoride etherate. The mixture was added under anhydrous conditions to a stirred solution of 500 mg (12.8 mmol) of NaH in 5 ml of diglyme at 0° over a period of 30 min. Stirring was continued for 30 min and the mixture was then poured into 50 ml of ice water and extracted with ether. The concentrate from the washed (twice with saturated NaCl solution) and dried extract was chromatographed over basic alumina. Elution with 1:1 petroleum ether–methylene chloride afforded 19 mg (7%) of **10a**, and ether then eluted 215 mg (*ca.* 100%) of blue oil: ir (neat) 2.9 μ (OH); uv (OD_{max}) (cyclohexane) 233 (0.60), 279 (1.02), 346 (0.10) and 362 mμ (0.07); visible (OD_{max}) 562 (0.68, sh), 585 (0.80), 607, (0.98), 633 (0.84), 666 (0.86), 700 (0.38 sh), and 738 mμ (0.35). The spectra indicated that the product was primarily 5-(1-azulyl)-1-pentanol (**9a**).

The blue oil (215 mg) and 0.5 ml (2.3 mmol) of ethyl N,N-diethylglutaramate were dissolved in 2 ml of dry tetrahydrofuran. To the cooled (0°), stirred solution was added, dropwise, 0.5 ml (3.9 mmol) of $POCl_3$ under anhydrous conditions. The mixture was stirred for 10 min at 0°, 30 min at room temperature, and 2 hr under reflux, then was cooled, diluted with 100 ml of water, made slightly basic with 10% KOH, and extracted with ether. The concentrate from the washed (twice with water and once with saturated NaCl) and dried extract was chromatographed over acidic alumina. Elution with 2:1 methylene chloride–petroleum ether removed a pale yellow-green oil (which was discarded) followed by 181 mg (48% from **8a**) of **11a** as an oil which crystallized as green needles, mp 40–42°. Rechromatography gave the analytical sample: mp 42–43°; ir (CCl_4) 5.75 and 6.07 μ; uv (OD_{max}) (cyclohexane) 231 (0.35), 265 (0.14, sh), 298 (0.36), 309 (0.43), 378 (0.08), and 397 mμ (0.08); visible (OD_{max}) 572 (0.84), 620 (0.66), and 688 mμ (0.22).

(40) Table I, ref *b*.

Anal. Calcd for $C_{22}H_{27}O_3Cl$: C, 70.49; H, 7.21; Cl, 9.48. Found: C, 70.63; H, 7.09; Cl, 9.29.

Azulene-1,3-bis(hexanenitrile) (14a).—To a solution of 187 mg (0.5 mmol) of the above chloro keto ester (**11a**) in 1.5 ml of ether was added 1 ml (8 mmol) of boron trifluoride etherate. This red solution was added dropwise to a stirred solution of 250 mg (6.4 mmol) of $NaBH_4$ in 2 ml of diglyme at 0° over a period of 30 min and the mixture was stirred an additional 30 min before it was added to 100 ml of ice water. The aqueous mixture was extracted with ether and the extract was washed with saturated NaCl and then dried. The concentrate was chromatographed over basic alumina. Petroleum ether–methylene chloride (1:1) eluted 10 mg of unchanged **11a** and then methylene chloride–ether (1:1) gave 153 mg (96%) of a blue oil presumed to be 1-(5′-chloropentyl)-3-(5′-hydroxypentyl)azulene (**12a**): ir (neat) 2.95 μ; uv (OD_{max}) (cyclohexane) 240 (0.28), 283 (1.03), 351 (0.12), and 368 mμ (0.10); visible (OD_{max}) 630 (1.13), 661 (0.41), and 774 mμ (0.34).

To a solution of 347 mg (1.19 mmol) of the blue oil in 5 ml of dry (KOH) pyridine stirred at 5–10° was added 573 mg (3 mmol) of *p*-toluenesulfonyl chloride over a 10-min period. The mixture was stirred at 18° for 3 hr, about 10 g of ice and 10 ml of 3 *N* hydrochloric acid was then added, and the whole was extracted with ether. The extract was washed twice with water and once with saturated NaCl and dried. The concentrate was chromatographed over basic alumina and 1:1 petroleum ether–methylene chloride eluted 359 mg (64%) of a blue oil presumed to be *p*-toluenesulfonate ester (**13a**) of the alcohol (**12a**): ir (neat) 6.25, 7.38, 8.43 and 8.51 μ (characteristic of tosylates) and no hydroxyl absorption. The visible spectrum (cyclohexane) was essentially identical with that of the immediate precursor alcohol.

A solution of 359 mg (0.76 mmol) of the preceding blue oil in 5 ml of dimethyl sulfoxide was added dropwise to a solution of 98 mg (2 mmol) of dry NaCN in 3 ml of dimethyl sulfoxide. The mixture was stirred for 5 min at 25°, heated at 80° for 30 min, cooled, diluted with 100 ml of water, and then extracted with ether. The extract was washed twice with water and once with saturated NaCl and dried. The concentrate was chromatographed over basic alumina. Elution with 2:1 petroleum ether–methylene chloride removed a trace of a blue oil, then 163 mg of a second blue oil was eluted with a 1:1 solution of the same solvents, and 47 mg of a third blue oil was eluted with CH_2Cl_2. The ir spectra (neat) of the two major fractions were very similar except that the absorption for nitrile was more intense in the latter. The former was therefore presumed to be the monochloromononitrile product and was subjected to a second identical treatment with sodium cyanide and work-up procedure. Rechromatography of the product from this, combined with the 47 mg from the initial reaction, over acidic alumina with CH_2Cl_2 as the eluent gave 175 mg (72%) of **14a** as a blue oil: ir (neat) 4.47 μ (CN); uv (OD_{max}) (cyclohexane) 230 (0.74), 282 (1.25), 350 (0.13), and 368 mμ (0.11); visible (OD_{max}) 580 (0.56, sh), 605 (0.67, sh), 628 (0.80), 660 (0.66), 688 (0.67), 730 (0.26, sh), and 767 mμ (0.22).

Anal. Calcd for $C_{22}H_{26}N_2$: C, 83.02; H, 8.18. Found: C, 83.05; H, 8.15.

Ethyl 4-(1-Azulyl)-4-oxobutanoate (8b).—To a cooled (0°) solution of 2.2 ml (11 mmol) of ethyl N,N-diethylsuccinamate, bp 114–115° (1.7 mm) [lit.[15] bp 102–104°, (0.8 mm)], prepared as described by Avison,[15] and 1.28 g (10 mmol) of azulene in 15 ml of dry tetrahydrofuran was added 1 ml (11 mmol) of $POCl_3$ over a period of 2 min. The mixture was stirred at 0° for 5 min and at room temperature for 15 min and was then heated under reflux for 3.5 hr. The cooled solution was diluted with 100 ml of saturated NaCl, made almost neutral (slightly acidic) with 10% KOH, and extracted with CH_2Cl_2. The extract was washed with saturated sodium chloride and dried. Chromatography of the concentrate over acidic alumina and elution with petroleum ether afforded 300 mg of azulene. Elution with 9:1 petroleum ether–diethyl ether removed a yellow oil (discarded) and then 1.131 g (44%, 60% net) of **8b** as a maroon oil: ir (neat) 5.75 and 6.09 μ; uv (OD_{max}) (cyclohexane) 229 (0.98, sh), 260 (0.39, sh), 288 (0.70, sh), 292 (0.80), 298 (0.75, sh), 304 (0.91), 367 (0.16), and 382 mμ (0.18); visible (OD_{max}) 547 (0.70), 565 (0.61, sh), and 591 mμ (0.60). The corresponding methyl ester and acid have been reported.[7b]

Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.99; H, 6.43.

1-(4'-Chlorobutyl)-3-(1'-oxo-3'-carbethoxypropyl)azulene (11b).—To a solution of 964 mg (3.76 mmol) of the above keto ester (**8b**) in 5 ml of dry ether was added 1.5 ml (12 mmol) of boron trifluoride etherate. The resulting red solution was added, under anhydrous conditions, over a 25-min period to 500 mg (13 mmol) of $NaBH_4$ in 5 ml of diglyme stirred at 0° and the mixture was stirred at 0° for an additional 30 min. The reaction mixture was then poured into 50 ml of cold (0°) 5% KOH and the whole was extracted with ether. The extract was washed twice with water and once with saturated NaCl and dried. On chromatography of the concentrate over basic alumina, 1:1 methylene chloride–petroleum ether eluted a trace of blue-green oil (discarded) and 4:1 methylene chloride–ether gave 381 mg (51%) of blue oil presumed to be 4-(1-azulyl)butanol (**9b**): ir (CCl_4) 3.00 μ; uv (OD_{max}) (cyclohexane) 242 (0.43), 278 (1.81), 283 (1.63), 298 (0.16), 346 (0.17), and 362 mμ (0.11); visible (OD_{max}) 560 (0.79, sh), 582 (0.94), 605 (1.15), 631 (0.98), 663 (1.01), 695 (0.45), and 734 mμ (0.41). An unidentified blue oil (136 mg) was finally eluted with 9:1 ether–methanol.

To a stirred solution of 317 mg (1.59 mmol) of the blue oil designated as **9b** and 0.5 ml (2.5 mmol) of ethyl N,N-diethylsuccinamate[15] in 1 ml of dry tetrahydrofuran was added 0.2 ml (2.1 mmol) of $POCl_3$ at 0° under anhydrous conditions. The mixture was stirred at 0° for 10 min, at room temperature for 20 min, and at 80° for 1 hr before being cooled, diluted with 100 ml of water, and made slightly basic with 10% KOH. The whole was extracted with CH_2Cl_2 and the extract was washed twice with saturated NaCl and dried. Chromatography of the concentrate over acidic alumina and elution with 9:1 petroleum ether–methylene chloride removed a blue oil (28 mg). A 2:1methylene chloride–petroleum ether solution then eluted a yellow-green oil (discarded) followed by 368 mg (67%) of **11b** as a violet oil: ir (neat) 5.75 and 6.08 μ; uv (OD_{max}) (cyclohexane) 235 (0.39), 296 (0.53), and 309 mμ (0.65); visible (OD_{max}) 570 (0.56), 618 (0.45), and 682 mμ (0.15).

Anal. Calcd for $C_{20}H_{23}ClO_3$: C, 69.26; H, 6.64. Found: C, 69.85; H, 6.54.

Azulene-1,3-bis(pentanenitrile) (14b). Method A.—To a solution of 263 mg (0.76 mmol) of the above chloro keto ester (**11b**) in 2 ml of anhydrous ether was added 1 ml (8 mmol) of boron trifluoride etherate. The resulting solution was added over a 30-min period under anhydrous conditions to a stirred solution of 150 mg (4 mmol) of $NaBH_4$ in 2 ml of diglyme at 0°. The mixture was stirred an additional 30 min, poured into 50 ml of cold 5% KOH, and extracted with ether. The extract was washed twice with water and once with saturated NaCl and then dried. Chromatography of the concentrate over basic alumina and elution with 1:1 petroleum ether–methylene chloride removed a blue oil (28 mg) and then elution with 9:1 methylene chloride–ether gave 158 mg (76%) of a blue oil presumed to be 1-(4'-chlorobutyl)-3-(4'-hydroxybutyl)azulene (**12b**): ir (neat) 2.96 μ; uv (OD_{max}) (cyclohexane) 233 (0.55), 282 (1.12), 350 (0.12), and 368 mμ (0.11); visible (OD_{max}) 608 (0.64), 629 (0.75), 659 (0.63), 691 (0.63), 725 (0.28, sh), and 770 mμ (0.23).

To a solution of 158 mg (0.57 mmol) of the product designated as **12b** in 5 ml of dry pyridine stirred at 0° was added 345 mg (1.8 mmol) of *p*-toluenesulfonyl chloride over a 10-min period and the mixture was stirred at 15° for 4.5 hr. About 10 g of ice and 10 ml of 2 *N* hydrochloric acid were added and the whole was extracted with ether. The extract was washed three times with cold water and once with saturated NaCl and then dried. The concentrate was chromatographed over basic alumina. A blue oil, 148 mg (58%) presumed to be the *p*-toluenesulfonate derivative (**13b**) of **12b**, was eluted with 1:1 methylene chloride–petroleum ether: ir (neat) 6.25, 7.36, 8.43, and 8.53 μ (tosylate) and no absorption for hydroxyl. The uv and visible spectra (cyclohexane) were very similar to those of **12b**.

A solution of 145 mg (0.33 mmol) of the product designated as **13b** in 5 ml of dry dimethyl sulfoxide was added under anhydrous conditions to 98 mg (2 mmol) of dry NaCN in 1 ml of dimethyl sulfoxide. The stirred mixture was heated at 80° for 30 min, then cooled, and diluted with 50 ml of water, and the whole was extracted with ether. The extract was washed several times with water and once with saturated NaCl and dried. Chromatography of the concentrate over basic alumina and development with 1:1 methylene chloride–petroleum ether gave two blue bands. The product (31 mg) from the first was assumed to be monochloride–mononitrile and was subjected to reaction with 98 mg (2 mmol) of NaCN in 5 ml of dimethyl sulfoxide as just described and the product was combined with the second fraction from the initial chromatograph. Rechromatography of the combined material with the same eluent gave a trace of blue oil as the first fraction and the main product (**14b**), 79 mg (82%), was removed with 2:1 methylene chloride–petroleum ether and obtained as a blue oil: ir (neat) 4.45 μ (CN); uv (log ϵ) (ethanol) 231 (4.47), 282 (4.74), 349 (3.70), and 366 mμ (3.58); visible (ϵ) 625 (313), 682 (258), and 765 mμ (88).

Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.76; H, 7.59. Found: C, 82.47; H, 7.86.

Method B.—Under anhydrous conditions a mixture of 2.2 g (22 mmol) of powdered succinic anhydride, 5.36 g (40 mmol) of anhydrous $AlCl_3$, and 100 ml of CH_2Cl_2 was warmed at 35° for 10 min with stirring. The mixture was cooled to 0° and, with stirring and purging with nitrogen, a solution of 1.28 g (10 mmol) of azulene in 50 ml of CH_2Cl_2 was added over a period of 20 min. Azulene remaining in the funnel was rinsed into the flask with 25 ml of CH_2Cl_2 and the total mixture was stirred at 15° for 3 hr and then poured into 50 ml of 2 *N* hydrochloric acid at 0°. The resulting red precipitate was collected by filtration and washed with cold CH_2Cl_2. The organic fraction of the filtrate was extracted three times with 10% Na_2CO_3 (extracts saved) and once with saturated NaCl and dried. Chromatography of the concentrate over acidic alumina and elution with petroleum ether afforded 640 mg (5 mmol) of azulene. The combined extracts were acidified with 6 *N* hydrochloric acid and the collected red precipitate was added to that obtained earlier. The combined product was rinsed with water and dried *in vacuo* over Drierite. This product was presumed to be mostly the bis keto acid (**15**) and appeared to be contaminated with succinic acid.

In a separate run, esterification of a methanol solution of this material with excess ethereal CH_2N_2 in the usual manner and purification by chromatography over acidic alumina (elution with 1:20 ether–methylene chloride to remove small yellow and red fractions and then with ether) gave a 15% (58% net) yield (0.537 g from 1.28 g of azulene) of 1,3-bis(1'-oxo-3'-carbomethoxypropyl)azulene (**16**) which crystallized from acetone as red needles: mp 108–109°; ir (KBr pellet) 5.79 and 6.06 μ; uv (OD_{max}) (ethanol) 305 (1.47), 375 (0.69), and 385 mμ (0.67); visible 500 mμ.

Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.72; H, 5.91.

The product designated as crude **15** was dissolved in 7 ml of diglyme and to this solution was added 3 ml (24 mmol) of boron trifluoride etherate. The resulting solution, in turn, was added over a 30-min period under anhydrous conditions to 500 mg (13 mmol) of $NaBH_4$ in 5 ml of diglyme stirred at 0°, and then a second equal portion of $NaBH_4$ was added in the same manner. The mixture was stirred an additional 30 min and then poured into 50 ml of cold 5% KOH. After extraction with ether (an emulsion formed which was broken by centrifugation), the extract was washed twice with water and once with saturated NaCl and dried over Na_2SO_4. The solvent was removed and the residue, presumed to be **17**, was taken up in 10 ml of dry pyridine. To the cold (0°) solution was added, with stirring, 3 g (15.8 mmol) of *p*-toluenesulfonyl chloride over a period of 1 hr. After the mixture was stirred 2 hr at 15°, about 10 g of ice and 20 ml of 3 *N* hydrochloric acid were added and the whole was extracted with ether. The extract was washed twice with water and once with saturated NaCl and dried. Chromatography of the concentrate over basic alumina and elution with 2:1 methylene chloride–petroleum ether gave 561 mg of blue oil presumed to be crude ditosylate (**18**): ir (neat) 6.25, 7.36, 8.43, and 8.53 μ (tosylate) along with a weak band at 5.75 μ; visible (cyclohexane–carbon tetrachloride) 629 mμ.

A solution of the blue product in 5 ml of dimethyl sulfoxide was added to 196 mg (4 mmol) of dry NaCN in 1 ml of dimethyl sulfoxide. The mixture was stirred for 5 min at room temperature and for 10 min at 80°. It was allowed to cool and diluted with 100 ml of water, and the whole was extracted with ether. The extract was washed three times with water and once with saturated NaCl and dried. Chromatography of the concentrate over basic alumina and elution with 2:1 methylene chloride–petroleum ether yielded 210 mg of blue oil which exhibited absorption at 4.48 (CN) and also at 5.75 μ (tosylate). Rechromatography over acidic alumina with 1:1 methylene chloride–petroleum ether eluent and fractional collection of the eluate effected the separation of the tosylate impurities (in the first fractions) from 116 mg (4%, 8% net from azulene) of **14b** identical (ir spectrum) with the product from method A.

N,N-Diethyl-10-(1-azulyl)decanamide (21). Method A.—To 24 g (0.1 mol) of decanedioyl chloride, mp −6 to −5°, bp 150° (3–4 mm) [lit.[41] bp 109–110° (1 mm)], in 50 ml of dry ether was added a solution of 50 ml (0.48 mol) of diethylamine in 50 ml of dry ether. The mixture was stirred for 3 hr and diluted with 100 ml of water, and the whole was extracted with ether. The extract was washed with 10% KOH, water, and saturated NaCl and then dried. Distillation gave 29.5 g (94%) of pale yellow oil presumed to be the tetraethyldiamide, bp 215–216° (1 mm).

Under anhydrous conditions a solution of 384 mg (3 mmol) of azulene in 1.67 g (5.4 mmol) of the diamide product was cooled to 0° and 0.28 ml (3 mmol) of $POCl_3$ was added with stirring over a 5-min period. The mixture was stirred at room temperature for 10 min and at 80° for 3 hr, cooled, and diluted with 100 ml of water. The solution was made slightly basic with 10% KOH and then extracted with ether. The concentrate from the washed (twice with water and once with saturated NaCl) and dried extract was chromatographed over acidic alumina. Petroleum ether–methylene chloride (4:1) eluted 19 mg of azulene and 1:1 petroleum ether–methylene chloride then removed 1.57 g of a maroon oil. The absorption spectra of this material indicated the presence of both the keto amide (**19**) and the tetraethyldecanediamide and rechromatography did not effect a separation. The material was dissolved in 10 ml of ethanol and to this solution was added 5 drops of 10% KOH and 500 mg (12.8 mmol) of $NaBH_4$. The mixture was stirred for 3 hr, then diluted with 100 ml of water, and extracted with ether. The concentrate from the washed (twice with water and once with saturated NaCl) and dried extract was chromatographed over basic alumina. A pale yellow-green oil was eluted with 1:1 petroleum ether–methylene chloride and then 1:1 methylene chloride–ether removed 756 mg (69%) of blue oil thought to be N,N-diethyl-10-(1-azulyl)-10-hydroxydecanamide (**20**): ir (neat) 2.90 and 6.10 μ; uv (OD_{max}) (ethanol) 240 (0.54), 278 (1.84), 282 (1.67), 330 (0.15, sh), 342 (0.19), and 358 mμ (0.09); visible (OD_{max}) 590 (0.56), 635 (0.47, sh), and 700 mμ (0.17 sh).

To 20 ml of dry ether and 3 ml of acetic anhydride under a nitrogen atmosphere at 0° in the apparatus described above for the preparation of 1-ethylazulene (method A) was added 1 ml of 70% perchloric acid. The solution was stirred for 30 min and then cooled in a Dry Ice–methanol bath, and 756 mg (2.07 mmol) of the above blue oil (**20**) dissolved in 10 ml of ether was added over a 15-min period. After the mixture stirred for an additional 30 min, the solvent was removed and the brown precipitate was washed with ether. The temperature was increased to 0° and 5 ml of dry CH_3NO_2 was added to give a brown solution which turned blue upon the addition of 500 mg (12.8 mmol) of $NaBH_4$. The solution was stirred for 15 min, diluted with ether, and then washed with water three times. The concentrate from the dried ethereal fraction was chromatographed over acidic alumina and elution with CH_2Cl_2 afforded 115 mg (16% from **20**, 11% from azulene) of **21** as a blue oil: ir (neat) 6.10 μ; uv (OD_{max}) (cyclohexane) 232 (0.48), 274 (0.77), 279 (0.85), 284 (0.79), 347 (0.08), and 362 mμ (0.06); visible (OD_{max}) 584 (1.16), 607 (1.40), 636 (1.23), 665 (1.24), 700 (0.61), and 739 mμ (0.50).

Anal. Calcd for $C_{24}H_{35}NO$: C, 81.59; H, 9.91; N, 3.97. Found: C, 81.61; H, 9.89; N, 3.81.

Ether–methylene chloride (1:1) eluted 285 mg of an unstable blue oil: ir (neat) 2.91 (small) and 6.10 μ; uv (OD_{max}) (cyclohexane) 243 (0.25), 284 (0.89), 352 (0.10), and 369 mμ (0.09); visible (OD_{max}) 610 (1.45), 633 (1.55), 663 (1.32), 693 (1.13), 733 (0.53), and 775 mμ (0.33). The material was not characterized further.

Method B.—The reaction of decanedioyl chloride with diethylamine, and the reaction of the presumed tetraethyldiamide product from this with azulene were carried out exactly and with the same quantities as described in method A. The maroon oil so obtained was dissolved in 8 ml of ether and to this was added 8 ml (64 mmol) of boron trifluoride etherate. The resulting red solution was added under anhydrous conditions to a stirred solution of 2 g (54 mmol) of $NaBH_4$ in 10 ml of diglyme at 0°. The mixture was stirred an additional 2 hr at 0° and then poured into 100 ml of water, and the whole was extracted with ether. The concentrate from the washed (twice with water and once with saturated NaCl) and dried extract was chromatographed over Woelm alumina. Petroleum ether–methylene chloride (9:1) eluted 25 mg of material isolated as blue crystals, mp 78–79°, which were not obtained analytically pure. The absorption spectra were consistent with the formula of 1,10-bis(1-azulyl)-decane: ir (CCl_4) 3.35, 3.45, 3.53, 6.35, 6.95, and 7.17 μ (characteristic for a 1-alkylazulene); uv (OD_{max}) (cyclohexane) 237 (0.36), 274 (0.83), 279 (0.95), 285 (0.86), 346 (0.11), and 362 mμ (0.07); visible (OD_{max}) 562 (0.61, sh), 583 (0.73), 607 (0.88), 532 (0.75), 665 (0.79), 698 (0.35), and 738 mμ (0.32). Elution with 4:1 methylene chloride–ether then gave 331 mg (31%) of **21** identical (ir, uv, and visible spectra) with the material from method A. A third fraction of 158 mg, eluted with ether, exhibited absorption spectra very similar to those of the by-product obtained in method A and was not characterized further.

N,N-Diethylpentanamide.—A solution of 25 g (0.15 mol) of valeryl bromide in 50 ml of dry ether was added over a 1-hr period to a stirred solution of 29 g (0.4 mol) of diethylamine in 50 ml of ether at 0°. The mixture was allowed to stand for 10 hr. Saturated NaCl (100 ml) was added and the whole was extracted with ether. Removal of the solvent from the washed (twice with saturated NaCl) and dried extract and distillation yielded 20 g (85%) of the amide product, bp 63–65° (1.5 mm) [lit.[42] bp 94–95° (10 mm)].

1-Pentylazulene (22). Method A.—To a solution of 384 mg (3 mmol) of azulene and 942 mg (6 mmol) of N,N-diethylpentanamide in 2 ml of dry tetrahydrofuran at 0° was added dropwise, under anhydrous conditions, 0.45 ml (5 mmol) of $POCl_3$. The mixture was stirred for 5 min at 0°, 30 min at room temperature, and 3 hr at 80°. It was then cooled to room temperature and diluted with 100 ml of water. The solution was made slightly basic with 10% KOH and was then extracted with CH_2Cl_2. The extract was washed three times with saturated NaCl, dried, concentrated, and chromatographed over acidic alumina. Petroleum ether eluted 35 mg of azulene and methylene chloride–petroleum ether (1:1) then removed a maroon oil (presumed to be crude 1-pentanoylazulene). The oil was dissolved in 3 ml of ether, 1 ml (8 mmol) of boron trifluoride etherate was added, and the resulting solution was added, under anhydrous conditions, over a 15-min period to 380 mg (10 mmol) of $NaBH_4$ in 5 ml of diglyme at 0°. The mixture was stirred an additional 30 min and then poured into 50 ml of cold 5% KOH, and the whole was extracted with ether. The extract was washed four times with 20 ml of water and once with saturated NaCl, dried, concentrated, and chromatographed over basic alumina. Petroleum ether eluted 463 mg (78%, 85% net) of **22** as a blue oil: ir (neat) 3.35, 3.45, 3.52, 6.35, 6.95, 7.16 μ (1-alkylazulene); uv (OD_{max}) (cyclohexane) 238 (0.40), 275 (1.12, sh), 279 (1.30), 298 (0.12), 347 (0.13), and 362 mμ (0.09); visible (OD_{max}) 562 (0.64, sh), 582 (0.77), 608 (0.93), 633 (0.79), 666 (0.82), 700 (0.36), and 737 mμ (0.34).

Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.75; H, 9.23.

Method B.—Azulene (256 mg, 2 mmol), N,N-diethylpentanamide (0.7 ml, 4 mmol), $POCl_3$ (0.3 ml, 0.33 mmol), and 2 ml of dry tetrahydrofuran were allowed to react and the reaction was worked up as described in method A. One-third of the maroon oil so obtained was dissolved in 10 ml of dry tetrahydrofuran and cooled to 0° with stirring. Diborane [generated in an adjacent flask by the slow addition of 380 mg (10 mmol) of $NaBH_4$ in 5 ml of diglyme to 1 ml (8 mmol) of boron trifluoride etherate] was carried into the reaction mixture by a nitrogen stream through a glass tube having a small exit orifice extending below the surface of the solution. The $NaBH_4$ addition was complete in 20 min, and the reaction mixture was stirred at 0° for an additional 30 min. Excess B_2H_6 was decomposed by the addition of a few ice chips and the mixture was then diluted with water and extracted with ether. The concentrate from the washed (twice with water and once with saturated NaCl) and dried extract was chromatographed over basic alumina. Elution with petroleum ether gave 76 mg (59%, 84% net) of **22** identical (ir, uv, and visible spectra) with the material from method A.

1,3-Dipentylazulene (23).—To a stirred solution of 404 mg (2.06 mmol) of 1-pentylazulene and 650 mg (4.15 mmol) of N,N-diethylvaleramide in 5 ml of tetrahydrofuran cooled to 0° was added dropwise under anhydrous conditions 0.32 ml (3.5 mmol) of $POCl_3$. The mixture was stirred for 5 min at 0°, 15 min at room temperature, and 1 hr at 80°. To the cooled mixture was added 100 ml of water and the solution was made slightly basic with 10% KOH. After extraction with CH_2Cl_2, the extract was washed twice with saturated NaCl and then dried. The con-

(41) T. Lieser and K. Macura, *Ann.*, **548**, 226 (1941).

(42) Y. K. Yurev and Z. U. Belyakova, *Zh. Obshch. Khim.*, **28**, 3 (1958) [*Chem. Abstr.*, **52**, 11765 (1958)].

centrate was chromatographed over acidic alumina. Petroleum ether eluted 44 mg (9%) of 1-pentylazulene and 2:1 petroleum ether–methylene chloride then removed an oil which was dissolved in 3 ml of ether. Boron trifluoride etherate (1 ml, 8 mmol) was added and the resulting solution was added over a 10-min period to a stirred solution of 380 mg (10 mmol) of $NaBH_4$ in 5 ml of diglyme at 0°. Stirring was continued for 30 min, the mixture poured into 50 ml of cold 5% KOH, and the whole was extracted with petroleum ether. The extract was washed twice with saturated NaCl, dried, concentrated, and chromatographed over acidic alumina. Elution with petroleum ether gave 410 mg (74%, 83% net) of **23** as a blue oil: uv (log ϵ) (cyclohexane) 241 (4.10), 282 (4.73), 351 (3.70), and 368 mμ (3.66); visible (ϵ) 588 (228, sh), 608 (264, sh), 632 (311), 663 (260), 695 (264), 735 (109, sh), and 776 mμ; mol wt 261 (calcd 268).

Anal. Calcd for $C_{20}H_{28}$: C, 89.49; H, 10.51. Found: 89.76; H, 10.25.

1,3-Dipropionylazulene (24).[43]—To a solution of 20 ml of propionic anhydride and 1.5 ml of $SnCl_4$ in 150 ml of CH_2Cl_2 was added 1 g of azulene dissolved in *ca.* 10 ml of CH_2Cl_2. The mixture was swirled occasionally over a 1-hr period and then shaken with 200 ml of 2 *N* hydrochloric acid. The aqueous layer was extracted with two 100-ml portions of CH_2Cl_2 and the combined extracts were washed four times with 100-ml portions of water, dried, and concentrated. Chromatography over acidic alumina and elution with *n*-hexane gave blue-green and purple fractions and then CH_2Cl_2 removed a red fraction. Rechromatography of the last and elution with *n*-hexane separated a small purple component from the red material, which was eluted with 1:1 *n*-hexane–methylene chloride and gave 114 mg (6%) of **24** as red crystals: mp 116.5–118.5°; ir ($CHCl_3$) 6.15 μ; uv (OD_{max}) (CH_2Cl_2) 259 (0.56), 289 (0.78), 309 (0.51), and 380 mμ (0.11, broad); visible (OD_{max}) 508 mμ.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.08; H, 6.83.

1,3-Dipropylazulene (25).—To a solution of 56 mg (0.23 mmol) of 1,3-dipropionylazulene in 3 ml of 1:1 ether–diglyme was added 0.5 ml (4 mmol) of boron trifluoride etherate. The resulting solution was added dropwise under anhydrous conditions to a stirred solution of 170 mg (4.6 mmol) of $NaBH_4$ in 2 ml of diglyme at 0°. The mixture was stirred at 0° for an additional 30 min and then poured into 50 ml of cold 5% KOH and the whole was extracted with petroleum ether. The organic extract was washed twice with water and once with saturated NaCl. The concentrate from the dried solution was chromatographed over acidic alumina. Petroleum ether eluted 45 mg (91%) of **25** as a blue oil: uv (OD_{max}) (cyclohexane) 235 (0.28), 282 (0.77), 288 (0.78), 352 (0.08), and 369 mμ (0.06); visible (OD_{max}) 587 (0.47, sh), 610 (0.55, sh), 631 (0.64), 662 (0.53), 694 (0.54), 733 (0.23, sh), and 775 (0.20).

(43) This experiment was performed by Robert G. Anderson.

Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.50; H, 9.63.

1,3-(5′-Cyano-6′-oxoundecamethylene)azulene (26).—An ethereal solution of phenyllithium[44] was determined to be 1.5 *N* by decomposing 1-ml samples of the reagent in water and titrating the aqueous solutions to the methyl orange end point with 0.1021 *N* perchloric acid. In a 2-l. three-necked flask fitted with a Trubore stirrer, dilution head, Hershberg dropping funnel, and condenser, the whole of which had been dried and filled with a nitrogen atmosphere, was placed a solution of 4 ml (6 mmol) of the phenyllithium solution and 1 l. of dry (distilled from $LiAlH_4$) ether. To the stirred solution was added through the dilution head, under reflux and nitrogen flow, 1 ml (9.5 mmol) of freshly distilled N-methylaniline. The mixture was stirred for 20 min and stirring was continued while a solution of 115 mg (0.36 mmol) of **14a** in 270 ml of dry ether was added over a period of 34 hr. The cooled (0°) reaction mixture was washed twice with water, shaken for 10 min with 50 ml of 3 *N* hydrochloric acid, and washed again with water and then with saturated NaCl. The concentrate from the dried organic solution was chromatographed over acidic alumina. Petroleum ether–methylene chloride (1:1) removed a light yellow semisolid and 2:1 petroleum ether–methylene chloride eluted a blue oil which was rechromatographed. Petroleum ether–methylene chloride (2:1) developed and eluted two bands. The second gave 15 mg of a blue oil that was not characterized. The first yielded 35 mg (31%, 5.4% from azulene) of **26** as blue crystals, mp 100–103°. The analytical sample melted at 105–107°: ir ($CHCl_3$) 4.48 (CN) and 5.80 μ; uv (log ϵ) (cyclohexane) 233 (4.39), 282 (4.65), 350 (3.71), and 368 mμ (3.65); visible (ϵ) 580 (215, sh), 605 (245), 629 (305), 660 (250), 689 (260), 732 (110), and 770 mμ (100); mol wt 289 (calcd 319).

Anal. Calcd for $C_{22}H_{25}NO$: C, 82.76; H, 7.84; N, 4.39. Found: C, 83.03; H, 8.03; N, 4.34.

Registry No.—**2**, 19981-45-4; **3**, 13502-43-7; **4**, 19981-47-6; **5**, 19981-48-7; **6**, 19981-49-8; **7**, 19981-50-1; **8a**, 19981-51-2; **8b**, 19981-52-3; **9b**, 19981-53-4; **10a**, 19981-54-5; **11a**, 19981-55-6; **11b**, 19981-56-7; **12a**, 19981-57-8; **12b**, 19981-58-9; **13a**, 19981-59-0; **13b**, 19981-60-3; **14a**, 19981-61-4; **14b**, 19981-62-5; **16**, 19981-63-6; **18**, 19981-64-7; **20**, 19981-65-8; **21**, 19981-66-9; **22**, 19981-67-0; **23**, 19981-68-1; **24**, 19981-69-2; **25**, 19981-70-5; **25**, 19981-70-5; **26**, 19981-71-6; tetraethyldiamide of decanedioyl chloride, 19268-68-9; 1-(α-hydroxyethyl)azulene, 19981-82-9; 1,10-bis(1-azulyl)decane, 19981-83-0.

(44) C. A. Walter, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 757.