lithium aluminum hydride. Excess reagent was destroyed by careful addition of aqueous tetrahydrofuran; the precipitate was removed by centrifugation and washed with tetrahydrofuran and subsequently with hot methanol. The methanol extract was evaporated and the residue was triturated with tetrahydrofuran.

The combined THF solutions yielded on evaporation 321 mg of a faintly pink oil. The oil was dissolved in propanol–ammonia (8:1), poured on a column of 50 g of silica gel, and eluted with the same solvent mixture to give 308 mg of colored material, which was rechromatographed on 10 g of alumina. Chloroform–methanol (4:1) eluted 88 mg of a pale yellow oil, identical with regard to infrared and chromatography (systems A, B, C) with V. Acetylation in pyridine–acetic anhydride gave a product which was identical in every respect with the diacetate VII. After three crystallizations from cyclohexane, the mp was 85–86°, undepressed on admixture with VII, 85°.

Dark Reduction of Dihydrothymidine. A solution of 500 mg of dihydrothymidine in 150 ml of water was stirred with 450 mg of $NaBH_4$ for 1 hr. After this period, the optical density (234 mμ) in 0.1 *N* alkali had fallen to zero, and the Archibald test[7] was negative. The reaction solution was neutralized by stirring with Dowex 50 W-H^+, filtered, and lyophilized. Boric acid was removed by repeated evaporation with methanol and the residue was taken up in water. The solution was cleared by centrifugation and again lyophilized to yield a colorless glassy material which was not uniform and could not be crystallized (III): infrared, 3400, 1650, 1510 cm^{-1} (Nujol); nmr (D_2O), poorly resolved multiplet at 0.95 (*sec*-methyl group), doublets at 3.02 (J = 6.5 cps, $-CH_2N<$), and 3.54 ppm (J = 6 cps, $-CH_2O-$).

Hydrolysis was effected by heating the photoreduction product in 0.3 *N* sulfuric acid for 1 hr in a boiling-water bath. After neutralization with baryta the solution was cleared by centrifugation and the supernatant evaporated. 3-Ureido-2-methylpropanol-1 and 2-deoxyribose could be identified by chromatography in systems A, B, C, and D. Similarly 200 mg of dihydrothymidine was treated with 200 mg of $NaBD_4$ in 50 ml of water. In the nmr spectrum (D_2O) of the isolated product the doublet at 3.54 ppm had disappeared.

Photoreduction of Thymidine. The reaction was carried out in semicircular quartz cells of approximately 1-cm thickness, each with a capacity of 100 ml. Two cells were fitted around a cylindrical quartz cooler, in the center of which the ultraviolet lamp was suspended. This apparatus was enclosed in a polished stainless steel cylinder. A solution with starting concentrations of 2 μmoles/ml of thymidine and 10 μmoles/ml of $NaBH_4$ showed less than 1% of the initial optical density at 260 mμ after irradiation for 2 hr at room temperature. In the control experiment, the optical density (260 mμ) of a thymidine solution irradiated in the absence of $NaBH_4$ remained unchanged over this period. The photoreduction of thymidine was carried out in the same manner with $NaBH_4$ in D_2O, $NaBD_4$ in water, and $NaBD_4$ in D_2O. The reaction was worked up in the same fashion as the reduction of dihydrothymine. The photoreduction product had the following properties: infrared absorption at 1650 cm^{-1} (Nujol); nmr (D_2O), two doublets centered at 0.97 and 1.03 ppm (J = 6.5 cps, secondary methyl group). The product was not uniform on chromatography in systems A and C. Hydrolysis yielded 3-ureido-2-methylpropanol-1 (V), 2-deoxyribose, and urea, identified by chromatography in systems A, B, C, and D.

Acknowledgment. We are greatly indebted to Dr. Udo Axen, Massachusetts Institute of Technology, for measuring the mass spectra and to Dr. R. G. Shulman for stimulating discussions.

A Study of the Synthesis and Properties of 2H-Benz[*cd*]azulene and Related Compounds[1,2]

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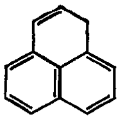
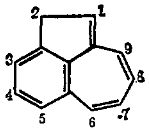
Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403. *Received March 26, 1966*

Abstract: A synthesis of 2H-benz[*cd*]azulene (II) is described. As predicted from molecular orbital calculations, the behavior of 2H-benz[*cd*]azulene on treatment with the appropiate reagents indicates easy formation of the corresponding carbonium ion, carbanion, and free-radical species. Various derivatives of 2H-benz[*cd*]azulene are described. The carbonyl derivatives have properties analogous to those of perinaphthenone and are relatively strong bases.

The synthesis[3] and studies[3–5] of the properties of perinaphthene (I) have demonstrated that the anion, carbonium ion, and radical derived from perinaphthene are all relatively stable. The usual explanation for this behavior is that perinaphthene, being an odd-alternant hydrocarbon, has a nonbonding orbital so that whether zero, one, or two electrons, corresponding to carbonium ion, radical, and anion, are placed in the nonbonding orbital there is little change in the delocalization energy.[6]



I



II

The ions or radical derived from perinaphthene, however, have a high degree of symmetry and the question of the degree to which symmetry plays a role in stabilizing these species is a pertinent one. For this reason we became interested in 2H-benz[*cd*]azulene (II) since it is isomeric with perinaphthene and is an odd-nonalternant hydrocarbon with a lower degree of symmetry.

Molecular orbital calculations for 2H-benz[*cd*]-azulene have been made both by the simple Hückel

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[1] A preliminary announcement of this work was made at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 20–22, 1964; *cf.* Abstracts, p 34C.

[2] We thank the Petroleum Research Fund of the American Chemical Society (Grant No. 914) for support of this research.

[3] V. Boekelheide and C. E. Larrabee, *J. Am. Chem. Soc.*, **72**, 1245 (1950).

[4] R. Pettit, *ibid.*, **82**, 1972 (1960).

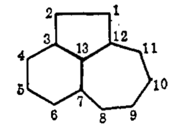
[5] (a) D. H. Reid, *Tetrahedron*, **3**, 339 (1958); (b) *Tetrahedron Letters*, No. **15**, 530 (1961).

[6] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 46.

Table I. Orbital Energy Levels of 2H-Benz[*cd*]azulene Carbonium Ion

	HMO	ω-SCF
1	2.50β	2.54β
2	1.74	1.90
3	1.73	1.85
4	1.17	1.30
5	1.00	1.12
6	0.68	0.70
7	0.00	0.14
8	−0.50	−0.36
9	−1.00	−0.89
10	−1.28	−1.12
11	−1.73	−1.61
12	−1.96	−1.85
13	−2.31	−2.23

Table II. Calculated Electron Density and Bond Orders for the 2H-Benz[*cd*]azulene Carbonium Ion



	Electron density			Bond Order	
Atom	HMO	SCF	Bond	HMO	SCF
1	1.0847	1.0300	1–2	0.7976	0.8048
2	0.9592	0.9600	2–3	0.4260	0.4054
3	1.0375	1.0000	3–4	0.6362	0.6520
4	0.8382	0.8800	3–13	0.5402	0.5372
5	0.9745	0.9500	4–5	0.5971	0.5867
6	0.8879	0.9200	5–6	0.7268	0.7328
7	0.9215	0.9200	6–7	0.5067	0.5003
8	0.8015	0.8400	7–8	0.5599	0.5633
9	0.8891	0.8900	7–13	0.5359	0.5360
10	0.8386	0.8600	8–9	0.6493	0.6580
11	0.8455	0.8700	9–10	0.6407	0.6350
12	0.9016	0.9000	10–11	0.6202	0.6314
13	1.0260	1.0000	11–12	0.6237	0.6238
			12–13	0.4620	0.4554
			1–12	0.4646	0.4583

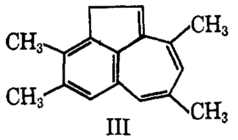
Table III. Calculated Electron Densities and Bond Orders for the 2H-Benz[*cd*]azulene Anion

	Electron density			Bond order	
Atom	HMO	SCF	Bond	HMO	SCF
1	1.1515	1.1414	1–2	0.6643	0.6757
2	1.2218	1.1815	2–3	0.5594	0.5621
3	1.1042	1.1042	3–4	0.5029	0.5018
4	1.1050	1.0827	3–13	0.5402	0.5342
5	1.0411	1.0614	4–5	0.7305	0.7326
6	1.1545	1.1157	5–6	0.5935	0.5866
7	0.9882	1.0226	6–7	0.6400	0.6510
8	1.0682	1.0433	7–8	0.4266	0.4119
9	0.9558	0.9990	7–13	0.5359	0.5337
10	1.1035	1.0770	8–9	0.7826	0.7902
11	0.9122	0.9793	9–10	0.5073	0.4988
12	1.1683	1.1463	10–11	0.7536	0.7541
13	1.0260	1.0427	11–12	0.4904	0.4951
			12–13	0.4620	0.4582
			1–12	0.5979	0.5941

and the ω-type, self-consistent-field procedures,[7,8] and these results are summarized in Table I. In contrast to the perinaphthene carbonium ion for which HMO calculations predict a delocalization energy of 5.83β,[9] the HMO prediction for the delocalization energy of 2H-benz[*cd*]azulene carbonium ion is 5.57β. Although the HMO calculation shows a nonbonding orbital, the ω-type, self-consistent-field calculation indicates a lowering of the energy of this orbital to 0.14β (Table I). In summary, then, the predictions for 2H-benz[*cd*]azulene from both HMO and the ω-type, self-consistent-field calculations (Tables I–III) are that its properties will be similar qualitatively to those of perinaphthene.

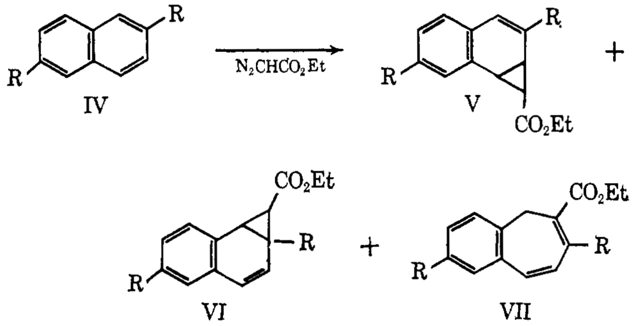
Synthesis

Although neither 2H-benz[*cd*]azulene nor simple derivatives of this system were known at the beginning of our studies, Hafner and Schaum published their elegant synthesis of the tetramethyl derivative III during the course of our work.[10] The properties of their product are discussed later in this paper. However, because their synthetic route cannot readily be modified to give the unsubstituted 2H-benz[*cd*]azulene and is quite different from ours, we will discuss in detail our synthesis of 2H-benz[*cd*]azulene itself and certain derivatives.



III

Acenaphthene was chosen as starting material in the expectation that the standard methods of ring expansion, used in azulene syntheses,[11] might apply. Of particular interest are the studies on the reaction of naphthalene[12,13] and substituted naphthalenes[14,15] with ethyl diazoacetate. As Huisgen and Juppe have shown,[14] naphthalenes (IV, R = H or CH_3) give three monoadducts of which VII is probably formed by thermal isomerization of VI. In any event the ring expansion of a naphthalene to a benzocycloheptatriene derivative by this procedure appeared quite feasible.



When molten acenaphthene was treated with ethyl diazoacetate at 150–160°, there formed in good yield the expected three monoadducts VIII, IX, and X, plus some of the diadduct XI. A crude separation of the

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(7) A. Streitwieser, Jr., ref 6, p 115; A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959).

(8) We are very much indebted to Charles Klopfenstein for making his computer programs available to us and assisting us in these calculations.

(9) R. J. Windgassen, Jr., W. W. Saunders, and V. Boekelheide, *J. Am. Chem. Soc.*, **81**, 1459 (1959).

(10) K. Hafner and H. Schaum, *Angew. Chem.*, **75**, 90 (1963).

(11) Pl. A. Plattner and J. Wyss, *Helv. Chim. Acta*, **23**, 907 (1940).

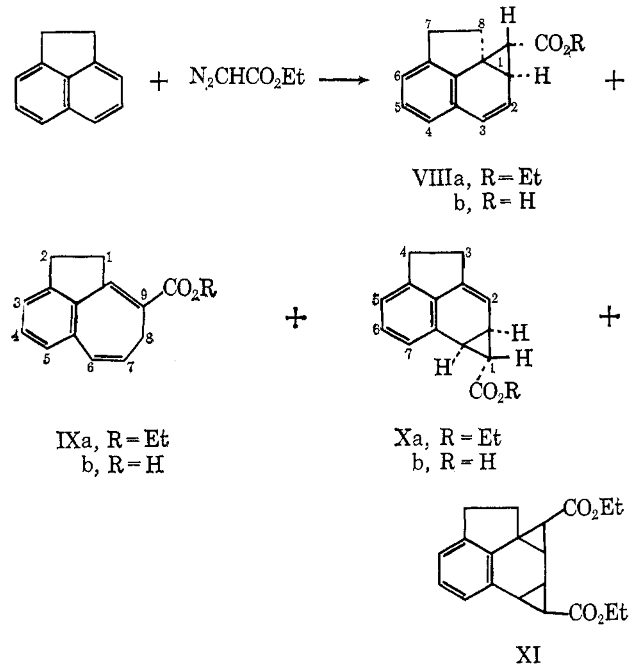
(12) G. M. Badger, B. J. Christie, H. J. Rodda, and J. M. Pyrke, *J. Chem. Soc.*, 1179 (1958).

(13) R. Huisgen and G. Juppe, *Ber.*, **94**, 2332 (1961).

(14) R. Huisgen and G. Juppe, *Tetrahedron*, **15**, 7 (1961).

(15) G. Juppe and R. Huisgen, *Ann.*, **646**, 1 (1961).

individual adducts was accomplished by fractional distillation, and subsequent purification was done through recrystallization and chromatography.



VIIIa, R=Et
b, R=H

IXa, R=Et
b, R=H

Xa, R=Et
b, R=H

XI

The assignment of structures VIII–XI is based both on spectral evidence and on the chemical behavior of these adducts. Thus, VIIIa shows the ultraviolet absorption of a typical 1,2-dihydronaphthalene[13] and an infrared band at 10.05 μ as would be expected for a cyclopropyl ring-bending vibration.[12] In its nmr spectrum, VIIIa shows a sharp doublet centered at τ 9.25 (J_{ab} = 3.5 cps) whose integrated area corresponds to one proton. The coupling constant of 3.5 cps is in accord with that found for *trans* protons in cyclopropane derivatives,[16] and the value of the chemical shift agrees with those found previously for cyclopropane protons α to a carbethoxy group. It can be deduced, therefore, that VIIIa has the stereochemistry shown. The remainder of its nmr spectrum is in keeping with this assignment.

When VIIIa was heated at 200–250° in a nitrogen atmosphere, rearrangement occurred to give IXa. Similar thermal rearrangements were observed by Huisgen and Juppe in the naphthalene series,[13] and it is probable that IXa is an artifact arising from the thermal rearrangement of VIIIa during distillation. Similarly, the corresponding acid VIIIb, obtained by hydrolysis of VIIIa, was readily converted by boiling in quinoline for 2 hr to IXb.

The change in structure during the thermal rearrangement of VIII to IX was readily observed from spectral data. A bathochromic shift occurred in the ultraviolet resulting in an absorption maximum for IX at 327 mμ, whereas in the infrared the absorption band corresponding to the cyclopropyl bending vibration disappeared. Likewise, in the nmr spectrum, the signals assigned to the cyclopropane protons disappeared giving rise to a multiplet at τ 6.88 corresponding to the six allylic protons. The aromatic protons of IX showed an ABX coupling pattern overlapping the vinyl hydrogen at the 6 position; the vinyl hydrogen at the 7 position, however, appeared as a distinct sextet centered at τ 4.58.

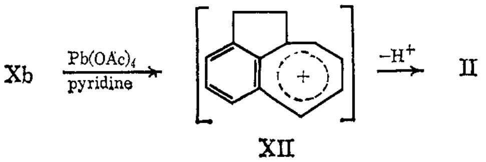
The third component, Xa, shows again a 1,2-dihydronaphthalene absorption in the ultraviolet and an absorption band at 10.05 cm^{-1} in the infrared corresponding to a cyclopropyl bending vibration. In the nmr spectrum, Xa shows a sharp triplet at τ 9.15 (J_{ab} = J_{bc} = 4.0 cps) indicative of a cyclopropyl proton α to the carbethoxy group split by two *trans*-cyclopropyl protons. From this the stereochemistry given by structure Xa can be deduced, and the remainder of the nmr spectrum is in accord with this assignment.

Attempts to effect a thermal rearrangement of Xa were either unsuccessful or under drastic conditions gave complex mixtures. However, the corresponding acid, Xb, when heated at 250–280° with copper chromite, was converted to the known 5-acenaphthenylacetic acid.[17–19]

In their studies on the adduct of naphthalene and ethyl diazoacetate, Huisgen and Juppe observed an acid-catalyzed rearrangement to give ethyl α-naphthylacetate. In a similar fashion we have found that Xa rearranges in acetic acid containing a drop of sulfuric acid to give ethyl 5-acenaphthenylacetate. The thermal and acid-catalyzed rearrangement of X provide additional proof for its structure.

Finally, the higher boiling component from the reaction of acenaphthene and ethyl diazoacetate was a mixture whose composition and spectral data are in accord with the over-all structure given by XI. Chromatography of this mixture over alumina effected separation of two of these isomers in a pure state. As discussed in the Experimental Section, tentative structural assignments for each of these isomers are suggested.

Returning now to a consideration of the possible use of these adducts for a synthesis of II one would expect Xb to be the most likely choice. For example, lead tetraacetate oxidative decarboxylation of acids is a generally useful reaction presumably involving an intermediate carbonium ion.[20–24] In the case of Xb it would be expected that ring opening of the cyclopropane ring would occur giving the more stable benzotropylium derivative XII, which with base would lead to the desired 2H-benz[*cd*]azulene (II). In fact, when Xb was treated with lead tetraacetate in pyridine, a vigorous evolution of carbon dioxide occurred and II was formed. However, under these conditions, there was extensive polymerization and the yield of II was very poor.



XII

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[16] J. D. Graham and M. T. Rodgers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

[17] H. J. Richter, *ibid.*, **75**, 2774 (1953).

[18] A. G. Anderson and R. H. Wade, *ibid.*, **75**, 2274 (1953).

[19] G. Lock and R. Schneider, *Ber.*, **88**, 564 (1955).

[20] W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953).

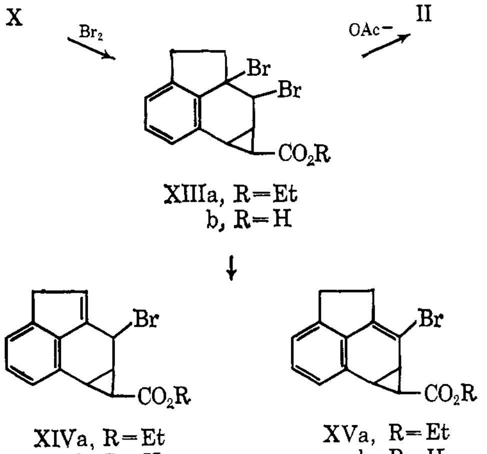
[21] L. L. McCoy and A. Zagalo, *J. Org. Chem.*, **25**, 824 (1960).

[22] G. Büchi, R. E. Erickson, and N. Wakabayashi, *J. Am. Chem. Soc.*, **83**, 927 (1961).

[23] E. J. Corey and R. L. Dawson, *ibid.*, **85**, 165 (1963).

[24] E. E. Van Tamelen and B. Pappas, *ibid.*, **85**, 3297 (1963).

Next, the reaction of X with bromine was studied. At low temperatures both Xa and Xb readily added bromine. Warming the resulting solutions to room temperature, though, led to evolution of hydrogen bromide and the formation of a mixture of the two monobromo derivatives XIV and XV, of which XV greatly predominated.

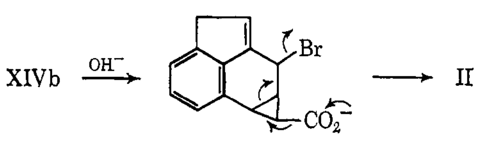


XIIIa, R=Et
b, R=H

XIVa, R=Et
b, R=H

XVa, R=Et
b, R=H

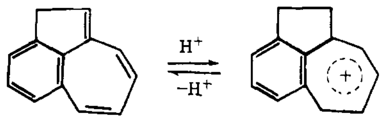
The original intent of the bromination studies had been to obtain XIVb in quantity with the expectation that treatment of XIVb with base would cause a fragmentation reaction, as shown by XVI, and lead to II. However, the mixture of monobromides, resulting from bromination of Xb followed by warming, contained so little of XIVb that it could not be isolated in the pure state.



XVI

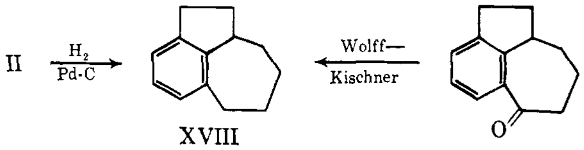
The difficulty in obtaining XIVb then led to a reconsideration of the dibromide XIIIb. If the fragmentation reaction of XIIIb were to proceed at a rate comparable to the rate of elimination of hydrogen bromide, the order of events might be reversed and so allow the direct formation of II from XIIIb. This proved to be true. When the addition of bromine to Xb in the cold was followed directly by the addition of an aqueous sodium acetate solution, instead of allowing the mixture to warm, formation of II occurred in a yield estimated to be 30%.

2H-Benz[*cd*]azulene (II) can be recognized as a derivative of heptafulvene, a substance which Doering has aptly characterized as being on the edge of existence.[25] This aspect of the chemistry of 2H-benz[*cd*]azulene was only too apparent and, in common with heptafulvene, 2H-benz[*cd*]azulene could not be isolated in the pure state so that our studies have been limited to its behavior in solution. Even at low temperatures concentration of a cyclohexane solution of II led to immediate polymerization. Similarly, the presence of a trace of acid caused the immediate separation of an insoluble white polymer. On the other hand, treatment of a cyclohexane solution of 2H-benz[*cd*]azulene with strong acid, sulfuric or hydrochloric, led to the extraction of the 2H-benz[*cd*]azulene into the aqueous layer from which it could be reextracted on treatment with base. Presumably, in the presence of strong acid there is rapid formation of the stable benzotropylium ion (XVII). This behavior would be anticipated and is in support of structure II.



II XVII

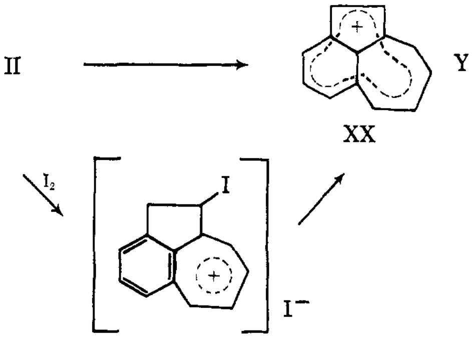
More definitive chemical proof for the structure of II was obtained, though, from hydrogenation experiments. Hydrogenation of 2H-benz[*cd*]azulene over a 10% palladium-on-charcoal catalyst gave a hydrocarbon (XVIII) identical in all respects with the product obtained by the Wolff–Kischner reduction of an authentic specimen of the tricyclic ketone XIX.[26]



XVIII

XIX

Although 2H-benz[*cd*]azulene is much more prone to polymerization than perinaphthene, its conversion to carbonium ion, carbanion, and radical occur as predicted and closely parallel the behavior of perinaphthene. Thus, treatment of II with a solution of trityl fluoroborate led to the immediate formation of a deep green color, and addition of ether caused the precipitation of a green solid. This solid, presumably the fluoroborate salt of the carbonium ion XX, was soluble in polar solvents, but attempts to isolate it in the pure state were frustrated by its sensitivity to both moisture and air and its ease of polymerization. Likewise, the procedure of Holmes and Pettit[27] gave the hexachloroantimonate salt as a deep green solid, but this too could not be purified. Treatment of a solution of II in carbon tetrachloride with iodine gave again a green precipitate. It would be expected that the reaction of II with iodine would yield an intermediate XXI which, on loss of hydrogen iodide, would generate the iodide salt of the carbonium ion XX.



XX

XXI

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[25] (a) W. von E. Doering, 16th National Organic Symposium, American Chemical Society, Seattle, Wash., June 15, 1959; (b) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).

[26] A. G. Anderson, Jr., and S. Y. Wang, *J. Org. Chem.*, **19**, 277 (1954). We are very much indebted to Professor Anderson for making available a generous supply of the tricyclic ketone XIX in order that we might prepare an authentic sample of XVIII for direct comparison.

[27] J. R. Holmes and R. Pettit, *ibid.*, **28**, 1695 (1963).

When 2H-benz[*cd*]azulene was added to a solution of lithium triphenylmethide,[28] the bright red color of the triphenylmethyl anion disappeared, and the solution became a deep blue-green, indicating that 2H-benz[*cd*]azulene is a more acidic hydrocarbon than triphenylmethane. With other bases, such as *n*-butyllithium, 2H-benz[*cd*]azulene underwent reaction to give the same deep blue-green color, but attempts to trap the anion were unsuccessful.

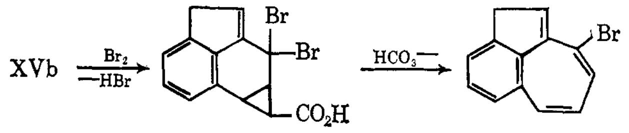
As with perinaphthene,[3] 2H-benz[*cd*]azulene underwent an exchange reaction with triphenylmethyl radical, but the resulting dark purple solution of the 2H-benz[*cd*]azulene began precipitating a black, insoluble polymer and could not be stored. Air oxidation of the anion of 2H-benz[*cd*]azulene, a procedure used by Reid to produce the perinaphthenyl radical,[5a] gave again a dark purple solution which deposited a black solid.

The ease with which 2H-benz[*cd*]azulene forms the corresponding anion would suggest that tautomerization must occur very readily and raises the question of whether the "extra" hydrogen is correctly assigned to the 2 position. This question is difficult to answer unequivocally and our assignment is based on the ultraviolet absorption spectrum of II (see Experimental Section). The absorption maximum at 427 mμ for II corresponds exactly to that found for heptafulvene[25b] and is close to the value (406 mμ) found for 3,4,7,9-tetramethyl-2H-benz[*cd*]azulene. Thus, the ultraviolet absorption spectrum provides a strong argument for the presence of the heptafulvene moiety and supports II as the correct structure for our benzazulene.

The fact that the tetramethyl derivative has its absorption maximum at a somewhat shorter wavelength than 2H-benz[*cd*]azulene itself can be rationalized on the basis that the tetramethyl derivative is a less planar molecule and that the position of the long wavelength maximum is quite sensitive to deformations from planarity of the heptafulvene system. This assumption is supported by the recent work of Bertelli and Ong,[29] who have synthesized both the 1,2- and 3,4-benzoheptafulvenes. Even though the 1,2-benzoheptafulvene is predicted to show absorption at longer wavelengths than 3,4-benzoheptafulvene, the opposite result is actually observed, presumably owing to a deviation from planarity for steric reasons in the case of the 1,2-benzoheptafulvene. The geometric relationship between 2H-benz[*cd*]azulene and 1,2-benzoheptafulvene has already been discussed by Bertelli and Ong.[29]

A reaction characteristic of heptafulvene is its addition of dimethyl acetylenedicarboxylate to give 1,2-dicarbomethoxyazulene. Attempts to effect a similar reaction with 2H-benz[*cd*]azulene were unsuccessful.

9-Bromo-2H-benz[*cd*]azulene. One of the difficulties encountered in our synthesis of 2H-benz[*cd*]azulene was the fact that XIII, on elimination of hydrogen bromide, gave almost entirely the wrong isomer (XV). However, it is apparent that a further addition of bromine to XV, followed by elimination of hydrogen bromide, can give only one isomer which has the structural features desired for the fragmentation reaction. Thus, addition of bromine in the cold to XVb followed by warming to room temperature gave the dibromo acid XXII. This, on solution in sodium bicarbonate solution, was rapidly converted, as expected, to 9-bromo-2H-benz[*cd*]azulene (XXIII).

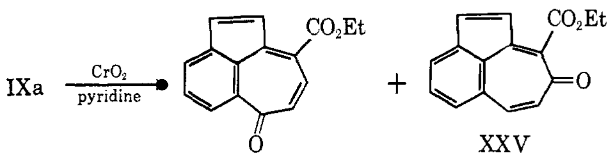


XXII XXIII

The structure of 9-bromo-2H-benz[*cd*]azulene (XXIII) was established from its spectral and chemical properties as well as its transformations discussed in the section on benz[*cd*]azulenones. The ultraviolet and visible absorption spectra of 9-bromo-2H-benz[*cd*]azulene (see Experimental Section) is very similar to that of 2H-benz[*cd*]azulene itself, but with the long wavelength maximum shifted to 421 mμ. Likewise, 9-bromo-2H-benz[*cd*]azulene readily formed the corresponding carbanion and carbonium ion in an analogous fashion to 2H-benz[*cd*]azulene. Unfortunately the analogy between the two benz[*cd*]azulenes was also true with regard to instability and ease of polymerization so that we have not been able to obtain 9-bromo-2H-benz[*cd*]azulene in a pure state, and our studies have been limited to its behavior in solution.

Benz[*cd*]azulenones. In view of the difficulty in handling the benz[*cd*]azulenes, our attention turned to possible derivatives which would show greater stability. In the perinaphthene series, the corresponding ketone, perinaphthenone, is a stable, well-known compound whose unusual basicity is attributed to a stabilization of positive charge over the perinaphthene moiety. A similar behavior would be predicted for suitable carbonyl derivatives in the benz[*cd*]azulene series, and so it was of interest to investigate their preparation.

Direct oxidation was explored first using the available IXa as a test substance in the hope that it might be converted to a benztropone derivative. In fact, when IXa was subjected to the action of chromium trioxide in pyridine, oxidation proceeded beyond the benztropone stage to give the two benz[*cd*]azulenones XXIV and XXV. These could be separated by chromatography, and XXIV was isolated as unstable red crystals whereas XXV formed stable yellow needles. Both showed the characteristic absorption in the 6.10- to 6.30-μ region of a benztropone.[30]



XXV

XXIV

A similar oxidation of 2H-benz[*cd*]azulene proceeded in poor yield but gave again two ketones: the red crystalline benz[*cd*]azulen-6-one (XXVI) and the yellow benz[*cd*]azulen-8-one (XXVII). In order to obtain chemical verification for these structural assignments an independent synthesis of the benz[*cd*]azulen-6-one was carried out. Treatment of the tricyclic ketone XIX with an excess of 2,3-dichloro-5,6-dicyanoquinone gave

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(28) P. T. Lansbury, *J. Am. Chem. Soc.*, **80**, 5449 (1958).

(29) D. J. Bertelli and C. C. Ong, *ibid.*, **87**, 3719 (1965).

(30) H. H. Rennhard, G. Di Modica, W. Simon, E. Heilbronner, and A. Eschenmoser, *Helv. Chim. Acta*, **40**, 957 (1957).

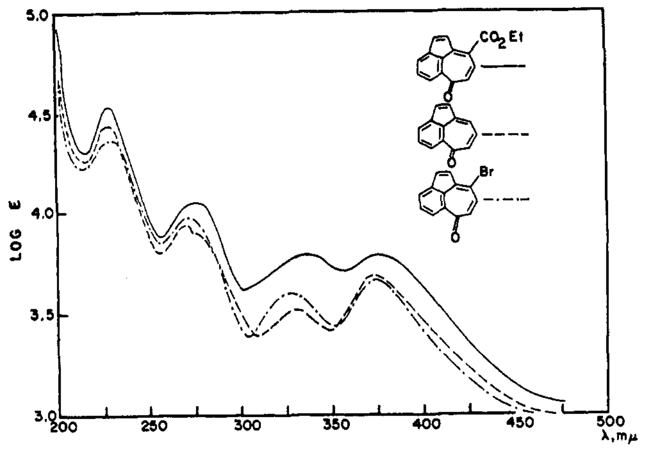


Figure 1. Ultraviolet absorption spectra of the benz[*cd*]azulen-6-ones taken in ethanol using a Cary 11 spectrophotometer.

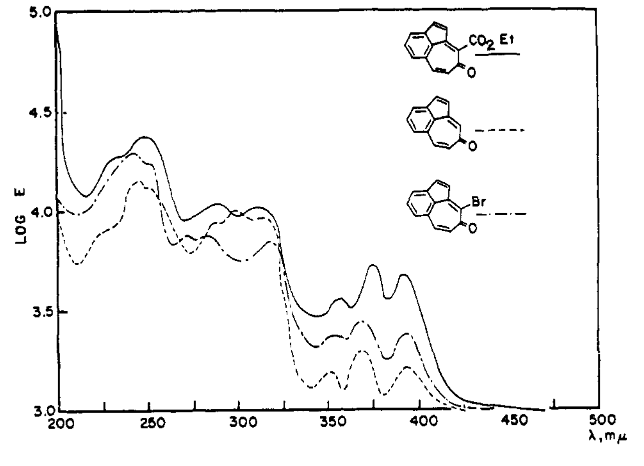
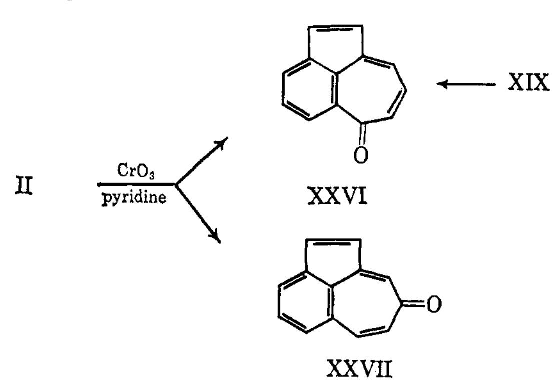
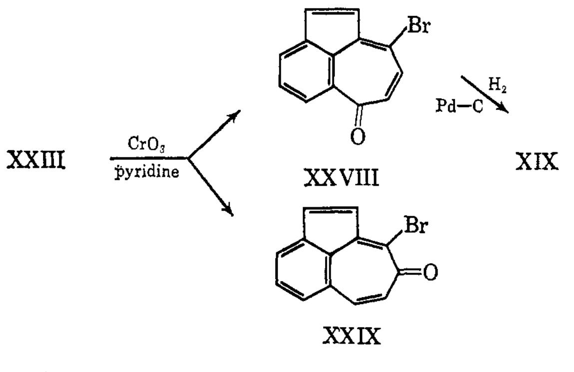


Figure 2. Ultraviolet absorption spectra of benz[*cd*]azulen-8-ones taken in ethanol using a Cary 11 spectrophotometer.

an authentic sample of benz[*cd*]azulen-6-one, identical in all respects with XXVI.



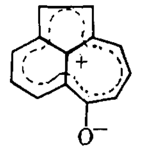
Finally, the oxidation of 9-bromo-2H-benz[*cd*]azulene (XXIII) with chromium trioxide in pyridine gave the two 9-bromobenz[*cd*]azulenones XXVIII and XXIX, as red and yellow crystals, respectively. Chemical proof that the red crystals corresponded to the 9-bromobenz[*cd*]azulen-6-one was provided when catalytic hydrogenation of XXVIII was shown to give the tricyclic ketone XIX.



In Figure 1, the ultraviolet absorption spectra of the benz[*cd*]azulen-6-ones are summarized, and in Figure 2 are given the corresponding spectra for the benz[*cd*]-azulen-8-ones. Although chemical evidence has been provided for the assignment of the benz[*cd*]azulen-6-ones, it is clear that the ultraviolet absorption provides a good criterion for classifying these compounds as 6- or 8-azulenones.

The fact that 6- and 8-azulenones are produced during these oxidations does not, of course, argue against the assignment of these compounds as 2H-benz[*cd*]azulenes. Quite probably these oxidations involve an intermediate ionic species, and so the eventual position taken by the carbonyl oxygen has no direct bearing on the position to be assigned to the "extra" hydrogen.

As predicted, all of these benz[*cd*]azulenones are readily soluble in strong aqueous acid and are regenerated on addition of base. Because of lack of material no dipole measurements were made, but the prediction that ionic structures such as XXX make an important contribution to the resonance hybrid appears well justified.



XXX

In summary, the properties of the benz[*cd*]azulenes are in accord with the predictions of simple Hückel molecular orbital calculations and parallel those of perinaphthene very closely. Likewise, the behavior of the benz[*cd*]azulenones is similar to that of perinaphthenone.

Experimental Section[31,32]

The Reaction of Acenaphthene with Ethyl Diazoacetate. The reaction conditions employed are similar to those described by Huisgen and Juppe for the addition of ethyl diazoacetate to naphthalene.[13] The highest yield (72%) of monoaddition products was obtained using the following procedure.

To 462 g (3 moles) of molten acenaphthene held at 160° there was added dropwise with stirring 57 g (0.5 mole) of ethyl diazoacetate over a period of 8 hr. After the addition of ethyl diazoacetate was complete, the dark brown mixture was stirred for an additional 0.5 hr or until nitrogen evolution ceased. The excess

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(31) Microanalyses are by Micro-Tech Laboratories and by Pascher and Pascher Laboratories. Infrared spectra were measured using a Beckman IR. 5-A and ultraviolet spectra were taken on a Cary Model 11.

(32) The nmr spectra were measured using a Varian A-60 spectrometer. We express our appreciation to the National Science Foundation for the funds allowing the purchase of this instrument.

acenaphthene was removed by distillation under reduced pressure (10 mm), and the residue was then subjected to a crude distillation from a Claisen flask. This gave 95 g of a crude oil (monoadduct), bp 155–165° (1 mm), and 15 g of a higher boiling fraction (diadduct), bp 180–200° (1 mm). The crude monoadduct was then carefully distilled using a spinning-band column to give four fractions: (1) 21.3 g, bp 94–96° (0.05 mm); (2) 5.0 g, bp 96–97° (0.05 mm); (3) 50.2 g, bp 97–99° (0.05 mm); and (4) 13.3 g, bp 99–101° (0.05 mm).

Ethyl 1a,8a-Dihydro-1H-cyclopropa[*c*]acenaphthene-1-carboxylate (VIIIa). Fractions 1 and 2 solidified and were shown to be identical white crystals, mp 81–82°, after recrystallization from ethanol. The ultraviolet absorption spectrum (ethanol) showed maxima (log ε) at 222 mμ (3.05), 230 (3.08), 237 (3.16), 245 (3.12), and 280 (2.86), whereas in the infrared, absorption bands at 5.80 μ (ester carbonyl) and 10.03 μ (cyclopropyl bending) were readily recognizable.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.97; H, 6.67.

Ethyl 1a,7b-Dihydro-1H-cyclopropa[*c*]acenaphthene-1-carboxylate (Xa). Fractions 3 and 4 were combined and dissolved in 250 ml of ethanol. When the solution was allowed to stand in the cold overnight, there separated 47 g of white crystals, mp 71–72°. The ultraviolet spectrum (ethanol) of these crystals showed absorption maxima (log ε) at 226 mμ (3.05), 232 (3.10), 239 (3.05), and 274 (2.79), whereas its infrared spectrum showed absorption at 5.79 μ (ester carbonyl) and 10.05 μ (cyclopropyl bending).

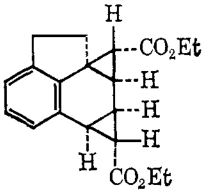
Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.97; H, 6.79.

Ethyl 1,2-Dihydro-8H-benz[*cd*]azulene-9-carboxylate (IXa). The mother liquor from the crystallization of ethyl 1a,7b-dihydro-1H-cyclopropa[*e*]acenaphthene-1-carboxylate (Xa) was concentrated under reduced pressure, taken up in cyclohexane, and chromatographed over neutral alumina (Woelm, activity 1). The first colorless fraction of eluate gave additional Xa on concentration. Later, the slightly yellow eluate was concentrated to give 1.0 g of a pale yellow oil. Treatment of this oil with ethanol gave crystals which were first sublimed and then recrystallized from petroleum ether (bp 30–60°) to give white needles, mp 62–63°. The ultraviolet spectrum (ethanol) of these crystals showed absorption maxima (log ε) at 214 mμ (4.48), 238 (3.98), and 327 (4.07), whereas in the infrared there was a strong absorption band at 5.85 μ (α,β-unsaturated carbonyl).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.57; H, 6.60.

Diethyl *cis*-1,1a,1b,2,2a,7b-Hexahydrodicyclopropa[*ce*]acenaphthene-1,2-dicarboxylate (XIa). The crude diadduct fraction was taken up in cyclohexane and chromatographed over neutral alumina (Woelm, activity 1). The first eluate fraction was an oil which, on treatment with ethanol, gave 1.5 g of large, white crystals, mp 88–89.5°. By analogy with the observations of Huisgen and Juppe[15] in the naphthalene series that the *cis* diadduct has the lower melting point and is formed in smaller amount, we assign the *cis* structure XIa to this product. Its nmr and infrared spectra are in accord with this assignment.

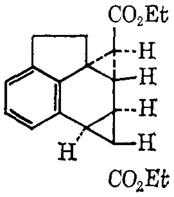
Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.38; H, 6.74.



XIa

Diethyl *trans*-1,1a,1b,2,2a,7b-Hexahydrodicyclopropa[*ce*]acenaphthene-1,2-dicarboxylate (XIb). The later fractions of eluate from chromatography of the diadduct were concentrated to give 3.0 g of white rods, mp 117–118°. Sublimation of these crystals raised their melting point to 120–120.5°. For the reasons indicated earlier this isomer is assigned the *trans* structure XIb. Again, its nmr and infrared spectra are in accord with this over-all structural assignment but are not useful for distinguishing between the *cis* and *trans* isomers.

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.91; H, 6.94.



XIb

1a,8a-Dihydro-1H-cyclopropa[*c*]acenaphthene-1-carboxylic Acid (VIIIb). To a solution of 5.0 g of ethyl 1a,8a-dihydro-1H-cyclopropa[*c*]acenaphthene-1-carboxylate (VIIIa) in 50 ml of ethanol there was added a solution of 50 ml of ethanol containing 3.5 g of potassium hydroxide, and the mixture was heated on a steam bath for 6 hr. After removal of the ethanol under reduced pressure, the residue was taken up in 150 ml of water and acidified. The precipitate was collected, dried, and recrystallized from ethanol to give 2.5 g (57%) of white prisms, mp 218–219°.

Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 78.99; H, 5.70.

1a,7b-Dihydro-1H-cyclopropa[*e*]acenaphthene-1-carboxylic Acid (Xb). The hydrolysis of Xa was carried out just as described above for the preparation of VIIIb. From 10.0 g of Xa there was obtained 7.0 g (80%) of white plates, mp 193–194°, after recrystallization from aqueous ethanol.

Anal. Calcd for $C_{14}H_{14}O_2$: C, 79.22; H, 5.70. Found: C, 78.79; H, 5.70.

1,2-Dihydro-8H-benz[*cd*]azulene-9-carboxylic Acid (IXb). Hydrolysis of IXa was carried out as described for the preparation of VIIIb. From 2.0 g of IXa acidification of the aqueous hydrolysate gave 1.2 g of a yellow-brown solid. This was dissolved in ethanol, treated with charcoal, and then crystallized. Sublimation of the resulting product gave 0.90 g (51%) of light yellow crystals, mp 228–229°. The ultraviolet spectrum (ethanol) of these crystals showed absorption maxima (log ε) at 212 mμ (4.27), 240 (3.77), and 322 (3.88).

Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 78.91; H, 5.69.

Thermal Isomerization of VIIIb to IXb. A solution of 1.0 g of VIIIb in 50 ml of redistilled quinoline was boiled under reflux for 2 hr. The mixture was then diluted with 200 ml of ether and extracted with aqueous acid. After the ether layer had been dried, it was concentrated, and the residual brown solid was recrystallized from ethanol. Sublimation of the resulting crystals (110° at 0.05 mm) gave 100 mg of light yellow crystals, mp 228–229°, undepressed by admixture of authentic IXb.

Thermal Isomerization of VIIIa to IXa. A 2.4-g sample of VIIIa was heated at 200–230° under an atmosphere of nitrogen for 4 hr. The oil was then taken up in cyclohexane and chromatographed over neutral alumina (Woelm, activity 1). Elution of the pale yellow band which appeared on the column gave, after concentration, 1.3 g (54%) of a pale yellow oil. This oil was shown by infrared and nmr spectral comparison to be identical with a sample of IXa as previously described.

Ethyl 5-Acenaphthenylacetate. To a solution of 1.0 g of Xa in 25 ml of acetic acid 2 drops of concentrated sulfuric acid was added, and the mixture was heated on a steam bath for 15 min. It was then poured onto crushed ice, neutralized with sodium bicarbonate, and extracted with ether. After the ether solution had been dried and concentrated, the residue was taken up in cyclohexane and chromatographed over alumina (Woelm, activity 1). Concentration of the main eluate fraction gave 0.5 g of a colorless oil whose infrared and nmr spectra were in accord with its being ethyl 5-acenaphthenylacetate. This was confirmed by subjecting a portion to basic hydrolysis whereupon it was converted to white needles, mp 179–180°. This melting point is in agreement with that reported for 5-acenaphthenylacetic acid,[17-19] and both its infrared and nmr spectra are in accord with this assignment.

Thermal Rearrangement of Xb to 5-Acenaphthenylacetic Acid. A mixture of 1.0 g of Xb and 2.0 g of copper chromite (Adkin's catalyst) was heated at 250–280° in a sublimation tube under slight vacuum. The white crystals, mp 179–180°, which formed on the cold finger were shown by spectral comparison and a mixture melting point determination to be identical with the 5-acenaphthenylacetic acid described above.

Ethyl 2-Bromo-1a,7b-dihydro-1H-cyclopropa[*e*]acenaphthene-1-carboxylate (XVa). To a stirred solution of 1.2 g of Xa in 30 ml of carbon tetrachloride at 0° there was added dropwise a solution of 0.8 g of bromine in 10 ml of carbon tetrachloride. After the addition of bromine was complete, the reaction mixture was allowed to warm to room temperature. Then, with a slow stream of nitrogen bubbling through the mixture it was heated under reflux until hydrogen bromide was no longer evolved (1 hr). The solution was concentrated under reduced pressure, and the residue was recrystallized from 100 ml of ethanol to give 1.2 g (75%) of pale yellow crystals, mp 101–102°. Its infrared spectrum showed absorption at 5.79 μ (ester carbonyl) and 9.90 μ (cyclopropyl bending).

Anal. Calcd for $C_{16}H_{15}O_2Br$: C, 59.81; H, 4.71; Br, 24.88. Found: C, 59.59; H, 4.65; Br, 25.56.

Ethyl 2,3-Dibromo-1a,8a-dihydro-1H-cyclopropa[*c*]acenaphthene-1-carboxylate. To a stirred solution of 1.2 g of VIIIa in 30 ml of carbon tetrachloride there was added dropwise a solution of 0.8 g of bromine in 10 ml of carbon tetrachloride. Concentration of the solution under reduced pressure followed by recrystallization of the residue from acetonitrile gave 1.8 g (90%) of white crystals, mp 165° dec; infrared absorption at 5.79 μ (ester carbonyl) and 9.90 μ (cyclopropyl bending).

Anal. Calcd for $C_{16}H_{16}O_2Br_2$: C, 48.10; H, 4.03; Br, 39.90. Found: C, 48.14; H, 4.14; Br, 39.36.

2,2-Dibromo-1a,7b-dihydro-1H,4H-cyclopropa[*e*]acenaphthene-1-carboxylic Acid (XXII). To a stirred solution of 2.12 g of Xb in 80 ml of chloroform maintained at −10 to −20°, there was added dropwise a solution of 1.6 g of bromine in 10 ml of chloroform. The reaction mixture was then warmed while bubbling a stream of nitrogen through until hydrogen bromide was no longer evolved. It was then cooled once again to −20°, and an additional 1.6 g of bromine in 10 ml of chloroform was added. The solution was again warmed while sweeping with nitrogen until evolution of hydrogen bromide ceased. The mixture was then allowed to stand overnight in the cold. The brown, crystalline precipitate was collected and recrystallized from chloroform to give 0.5 g of light brown needles, mp 250° dec.

Anal. Calcd for $C_{14}H_{10}O_2Br_2$: C, 45.44; H, 2.72; Br, 43.30. Found: C, 45.68; H, 2.86; Br, 43.32.

2H-Benz[*cd*]azulene (II). (A) *Via* the Bromination Procedure. A solution of 0.8 g of bromine in 10 ml of dioxane was added dropwise with stirring to a solution of 1.06 g of Xb in 50 ml of dioxane while maintaining the temperature of the mixture between 10 and 15°. A mixture of 2.0 g of sodium acetate in 85% aqueous dioxane was added, and the resulting mixture was boiled under reflux in a nitrogen atmosphere for 0.5 hr. The mixture was then diluted with 100 ml of benzene and washed successively with aqueous bicarbonate and water. Based on the evolution of carbon dioxide the yield of 2H-benz[*cd*]azulene is estimated at 30%. The organic layer was then chromatographed over neutral alumina (Woelm, activity 3) with the column being eluted by cyclohexane. The cyclohexane eluate of the main fraction could not be concentrated without causing polymerization of the 2H-benz[*cd*]azulene. Thus, it was not possible to obtain solutions of a high enough concentration for an nmr spectrum. The infrared spectrum (cyclohexane) showed major absorption bands at 3.25 μ, 6.26, and 14.20. The ultraviolet spectrum (cyclohexane) showed absorption maxima at 232 mμ, 257 (sh), 275, 284, 295, 315 (sh), 326 (sh), 403 (sh), 427, 451, 472, 521, and 545. The ultraviolet spectrum is reproduced in Figure 3. Because the concentration is not known, the value of the extinction coefficients is uncertain. For the study of the chemical properties of 2H-benz[*cd*]azulene, dilute cyclohexane solutions prepared in this way were employed.

(B) *Via* the Lead Tetraacetate Procedure. A mixture of 212 mg of Xb, 443 mg of lead tetraacetate, and 158 mg of pyridine in 20 ml of benzene was boiled under reflux in a nitrogen atmosphere for 2 hr. The dark green mixture was cooled, filtered to remove insoluble material, and washed with water. The filtrate was then partially concentrated under reduced pressure and chromatographed over neutral alumina (Woelm, activity 3). The column was eluted with cyclohexane and, after removal of the first orange, blue-green, and orange bands, a yellow eluate fraction was obtained. This solution showed the same infrared and ultraviolet absorption spectra as the solution described in part A. It also showed the same tendency to give a white, polymeric solid on concentration.

Hydrogenation of 2H-Benz[*cd*]azulene. A cyclohexane solution of 2H-benz[*cd*]azulene (obtained *via* procedure A from 1.06 g of Xb) was subjected to hydrogenation over a 10% palladium-on-charcoal catalyst at room temperature and an atmospheric pressure of hydrogen. When hydrogen was no longer absorbed, the catalyst and solvent were removed. The residual oil was taken up in cyclohexane and chromatographed over neutral alumina (Woelm, activity 1). The main eluate fraction gave 130 mg of a colorless oil whose nmr spectrum showed three kinds of protons: aromatic (centered at τ 3.2), benzylic (centered at τ 6.2–6.8), and aliphatic (centered at τ 8.9), in the ratio of 3:5:8, as would be expected for structure XVIII.

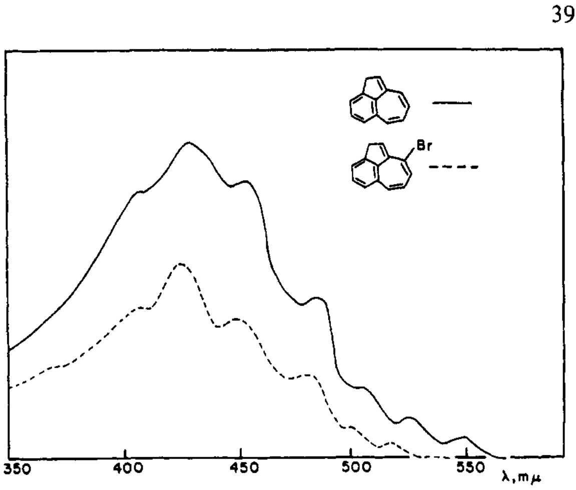


Figure 3. Ultraviolet absorption spectra in cyclohexane of 2H-benz[*c,d*]azulene and 9-bromo-2H-benz[*c,d*]azulene. Since the concentrations could not be determined accurately, no values are given for the extinction coefficient.

For independent confirmation of the structure of the hydrogenation product, a sample of the tricyclic ketone XIX was subjected to a Wolff–Kishner reduction as described by Anderson and Wang.[26] This gave an authentic sample of XVIII which, as a colorless oil, showed superimposable nmr and infrared spectra with those of the hydrogenation product from 2H-benz[*cd*]azulene.

Formation of the 2H-Benz[*cd*]azulene Carbonium Ion. A solution of 2H-benz[*cd*]azulene in 100 ml of benzene (prepared from 1.06 g of Xb) was chromatographed over neutral alumina (Woelm, activity 3), concentrated under reduced pressure to a volume of 15 ml, and then diluted with 15 ml of methylene chloride. To this yellow-orange solution was then added 0.2 g of trityl fluoroborate in 10 ml of methylene chloride, causing the solution to change immediately to a dark green. Addition of ether resulted in the precipitation of a dark green solid. However, attempts to isolate this solid or purify it by recrystallization led to a dark, insoluble, amorphous polymer.

In a similar way a solution of 2H-benz[*cd*]azulene in carbon tetrachloride was prepared and treated with a solution of 100 mg of iodine in carbon tetrachloride. There separated a dark green solid which was collected and redissolved in acetonitrile. Again addition of anhydrous ether caused precipitation of the dark green solid which could be collected and redissolved in acetonitrile. The ultraviolet absorption spectrum of the acetonitrile solution showed absorption maxima at 225 mμ, 245, 295, 350, and 680. Attempts to recrystallize the dark green solid or prolonged handling led to a dark, insoluble, amorphous solid.

Likewise, the use of antimony pentachloride, following the procedure of Holmes and Pettit,[27] with 2H-benz[*cd*]azulene in benzene gave a dark green solid. This could be collected by filtration and redissolved in acetonitrile or nitromethane, but its rapid decomposition prevented purification.

Formation of the 2H-Benz[*cd*]azulene Carbanion. To a solution of 2H-benz[*cd*]azulene in dry pyridine was added a solution of lithium triphenylmethide.[28] The bright red color of the triphenylmethide ion rapidly disappeared and the solution turned dark green. Addition of water caused the dark green color to be lost and left the solution an orange-yellow.

Likewise, treatment of a solution of 2H-benz[*cd*]azulene in dry pyridine with a pyridine solution of the lithium aluminum hydride–pyridine complex[28] produced a deep blue-green color. This solution seemed relatively stable for short periods of time but, on standing overnight, its color changed to a purple-black. When the deep blue-green solution was exposed to air, a rapid development of a purple-black color occurred, suggesting oxidation to the corresponding radical.

Formation of the Free Radical Derived from 2H-Benz[*cd*]azulene. To a solution of 2H-benz[*cd*]azulene (prepared from 1.06 g of Xb) in 100 ml of dry benzene there was added a solution of triphenylmethyl radical (prepared from 100 mg of triphenylmethyl chloride and 100 mg of zinc dust) in 50 ml of benzene. The solution quickly became deep purple in color and, on standing, a black amorphous solid precipitated. After filtration the filtrate was chromatographed and the principal component was shown to be triphenylmethane, mp 92–94°, undepressed by admixture of an authentic sample.

9-Bromo-2H-Benz[*cd*]azulene (XXIII). A solution of 500 mg of 2,2-dibromo-1a,7b-dihydro-1H,4H-cyclopropa[*e*]acenaphthene-1-carboxylic acid (XXII) in 25 ml of chloroform was stirred with a solution of 3.0 g of sodium bicarbonate in 50 ml of water. The mixture was warmed to 50–60° for 0.5 hr. The yellow-orange chloroform layer was then separated, washed with water, and diluted with cyclohexane. Partial concentration under reduced pressure followed by further additions of cyclohexane led eventually to a solution of 9-bromo-2H-benz[*cd*]azulene in essentially pure cyclohexane. Its ultraviolet absorption spectrum (see Figure 3) showed maxima at 230 mμ, 248, 252, 288, 298, 322, 337, 368 (sh), 403 (sh), 421, 450, 480, and 517.

Treatment of the 9-bromo-2H-benz[*cd*]azulene solution under the conditions described for conversion of 2H-benz[*cd*]azulene to carbonium ion, carbanion, and free radical led to essentially the same results and the development of essentially the same colors as with 2H-benz[*cd*]azulene.

Oxidation of Ethyl 1,2-Dihydro-8H-benz[*cd*]azulene-9-carboxylate. To a suspension of 15.0 g of chromium trioxide in 500 ml of dry pyridine at room temperature there was added dropwise with stirring a solution of 2.2 g of ethyl 1,2-dihydro-8H-benz[*cd*]azulene-1-carboxylate (IXa) in 20 ml of pyridine, and the resulting mixture was allowed to stand for 12 hr. It was then poured onto crushed ice and extracted with three 200-ml portions of ether. The combined ether extracts were washed successively with dilute aqueous hydrochloric acid, water, aqueous sodium bicarbonate, and water. After the ether solution had been dried, it was concentrated to give 1.5 g of a dark red oil. This was taken up in benzene and chromatographed over neutral alumina (Woelm, activity 3). Concentration of the first fraction of eluate gave in poor yield dark red crystals, mp 59–61°. In the infrared these crystals showed absorption bands at 5.81 μ, 6.21, and 6.29. In the ultraviolet the absorption spectrum (ethanol) showed maxima (log ε) at 227 mμ (4.52), 274 (4.06), 335 (3.79), and 374 (3.79). The crystals were difficult to handle and decomposed on standing. Structure XXIV is assigned to these crystals by spectral analogy.

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 75.92; H, 4.96.

The second fraction of eluate on concentration gave in fair yield bright yellow crystals. These, after recrystallization from ethanol, were obtained as yellow needles, mp 108–109°. By spectral analogy these have been assigned structure XXV. In the infrared they showed absorption bands at 5.81 μ, 6.11, and 6.28. In the ultraviolet absorption spectrum maxima (log ε) were observed at 227 (4.26, sh), 247 (4.45), 287 (4.04), 308 (4.02), 359 (3.55), 374 (3.67), and 394 (3.64).

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.07; H, 4.78.

Oxidation of 2H-Benz[*cd*]azulene. To 3.0 g of chromium oxide in 100 ml of dry pyridine was added a solution of 2H-benz[*cd*]azulene (prepared from 1.06 g of Xb) in 20 ml of pyridine. After the mixture had stood for 12 hr, it was poured onto crushed ice and extracted with three 100-ml portions of ether. The combined ether extracts were washed successively with dilute acid, water, aqueous sodium carbonate, and water, then dried and concentrated. The residue was taken up in benzene and chromatographed over neutral alumina (Woelm, activity 3). Concentration of the first eluate fraction gave 7 mg of red crystals, mp 128–129°. These have been assigned structure XXVI on the basis of their independent synthesis from the tricyclic ketone XIX. In the infrared XXVI shows strong absorption at 6.20 μ and 6.28 μ. Its ultraviolet spectrum (ethanol) shows absorption maxima (log ε) at 226 mμ (4.37), 266 (3.85), 310 (3.44, sh), 3.24 (3.47), and 3.70 (3.65).

Anal. Calcd for $C_{13}H_8O$: C, 86.65; H, 4.48. Found: C, 86.40; H, 4.74.

Concentration of the second eluate fraction gave 4 mg of bright yellow crystals, mp 102–103°. These have been assigned structure XXVII by spectral analogy. In the infrared they show strong absorption at 6.12 μ and 6.24 μ. In their ultraviolet spectrum (ethanol) they show absorption maxima (log ε) at 243 mμ (4.18), 248 (4.17, sh), 275 (3.94, sh), 282 (3.96), 320 (3.94), 350 (3.11), 367 (3.22), and 385 (3.15).

Anal. Calcd for $C_{13}H_8O$: C, 86.65; H, 4.48. Found: C, 86.85; H, 4.85.

Reaction of 6H-Hexahydrobenz[*cd*]azulen-6-one (XIX) with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone. A mixture of 50 mg of XIX[26] and 186 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 50 ml of dioxane was boiled under reflux for 2 hr. It was then poured into ice–water and extracted with two 50-ml portions of benzene. The combined benzene extracts were concentrated and then chromatographed over neutral alumina (Woelm, activity 3). Concentration of the main eluate fraction gave 10 mg of dark red crystals, mp 128–130°. The identity of these crystals with XXVI, obtained by oxidation of 2H-benz[*cd*]azulene, was established by a mixture melting point determination as well as by infrared and ultraviolet spectral comparison.

Oxidation of 9-Bromo-2H-benz[*cd*]azulene. A mixture of 10.0 g of chromium trioxide and 9-bromo-2H-benz[*cd*]azulene (prepared from 1.06 g of XXII) in 150 ml of dry pyridine was allowed to stand overnight at room temperature. The mixture was worked up as previously described for the oxidation of 2H-benz[*cd*]azulene, and concentration of the first eluate fraction gave 286 mg of red crystals, mp dec >200°. From spectral data and its catalytic hydrogenation (see below), these crystals are assigned structure XXVIII. In the infrared they show strong absorption at 6.12 μ and 6.32 μ. Their ultraviolet spectrum (ethanol) shows absorption maxima (log ε) at 232 mμ (4.33), 271 (3.90), 314 (3.61), 324 (3.60), and 380 (3.60).

Anal. Calcd for $C_{13}H_7OBr$: C, 60.02; H, 2.72. Found: C, 59.57; H, 3.15.

Concentration of the second eluate fraction gave 110 mg of yellow crystals, mp dec >190°. By spectral analogy these crystals have been assigned structure XXIX. In the infrared they show strong absorption at 6.10 μ and 6.23 μ. Their ultraviolet spectrum (ethanol) shows absorption maxima (log ε) at 243 mμ (4.29), 248 (4.19, sh), 273 (3.83), 282 (3.86), 318 (3.82), 354 (3.34), 371 (3.45), and 390 (334).

Anal. Calcd for $C_{13}H_7OBr$: C, 60.02; H, 2.72; Br, 30.81. Found: C, 60.17; H, 2.87; Br, 30.46.

Hydrogenation of 9-Bromo-6H-benz[*cd*]azulen-6-one (XXVIII). A mixture of 100 mg of 9-bromo-6H-benz[*cd*]azulen-6-one (XXVIII) and 10 mg of a 10% palladium-on-charcoal catalyst in 20 ml of ethyl acetate was subjected to hydrogenation at room temperature and atmospheric pressure of hydrogen for 36 hr. After removal of the catalyst and solvent, the residual oil was taken up in benzene and chromatographed over neutral alumina (Woelm, activity 3). The main eluate fraction gave 15 mg of a colorless oil whose infrared spectrum was superimposable with that of an authentic sample of 6H-hexahydrobenz[*cd*]azulen-6-one (XIX).