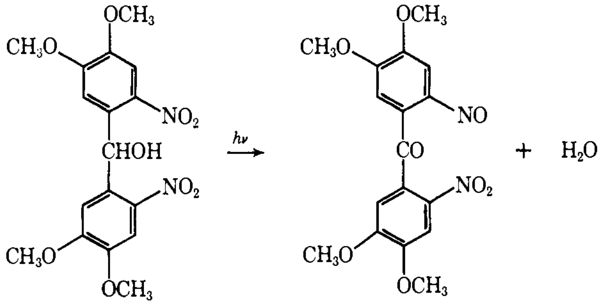
mixture of acids or of aldehyde reagents such as hydrazine, hydroxylamine hydrochloride, or semicarbazide hydrochloride (see Table I).

In an attempt to avoid the side reaction with the aldehyde intermediate formed during irradiation, we used α-substituted *o*-nitrobenzyl alcohol derivatives as starting materials for a second kind of blocking group. Symmetrical carbinols were chosen in order to avoid formation of diastereoisomers during the blocking step. We have shown that on irradiation of such alcohols, a ketonic product is formed, which is less reactive toward the amino function than the aldehydic intermediate mentioned above. Such a ketone was isolated and characterized as shown in Scheme II.

Scheme II



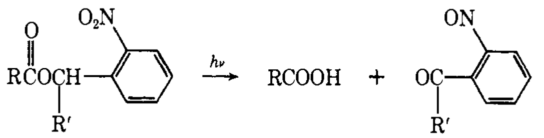
2, mp 202–203° **3**, mp 190–192°

A comparison of yields of photoremoval of 2,2′-dinitrodiphenylmethyloxycarbonyl (DNBOC) amino acid derivatives and (NBOC) and (NVOC) amino acid derivatives is given in Table II. It can be seen that in the case of DNBOC derivatives, the highest yields of deblocking were obtained.

We have also used 2,2′-dinitrodiphenylmethanol as a blocking group for the carboxylic function. Conditions for photoremoval of this blocking group were similar to those required for deblocking of the amino function. In this case, however, no auxiliary reagents were needed. Some examples are given in Table III.

The photoremoval of *o*-nitrobenzyl derivatives from the carboxylic function can be illustrated generally as in Scheme III.

Scheme III



In accordance with this scheme, it is likely that such groups could also be used for the protection of hydroxyl and phosphate functions. Work is now in progress to elucidate the applicability of this approach for carbohydrate and nucleotide synthesis.

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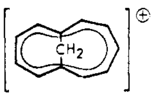
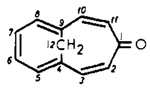
4,9-Methano[11]annulenone.[1a,b] A Ten-π-Electron Analog of Tropone

Sir:

In the course of our studies on aromatic bridged [10]annulenes[2] we recently synthesized the bicyclo[5.4.1]dodecapentaenylium ion (**1**) (as its BF$_4^-$ and ClO$_4^-$ salts),[3] a carbonium ion that can be looked upon as a 10π-electron analog of the tropylium ion.[4] The ion **1** has a pK_{R^+} value of 6.2 ± 0.1,[5] as compared with pK_{R^+} = 4.7 of the tropylium ion[6] and pK_{R^+} = -7.4 of the cyclopropenylium ion,[7] and thus represents the most stable unsubstituted (disregarding the CH$_2$ bridge) Hückel-type carbonium ion known. Although X-ray data for **1** are not yet available[8] the resonance stabilization of the ion strongly implies that its peripheral 11-membered ring is approximately planar. The similarities between **1** and the tropylium ion suggested the interesting possibility that the keto and ketohydroxy derivatives of **1**, such as **2** and **3**, would have chemical properties analogous to those of tropone and tropolone.[9] These expectations have now been borne out by the syntheses of **2** and some of its isomers.[2c,10] In this communication we elaborate on the preparation and properties of **2**.



1



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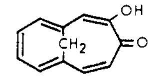

3

Our approach to 4,9-methano[11]annulenone (**2**) started out from 4,5-benzocycloheptenone and followed the pattern, previously developed in this laboratory, for the synthesis of 1,6-bridged cycloheptatrienes.[11] Treatment of 4,5-benzocycloheptenone with ethylene glycol and a catalytic amount of *p*-toluenesulfonic acid in benzene afforded the ketal **4**, mp 110°, in 94% yield. This ketal was submitted to the Birch reduction

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[1] (a) In the terminology proposed by Pilling and Sondheimer[1b] 4,9-methano[11]annulenone is a [4*n* + 3]annulenone with *n* = 2. (b) G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 5610 (1968).

[2] For reviews see: (a) E. Vogel, *Chem. Soc. Spec. Publ.*, No. 21, 113 (1967); (b) E. Vogel, *Chimia*, **22**, 21 (1968); (c) E. Vogel, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **12**, 215 (1968).

[3] (a) W. Grimme, H. Hoffmann, and E. Vogel, *Angew. Chem.*, **77**, 348 (1965); (b) E. Vogel, R. Feldmann, and H. Düwel, *Tetrahedron Lett.*, 1941 (1970).

[4] W. Grimme, E. Heilbronner, G. Hohlneicher, E. Vogel, and J.-P. Weber, *Helv. Chim. Acta*, **51**, 225 (1968).

[5] As determined by potentiometric titration in water as solvent.

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

[7] R. Breslow and J. T. Groves, *ibid.*, **92**, 984 (1970).

[8] An X-ray structure determination of the ion **1** is being carried out by Professor M. Simonetta, University of Milan, Italy.

[9] Macrocyclic [4*n* + 1]annulenones, specifically derivatives of [13]- and [17]annulenone, have recently been synthesized by G. M. Pilling and F. Sondheimer (see ref 1b) and by G. W. Brown and F. Sondheimer, *J. Amer. Chem. Soc.*, **91**, 760 (1969), respectively.

[10] Methano-bridged [11]annulenones with the bicyclo[5.4.1]dodecane carbon skeleton were first obtained by H. Hoffmann in this laboratory (Dissertation, University of Cologne, 1967) by the SeO$_2$ oxidation of bicyclo[5.4.1]dodeca-2,4,7,9,11-pentaene[3] following the procedure of P. Radlick (*J. Org. Chem.*, **29**, 960 (1964)), for the conversion of tropilidene into tropone. This method leads to a mixture of at least four methano[11]annulenones from which apart from **2**, 2,7-methano[11]annulenone and 3,8-methano[11]annulenone could be isolated by laborious chromatography on alumina.[2c] Rational syntheses of 2,7-methano- and 3,8-methano[11]annulenone are currently in progress and will be reported later.

[11] (a) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963); (b) E. Vogel, *Pure Appl. Chem.*, **20**, 237 (1969).

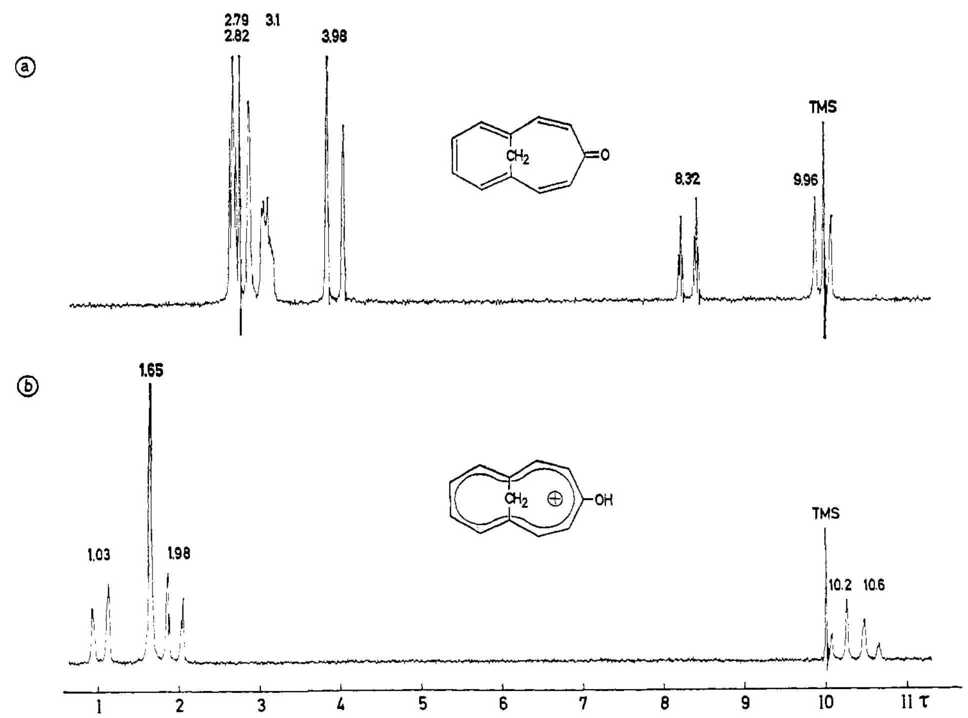
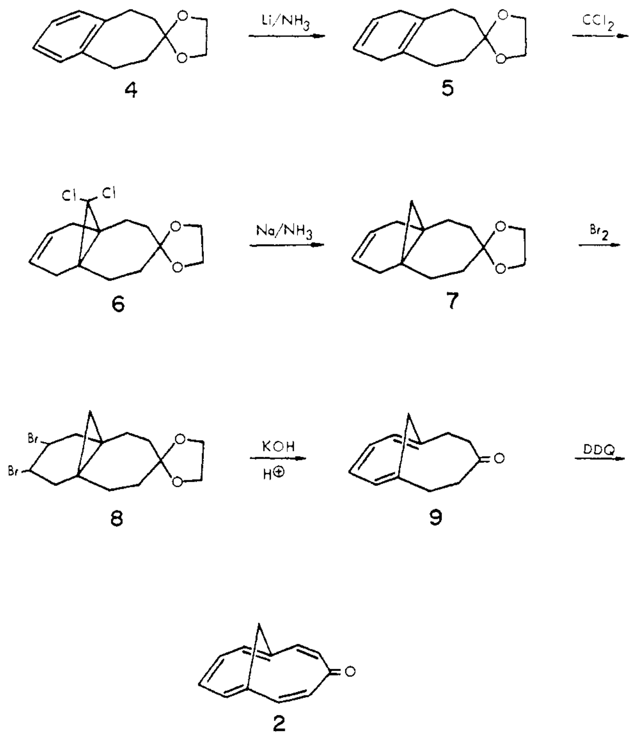


Figure 1. Nmr spectra of 4,9-methano[11]annulenone (2) in (a) CCl_4 and (b) deuteriotrifluoroacetic acid (60 MHz; TMS as internal standard).

Scheme I



using lithium in liquid ammonia with ethanol as a proton source and tetrahydrofuran as a cosolvent. The resulting reduction product, isolated in *ca.* 75% yield by one crystallization from methanol, melted at 57–61° and was found by nmr and glpc analysis to be 95% pure dihydroketal **5** (further purification was not deemed necessary, but could be achieved by repeated crystallizations; pure **5** had mp 70°). The subsequent cyclopropanation of **5** employing dichlorocarbene, generated from chloroform and potassium *tert*-butoxide, was based on the idea that the ketal oxygens might coordinate with the dichlorocarbene and might thus assist in directing the carbene to the central double bond. In line with this reasoning the dihydroketal **5**, when treated with chloroform and potassium *tert*-butoxide, gave the desired dichlorocarbene adduct **6**, mp 108–109°, in *ca.* 70% yield. That the selectivity exerted by dichlorocarbene in the addition to **5** cannot be solely due to the enhanced nucleophilicity of the central double bond, as compared with that of the outer double bond, becomes apparent from the course of the dichlorocarbene addition to bicyclo[5.4.0]-undeca-1(7),9-diene.[11] In the latter case, attack of dichlorocarbene at the central double bond is not markedly favored, even though the absence of the bulky ketal group renders this double bond more accessible to the carbene. The reductive elimination of the chlorine atoms from **6** with sodium in liquid ammonia yielded pure **7** (mp 38–39°; yield 97%). Compound **7** readily absorbed 1 mol of bromine in methylene chloride at −70° to give the dibromide **8**, mp 156° dec, and this on heating with potassium hydroxide in methanol, followed by treatment of the crude dehydrohalogenation product with dilute perchloric acid in tetrahydrofuran–water at 50–60°, produced the ketone **9** of mp 52–53° in 80% yield (based on **7**). The cycloheptatriene structure of the ketone is evident from the close agreement of its uv spectrum [λ_{max} (cyclohexane) 271 mμ (ϵ 4300)] with that of the corresponding hydrocarbon, *i.e.*, bicyclo[5.4.1]dodeca-7,9,11-triene,[11] as well as from its nmr spectrum [AA′BB′ system at τ 3.56 and 4.02 (four olefinic protons), multiplet at 7.1–8.0 (eight CH_2 protons plus one bridge proton), and doublet at 8.44 with J = 12.4 Hz (bridge proton located above the triene system)]. Dehydrogenation of **9** was best effected by heating the ketone with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in benzene at 115–125° (sealed tube) for 6 hr. The dehydrogenation product consisted, according to glpc assay, of two compounds in the ratio of 1:4.5 which could be separated by chromatography on alumina. The compound formed in minor amount (yield 9%), mp 27°, was identified as the 2,3-dihydro derivative of **2**, while the major product (46%) proved to be **2**.

4,9-Methano[11]annulenone (**2**), which was obtained as lemon yellow crystals of mp 74° (from cyclohexane), is a perfectly stable compound, remaining unchanged even after prolonged exposure to air. The ir spectrum of **2** (neat) displays one broad band in the 6–7-μ region, at 6.22 μ (1607 cm^{-1}), which apparently arises from coupled carbonyl and carbon double bond vibrations. The uv spectrum is found to be strongly solvent dependent: λ_{max} (cyclohexane) 227 (ε 15,000), 285 (38,000), 330 (4900, shoulder), and 392 mμ (1250, shoulder); λ_{max} (methanol) 226 (ε 15,700), 250 (10,300, shoulder), 292 (34,000), 335 (5300, shoulder), and 393 mμ (2600, shoulder). In the mass spectrum prominent peaks appear at *m/e* 170 (molecular ion), 142 (M − CO), and 141 (M − CO − H, base peak).

The nmr spectra of **2** in carbon tetrachloride and in acidic solvents confirm the proposed structure (Figure 1). The spectrum in carbon tetrachloride shows an AA′BB′ system at τ 2.79 and 3.1 (H_6, H_7 and H_5, H_8, respectively), an AB system at 2.82 and 3.98 with $J = 12.2$ Hz (H_3, H_{10} and H_2, H_{11}),[12] and another AB system at 8.32 and 9.96 with $J = 11.4$ Hz [*anti*-H_{12} (anti with respect to the cycloheptatriene system) and *syn*-H_{12}]. The assignments of both the olefinic protons H_5–H_8 and the bridge protons are based on the long-range couplings between H_5, H_8 and *anti*-H_{12} ($J = 1.5$ Hz). From a detailed analysis of the 100-MHz nmr spectrum[13] it appears that the ground state of the molecule is best represented by the polyenone structure **2**.[14] When the spectrum of **2** is recorded in deuteriotrifluoroacetic acid dramatic shifts are exhibited in accord with the expected formation of the aromatic 4-hydroxybicyclo[5.4.1]dodecapentaenylium ion (**10**). The most noticeable effect on the spectrum caused by the protonation of **2** is the large downfield shift of all the olefinic protons which now give rise to an AB system at τ 1.03 and 1.98 with $J = 11.0$ Hz (H_3, H_{10} and H_2, H_{11})[12] and to a singlet at 1.65 (H_5, H_6, H_7, H_8). The bridge protons on the other hand experience an upfield shift and give an AB system at τ 10.2 and 10.6 with $J = 11.0$ Hz. The opposite directions of shift for the protons in and above the plane of the peripheral 11-membered ring clearly indicate the presence of an induced diamagnetic ring current in the ion **10**. The aromatic stabilization of the ion **10** derives additional support from the finding that the pK_a of **10**, determined to be −0.6 ± 0.1,[15] compares well with that of protonated tropone (pK_a = −0.6 ± 0.3).[16]

4,9-Methano[11]annulenone (**2**) exhibits normal reactivity toward carbonyl reagents, *e.g.*, it forms an orange oxime (mp 197–198°) and a bright red phenylhydrazone (mp 178–179°).

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[12] This assignment is based on a comparison with the spectrum of 2,11-dideuterio-4,9-methano[11]annulenone.

[13] The analysis provides the following vicinal coupling constants for the olefinic protons H_5, H_6, H_7, and H_8 of **2**: $J_{5,6} = J_{7,8} = 6.74$ Hz and $J_{6,7} = 10.5$ Hz. These values are in close agreement with the corresponding constants of the parent hydrocarbon bicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene[3] (6.02 and 10.58 Hz), but differ markedly from the nonalternating constants of the ion **1** (9.46 and 9.46 Hz) (these findings will be the subject of a separate forthcoming publication by K. Müllen, H. Günther, and E. Vogel).

[14] For a similar evaluation of the electronic structure of tropone see: D. J. Bertelli and T. G. Andrews, Jr., *J. Amer. Chem. Soc.*, **91**, 5280 (1969), and D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, *ibid.*, **91**, 5286 (1969).

[15] Determined spectrophotometrically in aqueous sulfuric acid solution using Hammett's H_0 acidity values.

[16] A. S. Kende, *Advan. Chem. Phys.*, **8**, 133 (1965). See also H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Jap.*, **39**, 1414 (1966).

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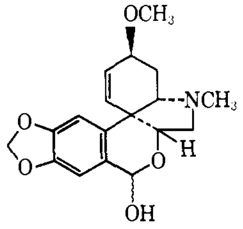
Molecular Structure and Absolute Configuration of Alkaloids Related to 5,10-Ethanophenanthridine[1]

Sir:

Previous chemical transformations have interrelated the alkaloids pretazettine (**1**), haemanthamine (**2a**), and montanine (**3**) as well as the artifact, tazettine (**4**).[2] Absolute configurations for these alkaloids and **4** were originally assigned by empirical arguments based on Mill's rule.[3] Extension of these observations in ORD and CD spectra[4,5] of the compounds led to ambiguous results. The elegant and detailed chemical degradations of dihydrotazettine[6] indicate that the assignments of absolute configurations shown for **1**–**4** were indeed correct. Because of biosynthetic interest in several laboratories concerning the mechanism of *in vivo* benzylic oxidation, and for better correlations of ORD and CD data with the absolute configuration and physiolog-



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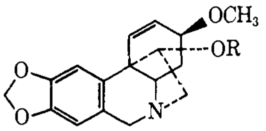
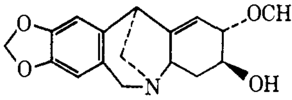


2a, R = H
b, R = COC_6H_4Br (para)



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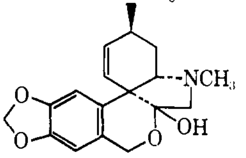

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 2796. Additional support was derived from a grant from the National Institutes of Health (HE-07503).

[2] W. C. Wildman and D. T. Bailey, *J. Amer. Chem. Soc.*, **91**, 150 (1969). For a summary of these alkaloid interconversions see: W. C. Wildman, *Alkaloids*, **6**, 343 (1960).

[3] J. A. Mills, *J. Chem. Soc.*, 4976 (1952).

[4] G. G. DeAngelis and W. C. Wildman, *Tetrahedron*, **25**, 5099 (1969).

[5] K. Kuriyama, T. Iwata, M. Moriyama, K. Kotera, Y. Hameda, R. Mitsui, and K. Takeda, *J. Chem. Soc. B*, **46** (1967).

[6] R. J. Highet and P. F. Highet, *Tetrahedron Lett.*, 4099 (1966).