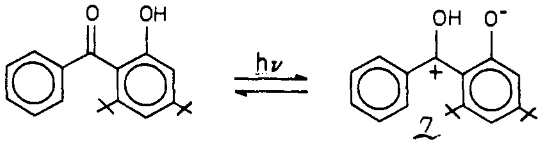
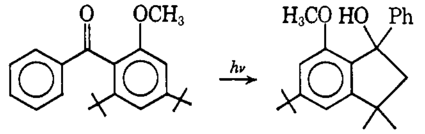
configuration of its excited states.[11] The role of intramolecular hydrogen bonding in the deactivation of excited states of **2** is not clear.[11] However, intramolecular hydrogen bonding has been proposed to provide a deactivation mechanism for excited states of amidophenylbenzotriazoles.[6] Since all the conditions postulated to explain the high photostability of **2** are sterically precluded in **1**, we ask: what is the mechanism of deactivation of excited states of **1**?

Using the technique of Weller[12] the pK_a* for 1 in its lowest excited singlet state was estimated at ~ -4 to -5. Such a low value for pK_a* suggests that rapid deprotonation competes with intersystem crossing from the n,π^* singlet state of **1**. The fact that **1** is photostable in hydrocarbon media demonstrates that the solvent is not involved as an accepting base. We propose that, subsequent to population of its n,π^* singlet state, **1** undergoes *reversible intramolecular proton transfer* of its phenolic hydrogen to the neighboring carbonyl oxygen. The zwitterionic species **7** formed in



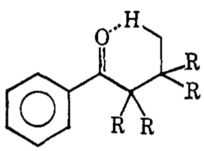
this reaction would not be expected to abstract a hydrogen atom from solvent but rather collapse to **1**.

An alternative explanation for the low photoreactivity of **1** is steric inaccessibility of the carbon group. This was dismissed by determining the quantum yield for photolysis of 2-methoxy-4,6-di-*t*-butylbenzophenone (**8**) in ethanol to be 0.5. The major product formed by irradiation of **8** in ethanol is the indanol **6**. No carbinol or pinacol reduction products were isolated. Compound **9** is presumably formed by intramolecular hydrogen abstraction from the *o*-*t*-butyl group of **8** followed by cyclization of the diradical thus generated. It is this intramolecular cyclization reaction with which reversible proton transfer in **1** must compete.



8 **9**

Our results on **1** prompt the question as to what contribution intramolecular hydrogen bonding makes to the high photostability of **2**. Does the intramolecular hydrogen bond itself provide an additional deactivation mechanism, or is reversible intramolecular proton transfer the only significant deactivation process for excited states of this class of compounds? Further work on the clarification of this point is anticipated on compounds of the general structure **10**. In **10**, effects directly attributable to intramolecular hydrogen bonding can be observed in the absence of complications due to low-lying charge-transfer states and to reversible proton-transfer reactions.



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Acknowledgment. The author is grateful to Dr. R. E. Kellogg of this laboratory for assistance in determining the phosphorescence lifetime of the title compound.

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(9) J. N. Pitts, Jr., H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(10) G. Porter and P. Suppan, *Pure Appl. Chem.*, **9**, 499 (1964).

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(12) A. Weller, "Progress in Reaction Kinetics," G. Porter, Ed., Pergamon Press, New York, N. Y., 1961, pp 189–191.

(13) Address inquiries to Department of Chemistry, Fairfield University, Fairfield, Conn.

E. J. O'Connell, Jr.[13]
Contribution No. 1326, Central Research Department
Experimental Station,
E. I. du Pont de Nemours and Company
Wilmington, Delaware

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Constituents of Hashish. A Novel Reaction of Olivetol with Citral in the Presence of Pyridine. Total Synthesis of *dl*-Cannabicyclol and *dl*-Cannabichromene[1]

Sir:

The components of hashish have received renewed interest in recent years.[2b] A synthesis of dl-$\Delta^{1(6)}$-3,4-*trans*-tetrahydrocannabinol (**3**) and $\Delta^{4(8)}$-isotetrahydrocannabinol (**4**) has been effected by condensation of olivetol (**1**) with citral (**2**) in the presence of 10% boron trifluoride etherate in benzene solution.[2c,d] However, when the reaction was carried out under the milder acidic conditions of 0.0005 *N* HCl in ethanol[2c] or of 1% boron trifluoride etherate in methylene chloride,[2b] dl-Δ^1-3,4-*cis*- (**6**) and dl-Δ^1-3,4-*trans*-THC (**5**) were isolated.

We now wish to report in this communication that the reaction of olivetol (**1**) with citral (**2**) in pyridine[3] takes a different course which provides a useful, simple, one-step synthesis of the racemic modifications of two

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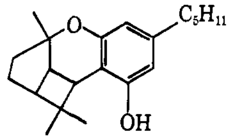
(1) Since submission of our paper, the synthesis of cannabicyclol and cannabichromene has been reported by L. Crombie and R. Ponsford, *Chem. Commun.*, 894 (1968). Another synthesis of cannabichromene has also been reported by G. Cardillo, R. Cricchio, and L. Merlini, *Tetrahedron*, **24**, 4825 (1968). In Crombie and Ponsford's paper a new structure was proposed for cannabicyclol. This structure does not

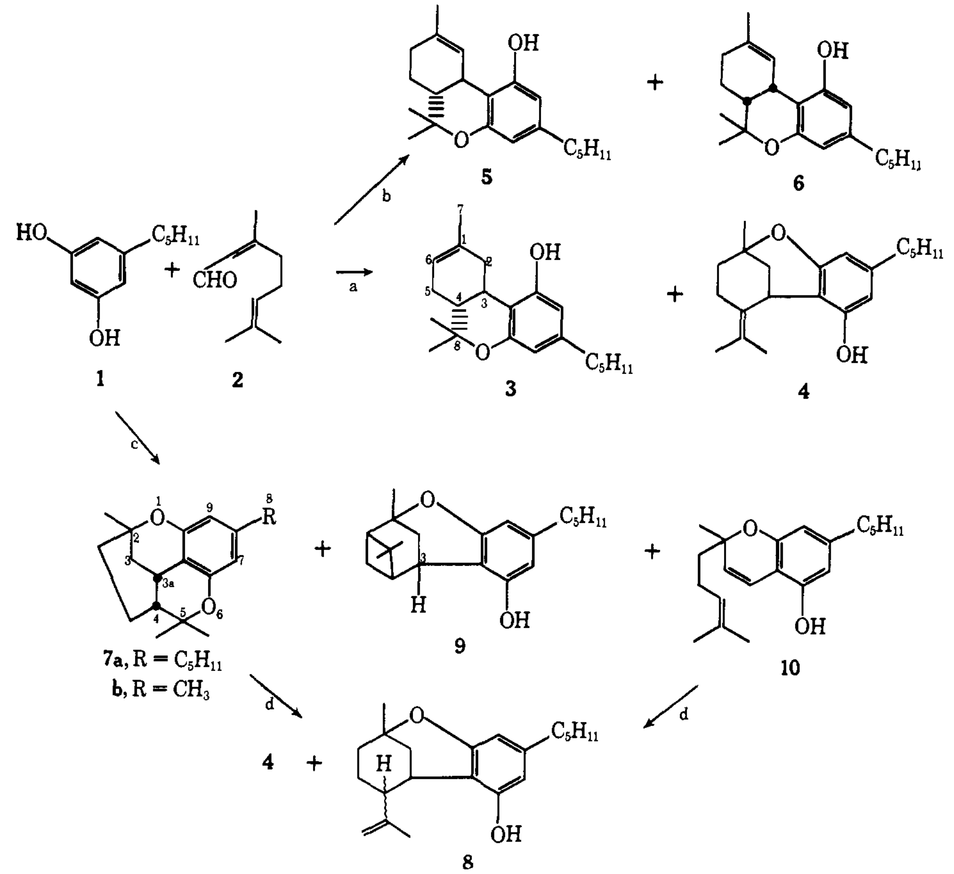


satisfactorily explain (a) the high-field methyl signal at 0.78 ppm in the nmr; (b) the fragment at *m/e* 232 in the mass spectral data; and (c) its formation from **10** on mechanistic grounds. We therefore suggest that in the absence of further experimental data the structure and stereochemistry as suggested by Korte[2a] and Mechoulam[2b] should not be discarded at the present time.

(2) (a) U. Claussen, F. V. Spulak, and F. Korte [*Tetrahedron*, **24**, 1021 (1968)] have isolated from hashish a crystalline compound, mp 144–146°, $[\alpha]^{20}D$ −3°, to which they have given the structure **9** on the basis of its nmr and mass spectral data and called it cannabipinol. They did not prove the identity of their cannabipinol with Mechoulam's[2b] cannabicyclol. However, Professor Korte (private communication) has kindly informed us that his sample and ours are the same as shown by ir (solution), mixture melting point, and mass spectrum. Hence this establishes the identity of cannabicyclol and cannabipinol. (b) R. Mechoulam and Y. Gaoni, *Fortschr. Chem. Org. Naturstoffe*, **25**, 175 (1967). (c) E. C. Taylor, K. Lenard, and Y. Shvo, *J. Am. Chem. Soc.*, **88**, 366 (1966). (d) Y. Gaoni and R. Mechoulam, *ibid.*, **88**, 5673 (1966).

(3) (a) C. E. Berkoff and L. Crombie, *J. Chem. Soc.*, 3734 (1960). (b) While our work was in progress, the potential synthetic utility of this reaction was also pointed out in a recent publication: L. Crombie and R. Ponsford, *Chem. Commun.*, 368 (1968).

Scheme I[a]



[a] Reagents: (a) 10% BF_3 in C_6H_6; (b) HCl in C_2H_5OH and 1% BF_3 in CH_2Cl_2; (c) pyridine; (d) *p*-toulenesulfonic acid in benzene.

of the minor constituents of hashish (Scheme I). It is, in effect, the first total synthesis of *dl*-cannabicyclol (**9**) as well as a one-step synthesis of *dl*-cannabichromene (**10**). A two-step synthesis of the latter has recently been reported.[4]

We have found that heating equimolar quantities of **1**, **2**, and pyridine under reflux for 5 hr gave a complex mixture of products, which was chromatographed on Florisil. Elution with 2:98 ether–petroleum ether (bp 30–40°) gave in 17% yield a colorless oil, homogenous on tlc; nmr (CCl_4), δ 0.87 (3 H, t, ω-CH_3), 0.94, 1.30, 1.44 (9 H, 3 s, 3-CH_3), 6.15 (2 H, broad, aromatic), no olefinic and no exchangeable protons; ir (CCl_4), no hydroxylic bands, 1064 and 1130 cm^{-1} (strong ether bands). These constants are in agreement for the tetracyclic ether obtained by treatment of cannabigerol with chloranil.[4] The mass spectrum indicated a molecular weight of 314, corresponding to a 1:1 adduct of **1** and **2**. In addition to the molecular ion peak, the mass spectrum included peaks at 299 (M − 15), 271, 258, 243, 232, 231, 193, and 174 which are completely explicable on the basis of structure **7a**.[5] Furthermore, when we treated **7a** with *p*-toluenesulfonic acid in refluxing benzene for 2 hr, we obtained **4**, together with an isomer, to which we tentatively assign structure **8**.[6] Mechoulam and coworkers[4] reported only the isolation of **4** from the same reaction. The spectroscopic data for **7a** and its acid-catalyzed conversion to **4** makes the structural assignment secure.

Orcinol also reacted with **2** under similar conditions (reflux in pyridine for 5 hr) to give an adduct $C_{17}H_{22}O_2$ (*m/e* calcd for $C_{17}H_{22}O_2$, 258.1619; found, 258.1612). The ir, nmr, and mass spectra confirmed **7b** as its formulation. Thus it appears that the reaction between substituted resorcinols and citral in pyridine to form tetracyclic ethers of type **7** is a general one, which leads to substituted iso-THC derivatives (**4**).

Elution with petroleum ether–ether (98:2 and 96:4) afforded a crystalline compound, mp 143–144° (Fisher-Johns apparatus), in 5% yield, which we consider to be cannabicyclol (**9**);[2b] nmr ($CDCl_3$), δ 0.89 (3 H, t, ω-CH_3), 0.78 (3 H, s, CH_3 on four-membered ring), 1.38 (6 H, s, CH_3 on a four-membered ring and α to OCH_3), 2.40 (4 H, t), 3.10 (1 H, broad m, C_3–H), 4.54 (1 H, s, OH, D_2O exchangeable), 6.17 (1 H, d, J = 2 cps, aromatic H), 6.34 (1 H, d, J = 2 cps, aromatic H); λ_{max}^{EtOH} 282 (ϵ 1165), 275 (1155), 226 sh (10,520), and 210 mμ (39,100); ν_{max}^{KBr} 3362 cm^{-1} (OH). Its uv, nmr, and ir (KBr) spectra were identical with those of natural cannabicyclol.[2b,7] The mass spectrum[8] confirms the molecular composition, $C_{21}H_{30}O_2$ (*m/e* calcd for $C_{21}H_{30}O_2$, 314.2245; found, 314.2241). Further, the mass

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[4] R. Mechoulam, B. Yagnitinsky, and Y. Gaoni, *J. Am. Chem. Soc.*, **90**, 2420 (1968).

[5] A rationalization of the complete spectrum will be provided in our detailed manuscript. From an examination of Dreiding models we suggest that 3,3a,4,5-tetrahydro-2,5,5-trimethyl-8-pentyl-2,4-ethano-2H-pyrano[4,3,2-*de*][1]benzopyran (**7a**) has a *cis*-3a,4 ring junction.

[6] The structure of **8** is based on the ir and nmr spectra.

[7] We are indebted to Professor R. Mechoulam for a sample of natural cannabicyclol, which was reported as having mp 152–153°,[2b] $[\alpha]^{22}D$ 0° (EtOH) (private communication); however, in our laboratory its melting point and mixture melting point with our sample was 145–146° (Fisher-Johns apparatus).

[8] The mass spectrum was run on a CEC 21-110B, block 110°, probe 95°.

spectrum of the synthetic product was identical with that of naturally occurring cannabicyclol: all the characteristic "cannabicyclol peaks"[2a] were exhibited, including the significant peaks at *m/e* 314 (M^+), 299 (M − 15), 232, 231 (base peak), 187, and 174.

Further elution with petroleum ether–ether (95:5 and 94:6) gave a reddish oil. This was rechromatographed twice on thick silica gel plates and evaporatively distilled at 150° (0.01 mm) to give a colorless liquid in 20% yield, homogenous by tlc and glc; nmr (CCl_4), δ 0.87 (3 H, t, ω-CH_3), 1.34 (3 H, s, α to OCH_3), 1.55 and 1.64 (6 H, 2 s, olefinic CH_3), 5.06 (1 H, broad t, olefinic H), 5.36 and 6.56 (2 H, AB quartet, J_{AB} = 10 cps, olefinic H), 5.99 (1 H, d, J = 2 cps, aromatic H), 6.16 (1 H, d, J = 2 cps, aromatic H), and 5.55 (1 H, s, OH; D_2O exchangeable; λ_{max}^{EtOH} 280 (ϵ 9700 and 225 mμ (27,500). The mass spectrum showed principal ions at *m/e* 314, 299, 232, 231 (base peak), and 174, in accord with the data presented for an authentic sample.[9] Furthermore, the ir spectrum of the synthetic cannabichromene in CCl_4 solution is virtually superimposable with that of natural cannabichromene (**10**).[2b] Also, as expected, heating **10** with *p*-toluenesulfonic acid in refluxing benzene gave mainly **4** along with **8**.[2d]

The success of these experiments has prompted us to continue an examination of this reaction and its mechanism, which will be the subject of future communications.

Acknowledgment. We are grateful to Arthur D. Little, Inc., for generous support of this work. The authors wish to thank Dr. P. Levins and Miss D. Wilson for recording the mass and nmr spectra, respectively, and Dr. Harry G. Pars for his encouragement of this work.

[9] (a) U. Claussen, F. V. Spulak, and F. Korte, *Tetrahedron*, **22**, 1477 (1966); (b) Y. Gaoni and R. Mechoulam, *Chem. Commun.*, 20 (1966).

Vinayak V. Kane, Raj K. Razdan
Organic and Medicinal Chemistry Laboratories
Arthur D. Little, Inc., Cambridge, Massachusetts 02140
Received July 15, 1968

1-Trimethylamino-1-beryl-2,3-dicarba-*closo*-dodecaborane(12). An Analog of the $B_{11}CH_{12}^-$ Ion

Sir:

The continued substitution of a beryllium atom–carbon atom pair for a pair of boron atoms in polyhedral-borane ions and carborane species would ultimately produce a series of beryllium–carbon species which are isoelectronic with the corresponding polyhedral $B_nH_n^{2-}$ ion and $B_{n-2}C_2H_n$ carborane (n = even number). Examples would include $Be_6C_6H_{12}^{2-}$, $BBe_5C_6H_{12}^-$, and $Be_5C_7H_{12}^0$ of probable icosahedral geometry which are isoelectronic with $B_{12}H_{12}^{2-}$, $B_{11}CH_{12}^-$, and $B_{10}C_2H_{12}$, respectively. We now wish to report the synthesis of species in which the first step of the Be + C for 2B substitution has been formally accomplished.

The reaction of a benzene solution of (3)-1,2-$B_9C_2H_{13}$[1] with a diethyl ether solution of dimethylberyllium produced 2 moles of CH_4 which was quantitatively determined and identified by its characteristic vpc retention time. Subsequent work-up of the reaction solution in the absence of air and moisture led to the

$$B_9C_2H_{13} + Be(CH_3)_2\cdot(OEt_2)_2 \longrightarrow B_9BeC_2H_{11}\cdot OEt_2 + OEt_2 + 2CH_4$$

isolation of a nonvolatile crystalline solid (I) which could be recrystallized from dry, oxygen-free CH_2Cl_2–pentane solutions. This substance was very sensitive to air and water and melted at 120–121°. Elemental analysis was unsuccessful because of the extreme air sensitivity of the compound. Proton nmr and infrared spectra suggested that I was $B_9BeC_2H_{11}\cdot O(C_2H_5)_2$ in which diethyl ether was coordinated with the beryllium atom, thus formally replacing a hydride ion in the parent $B_9BeC_2H_{12}^-$ ion. The latter ion is isoelectronic with the $B_{11}CH_{12}^-$ ion,[2] as suggested above, and would most likely possess an icosahedral geometry.

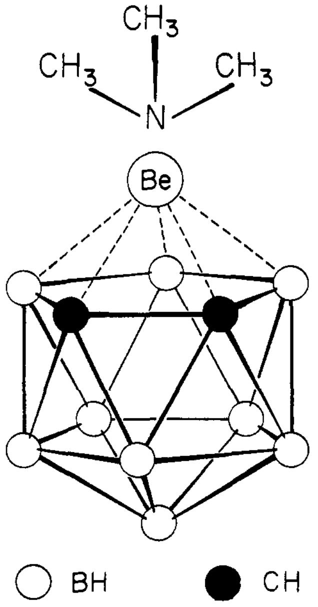

Figure 1. Proposed schematic structure of $B_9BeC_2H_{11}N(CH_3)_3$.

When anhydrous trimethylamine was passed through a solution of I in dry CH_2Cl_2, white crystals (II) precipitated which could be recrystallized from CH_2Cl_2–pentane solutions. The melting point of II was 221–223° dec, and II was much less reactive with moist air than I. *Anal.* Calcd for $B_9BeC_2H_{11}\cdot N(CH_3)_3$: B, 48.54; C, 29.93; H, 10.05; Be, 4.50; N, 6.98. Found: B, 47.45; C, 28.46; H, 9.67; Be, 3.79; N, 7.19. The parent peak in the mass spectrum[3] of II appeared at *m/e* 202 and corresponds to the $(^{11}B_9{}^9Be^{12}C_5{}^1H_{20}{}^{14}N)^+$ ion. The ^1H nmr spectrum of II in methylene chloride showed a broad singlet at δ −2.55 (relative intensity 2) and a sharp singlet at δ −2.90 (relative intensity 9) relative to tetramethylsilane. The ^1H nmr spectrum of I in methylene chloride showed the broad singlet at δ −2.75 (relative intensity 2) together with a triplet at δ −1.80 (relative intensity 6) and a quartet at δ −4.62 (relative intensity 4). The signals at δ −2.55 and −2.75 were assigned to the hydrogen atoms bonded to the carborane carbon atoms, whereas the singlet at δ −2.90 was assigned to the coordinated trimethyl-

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[1] R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

[2] (a) D. E. Hyatt, F. R. Scholer, L. J. Todd, and J. L. Warner, *Inorg. Chem.*, **6**, 2229 (1967); (b) W. H. Knoth, *J. Am. Chem. Soc.*, **89**, 1274 (1967).

[3] We are indebted to Professor H. D. Kaesz for the determination of the mass spectrum of II.