metrically linear bridging hydrogen located on the *idealized* center of symmetry occupies the sixth coordination site about each chromium and thereby enables the molecular geometry of $HCr_2(CO)_{10}^-$ ideally to possess D_{4h} symmetry.[12] Since metal-coordinated hydrogen atoms have been found *without exception* to occupy regular coordination sites about the metal,[10] the coincidence of the principal fourfold axes of the two $Cr(CO)_5$ fragments with each other demands a *linear* Cr–H–Cr bond in order for the hydrogen to be octahedrally coordinated to both chromium atoms; a nonlinear bridging hydrogen octahedrally bonded to both chromium atoms would result in loss of the D_{4h} molecular symmetry. A salient feature is the Cr–Cr distance of 3.41 ± 0.01 Å from which an equidistant bridging hydrogen yields a Cr–H bond length of 1.70 Å; this value is in good agreement with the limited M–H data available for other transition metal hydride complexes.[15]

It is expected that other polynuclear transition metal complexes with direct metal–metal bonds can be protonated to give linear three-center, electron-pair metal–hydrogen–metal bonds. In fact, Hayter[20] has shown that the dimeric monohydridic molybdenum and tungsten carbonyl analogs, $HMo_2(CO)_{10}^-$ and $HW_2(CO)_{10}^-$, are isostructural with that of $HCr_2(CO)_{10}^-$ from the similar infrared and nmr spectral properties of these three anions containing congeneric transition metals. No doubt, the protonated, electron-deficient complex $HFe_2(CO)_8^-$ also contains a linear three-center, two-electron bond.

the $HFe_3(CO)_{11}^-$ anion.[13] For this trinuclear iron carbonyl complex direct substantiation for the bridging hydrogen being equidistant from two iron atoms was given by the anion's Mössbauer spectrum, which shows the two hydrogen-coordinated iron atoms to be equivalent.[14]

(12) The possibility that a symmetrical bridging hydrogen lying on a mirror plane or center of symmetry may be statistically symmetrical (or time-averaged) owing to a double minimum potential function cannot be ruled out but is regarded as much less likely for these monobridging hydrogen–metal complexes. For discussions with references of single- and double-well potentials pertaining to symmetrical hydrogen bonding, see W. C. Hamilton, *Ann. Rev. Phys. Chem.*, 13, 19 (1962); R. E. Rundle, *J. Phys. Radium*, 25, 487 (1964).

(13) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, 4, 1373 (1965).

(14) N. E. Erickson and A. W. Fairhall, *ibid.*, 4, 1320 (1965).

(15) To date the only *accurately* known transition metal-hydride distance is the terminal Re–H distance of 1.68 ± 0.01 Å reported from a neutron diffraction study of K_2ReH_9.[16] A three-dimensional X-ray analysis of $HRh(CO)[P(C_6H_5)_3]_3$[17] located the hydrogen at a terminal Rh–H distance of 1.60 ± 0.12 Å, while a three-dimensional X-ray investigation of $HMn_3(CO)_{10}(BH_3)_2$, for which approximate coordinates were obtained for all hydrogen atoms, yielded an average value of 1.65 Å (with esd, 0.1 Å,) for the five independent bridging Mn–H distances.[18] Although not directly established from the X-ray work, a terminal Mn–H distance of 1.5–1.6 Å was estimated for $HMn(CO)_5$[19] and a bridging Mo–H distance of 1.8 Å was predicted for $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$[10b] from stereochemical considerations.

The approximate *single* bond covalent radii obtained for the earlier members of the transition metal series by the use of one-half the metal-metal bond length[10b] together with an empirical value of 0.2 Å for the hydrogen radius give a reasonably self-consistent set of M–H distances when compared with the values quoted above. The empirically estimated M–H distances (i.e., (M–M) Å/2 + 0.2 Å) are as follows (in Å) Cr–H, 1.7; Mo–H, 1.8; Mn–H, 1.65; Tc–H, 1.7; Re–H, 1.7; Ru–H, 1.65; Os–H, 1.65; Rh–H, 1.55; Ir–H, 1.55. The dependence of covalent radii on such factors as effective metal charge (or valency) and $d\pi$–$d\pi$ electronic repulsion, metal coordination number, and metal hybridization is ignored here along with the fact that a bridged M–H distance is expected to be longer than a terminal M–H distance.

(16) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, 3, 558 (1964).

(17) S. J. La Placa and J. A. Ibers, *Acta Cryst.*, 18, 511 (1965).

(18) G. R. Wilkes, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1965, G. R. Wilkes and L. F. Dahl, to be published.

(19) S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, 3, 1491 (1964).

(20) R. G. Hayter, presented at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965; to be published.

A stereochemical implication of the structure of $HM_2(CO)_{10}^-$ (where M = Cr, Mo, W) (and the presumed structure of $HFe_2(CO)_8^-$) is that these monohydridic anions cannot be further protonated[21] to give stable dihydridic dimeric complexes without a complete molecular rearrangement or breakdown into monomeric species. Consequently, the nonisolation of such dihydric dimeric complexes is not surprising.

Single crystal X-ray investigations of the other metal carbonyl anions are in progress in order to compare the geometries of the protonated and unprotonated species.

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Active Constituents of Hashish.
Synthesis of dl-Δ^6-3,4-*trans*-Tetrahydrocannabinol

Sir:

"Tetrahydrocannabinol," the active component(s) of hashish (marijuana), the psychotomimetically active resin of the female flowering tops of *Cannabis sativa* L., has long been known to possess the carbon skeleton indicated in structure **1**. Until recently, however, the stereochemistry of the ring fusion (positions 3 and 4), the position of the alicyclic double bond, and, indeed, even the homogeneity of the "active component," were not known. The correct structures of the biogenetic precursor cannabidiol (**2**)[2] and two isomeric tetrahydrocannabinols (**1** and **3**) have recently been established. The major member of the "tetrahydrocannabinol" fraction present in most hemp plants is the Δ^1-3,4-*trans* isomer (**1**),[3] but the isomeric Δ^6-3,4-*trans* isomer (**3**) also occurs naturally and is similar to **1** in physiological potency.[4,5] It has been demonstrated that **1** is formed by acid cyclization of cannabidiol;[3] under more strongly acidic conditions a mixture of **1** and **3** is formed, the latter arising by acid isomerization of the former.[4]

We wish to describe in this communication a simple, one-step synthesis of dl-Δ^6-3,4-*trans*-tetrahydrocannabinol (**3**), the racemic modification of one of the physiologically active principles of marijuana, and of two
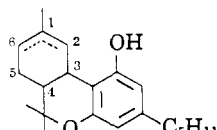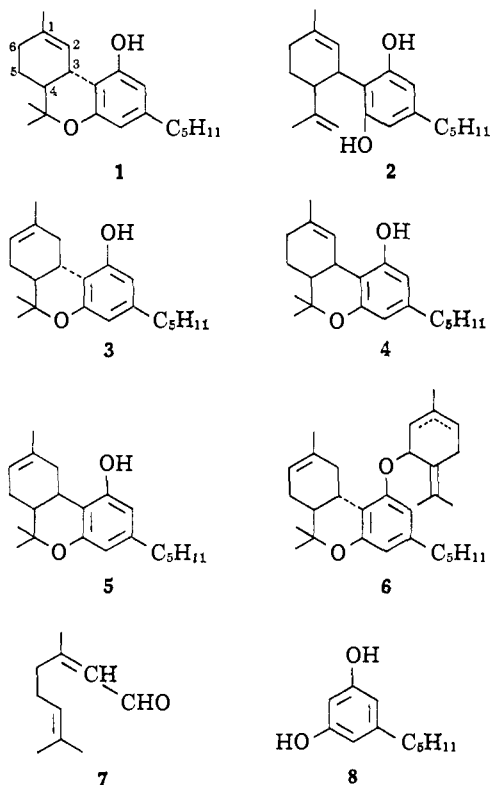
additional isomers, *dl*-Δ¹-3,4-*cis*-tetrahydrocannabinol (4) and *dl*-Δ⁶-3,4-*cis*-tetrahydrocannabinol (5).

We have found that the reaction of citral (7) with olivetol (8) at 5–10° in benzene solution in the presence of 10% boron trifluoride etherate, followed by extraction of the reaction mixture with dilute alkali (to remove unreacted olivetol), chromatography of the

the proton α to oxygen.[6] Subsequent elution of the Florisil column with hexane–ethyl ether (95:5) gave a resin which was separated by preparative vpc (column 10% GE-SE30 on Diatoport S; gas, helium; oven temperature, 280°) into *dl*-Δ⁶-3,4-*cis*-tetrahydrocannabinol (5) (20% yield. *Anal.* Calcd. for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.47; H, 9.62) and *dl*-Δ⁶-3,4-*trans*-tetrahydrocannabinol (3) (20% yield. *Anal.* Found: C, 80.40; H, 9.82). This latter compound was identical in all respects (nmr, ultraviolet, infrared) except optical activity with the natural product isolated from hemp.[4,7] The former compound (5) was identical with a sample of 5 prepared independently by an unequivocal route.[4]

When the condensation of citral with olivetol was carried out under milder acidic conditions (0.0005 N hydrochloric acid in ethanol), the first compound eluted from the Florisil column was *dl*-Δ¹-3,4-*cis*-tetrahydrocannabinol (4) (12% yield. *Anal.* Found: C, 80.49; H, 9.88), followed by impure 4 (∼25% yield) containing (by nmr) some *dl*-Δ¹-3,4-*trans*-tetrahydrocannabinol (1) (*vide infra*). The establishment of 4 as a Δ¹ isomer was indicated by the 6.33 ppm resonance line of the olefinic alicyclic proton (H-2). It can be seen from Table I, in which the nmr spectra of all four isomeric tetrahydrocannabinols (1, 3, 4, and 5) are summarized, that the olefinic H-2 proton in the Δ¹ series is considerably deshielded with respect to the olefinic proton in the Δ⁶ series. This is reasonable since the H-2 proton is subjected to an induced diamagnetic field arising from the aromatic ring; by contrast, the H-6 olefinic proton is completely removed from this environment. Assignment of *cis* stereochemistry to the ring fusion in compound 4 follows from a comparison of the band width of the signal at 3.59 ppm due to the H-3 proton (11 cps

Table I. Summation of Nmr Spectra[a] of Tetrahydrocannabinols

Type of proton	Δ¹-3,4-*trans*	Δ⁶-3,4-*trans*	Δ¹-3,4-*cis*	Δ⁶-3,4-*cis*	6
Aromatic	6.12 (d) (1)	6.12 (d) (1)	6.14 (d) (1)	6.13 (d) (1)	6.28 (br) (2)
	6.32 (d) (1)	6.32 (d) (1)	6.27 (d) (1)	6.31 (d) (1)	
Olefinic (C-2 or C-6)	6.42 (br) (1)	5.45 (br) (1)	6.33 (br) (1)	4.19 (br) (1)	5.42 (br) (2)
C-3	3.14 (br d) (1)	3.25 (br d) (1)	3.59 (br) (1)		3.1–3.7 (br) (2)[b]
Olefinic -CH₃	1.65 (s) (3)	1.70 (s) (3)	1.68 (s) (3)	1.94 (s) (3)	1.65 (s)[c]
gem di-CH₃	1.08 (s) (3)	1.11 (s) (3)	1.24 (s) (3)	1.36 (s) (3)	1.35 (s)
	1.38 (s) (3)	1.38 (s) (3)	1.40 (s) (3)	1.69 (s) (3)	
ω-CH₃	0.88 (t) (3)	0.88 (t) (3)	0.89 (t) (3)	0.89 (t) (3)	0.89 (t) (3)

[a] All spectra were determined on a Varian A-60 spectrometer in DCCl₃ solution. Values are given in parts per million relative to TMS as internal standard; s, singlet; d, doublet; t, triplet; br, broad. [b] A contribution to this signal is from the aliphatic proton α to oxygen. [c] The methyl signals in this compound cannot be assigned unequivocally.

organic phase on Florisil, and elution with hexane, gave as the first eluted product the tetrahydrocannabinol derivative 6 (10–20% yield. *Anal.* Calcd for $C_{31}H_{44}O_2$: C, 82.98; H, 9.89. Found: C, 82.38; H, 9.85). In agreement with the proposed structure, the nmr spectrum of 6 indicated a 1:1 ratio of olefinic to aromatic protons. A broad signal at 3.1–3.7 ppm, integrating for two protons, was assigned to H-3 and to

at half-height, unresolved) with the signal due to the H-3 proton in the known Δ¹-3,4-*trans* isomer 1 (3.14 ppm, 20 cps at half-height, unresolved).

(6) The position of the cyclohexene double bond and the stereochemistry of the ring fusion (*trans*) follow from arguments presented in support of the structure assigned to 4 (*vide infra*).

(7) We are indebted to Professor W. A. Mosher and Mr. R. Hively for the opportunity to make this direct comparison of our synthetic material with the natural product.

It appears that the condensation of citral with olivetol under acidic conditions gives an initial mixture of the Δ^1 isomers (**1** and **4**) which then rearrange to the Δ^6 isomers, with **1** rearranging more readily than **4**. In confirmation of this assumption, we have been able to show that **4** is indeed isomerized by boron trifluoride etherate to **5**; it is known that **1** isomerizes similarly under milder acidic conditions to **3**.[4] Separation of the natural Δ^1-3,4-*trans* isomer (**1**) from the Δ^1-3,4-*cis* isomer (**4**) by chromatography was not possible in our hands; separation by vpc was frustrated by facile thermal isomerization of **1** to **3**. We could show independently that pure **1**[8] was partially converted to **3** after one pass through a vapor phase partition chromatograph (column, 10% GE-SE30 on Diatoport S; gas, helium; oven temperature, 280°). Indeed, in view of this demonstrably facile heat isomerization, it seems possible that the physiological effects attendant upon smoking of hashish, now ascribed to the Δ^1 isomer, may in actuality be due to the Δ^6 isomer.

(8) We are indebted to Professor W. A. Mosher and Mr. R. Hively for a generous sample of pure **1**, isolated from hemp.

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A Method for Relating Rates of Interconversion and Destruction of Classical Carbonium Ions[1]

Sir:

How fast do equilibrating, classical ions interconvert with respect to the rates with which they react with entering groups or eject protons? This question goes to the heart of the debate[2-5] over nonclassical ions. Cram[3] implies, without saying why, that a factor of 100 in favor of phenyl migration would be too great for acetolysis, through classical ions, of *threo*-3-phenyl-2-butyl tosylate. Winstein[2] argues that a factor of 2000 in favor of interconversion of classical norbornyl ions would cause the rate of interconversion to exceed kT/h in the absolute rate equation.

The question is not easily answered, for we seek a ratio of two rates, the absolute values of which are unknown, and which can, conceivably, fluctuate over wide ranges. In addition, a determination of this ratio by ordinary[6] means strains the limits of experimental error for normal polarimetric, stoichiometric, or isotopic tracer techniques.

We attacked the problem first by studying reactions which are known[7] to proceed through equilibrating, classical ions, and outline here an approach which circumvents the need for extraordinary experimental precision.

Dehydration of either 1-*p*-tolyl-2,2-diphenylethanol

(1) This research was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.
(2) S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).
(3) D. J. Cram, *ibid.*, **86**, 3767 (1964).
(4) C. J. Collins, B. M. Benjamin, and M. H. Lietzke, *Ann.*, **687**, 150 (1965).
(5) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965).
(6) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965), for example, measured the racemization of *exo*-norbornyl acetate with a precision they state to be within ±0.05%.
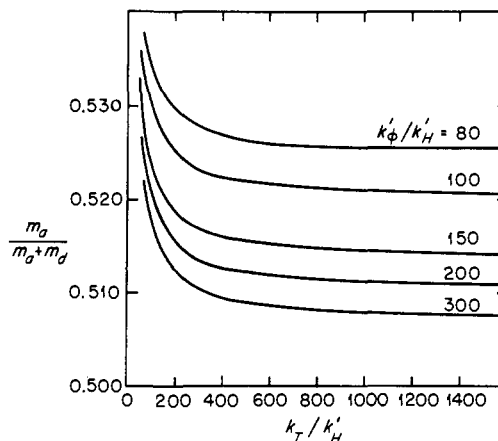(7) C. J. Collins and W. A. Bonner, *ibid.*, **77**, 92, 6725 (1955).

Figure 1. Plot of carbon-14 distribution in **3** *vs.* k_T/k'_H (Chart I) in the reaction **1** → **3** (76.0%) and **4** (24.0%).

(**1**) or 1,2-diphenyl-2-*p*-tolylethanol (**2**, *erythro* or *threo* forms) in boiling formic acid (containing a trace of *p*-toluenesulfonic acid) produces the olefins **3** and **4** (two geometrical isomers obtained in equal amounts) in yields of 76.0 and 24.0%, respectively. By the use of a carbon-14 label, the four ions a–d (Chart I) can be recognized, and these go irreversibly

Chart I
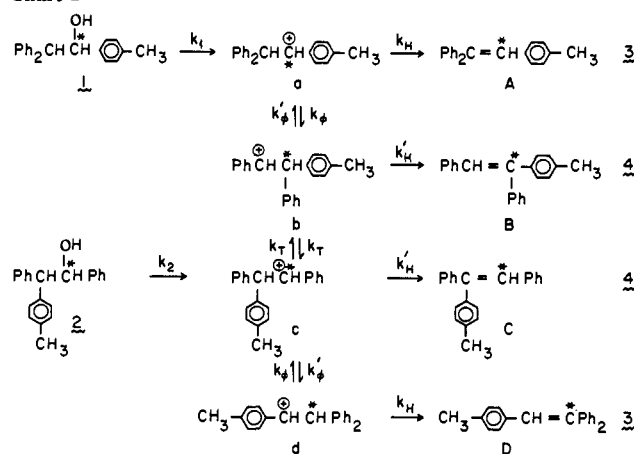
to olefins **3** and **4** through paths A–D.[8] By a method previously reported,[4] eq 1–4 were derived. These

$$\frac{k_\phi}{k_H}m_a + \frac{k_T}{k'_H}m_c = m_b\left[\frac{k'_\phi}{k'_H} + \frac{k_T}{k'_H} + 1\right] \quad (1)$$

$$\frac{k_T}{k'_H}m_b + \frac{k_\phi}{k_H}m_d = m_c\left[\frac{k_T}{k'_H} + \frac{k'_\phi}{k'_H} + 1\right] \quad (2)$$

$$\frac{k'_\phi}{k'_H}m_c = m_d\left[\frac{k_\phi}{k_H} + 1\right] \quad (3)$$

$$\frac{k_\phi}{k_H}(m_a + m_d) = (m_b + m_c)\left[\frac{k'_\phi}{k'_H} + 1\right] \quad (4)$$

equations exactly describe the mechanism given in Chart I for the dehydration of **1**. Equation 4 relates the ratio $k'_\phi/k'_H : k_\phi/k_H$ to the yields of the two olefins, and the extent of carbon-14 rearrangement in **3** and **4** determines the mole fractions m_a, m_b, m_c, m_d

(8) Although the ions a–d yield formate esters reversibly, all functions describing these processes cancel in the derivation of eq 1–4.