fusion controlled. These conclusions, if true, would be of considerable importance in our attempts to understand the behavior of excited states. However, they were apparently based on the assumption that photoreduction of acetone proceeds with negligible quantum efficiency. The data to be described do not support this assumption, and permit reasonable alternatives to Borkman and Kearns' conclusions.

Degassed hexane solutions containing 1.0 *M* acetone, 0.02 *M* benzene as internal standard, and various concentrations (0 to 0.0015 *M*) of 2,5-dimethyl-2,4-hexadiene were irradiated at room temperature at 3130 A to less than 2% conversion. Relative quantum yields of 2-propanol formation were determined by glpc analysis. A Stern–Volmer plot of $\phi_0/\phi$ values was linear with a slope, representing $k_q\tau_T$, of 9400 $M^{-1}$. With $1 \times 10^{10}$ $M^{-1}$ sec$^{-1}$ as the rate constant, $k_q$, for diffusion-controlled quenching in hexane,[5] the lifetime of triplet acetone, $\tau_T$, calculated from these experiments, is $0.94 \times 10^{-6}$ sec, in excellent agreement with the values $1 \times 10^{-6}$ sec determined by Borkman and Kearns[4] and $0.8 \times 10^{-6}$ sec measured by Wilkinson and Dubois[6] in studies of the acetone-sensitized phosphorescence of biacetyl.

The lifetime of an excited state is, of course, the reciprocal of the sum of the rates of all processes, both physical and chemical, which destroy it, in this case hydrogen abstraction from solvent and radiationless decay

$$\tau_T = 1/(k_H[SH] + k_d)$$

The sensitization studies in the literature provide no means for apportioning the relative importance of the two processes. In order to actually measure the quantum yield of photoreduction, degassed hexane solutions 0.24 *M* in acetone and 0.08 *M* in fluorobenzene were irradiated at 3130 A in parallel with degassed hexane solutions 0.20 *M* in 2-hexanone and 0.20 *M* in chlorobenzene. Relative quantum yields of disappearance of the two ketones and of appearance of 2-propanol were again determined by glpc analysis. Assuming a quantum yield of 0.50 for photolysis of 2-hexanone in solution,[7,8] the quantum yields for acetone disappearance and 2-propanol appearance were found to be 0.80 and 0.42, respectively. Several long retention time peaks on the glpc traces of the acetone–hexane system revealed the expected[2] formation of pinacol and various hexyldimethylcarbinols and bihexyls.

The important point of the present experiments is that 80% of the decay of triplet acetone in hexane occurs by hydrogen abstraction from the solvent, yielding estimates of $8 \times 10^5$ and $2 \times 10^5$ sec$^{-1}$ for $k_H$[SH] and $k_d$, respectively.

Borkman and Kearns[4] found that $k_q\tau_T$ for the acetone–2-pentene system is approximately 10 $M^{-1}$ in hexane, heptane, 3-methylpentane, and methanol, but five times larger in concentrated acetone. Moreover, they found no difference for acetone-$d_6$. We thus have to explain the constancy of $\tau_T$[9] for the first four solvents and the increase in $k_q\tau_T$ in acetone.

From Walling and Gibian's data,[8] it is possible to state that triplet acetone would abstract hydrogen from the three hydrocarbons at virtually indistinguishable rates. The exact reactivity of methanol has not been ascertained, but, by analogy with the behavior of alkoxy radicals, its reactivity is probably on the same order as that of the three alkanes. However, because of its electron-withdrawing carbonyl group, acetone is a very poor hydrogen donor toward electrophilic species such as ketone triplets.[8] Therefore, probably the entire increase in $k_q\tau_T$ in pure acetone can be attributed to the greater triplet lifetime in this unreactive solvent and not to an enhanced value of $k_q$ such as Borkman and Kearns[4] suggested.

The value of $2 \times 10^5$ sec$^{-1}$ for the rate of radiationless decay of triplet acetone in solution is very similar to the values found for triplet benzophenone in benzene[10] and triplet acetophenone in isopropyl alcohol.[11] Borkman and Kearns[4] presented a very good discussion as to why this value is probably intrinsic and not due to impurity quenching. Their conclusion that acetone-$d_6$ has the same triplet lifetime is readily understood, since most of its decay occurs by chemical reaction. Any change in the rate of the minor radiationless decay process could have been lost in experimental error. More likely, the rapid rate of radiationless decay of excited triplet species at room temperature in solution involves vibrational coupling with solvent C–H bonds and not with those of the excited species.

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(5) A manuscript describing the effect of solvents on quenching rates is in preparation.

(6) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

(7) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 398.

(8) 2-Hexanone was employed as an actinometer rather than more conventional systems because its absorption spectrum is so similar to that of acetone.

(9) The viscosities of these solvents are all similar; hence $k_q$ would be expected to have an almost identical value in each.

(10) J. A. Bell and J. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).

(11) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *ibid.*, **86**, 3060 (1964).

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## Concerning the Isomerization of $\Delta^1$- to $\Delta^{1(6)}$-Tetrahydrocannabinol[1]

*Sir:*

The acid-catalyzed isomerization of $\Delta^1$-3,4-*trans*-tetrahydrocannabinol ($\Delta^1$-3,4-*trans*-THC) (Ia),[2] the major psychotomimetic principle in hashish, to $\Delta^{1(6)}$-3,4-*trans*-THC (IIa)[3] is well documented.[3c,e] In a recent communication Taylor, *et al.*,[3d] have reported the synthesis of *dl*-$\Delta^1$-3,4-*cis*-THC (IIIa) and have claimed that this compound is similarly isomerized to *dl*-$\Delta^{1(6)}$-3,4-*cis*-THC (IVa). We wish to point out that the compound described as IVa possesses in fact structure V, for which we suggest the name $\Delta^{4(8)}$-iso-THC.[4]

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(1) Hashish. IX. For part VIII see Y. Gaoni and R. Mechoulam, *Chem. Commun.*, 20 (1966).

(2) (a) Y. Gaoni and R. Mechoulam, *J. Am. Chem. Soc.*, **86**, 1646 (1964); (b) R. Mechoulam and Y. Gaoni, *ibid.*, **87**, 3273 (1965); (c) K. E. Fahrenholtz, M. Lurie, and R. W. Kierstead, *ibid.*, **88**, 2079 (1966).

(3) (a) R. Adams, C. K. Cain, W. D. McPhee, and R. B. Wearn, *ibid.*, **63**, 2209 (1941); (b) H. Budzikiewicz, R. T. Alpin, D. A. Lightner, C. Djerassi, R. Mechoulam, and Y. Gaoni, *Tetrahedron*, **21**, 1881 (1965); (c) Y. Gaoni and R. Mechoulam, *ibid.*, **22**, 1481 (1966); (d) E. C. Taylor, K. Lenard, and Y. Shvo, *J. Am. Chem. Soc.*, **88**, 367 (1966); (e) R. Hively, W. A. Mosher, and F. Hoffmann, *ibid.*, **88**, 1832 (1966).

(4) Taylor, *et al.*,[3d] report that IVa (now shown to be V) has been prepared also by Hively, Hoffmann, and Mosher *via* an as yet unpublished

The nmr spectrum published[3d] and confirmed by us[5] is more compatible with structure V than with IVa.[6] The following revised assignments can be made: $\delta$ ($CDCl_3$)[7] 1.94 (s) and 1.69 (s) (two olefinic methyl groups), 1.36 (s) (one methyl group $\alpha$ to an oxygen atom), and 4.19 (br) (C-3 proton). The allylic benzylic C-3 proton in V is nearly in the plane of the aromatic ring and is therefore strongly deshielded.[8]

Hydrogenation of IIIa and V gave in each case a mixture of two isomers which were separated on Florisil.[10] The dihydro-V isomers were different from the dihydro-IIIa isomers and from the known dihydro-Ia isomers.[3c,11] The chromatographically more polar dihydro-V (isomer B) was, however, identical,[11] except for optical activity, with the reduction product of (−)-$\Delta^8$-iso-THC (VI).[12] The nmr spectrum of isomer B contains the isopropyl splitting as two doublets ($\delta$ 0.92 and 1.07; $J$ = 6.5 cps), while in the spectrum of the chromatographically less polar isomer A it appears as one broader doublet ($\delta$ 0.75; $J$ = 5 cps).

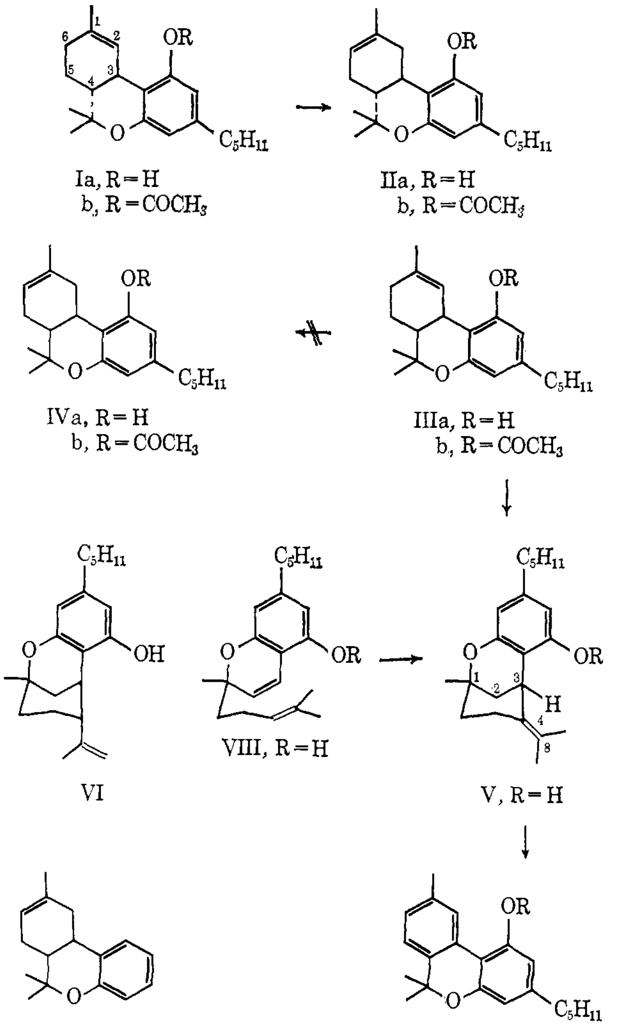
Acid treatment of (−)-$\Delta^1$-3,4-*trans*-THC acetate (Ib) gives (−)-$\Delta^{1(6)}$-3,4-*trans*-THC acetate (IIb), while *dl*-$\Delta^1$-3,4-*cis*-THC acetate (IIIb) is stable under identical (or more drastic) acidic conditions, in contrast to the isomerization of the free phenol IIIa. If acid-catalyzed isomerization of $\Delta^1$- to $\Delta^{1(6)}$-THC took place in both the *cis* and *trans* series as suggested,[3d] the yet unknown *dl*-$\Delta^{1(6)}$-3,4-*cis*-THC acetate (IVb) should have been obtained from IIIb.

The facile double bond isomerization in the *trans* series can be explained by decrease in steric strain. The nonbonded interactions between the phenolic group and the C-2 protons in the *trans*-$\Delta^{1(6)}$ compounds (IIa and IIb) are considerably smaller than those between the phenolic group and the C-2 proton in the *trans*-$\Delta^1$ compounds (Ia and Ib). In the *cis* series a driving force of this type would be very small, or nonexistent, for steric reasons.[13]

Boiling cannabichromene (VIII)[1,14] in benzene in the presence of *p*-toluenesulfonic acid gave partially synthetic V (in 80% yield), the infrared, nmr, and ultraviolet spectra of which were identical with those of the totally synthetic product. Ollis, *et al.*,[9] have recently described the closely related isomerization of gambogic to gamboginic acid.

On dehydrogenation with sulfur V gave cannabinol (IX). On mechanistic grounds this reaction is not exceptional.

Taylor[3d] has reported that the isomerization of $\Delta^1$-3,4-*trans*-THC (Ia) to the $\Delta^{1(6)}$ isomer (IIa) takes place also on a vapor phase chromatograph at 280°. In view of this reaction, which is considered to be thermal, it is suggested that "the physiological effects attendant upon smoking of hashish now ascribed to the $\Delta^1$ isomer may in actuality be due to the $\Delta^6$ isomer." In our hands on a different column (SE-30 on Chromosorb W, up to 300°) no such isomerization takes place. The $\Delta^1$ isomer (Ia) was collected unchanged (infrared, tlc) after passage through the column. Several instances of isomerization of terpenes on vpc have been reported.[15] The resulting products are those experimentally produced on acid isomerization and have been attributed to the column support.[15] It is hence doubtful whether on smoking of marihuana or hashish by means of cigarettes or narghiles, which are probably chemically neutral, the $\Delta^1$ isomer is converted into the $\Delta^{1(6)}$ isomer.



Ia, R = H
b, R = $COCH_3$

IIa, R = H
b, R = $COCH_3$

IVa, R = H
b, R = $COCH_3$

IIIa, R = H
b, R = $COCH_3$

VI

VIII, R = H

V, R = H

VII

IX, R = H

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route. The compound as prepared by both groups has been found to be identical by direct comparison.[3d]

(5) We have prepared compounds IIIa and V according to the published procedure[3d] and have found V to be identical with a sample[4] generously sent to us by Professor Mosher, to whom we are grateful.

(6) For example, the signal at $\delta$ 4.19 is assigned to an olefinic proton. Such an unusually strong shielding effect cannot be expected in IVa. The signal for the C-3 proton is missing entirely.

(7) Determined on a Varian A-60 spectrometer. Values are given in parts per million relative to $(CH_3)_4Si$ as an internal standard. Letters denote broad (br), singlet (s), triplet (t).

(8) These nmr assignments are similar to those reported for monomethylgamboginate,[9] which possesses a chemical moiety closely related to V.

(9) W. D. Ollis, M. V. J. Ramsey, I. O. Sutherland, and S. Mongkolsuk, *Tetrahedron*, **21**, 1453 (1965).

(10) Satisfactory analytical data have been obtained for all new compounds.

(11) Infrared, nmr, and mass spectral comparisons.

(12) The structure of compound VI which was previously only tentatively put forward[3c] has been confirmed by chemical transformations and mass spectral data, and will be discussed in the full paper.

(13) The facile cyclization of the free phenol in the *cis* series at the C-1 carbon puts in doubt the structure (VII, 3,4-*cis*) put forward for a synthetic model compound prepared through a reaction sequence the last step of which involves acidic cyclization [E. C. Taylor and E. J. Strojny, *J. Am. Chem. Soc.*, **82**, 5198 (1960)].

(14) V. Claussen, F. V. Spulak, and F. Korte, *Tetrahedron*, **22**, 1477 (1966).

(15) W. J. Zubyk and A. Z. Conner, *Anal. Chem.*, **32**, 912 (1960).

**Acknowledgment.** We are indebted to Dr. E. Gil-Av for stimulating discussions concerning vapor phase chromatography.

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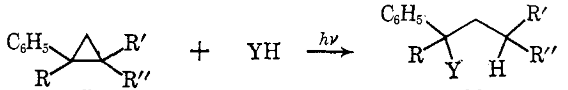
## Heterolytic Photocleavage of Cyclopropanes

*Sir:*

Previous communications from our laboratories have described a number of photochemical reactions of cyclopropanes including *cis–trans* isomerization,[1] rearrangement to olefins and indans,[1a,2,3] and fragmentation to carbenes,[4] all presumably by homolytic mechanisms. We now wish to report the first unequivocal examples of a new photochemical reaction, the addition of protic compounds, YH, such as methanol, acetic acid, and water, to ordinary cyclopropanes I in *ionic* fashion to give substituted propanes II.



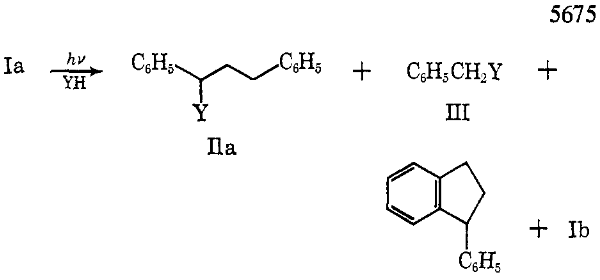
I II

a, R = R′ = H; R″ = $C_6H_5$
b, R = R″ = H; R′ = $C_6H_5$
c, R = R′ = $C_6H_5$; R″ = H

Y = OMe, OAc, or OH

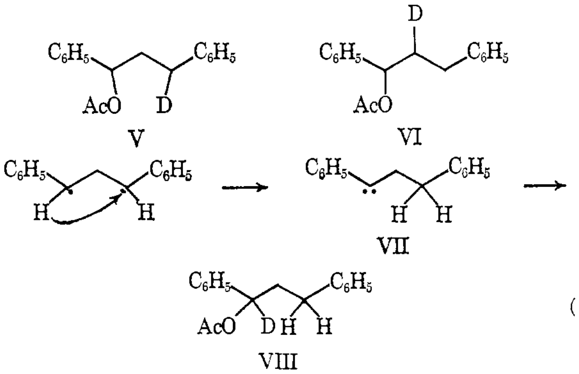
When a 0.1 *M* solution of *trans*-1,2-diphenylcyclopropane (Ia)[5] in methanol was irradiated[6] the major product (40 ± 3%) was 1,3-diphenyl-1-propyl methyl ether (IIa, Y = OMe), $\nu_{\max}^{CS_2}$ 2815 (w) and 1100 (vs) (OMe), 1025 (m), 960 (m), 902 (m), 760 (s), 740 (vs), and 695 cm$^{-1}$ (vs), identified by infrared, nmr, and elemental analysis and by independent synthesis.[7] Also present were benzyl methyl ether (III, Y = OMe; 2%) undoubtedly formed from phenylcarbene,[4] 1-phenylindan (IV; 12%), *cis*-1,2-diphenylcyclopropane (Ib; 2%), and Ia (6%).[1a,2] In the absence of light methanol did not react with 1,2-diphenylcyclopropane.

1,3-Diphenyl-1-propyl acetate (IIa, Y = OAc) was obtained (20% conversion) together with benzyl acetate (3%, from phenylcarbene) and other products when acetic acid was employed as the solvent. The transformation must be entirely photochemical since Ia was unaffected by heating to 190° in acetic acid for 23 hr. Acetate IIa (Y = OAc) was identical with a synthetic sample[8] in all respects, and its structure was consistent with its infrared ($\nu_{\max}^{CS_2}$ 1735 and 1230 cm$^{-1}$) and nmr spectra. The latter was distinguished by a triplet centered at $\tau^{CCl_4}$ 4.29 (one proton, $J$ = 11 cps), singlets at $\tau$ 2.75 and 2.88 (five protons each), and a complex multiplet at $\tau$ 7.2–8.3 (seven protons).



IV

Two possible pathways from I to IIa were excluded by examining the nmr spectrum of the acetate isolated from a similar irradiation in deuterioacetic acid. The infrared spectrum of the resulting acetate closely resembles that of IIa (Y = OAc) but possesses an additional peak at 2150 cm$^{-1}$ (m) (C–D). The nmr spectrum exhibited a triplet (one proton) identical with that which characterizes the benzylic proton adjacent to oxygen in the undeuterated acetate. The presence of this triplet together with the decrease in relative area of the $\tau$ 7.2–8.3 multiplet to six protons forces the conclusion that deuterium addition occurred at $C_3$ as formulated in structure V. Preliminary mass spectral data are also compatible with this interpretation.

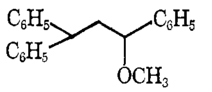


(1)

Thus, deuterioacetic acid did not react with 1,3-diphenylpropene (a known irradiation product of Ia[1a]), which would have given VI, nor with conceivable[9] carbene VII, the addition product of which would have been VIII (eq 1).

Irradiation of a supersaturated 0.1 *M* solution of Ia in an equimolar water–acetic acid mixture gave propanol IIa (Y = OH; *ca.* 12%),[10] identical with the alcohol obtained by reaction of hydrocinnamaldehyde with phenylmagnesium bromide; $\nu_{\max}^{CS_2}$ 3535, 3330, 1050, 905, 740, 695, and 530 cm$^{-1}$.

1,1,2-Triphenylcyclopropane (Ic) was irradiated in methanol to find out whether the methoxy group would add preferentially at the benzhydrylic carbon to give IIc or at the benzylic carbon to yield IX. The former



IX

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[1] (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem. Soc.*, **87**, 1410 (1965); (b) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *ibid.*, **85**, 1001 (1963).

[2] G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Letters*, 2951 (1965).

[3] H. Kristinsson and G. W. Griffin, *ibid.*, 3259 (1966).

[4] H. Kristinsson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind.* (London), 1562 (1966).

[5] S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952); R. M. Dodson and G. Klose, *Chem. Ind.* (London), 450 (1963); We thank Professor Dodson for generous samples of Ia and Ib with which this study was initiated. Ia containing 17% *cis* isomer Ib was used in most experiments.

[6] Unless stated otherwise, 0.1 *M* solutions in quartz tubes were carefully degassed and irradiated for 24 hr at 30° in a Rayonet chamber reactor (Southern New England Ultraviolet Company, Middletown, Conn.) equipped with 16 8-w low-pressure mercury lamps; products were isolated and yields determined by glpc on a 2 m × 0.6 cm i.d. silicone grease column using methyl laurate as an internal standard. No attempt was made to find optimum conditions.

[7] Prepared from III (R = OH) by a Williamson synthesis. *Cf.* A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 3723 (1953).

[8] L. F. Hewitt and J. Kenyon, *J. Chem. Soc.*, **127**, 1094 (1925).

[9] The hypothetical reaction leading to VIII is the reverse of the well-known hydrogen abstraction process known to occur with arylcarbenes; it has not yet been observed. See W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 86.

[10] A heavy precipitate formed on the walls during irradiation, and yields of IIa (Y = OH and OAc) were erratic.