The results obtained here confirm further the correctness of the structure of tyrocidine A given as I_n by Craig, *et al.*[20]

Work on syntheses of the cyclic decapeptides corresponding to the proposed structures for tyrocidine B[4] and C[5] is in progress in this laboratory.

(20) This work will be described in full in *Bull. Chem. Soc. Japan.*

Motonori Ohno, Nobuo Izumiya
Laboratory of Biochemistry, Faculty of Science
Kyushu University, Fukuoka, Japan

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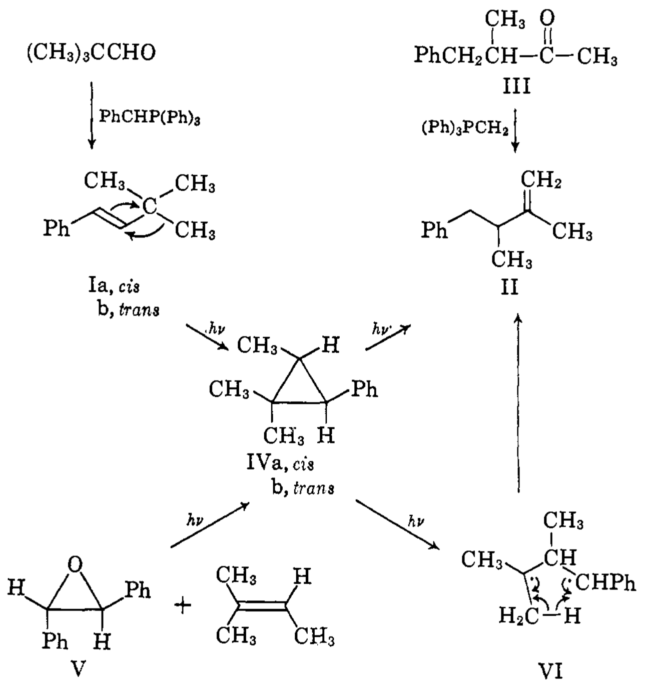
Photocyclization of 3,3-Dimethyl-1-phenylbutene-1. A Novel Photoinduced 1,2-Methyl Migration

Sir:

We wish to report the first example of a photoinduced 1,2-methyl migration in a simple hydrocarbon system.[1] Recent work on the photocyclization of propenes (which proceed with phenyl and/or hydrogen migration)[2] led us to believe that 1,2-alkyl migrations might be induced photochemically in such systems despite the absence of any confirmed reports of ground-state homolytic reactions of this type.[3] Comparatively little "ionic" character may be attributed to the π,π^* singlet and triplet states of alkyl- and aryl-substituted propenes. Presumably, then, the photochemistry of these hydrocarbons should approximate the unknown ground state homolytic processes more closely than the corresponding n,π^* reactions.[1]

A mixture (1.3:1) of *cis*- and *trans*-3,3-dimethyl-1-phenylbutene-1 (Ia and Ib, respectively) was synthesized by condensation of trimethylacetaldehyde[4] with the ylid prepared from benzyltriphenylphosphonium bromide and phenyllithium (63% yield); Ia: $\nu_{\max}$ (cm^{-1}) 3060, 2960, 2870, 1600, 1475, 1360, 1230, 1200, 1070, 1028, 935, 918, 898, 828, 752, 698, and 660; $\lambda_{\max}$ 220 mμ (ϵ 6400); nmr τ 2.90 (5 H singlet), 3.54 and 3.75 (1 H doublet), 4.38 and 4.60 (1 H doublet), and 9.05 (9 H singlet); Ib: $\nu_{\max}$ (cm^{-1}) 3030, 2960, 2900, 2870, 1360, 1266, 1203, 1070, 1026, 966, 744, and 690; $\lambda_{\max}$ 251 mμ (ϵ 18,100);[5] nmr τ 2.83 (5 H multiplet), 3.83 (2 H singlet), and 8.91 (9 H singlet). The assignment of *cis* stereochemistry to Ia and *trans* stereochemistry to Ib was made on the basis of the following spectroscopic evidence. The *trans* isomer Ib exhibits the characteristic out-of-plane deformation band for the vinyl hydrogens at 966 cm^{-1}. The ultraviolet spectra of Ia and Ib support this assignment. The $\lambda_{\max}$ of Ia is displaced approximately 20 mμ toward shorter wavelength than that of Ib, as might be anticipated. Furthermore, the *t*-butyl protons in the nmr spectrum of Ib are found at lower field than those of Ia, in agreement with prediction. A photoequilibrium between Ia and Ib is established rapidly under the irradiation conditions, and therefore separation was deemed unnecessary. Irradiation[6] of I in benzene (0.1 *M*) for 70 hr afforded almost exclusively 2,3-dimethyl-4-phenylbutene-1 (II).



Identification of the photoproduct II, $\nu_{\max}$ (cm^{-1}) 3080, 3065, 3025, 2970, 2930, 1635, 1600, 1485, 1450, 1370, 1112, 1100, 1078, 1030, 890, 757, 736, 720, and 698; nmr τ 2.95 (5 H singlet), 5.37 (2 H singlet), 7.67–7.17 (3 H multiplet), 8.33 (3 H singlet), and 9.00 and 9.10 (3 H doublet), was achieved by comparison with an authentic sample prepared by condensation of triphenylmethylenephosphorane with 3-methyl-4-phenylbutanone-2 (III).[7]

The primary products in this photoreaction are presumably *cis*- and *trans*-2,2,3-trimethyl-1-phenylcyclopropane (IVa and b, respectively), whose presence in the irradiation mixtures is apparent from comparisons of gas chromatographic retention times. However, variation of the concentration and irradiation time did not permit maximization of the concentration of IVa and IVb to isolable levels.

Our conclusion that IVa and IVb are intermediates in the conversion of I to II is supported by the observation that the isomeric cyclopropanes (IVa and IVb) are *completely* converted to the olefin II after only 24-hr irradiation in benzene (0.1 *M*). It is clear in view of this result why the cyclopropanes do not accumulate upon photolysis of I. IVa and IVb were synthesized

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[1] A methyl migration accompanying photochemical ring opening of an epoxy ketone has been reported; see H. E. Zimmerman, B. R. Crowley, C. Y. Tseng, and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 947 (1964); see also C. K. Johnson, B. Dominy, and W. Reusch, *ibid.*, **85**, 3894 (1963); C. Lehmann, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 45, 1031 (1962).

[2] G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Letters*, **34**, 2951 (1965); G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem. Soc.*, **87**, 1410 (1965).

[3] C. Walling in "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 416.

[4] H. C. Brown, H. I. Schlesinger, and A. B. Burg, *J. Am. Chem. Soc.*, **61**, 673 (1939).

[5] Infrared spectra were determined as neat films on a Perkin-Elmer Model 337 infrared spectrophotometer while ultraviolet spectra were obtained in 95% ethanol on a Model 202 ultraviolet–visible spectrophotometer.

[6] An air-cooled (40°) Rayonet chamber reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 8-w low-pressure mercury lamps was employed as a light source. All solutions were rigorously degassed. Gas chromatographic analyses and separations were conducted on a 210 × 0.6 cm i.d. glass column packed with 30% silicone gum (SE-30) on 60–80 mesh acid- and base-washed Chromosorb P. Satisfactory elemental analyses were obtained on all new compounds.

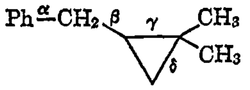
[7] C. Harries and G. H. Müller, *Ber.*, **35**, 966 (1902).

conveniently in high yield by irradiating stilbene oxide (0.3 *M*)[8] in neat 2-methyl-2-butene for 50 hr. Both IVa and IVb had been prepared previously from 2-methyl-2-butene, benzal bromide, and methyllithium.[9] However, the generation of arylcarbenes by photofragmentation of epoxides in the presence of alkenes currently appears to be the method of choice for the synthesis of aryl-substituted cyclopropanes.[10] It should be noted that, in spite of the photoinstability of IVa and IVb in benzene, they may be prepared in very high yield photochemically from IV without formation of substantial amounts of II if the conditions described above are employed.

It is assumed that the conversion of I to IV occurs in a concerted fashion with methyl migration accompanying cyclization. A mechanism involving formation of a common transitory intermediate (perhaps related to VI; *vide infra*) which collapses to II directly or alternatively to IVa and IVb cannot be excluded, however, even though a pathway exists for facile conversion of IV to II.

If II is indeed the primary photolysis product of IVa and IVb it is inviting to propose that a hydrogen atom is transferred in a cyclic five-membered transition state (VI) accompanying cleavage of the cyclopropane ring. Such intramolecular hydrogen migrations have been[11] proposed in related n,π* and π,π* excited states and would account for the seemingly unfavorable 1,4 transfer of a *primary* hydrogen atom in this case as well as in four other related alkyl-substituted phenylcyclopropyl systems.[12]

The formation of II could be rationalized by homolysis of the γ bond of the cyclopropane VII (formally derived from I by an unprecedented 1,4-hydrogen shift), subsequent hydrogen transfer, and cyclization. This alternate mechanism for the conversion of I to II without methyl migration has been considered and rejected for the following reasons. Photolysis of cyclopropylphenylmethane in the vapor phase, studied by Leermakers and co-workers,[13] gave a complicated spectrum of products together with extensive formation of polymer. No rearrangement to isomeric hydrocarbons was observed. Photochemical transformation of cyclopropylphenylmethane or its alkyl derivatives in solution is unknown and unlikely. Furthermore, the δ bond, in closer proximity to the chromophore, would certainly, in case of homolysis, cleave in preference to the γ bond.



VII

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H. Kristinsson, G. W. Griffin
Departments of Chemistry
Tulane University and Louisiana State University
in New Orleans, New Orleans, Louisiana
Received October 25, 1965

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[8] A. C. Cope, P. A. Trumbull, and E. R. Trumbull, *J. Am. Chem. Soc.*, **80**, 2844 (1958).

[9] G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964).

[10] H. Kristinsson and G. W. Griffin, *Angew. Chem.*, **77**, 859 (1965).

[11] M. J. Jorgenson and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 1698 (1963); J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964), and references cited therein.

[12] H. Kristinsson and G. W. Griffin, unpublished results.

[13] P. A. Leermakers and G. F. Vesley, *J. Org. Chem.*, 30, 539 (1965).

Synthetic Studies on Insect Hormones. I. Synthesis of the Tetracyclic Nucleus of Ecdysone[1]

Sir:

The insect hormone ecdysone[2] has been shown recently by X-ray study to have the structure and stereochemistry represented by Ia.[3] The first synthesis of the complete tetracyclic skeleton of this vital compound from readily available starting materials is the subject of this communication.

3β-Acetoxy-23,24-bisnorchol-5-en-22-oic acid methyl ester[4] was prepared in quantity from 3β-hydroxy-23,24-bisnorchol-5-en-22-oic acid by successive acetylation, then methylation with diazomethane. *trans* hydroxylation of the double bond according to the Fieser procedure[5] followed by mild methanolic sodium hydroxide hydrolysis of the 3β-acetate function led to 3β,5α,6β-trihydroxy-23,24-bisnorcholan-22-oic acid methyl ester (IIa; mp 232–234°, $[\alpha]_D$ −17°). The 6-ketone IIb (mp 227–229°, $[\alpha]_D$ −49°) was obtained from the triol IIa by selective oxidation with N-bromosuccinimide in aqueous dioxane.[5] The derived tosylate IIc (mp 153–155°, $[\alpha]_D$ −62°) underwent elimination on treatment with lithium carbonate–dimethylacetamide to furnish the desired 6-keto-5α-hydroxy-23,24-bisnorchol-2-en-22-oic acid methyl ester (III; mp 149–151°, $[\alpha]_D$ −27°) in 50% over-all yield by the seven-step sequence from the starting acid.[6]

cis hydroxylation of the olefin III with silver acetate and iodine in moist acetic acid[7] led to an amorphous triol IId which was converted by conventional methods (acetic anhydride–pyridine) to the corresponding diacetate IIe (mp 251–253°, $[\alpha]_D$ −52°). The 19-proton resonance frequency of the latter ($\nu_{19\text{-H}}$ 61 cps) confirmed β-face hydroxylation.[8] Bromination of the 6-ketone IIe under acid catalysis (Br_2–HBr–AcOH) afforded a monobromo analog (IIe, 7α-bromo; mp 195–196.5°, $[\alpha]_D$ +4°, λ_{max} 332 mμ (ε 120)). Dehydrobromination with lithium carbonate–dimethyl-

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[1] Steroids. CCXCI. For Steroids CCXC, see J. P. Turnbull and J. H. Fried, *Tetrahedron Letters*, in press.

[2] For a review of published researches at the biological and chemical level up to 1963, see P. Karlson, *Angew. Chem.*, **75**, 257 (1963). Later work is covered in a series of four articles by Karlson, Hoffmeister, and their collaborators, *Chem. Ber.*, **98**, 2361 (1965).

[3] R. Huber and W. Hoppe, *ibid.*, **98**, 2403 (1965).

[4] E. Fernholz, *Ann.*, 507, 128 (1933).

[5] L. F. Fieser and S. Rajagopalan, *J. Am. Chem. Soc.*, **71**, 3938 (1949).

[6] Several other routes to 5,6-dioxygenated Δ^2-steroids were explored. A discussion of these experiments and of much related chemistry will be the subject of later detailed reports.

[7] L. B. Barkley, M. W. Farrar, W. S. Knowles, H. Raffelson, and Q. E. Thompson, *J. Am. Chem. Soc.*, **76**, 5014 (1954).

[8] Nmr spectra were recorded on a Varian A-60 spectrometer using deuteriochloroform as solvent when possible. Comparisons of calculated *vs.* observed frequencies for angular methyl proton resonances were used throughout to check structure and stereochemistry. Nmr spectra for all reported compounds are consistent with the assigned structures, as are other physical and analytical data.