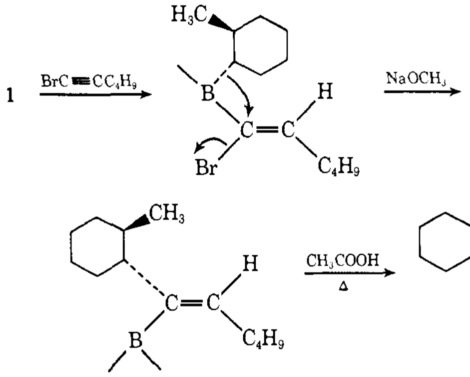
duced *trans*-1-methyl-2-(*trans*-1-hexenyl)cyclohexane,[5] again pointing to retention of configuration in the migrating 2-methylcyclohexyl group.[5,11] Similar results were obtained *via* the corresponding reaction with diisopinocampheylborane. A summary of the yields observed in each of these reactions is given in Table I.



Thus, procedures have now been developed for the stereoselective introduction of simple vinyl groups, cis and trans 2-substituted vinyl groups, and 1,2-disubstituted vinyl groups onto cycloalkane rings. These procedures should be exceedingly useful in stereospecific syntheses of compounds for natural product studies. We are currently exploring the synthetic potentialities of the hydroboration–iodination reaction with alkynes containing various functional groups.

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[11] The experimental conditions for the synthesis of this olefin are analogous to those reported in ref 10.

[12] National Defense Education Act Fellow (Title IV) at the University of California, Davis, for 1970–1971.

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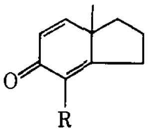
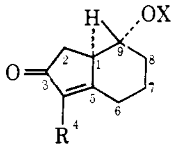
Photochemical Rearrangements of 6/5-Fused Cross-Conjugated Cyclohexadienones. Application to the Total Synthesis of *dl*-Oplopanone[1]

Sir:

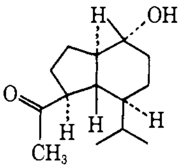
Earlier we reported that the methyl-substituted 6/5-fused cross-conjugated cyclohexadienone Ia undergoes photochemical rearrangement in aqueous acetic acid to produce the 5/6-fused hydroxy IIa (X = H) in high yield.[2] We have now found that the corresponding methoxydienone Ib[3] undergoes a similar rearrangement on irradiation in glacial acetic acid for 4 hr using a 450-W Hanovia lamp fitted with a Pyrex sleeve to give an 85% yield of the acetoxy ketone IIb (X = Ac), mp 54.5–55°. The stereochemistry of IIb (X = Ac) was assigned on the basis of the similarity of its nmr spectrum to that of IIa (X = H) and to the related 5/7-fused hydroxy and acetoxy ketones prepared by irradiation of the corresponding 4-methyl[5a,b] and 4-methoxy[5c] 6/6-fused systems, respectively. The nmr spectrum (CCl_4) of IIb (X = Ac) showed a singlet at δ 1.28 for the C-9 methyl group, a singlet at δ 1.97 for the acetate methyl group, and a singlet at δ 3.90 for the methoxy group. An apparent triplet (J = 4 Hz) at δ 3.08 and an apparent doublet (J = 4 Hz) at δ 2.27 were assigned to the C-1 proton and to the C-2 methylene protons, respectively. The ir spectrum (film) of IIb (X = Ac) showed absorptions at 1732 (acetate C=O), 1710 (C=O), 1650 cm^{-1} (C=C).



I



II



III

a, R = CH_3
b, R = OCH_3

The similarity of the skeleton and stereochemistry of IIb (X = Ac) to that of the sesquiterpene oplopanone III, isolated from *Oplopanax japonicus* by Minato and coworkers,[6] made a synthetic route to the natural product involving the photochemical rearrangement of the dienone IVa appear attractive. Condensation of 1,4-dimethoxy-2-butanone[4] with 2-methyl-5-isopropylcyclopentanone[7] using potassium ethoxide in ether at 10° followed by cyclization of the diketone intermediate with ethanolic potassium hydroxide gave the methoxy enone V (~20%): bp 89–90° (0.04 mm); nmr (CCl_4) δ 0.83 and 0.95 (d of d, J = 7 Hz, 6 H, C-6 $(CH_3)_2CH$–), 1.19 (s, 3 H, C-9 CH_3), 3.61 ppm (s, 3 H, OCH_3); ir (film) 1675 (C=O), 1631 cm^{-1} (C=C). The assignment of the β configuration of the isopropyl side chain in V was based upon subsequent conversions and the fact that examination of models suggests that $A^{1,3}$ strain[8] involving the C-4 methoxy group and the C-6 isopropyl group appears to be greater when the isopropyl side chain is in the α configuration.

Oxidation of V with freshly prepared selenium dioxide in *tert*-butyl alcohol gave a 5:1 mixture (apparently the equilibrium mixture)[9] of compounds IVa and IVb in 65% yield. The isomers were separated by chromatography on silica gel. The major isomer (IVa) showed bp 94–97° (0.07 mm); nmr (CCl_4) δ 0.92 and 0.97 (d of d, J = 7 Hz, 6 H, C-6 $(CH_3)_2CH$), 1.21 (s, 3 H, C-1 CH_3), 3.79 (s, 3 H, OCH_3), 5.99 and 6.88 ppm (AB

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[1] This investigation was supported by Public Health Service Research Grants No. GM 15044 from the National Institute of General Medicine and No. CA 12193 from the National Cancer Institute.

[2] D. Caine, W. J. Powers, III, and J. T. Gupton, Abstracts of Papers, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 23–27, 1970, No. ORGN 97.

[3] (a) The dienone Ib was prepared by condensation of 1,4-dimethoxy-2-butanone (ref 4) with 2-methylcyclopentanone using potassium ethoxide in ether, followed by oxidation of the resulting 6/5-fused enone with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in *p*-dioxane. This compound showed bp 74–77° (0.03 mm); nmr (CCl_4) δ 1.22 (s, 3 H, C-9 CH_3), 3.68 (s, 3 H, C-4 OCH_3), 6.01 and 6.99 ppm (AB quartet, J_{AB} = 10 Hz, 2 H, C-1 and C-2 H); ir (film) 1649 (C=O), 1608 cm^{-1} (C=C). (b) Correct elemental analysis and exact mass data have been obtained for all new compounds herein.

[4] E. Wenkert and D. A. Berges, *J. Amer. Chem. Soc.*, **89**, 2507 (1967).

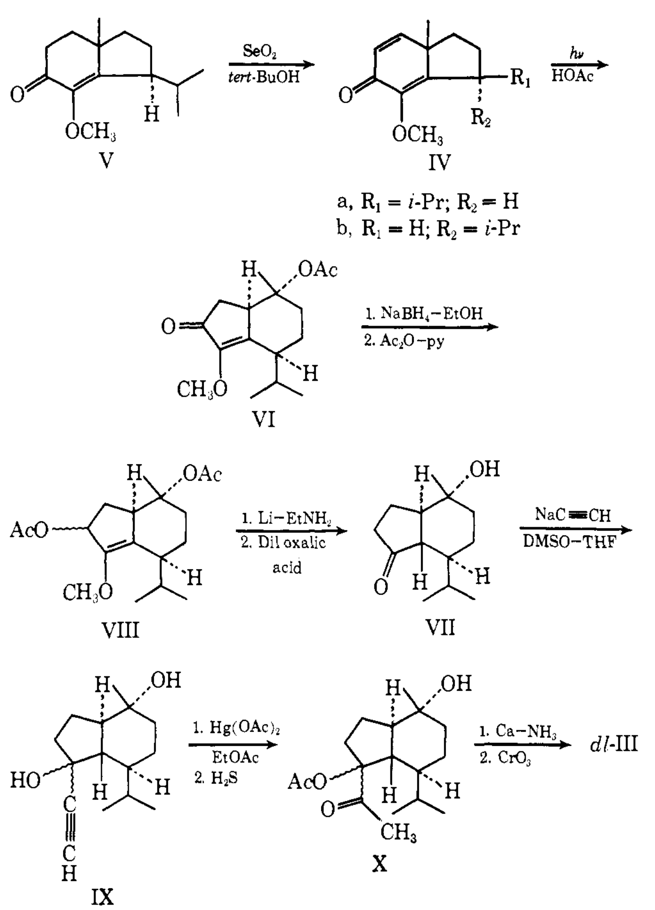
[5] (a) D. Caine and J. B. Dawson, *J. Org. Chem.*, **29**, 3108 (1964); (b) P. J. Kropp, *ibid.*, **29**, 3110 (1964); (c) Caine and P. F. Ingwalson, unpublished work.

[6] K. Takeda, H. Minato, and M. Ishikawa, *Tetrahedron, Suppl.*, No. 7, 219 (1965).

[7] This compound was prepared by a modification of the method of K. Sisido, S. Kurozumi, K. Utimoto, and T. Isida, *J. Org. Chem.*, **31**, 2795 (1966).

[8] F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

[9] The composition of the mixture was unchanged when it was treated under a variety of equilibrating conditions, and pure IVa was converted into the same 5:1 mixture on being allowed to stand on a silica gel column for several days.



quartet, J_{AB} = 10 Hz, 2 H, C-1 and C-2 H); ir (film) 1659 (C═O), 1608 cm^{-1} (C═C). The minor isomer (IVb) showed bp 94–97° (0.07 mm); nmr (CCl_4) δ 0.68 and 0.97 (d of d, J = 7 Hz, C-6 $(CH_3)_2CH$–), 1.22 (s, 3 H, C-1 CH_3), 3.69 (s, 3 H, OCH_3), 5.99 and 6.94 ppm (AB quartet, J_{AB} = 10 Hz, 2 H, C-1 and C-2 H); ir (film) 1661 (C═O), 1609 cm^{-1} (C═C). Examination of models of IVa and IVb suggests that $A^{1,3}$ strain should be less in the fomer, and thus IVa should be the more stable isomer. The stereochemical assignment of IVa was borne out by its subsequent conversion into *dl*-oplopanone (III).

Irradiation of IVa under the conditions described for Ib gave the acetoxy ketone VI: 91% yield; mp 73–74.5°; nmr (CCl_4) δ 0.88 and 0.97 (d of d, J = 6 Hz, 6 H, C-6 $(CH_3)_2CH$–), 1.22 (s, 3 H, C-9 CH_3), 1.91 (s, 3 H, Ac), 2.18 (d, J = 4.5 Hz, 2 H, C-2 CH_2), 3.01 (t, J = 4.5 Hz, 1 H, C-1 H), 3.84 ppm (s, 3 H, OCH_3); ir (CCl_4) 1738 (acetate C═O), 1714 (C═O), 1630 cm^{-1} (C═C).[10] The nmr absorption for the C-1 and C-2 protons indicated that the stereochemistry of VI at C-1 and C-9 was the same as that present in IIb (X = Ac).

A procedure similar to that described by Ireland and coworkers[11] and by us[12] was employed for the conversion of VI into VII, a degradation product of oplopanone.[6] Treatment of VI with sodium borohydride in ethanol followed by acetylation of the allylic hydroxyl group with acetic anhydride in pyridine gave the diacetate VIII (94%), mp *ca.* 20°,[13] as a mixture of C-2 isomers. The mixture showed nmr (CCl_4) δ 0.89 and 0.93 (d of d, J = 6 Hz, 6 H, C-6 $(CH_3)_2CH$'s), 1.27 and 1.33 (singlets for the C-9 CH_3's of the two isomers), 1.89 (s, 3 H, C-2 Ac's), 2.01 (s, 3 H, C-9 Ac's), 3.51 (s, 3 H, OCH_3's), 5.63–5.92 ppm (m, 1 H, C-3 H's); ir (film) 1720 cm^{-1} (acetate C═O).

Treatment of VIII with lithium in ethylamine (inverse addition) at −78° led to cleavage of the allylic acetate and reduction of the tertiary acetate grouping to give a hydroxy enol ether which was converted into VII (50%) by hydrolysis with 0.25 equiv of oxalic acid in aqueous methanol for 2 hr. The hydroxy ketone VII showed the same nmr and ir spectral properties as those reported[6] for the hydroxy ketone from the natural source.

Compound VII was converted into *dl*-oplopanone by reaction with excess sodium acetylide in dimethyl sulfoxide–THF[14] to give an ethynyl carbinol (IX), reaction of this compound with mercuric acetate in ethyl acetate[15] to give an α-acetoxy ketone (X), and removal of the acetoxyl grouping with calcium in liquid ammonia followed by oxidation with Jones reagent.[16] Although intermediates IX and X were not purified and fully characterized, they exhibited spectral properties consistent with the indicated structures. The synthetic oplopanone exhibited nmr, ir, and glc properties identical with those of an authentic sample of the natural product.[17]

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[10] That epimerization at C-6 did not occur during irradiation was shown by the fact that pure IVa gave pure VI, while irradiation of the 5:1 mixture of IVa and IVb gave a 5:1 mixture of VI and the corresponding C-6α isopropyl compound.

[11] R. E. Ireland, D. R. Marshall, and J. W. Tilley, *J. Amer. Chem. Soc.*, **92**, 4754 (1970).

[12] D. Caine and J. B. Dawson, *Chem. Commun.*, 1232 (1970).

[13] Purification of VIII was carried out by recrystallization from ether–hexane at −20°.

[14] J. Kříž, M. J. Beneš and J. Peška, *Tetrahedron Lett.*, 2881 (1965).

[15] H. B. Kagan, A. Marquet, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1079 (1960).

[16] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[17] We wish to express our deep appreciation to Dr. H. Minato for supplying us with an authentic sample of oplopanone.

[18] NDEA Title IV Fellow, 1966–1967; Union Camp Fellow, 1969–1970.

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On the Geometry of Tetraphenylethylene Dianion

Sir:

Reductions of arylethylenes, like tetraphenylethylene (:TPE), by two electrons lead to arylethylene dianions. Indirect evidence suggests, but does not demand, that the dianions have substantially different geometries from the parent hydrocarbons.[1–7] One

$$:\text{TPE} \xrightarrow{2\text{Na}} :\text{TPE}:^{2-},2\text{Na}^+ \qquad (1)$$

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[1] D. W. Ovenall and D. H. Whiffen, *Chem. Soc., Spec. Publ.*, No. 12, 139 (1958), and ensuing discussions by M. J. S. Dewar, N. S. Hush, and P. Gray, *ibid.*, 164, 166 (1958).

[2] N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

[3] J. F. Garst, E. R. Zabolotny, and R. S. Cole, *J. Amer. Chem. Soc.*, **86**, 2257 (1964).

[4] J. F. Garst, J. G. Pacifici, and E. R. Zabolotny, *ibid.*, **88**, 3872 (1966).

[5] R. C. Roberts and M. Szwarc, *ibid.*, **87**, 5542 (1965).

[6] A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **91**, 1892 (1969).

[7] M. Szwarc, "Carbanions, Living Polymers, and Electron Transfer Processes," Interscience, New York, N. Y., 1968, pp 361 ff.