nistic discussion of other relevant systems has been made by Parshall and coworkers.[6]

A number of organoaluminum dihalides have been used for this work besides ethylaluminum dichloride. These include methyl-, isobutyl-, and phenylaluminum dichlorides and various alkylaluminum dibromides. All these catalysts have the advantage of being soluble in the organic exchange medium. Perdeuteriobenzene is the most readily available of the various deuterated aromatic hydrocarbons suitable for use as the source of deuterium.

A significant aspect of our results is the high ring selectivity of these catalysts for exchange of protons bound to the aromatic nucleus. Thus toluene is converted to toluene-$d_5$, not toluene-$d_8$. Bromobenzene gives bromobenzene-$d_5$ which is a most useful intermediate for the preparation of other deuterated aromatics.

The present catalytic method thus presents substantial advantages, as compared with other deuterium labeling procedures, because of its simplicity, speed, selectivity, freedom from steric effects, and freedom from side reactions. Moreover, when used in conjunction with other catalytic labeling methods, the current procedure enables specific labeling of the nonaromatic protons. Thus toluene-$d_8$, deuterated using heterogeneous platinum, can be back-exchanged with benzene using ethylaluminum dichloride to give toluene-$d_3$, labeled exclusively in the side chain.

**Acknowledgment.** We thank the Australian Research Grants Committee and the Australian Institute of Nuclear Science and Engineering for the support of the research at The University of New South Wales.

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**J. L. Garnett,* M. A. Long, R. F. W. Vining**
*School of Chemistry, The University of New South Wales*
*Kensington, N.S.W., Australia*

**T. Mole**
*CSIRO, Division of Applied Chemistry*
*Melbourne, Australia*

*Received May 15, 1972*

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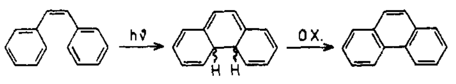
## Photodehydrocyclizations of Stilbene-Like Compounds. VI.[1] Chemical Evidence of an Excited State Mechanism

*Sir:*

Although the photocyclization of stilbene or analogs into phenanthrene, its derivatives, or benzologs is one of the most studied reactions in organic photochemistry,[2] Blackburn and Timmons stated in 1969 that the mechanism of the reaction is still the subject of much controversy.[2b]

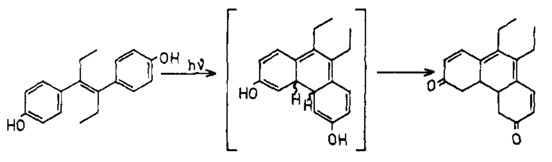
The controversy concerns two questions. (a) Is the reactive state an excited singlet state or a vibrationally excited ground state?[3] (b) Has the accepted intermediate II a cis or a trans configuration? The questions are related because orbital symmetry rules prescribe that cyclization in the excited state proceeds conrotatory giving *trans*-II, whereas a ground-state reaction should involve *cis*-II as an intermediate.



I II III

Arguments for an excited state mechanism, given by Muszkat and Fischer,[3] have been based on fluorescence measurements and quantum yields. Indications for a trans configuration of II, based on calculations using Hess' law,[4] or an extended Hückel MO treatment,[5] and on the observation that no molecular hydrogen is formed in solution,[6,7] are consistent with an excited state reaction. However, Güsten and Klasinc[8] favored a hot ground-state reaction because of the linear correlation between quantum yields of photocyclizations with meta substituted stilbenes and calculated electron densities on the ortho carbon atoms in the ground state.

The major difficulty in the establishment of the mechanism originates in the failure to isolate II and so to elucidate its configuration. Recently, Doyle, *et al.*, isolated,[9] however, as the irradiation product of $\alpha,\alpha'$-diethyl-4,4′-stilbenediol (IV) a stable tautomer VI of the primary cyclization product V. We have found that VI reacts as a normal dehydrophenanthrene derivative; on irradiation of a methanolic solution in the presence of iodine at 360 m$\mu$ (outside the absorption range of IV) 9,10-diethyl-3,6-phenanthrenediol was formed in good yield.



IV V VI

Because IV can be formed back by irradiation of VI, configurations of V and VI must be equal. Doyle, *et al.*, accepted a trans configuration because the $M^+ - 2$ peak in the mass spectrum was only a minor peak (1.3%).

Such conclusions from mass spectra should be taken carefully because comparison with cis and trans isomers of this kind of compounds is not possible.

We found a chemical proof of the trans configuration of VI. The compound (500 mg) was ozonolyzed in 50 ml of 80% acetic acid at room temperature for 5 hr. After addition of 20 ml of perhydrol the mixture was boiled for 1 hr, the solvent evaporated *in vacuo*, and the residue taken up in 10 ml of acetone. Dilution with benzene (50 ml) and boiling to remove the acetone yielded 230 mg (54%) of a crystalline product: mp 224–230°; after crystallization from acetone, 234–236° (lit.[10] *rac*-butane-1,2,3,4-tetracarboxylic acid

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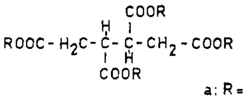
(VIIa), mp 236–237°; *meso*-VIIa, mp 188–189°).



$$\mathrm{ROOC{-}H_2C{-}\underset{\displaystyle COOR}{\overset{H}{C}}{-}\underset{H}{\overset{\displaystyle COOR}{C}}{-}CH_2{-}COOR}$$

VII

a: R = H

b: $R = CH_3$

The mixture melting point with authentic *rac*-VIIa[11] was undepressed. Esterification of the product with diazomethane gave a tetramethyl ester with mp 61.5–62.5° (lit.[10] *rac*-VIIb, mp 62°; *meso*-VIIb, mp 74–75°). The mixture melting point with authentic *rac*-VIIb was undepressed, with *meso*-VIIb it was 40–55°. Boiling of the product VIIa with acetyl chloride for several hours yielded a dianhydride with mp 172–173° (lit.[10] racemic, 172–173°; meso, 248°).

The racemic configuration of our product could also be established from small differences between the nmr spectra of *rac*- and *meso*-VIIb: *rac*-VIIb $\delta$ 3.72 (s, 6 H, 2 $CH_3$), 3.69 (s, 6 H, 2 $CH_3$), 3.45–3.26 (m, 2 H), 2.94–2.37 (m, 4 H), $|J_{\text{vic}}| = 4.5$ and 8.5 Hz, $|J_{\text{gem}}| = 16.5$ Hz; *meso*-VIIb $\delta$ 3.71 (s, 6 H, 2 $CH_3$), 3.69 (s, 6 H, 2 $CH_3$), 3.44–3.23 (m, 2 H), 2.87–2.31 (m, 4 H), $|J_{\text{vic}}| = 4.5$ and 8.5 Hz, $|J_{\text{gem}}| = 16.5$ Hz.

This unambiguous establishment of the trans configuration of VI firmly settles in our opinion that photocyclization of IV proceeds in the first excited state.

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[11] Authentic samples of *rac*- and *meso*-VIIa were obtained as described by Alder,[10] but the oxidation of the intermediate Diels–Alder adduct was carried out with ozone instead of potassium permanganate or nitric acid. The similarity between our products and those of Alder excludes the fact that unexpected rearrangements or isomerizations may occur during ozonolysis.

**Th. J. H. M. Cuppen, W. H. Laarhoven***
*Department of Organic Chemistry, R. C. University*
*Toernooiveld, Nijmegen, The Netherlands*

*Received May 31, 1972*

## Microwave Spectrum and Dipole Moment of Benzvalene

*Sir:*

The benzene isomers ($C_6H_6$) represent a class of compounds of great theoretical and experimental interest. Their synthesis and characterization is largely of recent origin, although in the case of fulvene[1] the history is considerably longer. Dewar benzene,[2] dimethylenecyclobutene,[3] and benzvalene[4] have been only recently synthesized, and, in the case of prismane,[5] the parent hydrocarbon has not yet been reported. All of the parent species share the common characteristic of relative instability, particularly when isolated.

Numerous theoretical studies[6] of these species have been performed. The number of experimental investigations of molecular properties has been relatively small, however, presumably because of the difficulties encountered in synthesizing, purifying, and handling the compounds. Molecular structure data have been obtained for fulvene and dimethylenecyclobutene from microwave[7] and electron diffraction[8] studies, and the structure of the hexamethyl derivative of Dewar benzene has been determined by electron diffraction[9] also.

We report here the microwave spectrum of benzvalene, tricyclo[3.1.0.$0^{2,6}$]hex-3-ene. The sample synthesis was performed by the method of Katz, *et al.*,[10] followed by vpc purification and nmr identification as described by Wilzbach,[4] *et al.* Microwave spectra were obtained by the conventional techniques. Benzvalene was found to be remarkably stable in our standard copper wave-guide cell at −78°, although some slow decomposition could be noted.

The microwave spectrum was that of an asymmetric rotor with a-type transitions and was assigned by its characteristic Stark effects and its agreement with preliminary predictions. Fourteen rotational transitions were measured, a portion of which are listed in Table I.

**Table I.** Rotational Transitions of Benzvalene

| Transition | Obsd[a] | Obsd − calcd[b] |
|---|---|---|
| $0_{00} \rightarrow 1_{01}$ | 9165.69 | −0.01 |
| $1_{11} \rightarrow 2_{12}$ | 16945.27 | 0.01 |
| $1_{01} \rightarrow 2_{02}$ | 17839.51 | 0.04 |
| $1_{10} \rightarrow 2_{11}$ | 19717.62 | 0.09 |
| $2_{12} \rightarrow 3_{13}$ | 25149.81 | 0.01 |
| $2_{02} \rightarrow 3_{03}$ | 25834.94 | 0.00 |
| $2_{11} \rightarrow 3_{12}$ | 29190.56 | 0.00 |
| $3_{13} \rightarrow 4_{14}$ | 33162.32 | −0.09 |
| $5_{05} \rightarrow 5_{24}$ | 19714.86 | −0.01 |
| $6_{15} \rightarrow 6_{34}$ | 20646.48 | −0.03 |

[a] All values in MHz. [b] Using best fit rotational constants given in text.

The complete set of transitions yielded rotational constants of $A = 7389.233 \pm 0.007$ MHz, $B = 5275.919 \pm 0.004$ MHz, and $C = 3889.779 \pm 0.003$ MHz.

We have also determined the electric dipole moment by measurements of the second-order Stark effect.[11] The data in Table II lead to $|\mu_T| = |\mu_a| = 0.88 \pm 0.01$ D. The vanishing values of $\mu_b$ and $\mu_c$ are in accord with the spectral observations and the $C_{2v}$ molecular symmetry.

**Table II.** Stark Effect Measurements

| Transition | $M$ | $(\Delta\nu/E^2) \times 10^5$ Obsd[a] | $(\Delta\nu/E^2) \times 10^5$ Calcd[b] |
|---|---|---|---|
| $1_{10} \rightarrow 2_{11}$ | 0 | 0.2418 | 0.2474 |
| $2_{11} \rightarrow 3_{12}$ | 2 | −0.3894 | −0.3813 |
| $2_{11} \rightarrow 3_{12}$ | 1 | −0.1141 | −0.1072 |
| $2_{12} \rightarrow 3_{13}$ | 2 | 0.5408 | 0.5497 |
| $2_{12} \rightarrow 3_{13}$ | 1 | 0.1256 | 0.1247 |

[a] Units are MHz/(V/cm)$^2$. Stark cell calibrated using $\mu_{\text{OCS}} = 0.71521$ D. [b] Calculated using $\mu_b = \mu_c = 0$; $\mu_a = 0.883$ D.

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