In order to further test our proposed mechanism, the deuterated phenyl propargyl ether **2** was prepared and pyrolyzed. The deuterium distribution of the phenyl used to prepare **2** was determined to be 19% in the ortho and para positions and *ca.* 100% in the meta positions.[13] The 2,4-dinitrophenylhydrazone of the 1,1-dimethyl-2-indanone obtained from the pyrolysis of **2** was prepared, and its deuterium distribution as determined by nmr analysis is that shown in **3**. This deuterium distribution is the one predicted by the above mechanism.

The production of the benzocyclobutene from the pyrolysis of the unsubstituted phenyl propargyl ether does not come from the decarbonylation of 2-indanone. A sample of 2-indanone was submitted to our pyrolysis conditions and recovered almost quantitatively.

(13) The deuterated phenol was prepared by converting benzene-d_6 to aniline[14] which was then diazotized and hydrolyzed to phenol.[15] The nmr spectrum of this product indicated that the ortho and para deuterium atoms had been exchanged for hydrogen atoms during its preparation. The nmr signals of the ortho and para protons of phenol are *ca.* 0.5 ppm upfield and those of the meta protons are *ca.* 0.2 ppm upfield from that of benzene.[16] The phenol was converted to anisole and analysis of it by nmr and mass spectroscopy indicated that the meta positions were fully deuterated and the ortho and para position contained 19% deuterium.

(14) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955.

(15) H. E. Ungnade and E. F. Orwoll, "Organic Syntheses," Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N. Y., 1955, p 130.

(16) J. C. Schug and J. C. Deck, *J. Chem. Phys.*, 37, 2618 (1962).

(17) Alfred P. Sloan Research Fellow, 1970–1972.

Walter S. Trahanovsky,*[17] Patrick W. Mullen
Department of Chemistry
Iowa State University of Science and Technology
Ames, Iowa 50010

Received April 17, 1972

A New Simple Method for Rapid, Selective Aromatic Deuteration Using Organoaluminum Dihalide Catalysts

Sir:

The most useful general methods for deuteration of aromatic and aliphatic compounds involve exchange with heavy water in the presence of a homogeneous[1,2] or heterogeneous[3] metal catalyst. Of these catalysts those containing platinum are most satisfactory.[4] With homogeneous $PtCl_4^{2-}$, aromatic deuteration is sterically retarded at hindered positions,[3] while with a heterogeneous platinum catalyst similar steric hindrance is encountered[4] as well as coupling of the aromatic as a side reaction.[5] For some aromatic compounds, such as naphthalene, the heterogeneous catalyst requires up to several weeks at 150° for the attainment of equilibrium.

We now report that organoaluminum dihalides, such as ethylaluminum dichloride, catalyze very rapid exchange of hydrogen atoms between aromatic nuclei. Equilibrium is attained within minutes at room temperature and there appears to be no steric hindrance. These catalysts afford a new, very rapid, and simple procedure whereby an aromatic compound can be deuterated using as the deuterium source an already deuterated aromatic compound such as perdeuteriobenzene.

In a typical experiment ethylaluminum dichloride (0.01 g) was added by syringe to a mixture of perdeuteriobenzene (0.2 ml) and bromobenzene (0.2 ml) in a small serum-capped vial at room temperature. The reactants were not dried prior to use as traces of water serve as a cocatalyst, greatly enhancing the rate of exchange. Reaction was terminated after a few minutes by the addition of excess water. Analysis of the quantitatively recovered bromobenzene by mass and nmr spectrometry showed that exchange equilibrium had been reached at *all* five aromatic positions. In contrast conventional homogeneous and heterogeneous platinum catalysis leads to exchange in only three positions in bromobenzene and a prolonged time at an elevated temperature is required.[3,4]

A wide range of compounds have been deuterated using the present technique. Examples are given in Table I.

Table I. Compounds Deuterated by Exchange with Perdeuterated Benzene Using $EtAlCl_2$[a]

Organic substrate	% approach to equilibrium	No. of exchangeable H per molecule
Chlorobenzene	100	5
Bromobenzene	100	5
Ethylbenzene	100	5
tert-Butylbenzene	100	5
p-Xylene	100	4
Mesitylene	100	3
Allylbenzene	100	5
Diphenyl	100	10
Dibenzyl	100	10
p-Terphenyl	100	14
Naphthalene	100	8
Anthracene[b]	0	
Chrysene[b]	0	
Pyrene[b]	0	

[a] Reaction conditions: room temperature, 30 min. [b] Anthracene, chrysene, and pyrene showed complete exchange of 10, 12, and 10 hydrogen atoms, respectively, after 1 week at 90°.

For some of the condensed polycyclic aromatic hydrocarbons, elevated temperature (90°) is necessary. The relatively low reactivity of pyrene and anthracene may be significant, since these hydrocarbons should be particularly reactive if isotope exchange were a simple electrophilic proton substitution.

Alkanes and alkenes, as well as oxygen- and nitrogen-containing compounds, do not exchange. Thus no deuteration was observed with hexane and cyclopentane. Pyridine and many aromatic compounds substituted by electronegative groups (*e.g.*, anisole, benzaldehyde, benzoic acid, phenol, and aniline) not only fail to exchange but also inhibit the deuteration of other aromatic compounds, presumably because of preferential complex formation with the aluminum catalyst.

Mechanistically, it is plausible to suggest that the catalyst acts as a proton-transfer agent and two aromatic compounds undergo exchange in turn, possibly complexing with the metal atoms of the catalyst through a π-associative-type species as proposed for other catalytic exchange systems.[3,4] A brief, critical, mecha-

(1) J. L. Garnett and R. S. Kenyon, *Chem. Commun.*, 1227 (1971), and references cited therein.

(2) R. J. Hodges, D. E. Webster, and P. B. Wells, *ibid.*, 462 (1971).

(3) J. L. Garnett, *Catal. Rev.*, 5, 229 (1971).

(4) J. L. Garnett, *Proc. Int. Conf. Methods Prep. Stor. Label. Compounds, 2nd*, 689 (1968).

(5) G. E. Calf and J. L. Garnett, *Chem. Commun.*, 373 (1969).

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.

---

[6] E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, **92**, 5234 (1970).

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

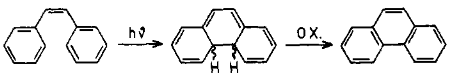
Received May 15, 1972

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]

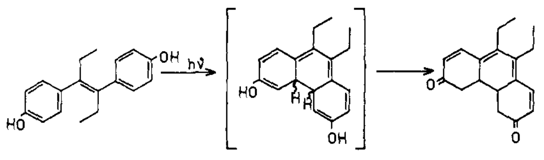
The controversy concerns two questions. (a) Is the reactive state an excited singlet state or a vibrationally excited ground state?[3] (b) Has the accepted intermediate II a cis or a trans configuration? The questions are related because orbital symmetry rules prescribe that cyclization in the excited 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 α,α'-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 mμ (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

---

[1] Part V: W. H. Laarhoven and Th. J. H. M. Cuppen, *J. Chem. Soc., Perkin Trans. 1*, in press.

[2] (a) F. R. Stermitz in "Organic Photochemistry I," O. L. Chapmann, Ed., Marcel Dekker, New York, N. Y., 1967; (b) E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, **23**, 482 (1969).

[3] Sensitization experiments indicate that a triplet state is unprobable: K. A. Muszkat and E. Fischer, *J. Chem. Soc. B*, 662 (1967).

[4] F. B. Mallory, C. S. Wood, and J. F. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964).

[5] K. A. Muszkat and W. Schmidt, *Helv. Chim. Acta*, **54**, 1195 (1971).

[6] E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. C*, 163 (1970).

[7] R. Srinivasan and J. C. Powers, *J. Chem. Phys.*, **39**, 580 (1963).

[8] H. Güsten and L. Klasinc, *Tetrahedron*, **24**, 5499 (1968).

[9] F. D. Doyle, N. Filipescu, W. R. Benson, and D. Banes, *J. Amer. Chem. Soc.*, **92**, 6371 (1970).

[10] K. Alder and M. Schumacher, *Justus Liebigs Ann. Chem.*, **564**, 96 (1949).