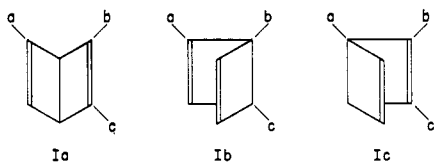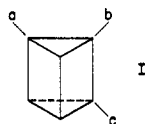# Phototransposition of Carbon Atoms in the Benzene Ring[1]

Sir:

A previous communication[2] disclosed a finding of alkyl group translocations, predominantly 1,2 shifts, in dimethyl- and diethylbenzenes as vapor or in solution under ultraviolet irradiation; similarly induced isomerizations in the *t*-butylbenzenes were discovered independently by Burgstahler and Chien.[3] We have now applied isotope-labeling criteria, as they also proposed, to differentiate between the two categories of mechanisms, those with detachment of the alkyl group from its ring carbon atom and, contrastingly, those in which convolutions of the benzene ring effect transposition of ring carbons together with their attached alkyl groups. Mesitylene-1,3,5-C^{14}_3 (from acetone-2-C^{14}),[4] upon photolysis (2537 Å.) in isohexane solution at 30°, isomerized to 1,2,4-trimethylbenzene labeled exclusively in the 1, 2, and 4 positions as shown by ozonolytic degradation[5] (*cf.* Table I). This constitutes a clear demonstration that the apparent 1,2 shift of a methyl group is an outcome of ring carbon interchange.

Whereas Burgstahler and Chien referred[3] to a Ladenburg-type mechanism as a possible alternative to alkyl migration, we consider the mechanistic possibilities that can be credibly invoked with reference to known types of photochemical transformations as threefold. The first is equivalent to the classical Ladenburg structure insofar as the allowed scrambling of ring carbons is concerned but is physically different in that each Ladenburg structure, *e.g.*, I, is replaced by a set of three folded (three-dimensional) Dewar structures,[6] Ia, b, and c, which have essentially similar geometry

but different dispositions of the single and double bonds. With the assumption of easy interconvertibility[7] under the prevailing excitation, the same possibilities for

Table I. Activities of Photoproduced 1,2,4-Trimethylbenzene and Derived Glyoximes[a]

| | Activity[b] | |
	μc./mole	Relative[c]
1,2,4-Trimethylbenzene[d]	218 ± 4	3
Glyoxime	0.4 ± 0.1	0.005
Methylglyoxime	74 ± 1	1.02
Dimethylglyoxime	146 ± 2	2.01

[a] The 1,2,4-trimethylbenzene formed with a quantum yield of 0.007 was separated by vapor phase chromatography, diluted 1500-fold with carrier, ozonized, and treated with hydroxylamine. The resulting glyoximes were recrystallized to constant melting point and specific activity. [b] Determined by liquid scintillation counting. [c] Expected for 1,2,4-trimethylbenzene-: 1,2,4-C^{14}_3, 3:0:1:2; 2,4,6-C^{14}_3, 3:1:1:1. [d] The initial mesitylene, at the same dilution, had an activity of 216 ± 3 μc./mole.

carbon atom transpositions upon re-aromatization are present as in the Ladenburg formulation. In either case apparent 1,3 shifts are allowed as well as apparent 1,2 shifts; to the extent that the latter appear to predominate steric or other special effects must be invoked.

Two additional mechanisms consistent with the labeling experiment are geometrically limited to 1,2 shifts. One is a conversion of the excited aromatic molecule to a fulvene, a known type of photochemical isomerization,[8] followed by re-aromatization, a step not supported by the reported[8] failure of fulvene to revert to benzene. A second and perhaps more plausible mechanism for pair wise involution of ring carbons is an out-of-plane twist through 180°. At the halfway point, probably a trough in the potential energy traverse, the structure passes through that of a tricyclohexene, II.[9] The formation of such a structure in photolysis is reminiscent of the formation of bicyclo-[1.1.0]butane from butadiene.[10]
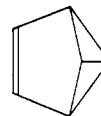
No single mechanism appears to be in accord with all the observations thus far accumulated. A mechanism which permits only a 1,2 shift of ring carbon atoms adequately accounts for the results of photolyses in the vapor phase.[11] It cannot, however, account for the products, corresponding to 1,3 shifts, which have now been identified in the photolysis of the dimethyl- and dimethylethylbenzenes in solution.[12] While all of the observed products can be accommodated through the mechanism of labile three-dimensional Dewar forms (or the equivalent in classical Ladenburg structures), the strong astatistical preference for 1,2 type transformations, easily rationalized

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **86**, 2307 (1964).

(3) A. W. Burgstahler and P. L. Chien, *ibid.*, **86**, 2940 (1964). These authors credit E. E. van Tamelen with similar findings (see their ref. 4).

(4) A. V. Grosse and S. Weinhouse, *Science*, **104**, 402 (1946); J. Bolle, *Mém. services chim. état* (Paris), **32**, 67 (1945); *Chem. Abstr.*, **42**, 4541 (1948).

(5) P. W. Haaijmman and J. P. Wibaut, *Rec. trav. chim.*, **60**, 842 (1941).

(6) The photochemical conversion of 1,2,4-tri-*t*-butylbenzene to the folded Dewar structure has been reported by E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962).

(7) Our assumption of easy interconvertibility of forms under the conditions applicable in the photochemical formation is not supported, nor is it excluded, by the fact that van Tamelen and Pappas (ref. 6) isolated only one of the Dewar forms and found that it reverts thermally to the starting material only.

(8) H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, 2003 (1960).

(9) A structure of this type was considered, and rejected on the basis of n.m.r. data, for the photoisomer of 1,2,4-tri-*t*-butylbenzene by van Tamelen and Pappas (*cf.* ref. 6).

(10) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 4045 (1963).

(11) The absence of a 1,3 shift has now been demonstrated for *p*-xylene as well as for *o*-xylene (ref. 2).

(12) At low conversion, the yield of *p*-xylene from *o*-xylene is 7% that of *m*-xylene. With each of the dimethylethylbenzenes (1,2,3-; 1,3,2-; and 1,4,2-) the predominant product corresponds to a 1,2 shift but a 1,3 shift product is formed with a yield one-tenth to one-third as large.

for *t*-butyl groups in terms of steric requirements, is less comprehensible for methyl substituents. It is likewise not an obvious consequence of this mechanism that the preference for 1,2 shifts should be more marked in the vapor than in the liquid. The results are readily interpreted on the assumption that both types of mechanism operate concurrently to varying degrees. If, as seems reasonable, the three-dimensional Dewar structure represents a lower energy form than the tricyclohexene, it should be favored in solution to the extent that the solvent drains off excess excitation energy.[12a]

(12a) NOTE ADDED IN PROOF. While this work was in press, H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem. Intern. Ed. Engl.*, **3**, 755 (1964), reported the isolation of isomers having the Ladenburg, tricyclohexene, and Dewar structures from the trimerization of *t*-butylfluoroacetylene.

(13) Resident student associate, summer 1964.

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Two New Porphyrin Syntheses

Sir:

Hitherto porphyrin syntheses have generally depended on final coupling of two dipyrrolic units.[1] We now wish to describe two syntheses proceeding through crystalline tetrapyrrolic intermediates III and VI, each of which is stabilized by an internuclear carbonyl group. Potentially this approach offers great advantages in the synthesis of diversely substituted porphyrins, but here it is merely exemplified by syntheses of mesoporphyrin IX and similar compounds.

Chlorination of the pyrroketone Ia[2] (ν_{max} CO, 1582 cm.$^{-1}$; λ_{max} 250, 303, and 348 mμ (log ϵ 4.23, 4.08, and 4.33) in methylene chloride; λ_{max} 422 mμ (log ϵ 4.51) in methylene chloride–HCl, *cf.* urea and tropone!) by *t*-butyl hypochlorite in tetrahydrofuran–ether (1:1) at 3° yielded Id, which was coupled[3] as its pyridinium derivative with the lithium salt of IIb (prepared by semihydrogenation of IIa) to yield 44% of the tetrapyrrolic ketone IIIa, m.p. 143–144°, mol. wt. 870 (mass spectrum[4]). The carbonyl group in IIIa was reduced by diborane[5] in tetrahydrofuran–ethyl acetate (1:1) to a methylene group.[6] The bilane dicarboxylic acid resulting from hydrogenolysis was dehydrogenated to principally the bilene-b hydrochloride IV (λ_{max} 505 mμ (log ϵ *ca.* 4.60)) by *t*-butyl hypochlorite (1 mole) in ether; *if this step was omitted the synthesis could*

(1) Exceptions with limited scope are described by A. H. Corwin and E. C. Coolidge, *J. Am. Chem. Soc.*, **74**, 5196 (1952), and A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 2418 (1961). The classical synthesis of chlorophyll by R. B. Woodward, *et al.*, *J. Am. Chem. Soc.*, **82**, 3800 (1960), includes a fleeting open-chain tetrapyrrolic intermediate.

(2) J. A. Ballantine, unpublished work; *cf. Proc. Chem. Soc.*, 198 (1961).

(3) (a) A. Hayes, G. W. Kenner, and N. R. Williams, *J. Chem. Soc.*, 3779 (1958); (b) A. H. Jackson, G. W. Kenner, and D. Warburton, *ibid.*, in press.

(4) All crystalline compounds isolated were characterized by their mass, n.m.r., infrared, and ultraviolet spectra and by microanalyses.

(5) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960).

(6) The intermediate pyromethenes can be detected spectroscopically during reduction of pyrroketones: unpublished work by Mr. L. E. Houghton shows that diborane also reduced diaryl ketones containing electron-releasing substituents, such as Michler's ketone and dianisyl ketone, to diarylmethanes.
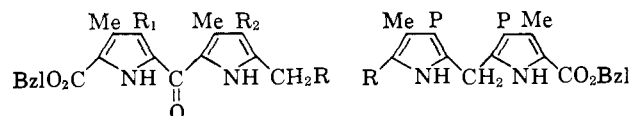
Ia, $R_1 = R_2 = C_2H_5$, R = H
b, $R_1 = CH_3$, $R_2 = C_2H_5$, R = H
c, $R_1 = C_2H_5$, $R_2 = CH_3$, R = H
d, $R_1 = R_2 = C_2H_5$, R = Cl

IIa, R = CO_2Bzl
b, R = CO_2H
c, R = H
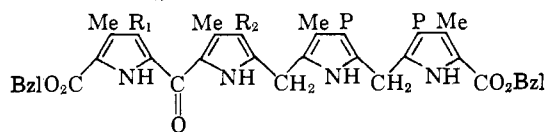
IIIa, $R_1 = R_2 = C_2H_5$
b, $R_1 = CH_3$, $R_2 = C_2H_5$
c, $R_1 = C_2H_5$, $R_2 = CH_3$

IV
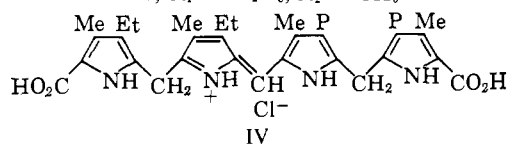
P = $CH_2CH_2CO_2CH_3$

still be carried through to porphyrins but the product was a mixture, arising from "jumbling" of the pyrrole nuclei.[7] Cyclization of IV with methyl orthoformate–trichloroacetic acid (1:3) in methylene chloride, followed by aeration, gave mesoporphyrin IX dimethyl ester as the only porphyrinic product in an over-all yield of 25% from IIIa. Analogous syntheses from Ib and Ic yielded tetrapyrrolic ketones IIIb, m.p. 142–143°, and IIIc, m.p. 153–154°, and thence 4-ethyl-1,2,3,5,8-pentamethyl-6,7-dimethoxycarbonylethylporphin, m.p. 255.5–256.5° (24% yield from IIIb), and 2-ethyl-1,3,4,5,8-pentamethyl-6,7-dimethoxycarbonylethylporphyrin, m.p. 295–296° (24% yield from IIIc).[8,9]

The second synthesis involves coupling of the pyrromethane amide V[3b] as its phosphoryl chloride complex (λ_{max} 390 mμ (log ϵ *ca.* 4.30)) with the pyrromethane IIc (derived from decarboxylation of IIb) in methylene chloride to an imine salt (λ_{max} 412 mμ (log ϵ *ca.* 4.23)). The latter was hydrolyzed by aqueous sodium carbonate to give the tetrapyrrolic ketone VI, m.p. 170° (38% yield from V and IIb). Hydrogenation of VI yielded the dicarboxylic acid, m.p. 178–179° dec.,

V

VI
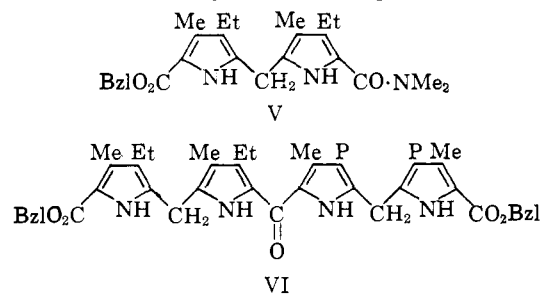
which was decarboxylated at 185° to an oil (characterized by n.m.r.). The latter was cyclized with methyl orthoformate and boron trifluoride etherate in methylene chloride and, after aeration in the presence of triethylamine, the blue "β-hydroxyporphyrin" VII[10] (λ_{max}

(7) D. Mauzerall, *J. Am. Chem. Soc.*, **82**, 2601 (1960).

(8) The good agreement with the published m.p. 255° and 290° [H. Fischer and E. Jordan, *Z. physiol. Chem.*, **191**, 38 (1930)] adds support to the accepted structure of chlorocruoroporphyrin.

(9) Mr. J. Wass has further extended the method to the syntheses of 2-ethyl-1,3,5,8-tetramethyl-4,6,7-trimethoxycarbonylethylporphin and of coproporphyrin III tetramethyl ester.

(10) A "hydroxyporphyrin" prepared from coproporphyrin I tetramethyl ester by H. Libowitsky and H. Fischer, *Z. physiol. Chem.*, **255**,