in the spectrum of **7**, **8**, and **9** is a downfield signal at about τ 3.1–3.2, characteristic of [2.2]paracyclophane protons pseudo-geminal to $-CH_2-X$ substituents ($X =$ OH, Cl, Br).[6] Thus **7**, **8**, and **9** do not contain protons pseudo-geminal to CH_2-X substituents, and the CH_2-X substituents themselves must be pseudo-geminal to one another. Since reactions link compounds **2** and **4–9**, the points of attachment of the substituents or new bridges all must be pseudo-geminal to one another. Although molecular models (Fisher–Hirschfelder–Taylor) can be made of [2.2]paracyclophanes containing extra *three*-atom bridges attached at pseudo-ortho positions, an extra *two-atom* bridge can only be assembled which spans the pseudo-geminal positions. The extra bridge of **2** contains two methylene groups, and should they be attached to pseudo-ortho positions, the compound would be extraordinarily strained.

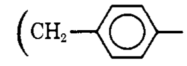
The pmr spectra contained other interesting features. Those of **3** and **4** were typical of [2.2]paracyclophane derivatives,[6] including a close doublet (τ 3.15 (1 H)) assigned to the proton ortho to the carbonyl-containing substituent.[6] In the spectrum of **5**, this proton was not moved downfield. The downfield shift of this proton in **3** and **4** appears associated with carbonyl conformations that are eliminated in **5** by the constraints of the additional bridge of which the carbonyl is a part. The usual meta coupling[6] between H_a and H_b of **5** was not detectable. In the pmr spectrum of **2** the aromatic protons were upfield of those in [2.2]paracyclophane (τ 3.63).[7] In **2**, H_a appeared as a doublet (τ 3.95 ($J_{a,b} =$ 1.9 Hz)), and H_b and H_c gave an AB quartet (τ 3.63 and 3.83, respectively ($J_{b,c} = 8.2$ Hz)). On the basis of its meta coupling H_b was assigned the downfield signal. In **6**, the chemical shifts of the corresponding protons followed a different pattern. Thus, H_a was furthest downfield (τ 3.57 (d, $J_{a,b} = 1.9$ Hz)) and H_b and H_c gave an AB quartet (τ 3.85 for H_b and 3.65 for H_c ($J_{b,c} = 8.1$ Hz)). Again H_b was assigned on the basis of its meta coupling, and in **6**, H_b gave the upfield signal. Molecular models (CPK) indicate that in **2** the rings are tilted so that C-5 and C-12 and their H_a protons are close to one another. In **6**, the relative positions of the aromatic rings and their protons are more similar to those of [2.2]paracyclophane itself.

The aromatic protons of **11** (τ 3.15–3.48) were shifted downfield relative to those of **2**, but were upfield of normal aromatic protons or of those of 3-carboxy[7]-paracyclophane (τ 2.8).[8] The barrelene bridgehead proton H_c and the olefinic proton H_b are coupled ($J_{b,c}$ = 10 Hz), the former giving a signal at τ 5.92 and the latter at 4.64. The other bridgehead proton H_a gave a doublet at τ 5.96 ($J_{a,b} = 2$ Hz), not far from the signal of the proton of C-1 of barrelene ($\tau \sim 5.4$).[9] Proton H_b was far upfield of its counterpart in barrelene (τ ~ 3.3).[9]

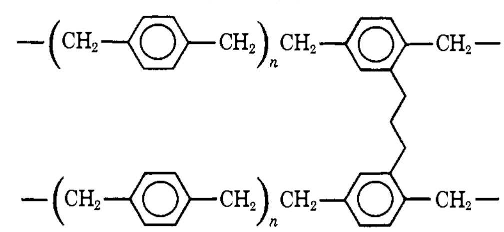
The differences in shape between **2** and **6** are also reflected in differences in their uv spectra. The spectrum of **6** (ethanol) was nearly superimposable on that of [2.2]paracyclophane, which gave[10] λ_{max} (ϵ) at 227 nm (18,000), 291 (200), and 302 (160, shoulder). The uv spectrum of **2** (ethanol) gave λ_{max} (ϵ) at 223 nm (12,000), 291 (440), and 305 (220, shoulder). The ultraviolet spectrum of adduct **11** (ethanol) gave λ_{max} (ϵ) at 220 nm (>20,000), 284 (1200), 291 (1130), and 323 (730). The band at 284 nm correlates with that observed for [7]paracyclophane[8,11] at 284 nm (1000), and for the mono-TCNE adduct of [2.2]paracyclophane at 284 nm (1100),[5] possibly indicating similar deformations of the benzene rings in the three systems.

The carbonyl stretching frequencies (μ) in the ir spectra of **3** (5.95), **4** (5.95), **5** (5.96), and **10** (5.98) indicate the carbonyl groups are at least partially conjugated with the rings. Compounds **3** and **4** also exhibit bands at 10.75 and 11.20 μ, characteristic of [2.2]paracyclophanes.[10]

At about 500° in the gas phase, [2.2]paracyclophane gives *p*-xylylene, which when condensed on cold surfaces produces a film of linear polyparaxylylene.[12] If our tris-bridged cyclophanes, **6** or **8**, behave similarly, a highly cross-linked polymer could be produced. Possibly pyrolysis and condensation of an appropriate mixture of **6** and [2.2]paracyclophane will give a film (**12**), cross-linked to a desired degree, much as the addition of *p*-divinylbenzene to styrene provides cross-linked polystyrene. This possibility is being examined.



polyparaxylylene



(6) H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, **91** 3534 (1969).
(7) D. J. Cram and R. C. Helgeson, *ibid.*, **88**, 3515 (1966).
(8) N. L. Allinger and T. J. Walter, *ibid.*, **94**, 9267 (1972).
(9) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. H. Sherwin, *ibid.*, **91**, 2330 (1969).
(10) D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1956).
(11) H. D. Wolf, V. V. Kane, R. H. Levin, and M. Jones, Jr., *ibid.*, **95**, 1680 (1973).
(12) (a) W. F. Gorham, *J. Polym. Sci., Part A-1*, 4, 3027 (1966); (b) *Chem. Eng. News*, 43, 35 (Feb 22, 1965); (c) *ibid.*, 43, 41 (Mar 1, 1965).
(13) National Science Foundation Trainee Fellowship, 1969–1973.

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Di-π-methane Interaction *vs.* Group Migration

Sir:

During the past several years we have been interested in intramolecular photochemical reaction between nonconjugated benzene rings. In the course of this work, photochemical interaction between rings separated by two, three, and four atoms[1] has been systematically investigated; however, similar attention has not been directed toward the parent reaction in this series, namely, that in which the interacting benzene rings are attached to the same carbon atom. This latter type of

(1) (a) J. A. Ross, W. C. Schumann, D. B. Vashi, and R. W. Binkley, *Tetrahedron Lett.*, 3283 (1971); (b) W. C. Schumann, D. B. Vashi, J. A. Ross, and R. W. Binkley, *J. Org. Chem.*, **37**, 21 (1972); (c) R. W. Binkley and W. C. Schumann, *J. Amer. Chem. Soc.*, **94**, 1769 (1972); (d) R. W. Binkley and W. C. Schumann, *ibid.*, **94**, 8743 (1972).

process would be analogous, at least in its early stages, to the well-known di-π-methane rearrangement.[2,3] We have now investigated a group of five compounds (**1**–**5**) capable of intramolecular reaction between benzene rings attached to the same atom and have found, surprisingly, that our results are best understood not in terms of a di-π-methane type reaction but rather a 1,2-shift process.

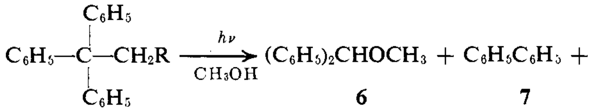
The five compounds listed in Table I were each synthesized from triphenylmethylsodium and the appropriate alkyl chloride according to the procedure of Hauser, *et al.*[4] Vycor-filtered irradiation of each of these five substituted triphenylmethanes (**1**–**5**) was conducted in methanol under nitrogen using a 450-W Hanovia mercury–vapor lamp. The reactions of the five (**1**–**5**) are shown in eq 1 and the product yields listed in Table I. The photoproducts, whose identities were established by comparison with known samples,[5] were separated from the starting materials by column chromatography on Florisil and, where necessary, purified by preparative glc.

Table I. Product Yields (Per Cent) from Reactions of Compounds **1**–**5**[a]

	6	7	8	9	10[b]
1,1,1-Triphenylbutane (**1**)	34	41	31	36	6
4,4,4-Triphenyl-1-butene (**2**)	45		35		
5,5,5-Triphenyl-2-methyl-2-pentene (**3**)	57		50		
1,1,1,2-Tetraphenylethane (**4**)	22	28	19	18	7
1,1,1-Triphenyl-2-*p*-tolylethane (**5**)	25	28	21	18	7

[a] Yields are calculated from the ratio of moles of product formed to moles of reactant consumed; thus, the total can exceed 100%. [b] Cis and trans isomers are not separated.

Two possible mechanisms merit consideration in attempting to understand the observed photochemical reactions (eq 1). These are the di-π-methane type interaction and the 1,2-shift process (Scheme I). The 1,2-shift process allows two types of rearrangement to take place, RCH_2 group migration and phenyl group migration. The di-π-methane process, on the other hand, predicts only a single type of rearrangement, one which at the intermediate stage **11** becomes indistinguishable from the phenyl 1,2-shift process; therefore, a means exists for differentiating, at least partially, between these two pathways. In examining the products from reaction of compounds **1**–**5**, one finds support for the existence of the migration process since reaction understandable in terms of RCH_2 group migration results from photolysis of all five compounds. In photolysis of **2** and **3** it is the sole rearrangement process. Since phenyl group migration and di-π-methane type reaction pass through a common intermediate (**11**), it is not possible to determine whether one or a combination of these two pathways is being followed for the remaining compounds **1**, **4**, and **5**. What is clear is that in choosing between these two mechanisms the 1,2-shift process must be recognized as accounting for some products and capable of accounting for all of them. Further, although it cannot be definitely excluded on the basis of the present evidence, no di-π-methane type of transformation is required to understand these reactions.

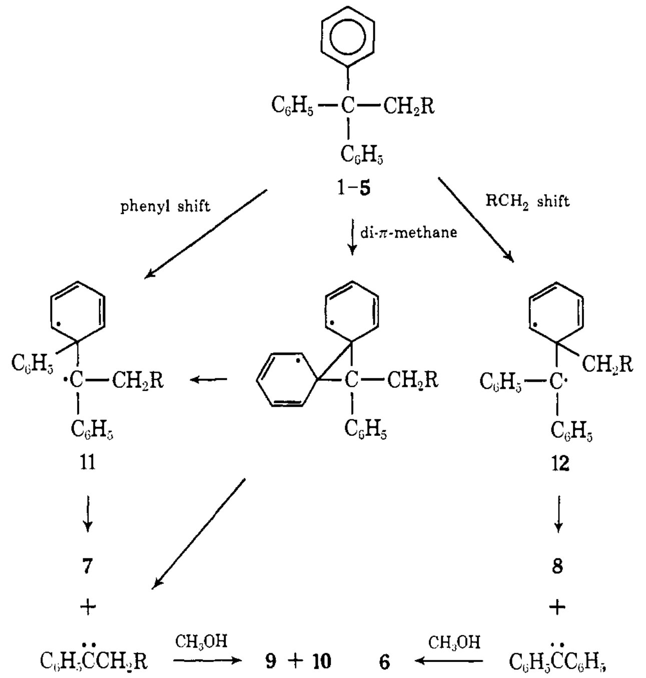


$$C_6H_5{-}\underset{C_6H_5}{\overset{C_6H_5}{C}}{-}CH_2R \xrightarrow[CH_3OH]{h\nu} \underset{6}{(C_6H_5)_2CHOCH_3} + \underset{7}{C_6H_5C_6H_5} +$$

1, R = CH_2CH_3
2, R = $CH{=}CH_2$
3, R = $CH{=}C(CH_3)_2$
4, R = C_6H_5
5, R = $C_6H_5CH_3$-*p*

$$\underset{8}{C_6H_5CH_2R} + \underset{9}{C_6H_5CH(OCH_3)CH_2R} + \underset{10}{C_6H_5CH{=}CHR} \quad (1)$$

Scheme I. Proposed Reaction Pathways



Both mechanisms pictured in Scheme I assume the reactions of **1**–**5** to be intramolecular. Although this seemed quite probable, it was desirable to have direct evidence supporting such an assumption.[6] The intramolecularity of the reaction of one of the five, 1,1,1,2-tetraphenylethane (**4**), was established by irradiating it in the presence of an equal molar amount of 1,1,1,2-tetra-*p*-tolylethane (**13**). Although **13** experiences the same type of reaction as **4**, no products from a "crossover" process were detected; that is, only photoproducts containing two phenyl groups or two *p*-tolyl groups were formed. Since compound **4** reacts in an intramolecular fashion, it is reasonable to assume that this

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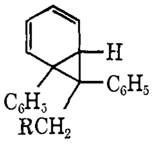
(2) Although others have made important contributions, study of the di-π-methane rearrangement has been primarily the work of Zimmerman and his students. The most recent publication from the Zimmerman laboratory on this reaction is H. E. Zimmerman and M. Viriot-Villaume, *J. Amer. Chem. Soc.*, **95**, 1274 (1973).

(3) Two molecules whose reactivity may be of the di-π-methane type between benzene rings are tetraphenylmethane (T. D. Walsh and D. R. Powers, *Tetrahedron Lett.*, 3855 (1970)) and triptycene (T. D. Walsh, *J. Amer. Chem. Soc.*, **91**, 515 (1969), and N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, *ibid.*, **91**, 516 (1969)).

(4) C. R. Hauser, C. F. Hauser, and P. J. Hamrick, *J. Org. Chem.*, **24**, 397 (1959). New compounds gave correct elemental analyses and spectra.

(5) The hydrocarbon photoproducts were either commercially available or synthesized by standard procedures. The ethers were synthesized from the corresponding alcohols *via* the Williamson synthesis. Although cis and trans isomers of **10** were not separated, identification of **10** is based upon comparison of its nmr and ir spectra with appropriate mixtures of the independently obtained cis and trans isomers as well as chromatographic (column and glc) behavior. Thus, although accurate cis:trans ratios were not determined, the identification procedure showed the cis isomer greatly (>80%) predominated in each case.

(6) We thank a referee for pointing out this fact.



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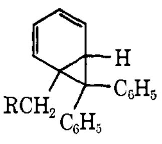

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type of reactivity extends to all of the triphenylmethane derivatives **1–5**.

It is worthwhile to consider the possible formation of the norcaradienes **14** and **15** as intermediates in the transformations of **1–5**. Compound **14** would be the "normal" di-π-methane rearrangement product[2] while both **14** and **15** would be the products of concerted $_{\pi}2_a + {}_{\sigma}2_a$ cycloaddition.[7] Since no evidence exists for formation of these molecules from compounds **1–5**,[8] they were not included in the proposed reaction mechanism (Scheme I). It is conceivable, however, that they (**14** and **15**) are intermediates in these reactions since their photochemical decomposition could yield the same products as the rearrangement of **11** and **12**.[9] Supporting this possibility is the fact that **14** and **15** should be indirectly excited by energy transfer with ease,[10] thus allowing their facile further reaction. Unfortunately, the question of the intermediacy of norcaradienes in the photochemical reactions of phenyl-substituted methanes does not appear to be answerable from study of the substituted triphenylmethanes **1–5**. We are continuing to explore this question as part of an effort to further understand the relationship between the various possible reaction pathways (di-π-methane, 1,2 shift, σ + π addition) available to excited aromatic systems attached to the same atom.

Acknowledgment. The authors wish to express their appreciation to Dr. Thomas W. Flechtner for his stimulating discussion of this work.

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(7) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 820 (1969).

(8) The nmr spectra of the crude reaction mixtures from photolyses of **1–5** were examined for the presence of olefinic absorptions not present in the starting materials or in **10**. None were detected.

(9) This type of reaction has been observed in similar systems. See: (a) T. Toda, M. Nitta, and T. Mukai, *Tetrahedron Lett.*, 4401 (1969); (b) M. Pomerantz and G. W. Gruber, *J. Amer. Chem. Soc.*, **89**, 6798 (1967); (c) D. B. Richardson, L. R. Darret, J. M. Martin, Jr., W. E. Putnam, S. C. Slaymaker, and I. Dvoretsky, *J. Amer. Chem. Soc.*, **87**, 2763 (1965).

(10) The triplet energy of compounds similar to **1–5** is 82 kcal/mol (ref 1d) while the norcaradiene system would be expected to have a triplet energy in the 50–60 kcal/mol range.[11]

(11) (a) D. F. Evans, *J. Chem. Soc.*, 1735 (1960); (b) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

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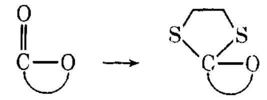
A Method for the Protection of Lactones and Esters against Nucleophilic Attack

Sir:

The direct application to lactones and esters of protecting groups which prevent attack at these sites by nucleophilic reagents (*e.g.*, RLi, AlH_4^-, OH^-) has not previously been part of synthetic practice, in contrast to the very widespread usage of ketal, thioketal, and acetal protection of ketones and aldehydes.[1] The need to effect such protection of a lactone function in connection with a synthetic program under way in these laboratories coupled with the inadequacy of existing methods for the conversion of lactones to suitable derivatives[2,3] led to the search for a mild and generally useful new method. This communication records a practical solution to the problem.

The ideal derivative for lactone protection appeared to be the corresponding 1,3-dithiolane structure. This type of unit is more stable to weakly acidic reagents than the highly labile ortho ester (oxygen) analog and can be removed by a variety of highly specific reagents under nearly neutral[4] conditions. It appeared possible that the lactone → 1,3-dithiolane conversion might be effected under mild nonacidic reaction conditions using a reagent of the type $MetSCH_2CH_2SMet$, in which Met represents a metallic unit having a larger affinity for oxygen than for sulfur substituents. Of the various candidates Met = dialkylaluminum was selected for initial studies. It was soon ascertained that such reagents performed the desired function and that the dimethylaluminum reagent (I) possessed superior reactivity.[5]



Bis(dimethylaluminum) 1,2-ethanedithiolate (I) can be generated from trimethylaluminum (as a *ca.* 1.7 *M* solution in toluene as obtained from Texas Alkyls, Inc.) and ethanedithiol (molar ratio 2:1) in toluene–methylene chloride at −78° initial temperature with gradual warming to room temperature.[6] Reaction of I (1.05 equiv) with the unsaturated lactone 11[7] in methylene chloride (at *ca.* 0.25 *M* reactants) first at −20° was com-

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(1) For a review of such protection see J. F. W. McOmie, *Advan. Org. Chem.*, **3**, 191 (1963); J. F. W. McOmie, "Protective Groups in Organic Chemistry," Plenum Press, London, 1973.

(2) For background information see R. H. De Wolfe, "Carboxylic Ortho Acid Derivatives," Academic Press, New York, N. Y., 1970, Chapters 1 and 6.

(3) Two methods for the conversion of lactones to ortho esters have been described by the Meerwein school: (a) the reaction with boron trifluoride and an oxirane to give 1,3-dioxolane derivatives [K. Bodenbenner, *Justus Liebigs Ann. Chem.*, **623**, 183 (1959)], and (b) the reaction with a trialkyloxonium salt followed by treatment with an alkoxide salt [H. Meerwein, P. Borner, O. Fuchs, H. J. Saase, H. Schrodt, and J. Spille, *Chem. Ber.*, **89**, 2060 (1967)]. The former method requires the use of a strongly acidic reagent and affords at best only moderate yields; the latter suffers from limitations of scope and efficiency.

(4) A number of methods which are applicable to thioketals (*e.g.*, 1,3-dithianes) can be mentioned in this regard including Hg^{2+}–HgO or *N*-halosuccinimide [E. J. Corey and B. W. Erickson, *J. Org. Chem.*, **36**, 3553 (1971); E. Vedejs and P. L. Fuchs, *ibid.*, **36**, 366 (1971)], chloramine-T [D. W. Emerson and H. Wynberg, *Tetrahedron Lett.*, 3445 (1971)], Ce(IV) [T.-L. Ho, H. C. Ho, and C. M. Wong, *J. Chem. Soc., Chem. Commun.*, 791 (1972)], and CH_3I or FSO_3CH_3 [M. Fetizon and M. Jurion, *ibid.*, 382 (1972)].

(5) Reagents based on other metals, *e.g.*, boron or titanium, have not been studied thus far.

(6) All operations involving organoaluminum reagents were conducted in an atmosphere of dry argon or nitrogen using oxygen-free, dry solvents. In a typical preparation of I, 15 ml of a cooled solution of trimethylaluminum (1.67 *M* in toluene) was diluted with 10 ml of dry methylene chloride, further cooled to −78°, and treated dropwise with 1.06 ml (12.5 mmol) of dry ethanedithiol (distilled from Linde 4A Molecular Sieve) to afford a colorless precipitate (*strongly exothermic* reaction). After warming to 25° over *ca.* 30 min, the partially soluble reagent (I) is ready for use *in situ*. Alternatively, the mixture may be concentrated to dryness to yield I as a colorless solid which may be stored under nitrogen and used for reactions as needed with methylene chloride as the preferred solvent.

(7) E. J. Corey, Z. Arnold, and J. Hutton, *Tetrahedron Lett.*, 307 (1970).