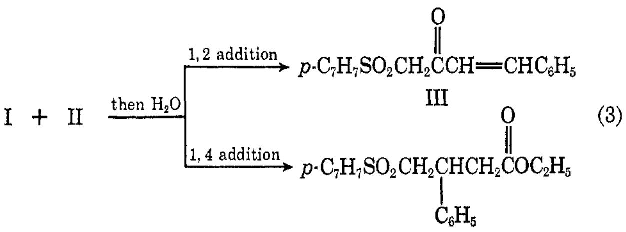
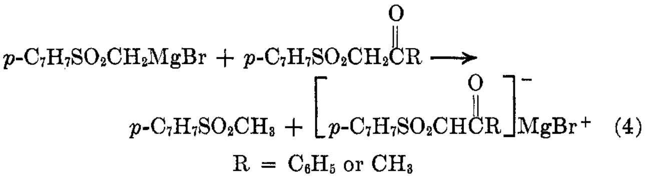
Two distinct products would be possible from the reaction of I and II, one from a 1,2-addition reaction and the other from 1,4 addition. It was not expected that ketone III would add a molecule of I in the conventional sense because Field and coworkers[7] had shown that the following reaction takes place.



$$\mathrm{I} + \mathrm{II} \xrightarrow{\text{then } H_2O} \begin{cases} \xrightarrow{1,2\ \text{addition}} p\text{-}C_7H_7SO_2CH_2C(=O)CH{=}CHC_6H_5 \quad \text{III} \\ \xrightarrow{1,4\ \text{addition}} p\text{-}C_7H_7SO_2CH_2CH(C_6H_5)CH_2C(=O)OC_2H_5 \end{cases} \quad (3)$$



$$p\text{-}C_7H_7SO_2CH_2MgBr + p\text{-}C_7H_7SO_2CH_2C(=O)R \longrightarrow p\text{-}C_7H_7SO_2CH_3 + \left[p\text{-}C_7H_7SO_2CHC(=O)R\right]^- MgBr^+ \quad (4)$$

$$R = C_6H_5 \text{ or } CH_3$$

In this paper we shown that the product from the reaction of I and II is always III. There was no evidence for 1,4 addition over a I/II ratio of 3:1 to 1:2 and a temperature range of 0–80°. Consistent with Field's results, the yield of III was less than the possible 50% when a 1:1 ratio of Grignard reagent and ester was used. Furthermore, one-half of the methyl p-tolyl sulfone and one-half of the ethyl cinnamate should be recovered. Our results approximated those predictions. The low yields of III in some cases may have been due to difficulty in the separation of mixtures. Fractional crystallization was found better for separating III from sulfone and unreacted II than was chromatography on alumina.

In conclusion, sulfonyl Grignard reagents undergo only 1,2 additions to cinnamate esters. This behavior is analogous to the reactions of I with α,β-unsaturated aldehydes and ketones. The sulfonyl Grignard reagent resembles vinyl Grignard reagents more than it does phenylmagnesium bromide in its reactions with cinnamate esters. The possible reasons for exclusive 1,2 addition have already been discussed.[1]

Experimental Section

Reaction of p-Tolylsulfonylmethylmagnesium Bromide (I) with Ethyl Cinnamate (II).—The p-tolylsulfonylmethylmagnesium bromide (I) was prepared from 12.75 g (0.075 mol) of methyl p-tolyl sulfone[8] by the procedure used previously.[1] To the slurry of I in ether–benzene was added during 20 min at room temperature 13.47 g (0.077 mol) of II in 80 ml of dry benzene. After the mixture was stirred an additional 4 hr at room temperature, hydrolysis was effected with 100 ml of cold 1 N HCl solution. Removal of solvent *in vacuo* gave 22.7 g of greasy solid, mp 70–80°. Recrystallization from benzene–petroleum ether afforded 6.4 g (28.4%) of white needles, mp 115–119°. Further recrystallization gave 1-(p-tolylsulfonyl)-4-phenyl-3-buten-2-one (III) with constant mp 127–128°. Ir and nmr spectroscopy confirmed the structure of III.

Anal. Calcd for $C_{17}H_{16}O_3S$: C, 68.00; H, 5.33; S, 10.67. Found: C, 67.86; H, 5.21; S, 10.82.

The addition of 2 vol. of petroleum ether to the filtrate gave 6.60 g (51.8%) of recovered methyl p-tolyl sulfone, mp 73–78°. Recrystallization from ethanol–water gave pure sulfone, mp 85–86°, which did not depress the melting point of an authentic sample.

Removal of solvent and distillation of the residue afforded 9.28 g (68.5% recovery) of unreacted ethyl cinnamate (II), bp 66–69° (0.10 mm). The ir spectrum was identical with that of starting material.

In other reactions at various temperatures and I/II ratios, the maximum yield of III (86.6%) was obtained at room temperature with a I/II ratio of 2:1.

Registry No.—I, 3048-28-0; II, 103-36-6; III, 23042-70-8.

Acknowledgment.—The authors wish to thank the donors of the Petroleum Research Fund for the PRF Grant No. 2571-B which partially supported this investigation.

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[7] L. Field, J. E. Lawson, and J. W. McFarland, *J. Amer. Chem. Soc.*, **78**, 4389 (1956).

[8] R. Otto, *Ber.*, **18**, 161 (1885).

Ring Inversion of Perfluoro-1,4-dithiane[1]

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Interconversion of chair conformations of six-membered rings containing two identical heteroatoms has been much studied by the nmr method,[3] with the exception of the 1,4-dithiane system. The results so far obtained for 1,2- and 1,3-dithianes in comparison with those of dioxanes and the corresponding diaza systems suggest that this barrier should be readily measureable by the nmr method. We are concerned here with the ring inversion of octafluoro-1,4-dithiane (**1**).

The ^{19}F nmr spectrum of **1**, kindly supplied by Dr. B. C. McKusick of the Central Research Department of E. I. du Pont de Nemours and Co., in 2:1 (v/v) acetone–chloroform at 70° is a single line of half band width of *ca.* 1.8 Hz, 71.8 ppm downfield from internal hexafluorobenzene. At $-90°$, the spectrum appears as an AB quartet, each line of which shows small additional splittings, centered 70.0 ppm downfield from internal hexafluorobenzene. The chemical-shift difference between the A and B parts is 15.02 ppm and J_{AB} is 230 Hz. The quartet coalesces to a broad singlet at $-32°$. To gain information about the barrier to inversion, spectra were recorded at 23 temperatures between -62 and 17°.

A series of spectra, calculated as a function of τ, the average lifetime spent in either chair confirmation, was generated by standard procedures[4] and compared with the experimental spectra to obtain a value of τ for each temperature. The variation of the rate constant k_{inv} ($= 1/\tau$) for interconversion of chair conformations with temperature gave the free energy of activation ($\Delta G^{\ddagger}$) as 10.05 ± 0.10 kcal/mol at $-32°$, the enthalpy of activation ($\Delta H^{\ddagger}$) as 9.74 ± 0.20 kcal/mol, and the entropy of activation ($\Delta S^{\ddagger}$) as -1.2 ± 1 eu.

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[1] Supported by the National Science Foundation.

[2] Harkness Fellow of the Commonwealth Fund of New York, 1966–1968. Chemistry Department, University College, Gower Street, London, W.C. 1.

[3] G. Binsch in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, Inc., New York, N. Y., 1968, p 97, provides an excellent review.

[4] J. T. Gerig and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 2791 (1966).

The barrier to ring inversion for **1** is slightly smaller than those of 1,2-dithiane, 11.6 kcal/mol,[5] and 1,3-dithiane, 10.4 kcal/mol,[6] although it would hardly be tenable to draw very detailed conclusions concerning dithiane itself from the results for **1**. On the basis of the fluorine chemical-shift differences at −90°, which compare reasonably well with those for noninverting (or slowly inverting) *gem*-fluorocyclohexanes,[7] we have assumed that the preferred conformation of **1** is a chair—possibly strongly puckered as for 1,4-dithiane.[8]

Registry No.—**1,** 710-65-6.

Acknowledgment.—We are grateful to Mr. J. E. Leininger for assistance with the computing.

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[5] C. Claesen, G. M. Androes, and M. Calvin, *J. Amer. Chem. Soc.*, **82,** 4428 (1960).

[6] H. Friebolin, S. Kabuss, W. Maier, and A. Luttringhaus, *Org. Magnetic Resonance*, **1,** 67 (1969).

[7] Cf. G. A. Yousif and J. D. Roberts, *ibid.*, **90,** 6428 (1968), and references cited therein.

[8] J. B. Lambert, *J. Amer. Chem. Soc.*, **89,** 1836 (1967); J. B. Lambert, R. E. Carhart, and P. W. R. Corfield, *ibid.*, **91,** 3567 (1969).

Observations Related to the Preparation of 2-Phenyliodoniobenzoate

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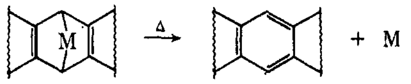
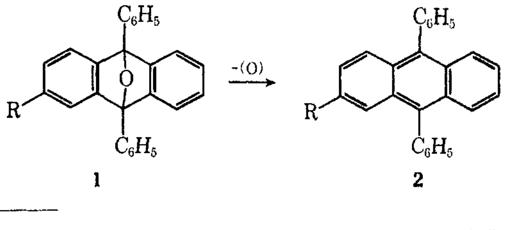
Several M-bridged polycyclic systems are known to undergo thermally induced extrusion of the bridging elements with concomitant formation of an aromatic system. When this operation is conducted in the presence of a reagent to trap M, it frequently constitutes a synthetically useful process.[1] With this notion in mind, we investigated the thermolysis of 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene (**1**, R = H), a compound previously reported to undergo thermal decay, ostensibly in accord with the above-mentioned principle, to produce 9,10-diphenylanthracene (**2**, R = H), although the fate of the oxygen bridge was not established.[2]

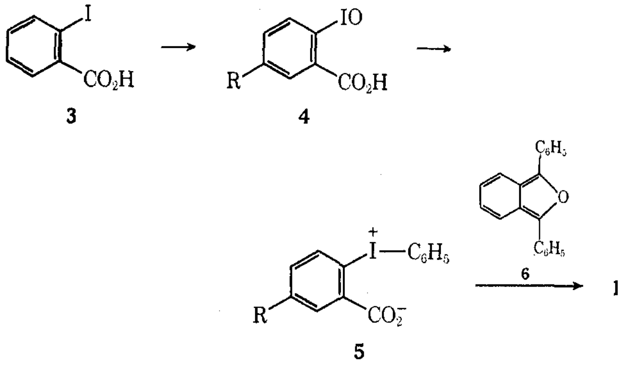




1 **2**

We reproduced the procedure (Scheme I) for the synthesis of **1** (R = H) from 2-phenyliodoniobenzoate (**5**) and 1,3-diphenylisobenzofuran (**6**), which involved:[2] oxidation (fuming nitric–sulfuric acid mixture) of *o*-iodobenzoic acid (**3**) to an *o*-iodosobenzoic acid (**4**); sulfuric acid-catalyzed condensation of **4** with benzene to produce betaine **5**, followed by thermal decomposition of the benzyne precursor **5** in the presence of **6**.

SCHEME I



The physical properties of compounds **4**, **5**, and **1** obtained by this route were in accord with those reported[2] for **4** (R = H), **5** (R = H), and **1** (R = H). However, **1** was recovered (91% yield) after being heated at reflux in triglyme solution.[3]

In view of the well-documented analogy between various thermolysis and electronolysis reactions,[4] the mass spectrum of **1** was investigated for an $M - 16$ ion. Although such fragmentation was not observed to be appreciable, the appearance of the molecular ion at *m/e* 391, consistent with the formulation $C_{26}H_{17}NO_3$, *requires reconstitution of* **1** (*R* = *H*), *prepared by this route, as* **1** (*R* = NO_2). Correspondingly, materials synthesized by this procedure are reassigned structures **4** (R = NO_2) and **5** (R = NO_2). All revised assignments are supported by correct compositional analyses, as well as corroborative ultraviolet, infrared, proton magnetic resonance, and mass spectroscopic evidence (*cf.* Experimental Section). Apparently the conditions selected for oxidation (ArI → ArIO) were adequate to effect electrophilic aromatic nitration as well.[5]

An authentic sample of **5** (R = H) was obtained by successively treating a mixture of **3** in concentrated sulfuric acid with potassium persulfate, benzene, then base, according to the method of LeGoff[6] and Fieser.[7] Compounds **5**-H and **5**-NO_2 were thereby readily distinguished; compounds **1**-H and **1**-NO_2 were also spectroscopically differentiated. Compound **1**-H was recovered (92% yield) after being heated at reflux in triglyme solution (2.5 hr),[3] and in 90% yield after a 2.25-hr reflux period in a diglyme solution containing cyclohexene.

Compound **5**-NO_2 serves as an effective "4-nitrobenzyne" precursor. Thermolysis of **5**-NO_2 in the

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[1] *Inter alia*, diimide (M = HNNH), E. J. Corey and W. L. Mock, *J. Amer. Chem. Soc.*, **84,** 685 (1962); dimethylsilylene [M = $Si(CH_3)_2$], H. Gilman, S. S. Cottis, and W. H. Atwell, *ibid.*, **86,** 1596 (1964); singlet oxgen, H. H. Wasserman, and J. R. Scheffer, *ibid.*, **89,** 3073 (1967); tetramethyldisilene, G. J. D. Peddle, D. N. Roark, A. M. Good, and S. G. McGeachin, *ibid.*, **91,** 2807 (1969). For a survey of other examples, see B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, New York, N. Y., 1967.

[2] F. M. Beringer and S. J. Huang, *J. Org. Chem.*, **29,** 445 (1964).

[3] Although this result differs from previous observations,[2] we cannot account for the discrepancy.

[4] A. Maccoll in "Modern Aspects of Mass Spectroscopy," R. I. Reed, Ed., Plenum Press, New York, N. Y., 1968, pp 143–168.

[5] This result is in accord with the observations of H. Goldstein and A. V. Grampoloff, *Helv. Chim. Acta*, **13,** 310 (1930).

[6] E. LeGoff, *J. Amer. Chem. Soc.*, **84,** 3786 (1962).

[7] L. F. Fieser, "Organic Experiments," D. C. Heath and Co., Boston, Mass., 1964, pp 311–313; L. F. Fieser and M. J. Haddadin, *Org. Syn.*, **46,** 107 (1966).