

- MeOH, but this was generally less satisfactory than the acid-catalyzed reactions.
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- (23) Enamides could also be obtained in good yields when the epoxysilanes were treated with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ for longer periods of time, or when the oxazolines or the hydroxyamides were treated with $\text{BF}_3 \cdot \text{Et}_2\text{O}$, but these reactions were accompanied by some cis-trans isomerization when carried out on a preparative scale.
- (24) However, the relative orientation of the C-Si bond and the β C-O bond greatly deviate from the parallel alignment favorable for the stabilization of a developing positive charge by the silicon (see ref 13b).
- (25) Enolates are useful precursors to other enol derivatives, e.g., silyl enol ethers (G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, **90**, 4462-4464 (1968); H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324-2336 (1969)) and vinyl triflates (P. J. Stang, M. G. Mangum, D. P. Fox, and P. Haak, *J. Am. Chem. Soc.*, **96**, 4562-4569 (1974); T. C. Clarke and R. G. Bergman, *ibid.*, **96**, 7934-7944 (1974)).
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The 9,10-Dihydro-9,10-(1,2-tropylio)anthracene Tetrafluoroborate. Transannular π - π Interaction between Tropylium Ion and Remote Benzene Rings

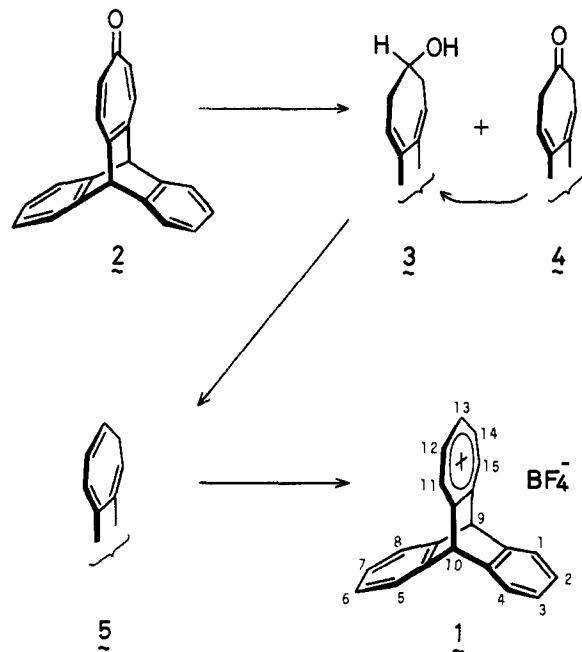
Sir:

In the time since the 1942 publication by Bartlett and co-workers of their first synthesis of triptycene,¹ the question of transannular π - π interaction between the remote (nonconjugated) benzene rings in triptycene still remains a subject of controversy.² Previous UV³ and CD⁴ spectroscopy measurements of some heterocyclic triptycenes have revealed that π - π interaction between all three rings in triptycene systems exists. On the other hand, intermolecular charge-transfer complex formation has been found between various stable carbonium ions and aromatic hydrocarbons.^{5,6} Quite recently, intramolecular charge-transfer interaction was observed in the [2.2](1,4)tropylioparacyclophane tetrafluoroborate independently by two research groups.^{7,8}

In view of these precedents, the 9,10-dihydro-9,10-(1,2-tropylio)anthracene tetrafluoroborate (**1**), which consists of the tropylium ion and two benzene rings with rigid spacial arrangement identical with triptycene, would be a pertinent model for the intramolecular remote π - π interaction. In this communication we wish to describe the synthesis and properties of **1**.

Our synthetic approach to **1** is outlined in the following scheme. The requisite tropone (**2**) was accessible conveniently by the reaction of 4,5-dehydrotropone with anthracene.⁹ Reaction of **2** with a threefold excess of lithium aluminum hydride¹⁰ in a mixture of benzene and ether for 2 h at ambient temperature gave the dienol (**3**). Chromatographic (Al_2O_3 ,

CH_2Cl_2) purification afforded a 35% yield of **3**,¹¹ pale yellow prisms, mp 184-186 °C (IR 3300 cm^{-1} OH; NMR δ (in CDCl_3 , 100 MHz) 1.57 (d, $J = 6$ Hz, OH), 2.43 (dd, $J = 5$ and 4 Hz, $-\text{CH}_2-$), 3.99 (dq, $J = 6$ and 5 Hz, $>\text{CHO}-$), 4.71 (s, $>\text{CH}$), 5.75 (t, $J = 4$ Hz, $-\text{CH}=\text{C}$), 7.00-7.38 (AA'BB', aromatic), along with 9% yield of the dienone (**4**). When the reduction was carried out at -70 to -65 °C with 3 molar equiv of lithium aluminum hydride, the dienone (**4**),¹¹ colorless prisms, mp 230 °C dec (IR 1699 cm^{-1} C=O; NMR δ (in CDCl_3 , 60 MHz) 3.04 (d, $J = 5$ Hz, $-\text{CH}_2\text{CO}-$), 4.88 (s, $>\text{CH}$), 5.74 (t, $J = 5$ Hz, $-\text{CH}=\text{C}$), 7.02-7.45 (AA'BB', aromatic), was obtained as a major product which afforded the dienol (**3**) as the sole product (70% yield) through further reduction with lithium aluminum hydride.



Attempts to prepare the cycloheptatriene (**5**) from **3** by direct dehydration failed. Instead conversion of **3** to its mesylate ($\text{CH}_3\text{SO}_2\text{Cl}$, Et_3N , CH_2Cl_2) which, without purification, was subjected to elimination with 1,8-diazabicyclo[5.4.0]undec-7-ene¹² in CH_2Cl_2 gave the cycloheptatriene (**5**)¹¹ in 33% yield, colorless prisms, mp 196-199 °C (NMR δ (in CDCl_3 , 100 MHz) 2.24 (t, $J = 6.5$ Hz, 2 H), 4.92 (s, 1 H), 4.95 (s, 1 H), 5.17 (dt, $J = 9.8$ and 6.5 Hz, 1 H), 5.40 (t, $J = 6.5$ Hz, 1 H), 5.96 (dd, $J = 9.8$ and 6.0 Hz, 1 H), 6.54 (d, $J = 6.0$ Hz, 1 H), 6.95-7.40 (m, aromatic)).¹³

Completion of the synthesis requires a hydride ion abstraction from **5** and was achieved by use of trityl tetrafluoroborate in CH_2Cl_2 . The cation, **1** (as tetrafluoroborate), which was obtained in ~70% yield as greenish yellow prisms, decomposed at around 110 °C. The structure of **1** was supported by its spectroscopic data (IR 1030-1125 cm^{-1} (broad strong, BF_4^-); NMR δ (in CD_2Cl_2 , 100 MHz) 6.26 (s, 2 H, H-9 and -10), 7.18 (AA' part) and 7.69 (BB' part of AA'BB' system, 8 H, aromatic), 8.60-8.94 (m, 3 H, H-12, -13, and -14), 9.14-9.32 (m, 2 H, H-11 and -15); δ (in CF_3COOH , 100 MHz) 6.15 (s, 2 H, H-9 and -10), 7.22 (AA' part) and 7.66 (BB' part of AA'BB' system, 8 H, aromatic), 8.74-8.92 (m, 3 H, H-12, -13, and -14), 9.04-9.24 (m, 2 H, H-11 and -15)). Although the NMR data obtained for the cation, **1** (slight downfield chemical shifts of the aromatic protons of **1** compared with those of **5** and triptycene¹⁴), suggested a certain degree of the positive charge delocalization over the two benzene rings, because of the complexity of the factors affecting the chemical shifts, no definite conclusion concerning the intramolecular π - π interaction could be made.

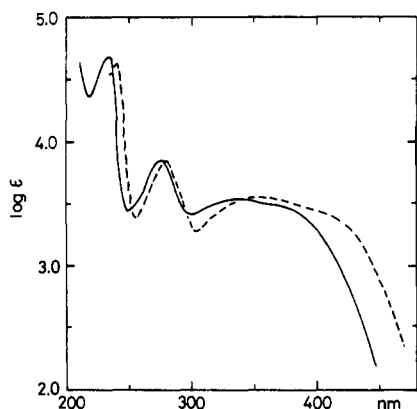


Figure 1. Electronic spectrum of **1** in CH_3CN (—) and CH_2Cl_2 (- - -).

However, the electronic spectrum of **1** (Figure 1) exhibited a broad long wavelength absorption at 300–450 nm ($\log \epsilon > 3.0$),¹⁵ not found in the spectra of either tropylium tetrafluoroborate¹⁶ or 1,2-dimethyltropylium tetrafluoroborate,¹⁷ clearly indicating a charge-transfer interaction between the tropylium ion and remote benzene rings in **1**. The substantial blue shift accompanying the change from methylene chloride to acetonitrile as solvent (Figure 1) is in accord with the solvent sensitivity of the charge-transfer band.¹⁸

An important aspect of the significance of the charge transfer interaction in **1** is the fact that donor and acceptor are not in parallel planes. In view of the fact that most charge-transfer interactions both intra- and intermolecular usually place the donor and acceptor in near parallel geometric orientation, we think it worthy to note that in this molecule the interaction is strong despite the minimized overlap of the orbital systems of both donor and acceptor. This of course raises the question of how much through bond interaction is responsible for charge-transfer in this system.¹⁹ Experimental and theoretical study on **1** with molecules containing much stronger donor moieties, e.g., naphthalene and methyl substituted benzene frameworks, which will offer further evidence on the charge-transfer interaction, is in progress.

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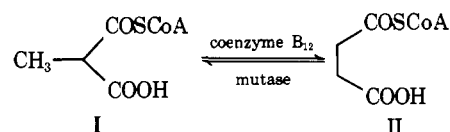
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The Mechanism of Action of Coenzyme B₁₂. The Role of Thioester in a Nonenzyme Model Reaction for Coenzyme B₁₂ Dependent Isomerization of Methylmalonyl Coenzyme A to Succinyl Coenzyme A

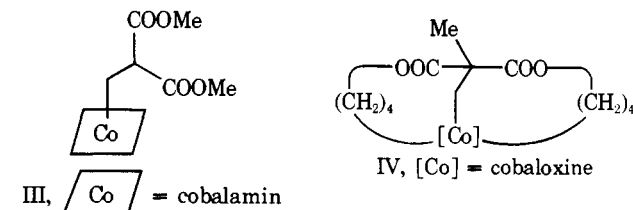
Sir:

Although much interest has been focused on the search for a mechanistic rationale for the biological reactions of adenosylcobalamin,¹ little parallel exists in organic chemistry for many of the processes involved. The evolution of working, nonenzymic models to uncover the requisite analogies has already led to some suggestive experiments.² In the case of the methylmalonyl CoA \rightleftharpoons succinyl CoA (**I** \rightleftharpoons **II**) conversion, such a model in its most sophisticated form would be required to simulate the following salient features of the enzyme catalyzed



process. (1) The thioester (COSC) group migrates³ in an intramolecular 1,2 shift.⁴ (2) Intermolecular hydrogen atom transfer from the CH_3 group via the 5'-methylene of deoxyadenosine and return to substrate is observed.⁵ (3) Configuration at both termini of the rearranging species is retained,⁶ a process which does not necessarily involve a σ -bonded organocobalt derivative of the substrate.

Recent nonenzymic studies of this reaction have uncovered (a) the conversion of the metastable alkyl cobalamin dimethyl ester **III** to succinic acid⁷ and (b) the rearrangement of the capped cobaloxime complex of dimethylmalonic acid (**IV**) to methyl succinic acid in an intramolecular process.⁸ It has also



been suggested⁸ that the low yield in reaction a is due to loss of contact of the radical (or ionic) substrate species with the central cobalt of reduced coenzyme or cobaloxime. As far as we are aware, the role of the thioester has not yet been evaluated in terms of stabilization of radical (or ionic) intermediates, reaction yield, or migratory aptitude. To this end we have