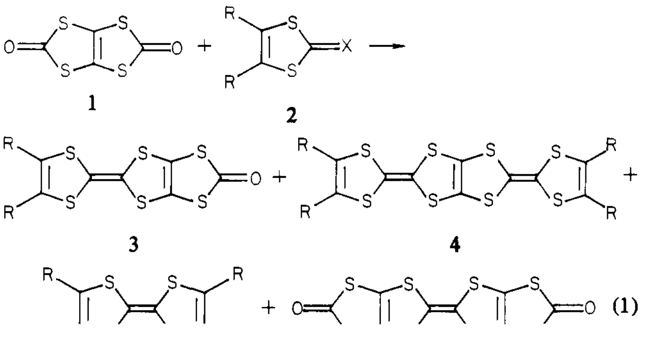
Table I. Experimental Data for 3, 4, 7, 9, and 11

compd	mp, °C	color (solvent)[a]	spectra[b]
3, R = CN	196 dec	magenta (CH_3CN)	(IR) 2210, 2205 (CN), 1675 (C=O)
3, R = CF_3	146-147	yellow (hexane)	(IR) 1680, 1665 (C=O), 1610, 1280, 1155 (CF_3); (^{19}F NMR) 49.6
4, R = CN	290 dec	black ($CHCl_3$ continuous extraction)	(IR) 2210 (CN)
4, R = CF_3	233-235	orange (benzene)	(IR) 1600, 1260, 1140 (CF_3)
7	252 dec	red (chlorobenzene)	(IR) 1605, 1270, 1165 (CF_3)
9, R = CO_2CH_3	204 dec	olive (nitrobenzene)	(IR) 1740, 1720, 1710 (ester), 1680 (C=O); (^1H NMR) 3.76, 3.80
11, R = CO_2CH_3	88-90	maroon (hexane)	(IR) 1725, 1710 (ester); (^1H NMR) 2.32, 3.72

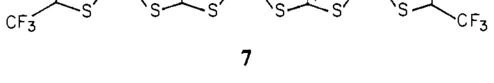
[a] Recrystallization solvent. [b] IR: KBr, cm^{-1}. ^{19}F NMR: $CHCl_3$, ppm relative to CCl_3F. ^1H NMR: ppm relative to Me_4Si.

acceptors to form the most conducting organic solids presently known.[1] The recent synthesis of 1,3,5,7-tetrathiapentalene-2,6-dione[2,3] (**1**, thiapendione) provided the possibility of elaborating a wide variety of novel TTF derivatives through cross-coupling reactions[4] with 1,3-dithioles (**2**) (eq 1).



The cross-coupling reaction depends on the nature of the R and X substituents in dithiole **2**. Mono and bis capping of dithiapen to give products **3** and **4**, respectively, occurs when R = CO_2CH_3 or CF_3 and X = S and when R = CN and X = O. No cross-coupling was observed for R = alkyl and/or X = Se. In a typical reaction, a 2–4 mol excess of dithiole derivative to thiapendione was refluxed with excess trimethyl phosphite in dry benzene under N_2 for several hours. The products (**3**–**6**) were isolated by chromatography and by their solubility differences. Identification of the products was based on their spectral properties, mass spectral data (except for **4**) and elemental analysis. Table I summarizes some of this data.[5]

Selective high-yield preparations of either **3** or **4** could be achieved by modifying the cross-coupling reaction conditions. At 60 °C in neat triethyl phosphite,[6] thiapendione (**1**) does not undergo self-coupling to dithiapendione (**6**) whereas dithioles **2** readily self-couple to their respective TTF derivatives **5**. Because of solubility differences, addition of dithiole to a 60 °C solution of thiapendione in triethyl phosphite selectively precipitates in good yield (50–75%, based on thiapen) only monocapped product **3**, when R = CO_2CH_3, and only biscapped product **4**, when R = CF_3 or CN. In refluxing triethyl phosphite, monocapped product **3** (R = CF_3) self-couples to provide, in about 10% yield, the first example of a trisfused TTF derivative, bis(dithiolyidene)dithiapen (**7**).



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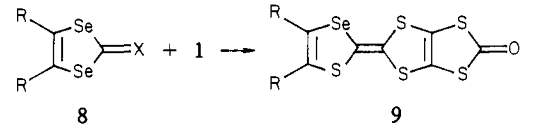
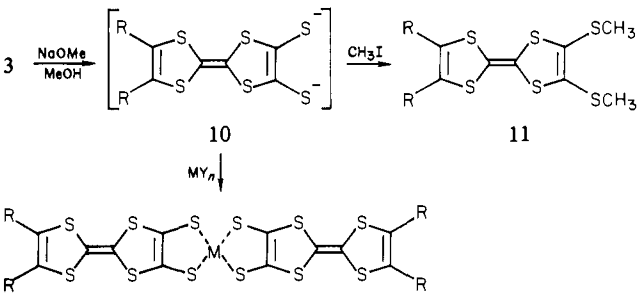
Extension of the cross-coupling reaction to 1,3-diselenoles (**8**, R = CO_2CH_3) failed when X = Se and led to a rearranged monocapped product **9** when X = S. As noted earlier[7] in the self-coupling of diselenole thiones, an interchange of a ring selenium with the carbonyl sulfur occurs to give a monocapped product (**9**) containing only one selenium.



Monocapped products can be converted in strong base (e.g., NaOMe) to the corresponding TTF dithiolate intermediates (**10**) which can then be treated with methyl iodide to provide unsymmetrically substituted TTF derivatives (**11**, R = CO_2CH_3). Alternately, treatment of **10** with transition-metal salts yielded a wide variety of novel metal dithiolene derivatives (**12**) which incorporate TTF as conjugated ligands.[8]



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Chemistry of Exciplexes. 10. Role of Excimers in Photocycloadditions of Arenes to 1,3-Dienes

Sir:

Photoexcited anthracenes and their catacondensed homologues form excimers,[1] and many are known to form exciplexes with

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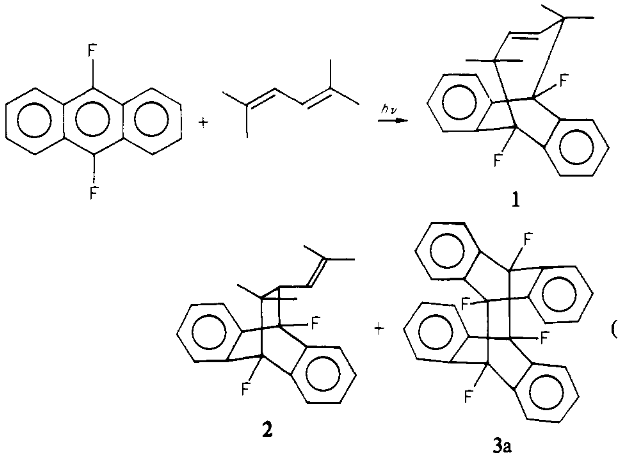
Table I[a]

arene (concn, M)[b]	diene (concn, M)[c]	solvent	Φ_{arene}	product (yield, %)			
				$4\pi_s + 4\pi_s$	$4\pi_s + 2\pi_s$	dimer	8 + 9[d]
DFA (9.3×10^{-4})[e]	DMHD (0.56)	cyclohexane	*f*	1 (45)	2 (4)	3a (33)	
DFA (8.3×10^{-3})[e,g]	DMHD (0.76)	cyclohexane	*f*		2 (6)	3a (76)	
a,j-DBA (4.4×10^{-4})[h]	CHD (1.8)	benzene	0.0015	4 (91)	5 (9)		
a,j-DBA (3.6×10^{-3})[h]	CHD (1.8)	benzene	0.0048	4 (11)	5 (89)		
anthracene (7.9×10^{-4})[h]	CHD (0.95)	benzene	0.34	6b (76)	7b (14)		(10)
anthracene (0.04)[h]	CHD (0.95)	benzene	0.81	6b (37)	7b (8)	3b (38)	(12)
anthracene (0.04)[h]		benzene	0.30			3b (100)	
9-PA (0.00134)[h]	CHD (0.95)	benzene	*f*	6c (17.5)	7c (67.5)		9c (15)
9-PA (0.134)[h]	CHD (0.95)	benzene	*f*	6c (14)	7c (50)		9c (36)

[a] All new products given in this table have been rigorously characterized by elemental and spectral analyses. [b] DFA, 9,10-difluoroanthracene; *a,j*-DBA, dibenz[*a,j*]anthracene; 9-PA, 9-phenylanthracene. [c] DMHD, 2,5-dimethyl-2,4-hexadiene; CHD, 1,3-cyclohexadiene. [d] Due to the instability of 8, the combined yield of 8 and 9 was estimated after the thermal conversion of 8 to 9. However, the relative increase in the yield of 9 was more pronounced than that of 8 at higher anthracene concentrations, and 8c was not detected in the reaction of 9-PA and CHD. [e] The yields given were estimated from the amount of products isolated by chromatography on alumina. [f] Not determined. [g] Anthraquinone was also obtained in 6% yield. [h] The yields of adducts given were determined by NMR spectroscopy of appropriate chromatographic fractions with a Bruker HX-270 NMR spectrometer, experimental uncertainty ±2%. [i] b series, X = Y = H; c series, X = Ph, Y = H.

1,3-dienes.[2] Arene excimers may decay to yield photodimers,[1,3] and arene–diene exciplexes may decay to yield photocycloadducts.[2] The mode of cycloaddition is highly selective, following the rule of conservation of orbital symmetry for an excited-state process.[4,5] Nevertheless, the mechanism of photocycloaddition of arenes to 1,3-dienes remains a subject of current interest as well as controversy.[2,6,7] Much of the controversy derives from the apparent discrepency between the relative ratio of different types of adducts formed in the reaction.[8,9] This communication deals with photocycloadditions of arenes to 1,3-dienes at various arene concentrations. Ratios of adducts formed and quantum yields of arene consumption varied dramatically as the concentration of arene in the reaction medium was changed. In general, the proportions of $4\pi_s + 4\pi_s$ adduct formed at the meso positions decrease at higher initial arene concentration, indicating that excimers, when compared to the corresponding monomeric singlet excited arenes, exhibit reduced impetus to undergo concerted cycloadditions at the meso positions with 1,3-dienes. The results clarify the apparent controversy in the reaction mechanism and also indicate that photochemical reaction pathways of arenes with 1,3-dienes may be controlled by varying the initial arene concentration to yield different products or different proportions of products.



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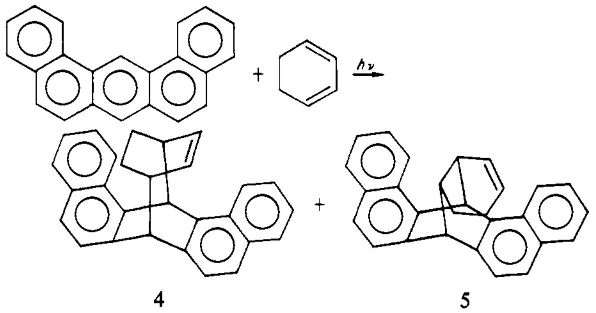

(2)

We have found that the major adduct from the photocycloaddition of 9,10-difluoroanthracene and 2,5-dimethyl-2,4-hexadiene (DMHD) changed from **1** to **2** as the initial concentration of the arene was increased (eq 1).[10] The major photocycloadduct from dibenz[*a,j*]anthracene and 1,3-cyclohexadiene (CHD) varied from **4** to **5** in a similar manner (eq 2). In both cases, the $4\pi_s + 4\pi_s$ adduct is the major product at low initial arene concentration, as was anticipated by orbital symmetry considerations for a bimolecular pericyclic reaction[4,5] while the $4\pi_s + 2\pi_s$ adduct is the major product formed at higher arene concentrations. These observations led us to a systematic analysis of photocycloadditions of anthracene and substituted anthracenes with CHD at various arene concentrations. Detailed product analysis on the photocycloaddition of anthracene to CHD revealed the formation of two minor adducts, **8** and **9**, in addition to adducts **6** and **7** which have been reported previously (eq 3).[9,11] Adduct **8** is labile and undergoes a facile Cope rearrangement to **9**. When the concentration of anthracene increases, there is a dramatic increase in the quantum yield of arene consumption, the yield of photodimer formation and the relative yield of **8** and **9** among the adducts. Since the disagreement on the relative amounts of adducts formed in this reaction in the literature was based on the reactions carried out with different anthracene concentrations, our current observation has resolved this discrepancy.[12] Investigation of the photocycloaddition of 9-phenylanthracene to CHD indicated a

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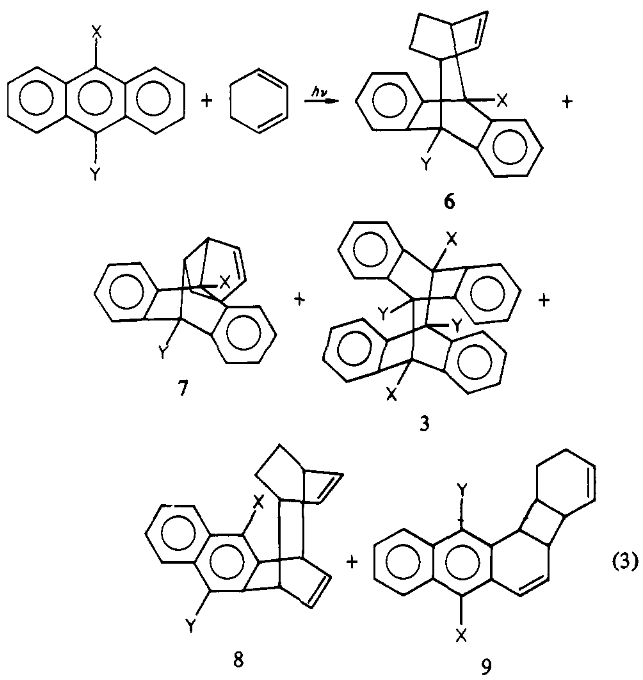

(3)

similar dependence of the proportions of adducts formed upon arene concentration. The results of representative cases are summarized in Table I.

As noted, photoexcited arene may react competitively either with another molecule of arene in its ground state to form an excimer or with a molecule of 1,3-diene to form an exciplex. The amount of excited arene which will decay via each pathway will depend on the relative concentrations of the two reactive species, the arene and 1,3-diene in their ground state, as well as on the relative extent of the equilibria for excimer and for exciplex formation. The meso positions are the most reactive positions in excited arenes since the MO coefficients of HOMO and LUMO are greatest in magnitude at these positions, i.e., the meso positions have the highest free valences.[13] The excited arene should react in a concerted manner at the meso positions to afford $4\pi_s + 4\pi_s$ adducts with 1,3-dienes, following the rule of conservation of orbital symmetry. However, the rate of this reaction is competitive against other decay processes of excited arene, such as intersystem crossing and radiative decay. In the cases we have studied, there appears to be a general trend in that $4\pi_s + 4\pi_s$ photocycloaddition at the meso positions is favored at lower initial arene concentration when the excited arene mainly decays via the arene–diene exciplex and the monomeric singlet excited arene. At higher initial arene concentration, excimer formation becomes more favorable. Since the excitation energy is delocalized between both components of excimer, each component will be less reactive at the meso positions toward the diene than will the monomeric excited arene. Thus, the formation of $4\pi_s + 4\pi_s$ adducts with 1,3-dienes in the expected manner is suppressed, and competitive processes such as nonconcerted $4\pi_s + 2\pi_s$ cycloaddition, addition at an alternative site, and arene photodimerization become the preferred modes of decay. Different products or different proportions of products are then formed in the reaction.

Liu and co-workers also have reported that 1,3-dienes promote the photodimerization of anthracenes and suggested that excimers are the intermediates in this reaction.[14] Since excimers of anthracenes have been characterized to have finite lifetimes,[3] the excimers may interact with 1,3-dienes to give enhanced yields of photodimers as an additional pathway of excimer decay when 1,3-dienes are present at sufficiently high concentrations in the reaction media. The enhanced quantum yield of anthracene consumption at high initial anthracene concentration in the presence of CHD may be justified by this pathway. Lewis and co-workers recently reported that the photocycloaddition of stilbene to dimethyl fumarate is concentration dependent, and the excimer of stilbene has been suggested as a intermediate at high stilbene concentration.[15] Therefore, excimers of arenes may play a more general role than previously anticipated in photocycloadditions of arenes to unsaturated systems.

Acknowledgment. We thank the National Science Foundation and the National Institute of General Medical Sciences for the support of this work, Dr. Bongsub Kim for carrying out the preliminary studies on the reaction of 9,10-difluoroanthracene, Professor L. M. Stock for a sample of 9,10-difluoroanthracene, and the Institute of Photographic Chemistry of the Academia Sinica (Beijing) for research fellowships to two of us (H.S. and T.W.) in the United States.

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[12] The discrepancy concerns the relative ratios of **6b** and **7b** reported from two different laboratories.[2,9] The reactions were carried out at different initial anthracene concentrations, and the results were analyzed by different types of NMR spectrometers, 60 MHz[9] vs. 270 MHz.[2] When the reaction was repeated in our laboratory at higher initial anthracene concentration and the results were analyzed with a 270-MHz NMR spectrometer, the higher yield of **7b** reported[9] may be attributed to the method of analysis as well as to the formation of **8b** and **9b** and their secondary reactions.

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[16] Visiting scholar from the Institute of Photographic Chemistry, the Academia Sinica (Beijing).

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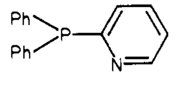
2-(Diphenylphosphino)pyridine as a Bridging Ligand. Synthesis and Structure of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ and $RhPd(Ph_2Ppy)_2(CO)Cl_3$

Sir:

There has been considerable current interest in the reactions between two metal complexes and in the reactivity of binuclear metal complexes.[1–5] The ligand 2-(diphenylphosphino)pyridine,[6,7] Ph_2Ppy (**1**), is a convenient building block for constructing binuclear complexes. Because of its similarity to triphenylphosphine, it should be capable of substitution for triphenylphosphine in any of the numerous complexes of this popular ligand while the presence of the pyridine nitrogen should allow the ligand to bind a second metal ion. Consequently, a metal complex containing



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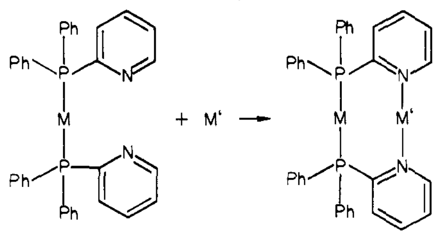

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