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(9) A similar spectrum was observed for benzyl alcohol in the presence of $Yb(fod)_3$.

(10) This observation is also consistent with, but does not require, the proposal of fluorine lone pair participation in p → p_π back bonding in fluorobenzene. For a summary of the supporting and conflicting evidence regarding this proposal as well as a list of leading references, see ref 8.

(11) Infrared spectra were determined within sodium chloride cells on a Perkin-Elmer Model 225 grating spectrophotometer. NMR (^1H and ^{19}F) spectra were determined with a JEOL and Varian NMR spectrometers at 100 and 94.1 MHz, respectively. ^1H chemical shifts are reported in parts per million relative to internal tetramethylsilane. The internal standard for ^{19}F chemical shifts is as noted. All coupling constants are in hertz. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7E mass spectrometer. Samples for spectral analyses were purified on a Hewlett-Packard Model 700 thermal conductivity gas chromatograph. Analytical GLC analyses were performed on a Hewlett-Packard Model 5750 flame ionization instrument. Absolute yields of products were calculated from peak areas using internal standard techniques.

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Secondary Orbital Effects vs. Steric Effects in Some Diels–Alder Additions

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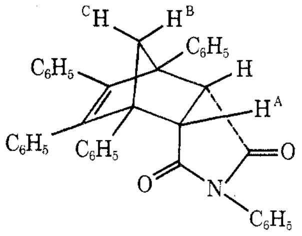
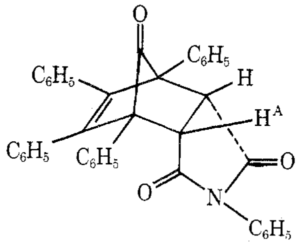
It has been found by several groups of workers that Diels–Alder addition of *N*-phenylmaleimide to heterocyclic dienes leads to formation of exo adducts.[1–4] The usual adduct, the endo isomer,[5] is not produced because either the nonbonded electrons on the heteroatom allow adequate overlap with the π electrons of the dienophile (*N*-phenylmaleimide) to produce the exo adduct or there is sufficient steric blocking to prevent formation of the endo adduct. The purpose of the study described below is to determine whether the possibility of exo-adduct formation results simply from steric hindrance or if the electronic interaction with π electrons of a bridged carbonyl group is operative.

We have determined the structures of endo adducts of *N*-phenylmaleimide to 1,2,3,4-tetraphenylcyclopentadiene (I) and 2,3,4,5-tetraphenylcyclopentadienone (II) which were isolated after 48 hr of reflux in xylene.



I
mp 241°



II
mp 226°

H_A (2 H, δ 4.26, singlet)
H_B (1 H, δ 2.36, doublet, $J = 9$ Hz)
H_C (1 H, δ 3.21, doublet, $J = 9$ Hz)

H_A (2 H, δ 4.28, singlet)

Several groups of workers have shown a four-bond spin–spin splitting coupling constant of approximately 3 Hz for the protons at the extremities of the fixed W formation in bicyclo[2.2.1]heptane systems;[6,7] specifically, the anti proton in the methylene bridge and the endo protons in the ethylene bridge show mutual splitting. The absence of coupling of H_A and H_C in I suggests the endo structure of the adduct.

The structure of II was shown by $Eu(fod)_3$-d_{27}–$CDCl_3$ NMR.[8,9] The exo hydrogens at δ 4.28 were shifted upfield as complexation with $Eu(fod)_3$-d_{27} took place. The aromatic hydrogens underwent no apparent shift. In order to determine complexation to be with the bridged carbonyl and not the imide carbonyls, the NMR of I with $Eu(fod)_3$-d_{27}–$CDCl_3$ was studied. The exo hydrogens at δ 4.26 underwent no apparent shift with $Eu(fod)_3$-d_{27}.[10]

The inclination for endo addition was ascribed by Alder and Stein[11] to the "maximum accumulation of double bonds". A quantum chemical restatement in terms of "secondary orbital interactions"[12] has emphasized the opinion[13–17] that secondary attractive forces in operation between centers not involved in eventual bond formation in the adduct account for the rule of endo addition.

There have been suggestions for the relative unimportance of secondary orbital relationships in favor of a steric repulsion hypothesis.[18–22] In the past decade, there have been several reports of exo adducts formed from the addition of *N*-phenylmaleimide to heterocyclic dienes.[1–4] The heteroatoms, each having at least one pair of nonbonded electrons, can participate in a secondary orbital effect leading to transition states which give rise to exo adducts. The carbonyl of 2,3,4,5-tetraphenylcyclopentadienone apparently does not sufficiently participate in secondary overlap in the transition state to form an exo adduct (instead, II is formed).

Experimental Section

***endo*-1,2,3,4-Tetraphenylbicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Acid *N*-Phenylimide (I).** A solution of 5.000 g (0.0135 mol) of 1,2,3,4-tetraphenylcyclopentadiene and 2.48 g (0.014 mol) of *N*-phenylmaleimide in 100 ml of dry xylene was refluxed for 3–48[23] hr and cooled, and solid was recrystallized twice (first from *p*-xylene, second from anhydrous ethanol) to give 5.36 g (73%) of colorless crystals (the endo isomer): mp 241°; NMR, vide supra.

Anal. Calcd for $C_{39}H_{29}NO_2$: C, 86.16; H, 5.38; N, 2.58. Found: C, 86.42; H, 5.36; N, 2.61.

***endo*-1,2,3,4-Tetraphenylbicyclo[2.2.1]hept-2-en-7-one-5,6-dicarboxylic Acid *N*-Phenylimide (II).** A solution of 5.000 g (0.0130 mol) of 2,3,4,5-tetraphenylcyclopentadienone and 2.57 g (0.015 mol) of *N*-phenylmaleimide in 100 ml of dry xylene was refluxed for 3–48[23] hr and cooled, and the colorless crystals which separated were collected by filtration and recrystallized once from *p*-xylene to give 4.21 g (58%) of the endo isomer: mp 226°; NMR, vide supra.

Anal. Calcd for $C_{39}H_{27}NO_3$: C, 84.00; H, 4.88; N, 8.61. Found: C, 83.83; H, 5.17; N, 2.61.

Acknowledgment. The author wishes to thank the American Philosophical Society for its generous support.

Registry No.—I, 57066-03-2; II, 57128-65-1; *N*-phenylmaleimide, 941-69-5; 1,2,3,4-tetraphenylcyclopentadiene, 15570-45-3; 2,3,4,5-tetraphenylcyclopentadienone, 479-33-4.

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(23) There was no observed change in yields in the variation of reaction time.

Thermal and Base-Catalyzed Decomposition of Ester and Nitrile Derivatives of 2-(2,2-Dicarboxyvinyl)-1,1,1-trimethylhydrazinium Hydroxide Inner Salt

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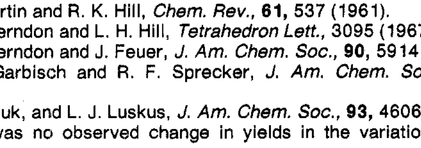
Curtius (path a) or Stevens (path b) rearrangements may be initiated by thermal decomposition of appropriately substituted aminimides derived from carboxylic acids (1).[1]



$$\mathrm{RCO\overset{-}{N}\overset{+}{N}(Me)_2R'}\ (\mathbf{1}) \xrightarrow{a} \mathrm{RNCO + Me_2R'N}\quad \mathrm{R'=alkyl\ or\ aryl}$$

$$\mathrm{RCO\overset{-}{N}\overset{+}{N}(Me)_2R'}\ (\mathbf{1}) \xrightarrow{b} \mathrm{RCONR'N(Me)_2}\quad \mathrm{R'=allyl\ or\ benzyl}$$

This note reports the results of our study of the thermal and base-catalyzed decomposition of three vinylogous aminimides (2) which were first synthesized by Brown[2] in 1967.

$$\mathrm{(CH_3)_3\overset{+}{N}\overset{-}{N}CH{=}CR_1R_2}$$

2a, $R_1 = R_2 = CO_2Et$
b, $R_1 = CN$; $R_2 = CO_2Et$
c, $R_1 = R_2 = CN$

Brown[2] reported that the diester **2a** decomposes in refluxing chloroform to give trimethylamine and unidentified products. The latter observation was of interest to us since **2a** is incapable of undergoing a Curtius-type rearrangement and the unidentified products could therefore derive from the vinyl nitrene, $NCH{=}C(CO_2Et)_2$. Although the odor of trimethylamine was apparent during the thermolysis of **2a** in refluxing chloroform, we have established that the major pathway for the thermal decomposition of **2a** is β elimination of trimethylammonium ion to give the trimethylammonium salt of diethyl cyanomalonate (3). Attempts to initiate similar eliminations by heating the more stable

$$\underset{\mathbf{2a}}{\mathrm{(Me)_3\overset{+}{N}\overset{-}{N}CH{=}C(CO_2Et)_2}} \longrightarrow \underset{\mathbf{3}}{\mathrm{(Me)_3\overset{+}{N}H\ NC\overset{-}{C}(CO_2Et)_2}}$$

nitrile derivatives **2b** and **2c** in *N,N*-dimethylformamide at 140° gave recovered starting materials and tarry, unidentified products.

When treated with 1 equiv of sodium ethoxide in refluxing ethanol, **2a** eliminated trimethylamine and was converted to diethyl sodiocyanomalonate (**4a**). Similar treatment of **2b** and **2c** afforded ethyl sodiodicyanoacetate (**4b**) and sodium tricyanomethide (**4c**), respectively.

$$\underset{\mathbf{2}}{\mathrm{(Me)_3\overset{+}{N}\overset{-}{N}CH{=}CR_1R_2}} \xrightarrow[\mathrm{EtOH}]{\mathrm{NaOEt}} \mathrm{(Me)_3N} + \underset{\mathbf{4}}{\mathrm{NaC(CN)R_1R_2}}$$

a, $R_1 = R_2 = CO_2Et$
b, $R_1 = CO_2Et$; $R_2 = CN$
c, $R_1 = R_2 = CN$

These nitrile-forming β-eliminations find precedence in our previously reported base-catalyzed conversion of aldehyde quaternary hydrazones to nitriles.[3]

Experimental Section

Melting points are uncorrected and were determined with a Mel-Temp apparatus. NMR spectra were determined on a Perkin-Elmer R-20 spectrometer utilizing hexamethyldisiloxane as an internal standard.

Thermolysis of 2-(2,2-Dicarbethoxyvinyl)-1,1,1-trimethylhydrazinium Hydroxide Inner Salt (2a) in Chloroform. A solution containing 2.5 g of **2a**[2] in 50 ml of chloroform was heated under reflux for 10.5 hr. Removal of the chloroform in vacuo afforded 2.5 g of the crude semisolid trimethylammonium salt of diethyl cyanomalonate. Recrystallization from ethanol–ether gave hygroscopic white crystals: mp 109–110°; NMR ($CDCl_3$) δ 2.86 (s, 9), 1.15 (t, 6, J = 8 Hz), 4.05 (q, 4, J = 8 Hz); ir (KBr) 2170 (CN, m), 1690 cm^{-1} (CO, s).

Anal. Calcd for $C_{11}H_{20}N_2O_4$: N, 11.5. Found: N, 11.3.

The salt was identical (ir, NMR) with that precipitated by addition of anhydrous ether to a solution prepared by adding diethyl cyanomalonate[4] to methanolic trimethylamine.

Reaction of Aminimides with Ethanolic Sodium Ethoxide. Ten percent ethanolic solutions of **2a**, **2b**, and **2c** containing 1 equiv of sodium ethoxide were heated under reflux for 5, 18, and 15 hr, respectively. Trimethylamine was evolved and was identified (from **2b**) by conversion to its picrate, mp 220–225° (ir identical with that of an authentic sample). The ethanol was evaporated in vacuo to give the crude sodium salts (**4a**, **4b**, and **4c**).

Crude diethyl sodiocyanomalonate (**4a**) from 2.0 g of **2a** was acidified with 10 ml of 6 *N* HCl and the resultant solution extracted with chloroform. Evaporation of the dried extract gave 1.0 g (66%) of pure diethyl cyanomalonate, which was identified by comparison of its NMR and ir spectra with those of an authentic sample.[4]

Crude ethyl sodiocyanoacetate (**4b**) obtained from 4.0 g of **2b** was recrystallized from ethanol–ether, affording 1.5 g (54%) of product whose structure was established to be **4b** by comparison of its NMR and ir spectra (KBr) with those of an authentic sample.[5] The NMR spectrum (CD_3COCD_3) indicated contamination with <5% of **4b**.

The crude sodium tricyanomethide (**4c**) obtained from 2.0 g of **2c** displayed an ir spectrum identical with that of an authentic sample.[6]

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Registry No.—**2a**, 18248-91-4; **2b**, 18248-92-5; **2c**, 18248-93-6; **3**, 57196-67-5; **4a**, 22466-42-8; **4b**, 4513-68-2; **4c**, 36603-80-2; chloroform, 67-66-3; sodium ethoxide, 141-52-6; diethyl cyanomalonate, 4513-67-1.

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