Heteropentalenes. The Thermal Addition of Pyrazolo- and Triazolobenzotriazoles to Dimethyl Acetylenedicarboxylate

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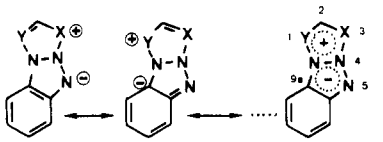
Pyrazolo[1,2-*a*]benzotriazole (**1a**), 1,2,3-triazolo[2,1-*a*]benzotriazole (**1b**), and 1,2,3-triazolo[1,2-*a*]benzotriazole (**1c**) undergo electrophilic attack by dimethyl acetylenedicarboxylate to reversibly form diradical or zwitterionic intermediates, which then evolve along different pathways. Thus initial attack at position 5 of the heteropentalene (path A, Scheme V) ends up in formal cycloaddition yielding the pyrazolo[1,2-*a*]pyrazolo[1,2-*b*]benzotriazole **2** from **1a** and the triazolo[2,1-*a*]pyrazolo[1,2-*b*]benzotriazole **10** from **1b**. The latter decomposes to dimethyl pyrazolo[1,2-*a*]benzotriazole-1,2-dicarboxylate (**11**), in turn capable of further cycloaddition. Protic media trap the intermediate giving dimethyl 2-methoxy-3-[(2-pyrazol-1-ylphenyl)amino]maleate (**7**) from **1a** and the analogous **14** from **1b**. Attack at position 1 or 3 (path D and B) leads to stable products only when a hydrogen atom is present at these positions; then a hydrogen intermolecular shift ensues to form pyrazolo- or triazolobenzotriazolylmaleates or fumarates (products **3**, **5**, **6**, **13**, **17**, and **18**). In the case of **1c** the initial adduct transfers a hydrogen atom and rearranges to a stable pyridazinobenzotriazine radical (compound **16**). The mechanistic scheme proposed also accounts for the results obtained with singlet oxygen with the same substrates.

Introduction

In the frame of our continuing effort[1] toward elucidation of the chemistry of polyazapentalenes, i.e., heterocyclic meso ionic betaines, which are isoelectronic analogues of the pentalene dianion, we report the reaction of the tri- and tetrazapentalenes **1a–d** with dimethyl acetylenedicarboxylate. Compounds **1a–d** pertain to class B in



1 a–d

	X	Y
a =	CH	CH
b =	CH	N
c =	N	CH
d =	CMe	CMe

Ramsden's classification of heteropentalenes.[2] They are characterized by the presence of two nitrogen atoms at the bridged positions; whereas the other positions can be occupied by either nitrogen or carbon atoms. No single formula gives a satisfactory representation of the bonding in heteropentalenes, and the explicit consideration of several mesomeric dipolar formulas is necessary. Simple heteropentalenes of this class have limited stability, but many benzo or dibenzo derivatives are stable compounds. Although several compounds of this series were first synthesized more than twenty years ago,[3] knowledge of the chemistry of these compounds is still limited. Scattered data regarding electrophilic addition or substitution have been reported for some compounds of this class.[3,4] A previous investigation of the heteropentalenes **1a–d** showed that singlet oxygen adds to compounds **1a** and **1d** in position 1 and 3 with cleavage of the pyrazole ring, and reacts also with **1c** with degradation, while no reaction with **1b** was observed.[1b] Thus the reactivity with another dipolarophile of similar structure, dimethyl acetylenedicarboxylate (DMAD) was studied in the hope of obtaining fuller characterization of the chemistry of these compounds.

Results and Discussion

Reaction of Pyrazolo[1,2-*a*]benzotriazole (1a).[1b] At room temperature the heteropentalene **1a** reacts completely with an equimolar amount of DMAD in 4 h in aprotic solvents to give three products which were separated by chromatography. The most abundant one is a 1:1 adduct and, in comparison with the starting material, is characterized by a marked upfield shift of the NMR signals corresponding both to heterocyclic and to aromatic protons, the latter appearing as an AB system centered at 7.1 δ. Thus this product is substantially symmetric and has conserved the aromaticity in the carbocyclic ring, but not in the heterocyclic moiety. Therefore it is identified as the tricyclic derivative dimethyl pyrazolo[1,2-*a*]-pyrazolo[1,2-*b*]benzotriazole-1,2-dicarboxylate (**2**), i.e., the formal product of the cycloaddition onto the azomethinimine part of the molecule.[5]

Of the other two products, one is again a 1:1 adduct while the other is a 1:2 adduct. The first shows a NMR spectrum remarkably similar to that of the starting material, apart from a low-field singlet and the signals of the methoxy groups. The identification as dimethyl 2-(pyrazolo[1,2-*a*]benzotriazol-1-yl)maleate (**3**) is finally confirmed by the catalytic reduction to the corresponding succinate **8**, which has the aromatic part of the NMR spectrum and the UV spectrum corresponding to those of compound **1a**. Under the conditions used the heteropentalenes **1a–d** are recovered unchanged. The 1:2 adduct (**4**) has both a pendant vinyl group in position 1 and a DMAD moiety added across positions 3 and 5, as shown by the comparison of its spectroscopic properties with those of the previously discussed products **2** and **3**. Thus this product arises from the cycloaddition of a further DMAD molecule onto the

(1) (a) Albini, A.; Bettinetti, G. F.; Minoli, G. *J. Chem. Soc., Perkin Trans. 1* **1983**, 581. (b) Albini, A.; Bettinetti, G. F.; Minoli, G. *J. Org. Chem.* **1983**, *48*, 1080.

(2) Ramsden, C. *Tetrahedron* **1977**, *33*, 3203.

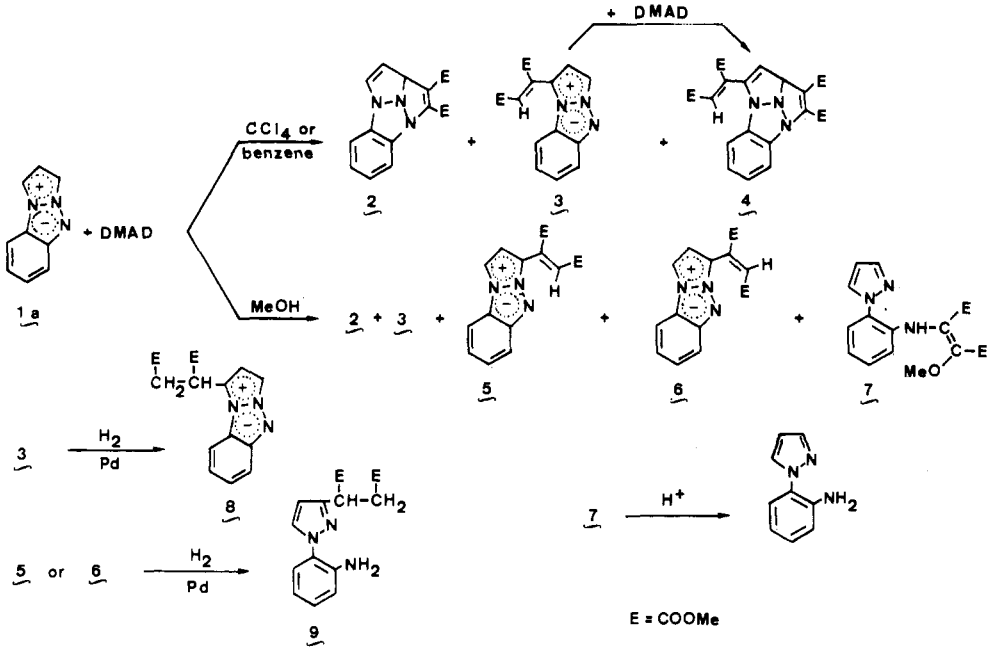
(3) (a) Linch, B. M.; Hung, Y. Y. *J. Heterocycl. Chem.* **1965**, *2*, 218. (b) Carboni, R. A.; Kauer, J. C.; Hatchard, W. R.; Harden, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 2626. (c) Kauer, J. C.; Carboni, R. A. *Ibid.* **1967**, *89*, 2633. (d) Hall, J. H.; Stephanie, J. G.; Nordstrom, D. K. *J. Org. Chem.* **1968**, *33*, 2951. (e) Trofimenko, S. *J. Am. Chem. Soc.* **1965**, *87*, 4393. (f) Solomons, T. W. G.; Voigt, C. F. *Ibid.* **1965**, *87*, 5256.

(4) (a) Koga, H.; Hirobe, M.; Okamoto, T. *Tetrahedron Lett.* **1978**, 1291. (b) Tsuge, O.; Samura, H. *J. Heterocycl. Chem.* **1971**, *8*, 707. (c) Tsuge, O.; Samura, H. *Org. Prep. Proced. Int.* **1972**, *4*, 273. (d) Tsuge, O.; Samura, H. *Tetrahedron Lett.* **1973**, 597. (e) Tsuge, O.; Samura, H. *Heterocycles* **1974**, *2*, 27.

(5) Crystallographic data have been obtained which confirm this structure: Bovio, B. *J. Crystallogr. Spectrosc. Res.* **1984**, *14*, 369.

0022-3263/84/1949-2670$01.50/0

Scheme I



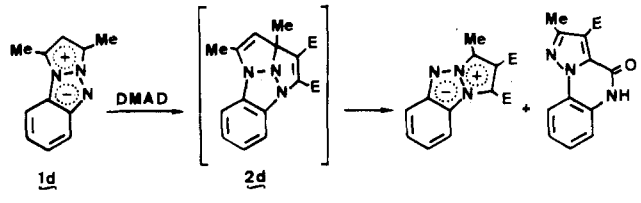
azomethinimine moiety of the primary adduct **3**. This reaction sequence is confirmed by direct experiments showing that **3** which contains the heteropentalene structure, adds DMAD under the same condition as **1a** to give **4**, while the other primary adduct **2** is unreactive.

In conclusion, the reaction of **1a** with DMAD in aprotic solvent, gives roughly equal amounts of products from two paths. One is the adduct **2** from cycloaddition onto the azomethinimine site (across positions 3 and 5). The concurrent mode of attack, rather than giving the cycloadduct onto the azomethinylide site (across positions 1 and 9a), yields product **3** with a pendant vinyl group in position 1.

In protic solvents, e.g., methanol, the reaction leads to different results. Thus compound **2** is obtained in about 3% yield, while the main product results from the addition of one molecule of solvent besides a DMAD unity, and was identified as dimethyl 2-methoxy-3-[(2-pyrazol-1-ylphenyl)amino]maleate (**7**) on the basis of spectroscopic comparison with the known 3,5-dimethylpyrazolyl analogue[5] and acid-catalyzed hydrolysis to 1-(2-aminophenyl)pyrazole (see Experimental Section). Moreover two further products, **5** and **6**, are formed, which have similar spectroscopic properties to compound **3**, in turn obtained also in these conditions, although in lower yield than in aprotic solvents. Both compounds **5** and **6** are catalytically hydrogenated to the same product **9** which is different from product **8** obtained from the hydrogenation of **3**. The structure of compound **9** is recognized as a derivative of the known 1-(2-aminophenyl)pyrazole having in position 3 a dimethyl succinyl group on the basis of comparison of their spectroscopic properties. Thus compounds **5** and **6** are the *E* and *Z* isomers arising from attack of DMAD onto position 3 of the heteropentalene **1a** instead of attack onto position 1 as in the case of compound **3**.

It is noteworthy that only in the case of 3-vinyl substituted heteropentalene **5** is the triazole ring cleaved by catalytic hydrogenation, whereas in the case of the 1-vinyl substituted heteropentalene **3** (as well as of the analogous compounds **17** and **18**) and of the parent compounds **1a–d**, the heterocyclic system is unaffected in these conditions. This result requires that in the former case the heterocyclic system participates in the first step of the hydrogenation, which can be envisaged as a hydrogenation involving the

Scheme II



extremes of the six π electron system from the pendant vinyl group to the nitrogen in position 5, followed by the absorption of a second mole of hydrogen and cleavage of the N(4)–N(5) bond. In the case of the 1-vinyl derivatives, the only reaction is the 1,2-hydrogenation of the ethylenic bond.

Compound **7**, the main product in methanol, could be envisaged as arising from the methanolysis of the cycloadduct **2**, obtained as the main product in aprotic medium. However, control experiments showed that the cycloadduct **2** is stable in methanol in these conditions. Thus compound **7** arises from the trapping by methanol of some intermediate preceding **2** (see Scheme I and Table I).

The reactivity of the heteropentalene **1a** can be compared with that of the 1,3-dimethyl derivative **1d**.[6] This latter compound reacts with DMAD in aprotic solvents to give cycloadduct **2d**, the analogue of **2**, which was identified in solution from its spectroscopic properties, but could not be isolated since it decomposes during the workup. On standing in solution a further spontaneous reaction is observed, which leads mainly to two stable products. The first arises from loss of propyne via a retrocycloaddition process, the latter involves rearrangement as well as fragmentation (see Scheme II).

Thus cycloaddition onto the azomethine imine site takes place in the case of **1d** as in the case of **1a**, but instability caused by the angular methyl group in compound **2d** prevents isolation.

Also analogous is the reaction between **1d** and DMAD in methanol, which yields the dimethyl analogue of **7** as a trapping product.

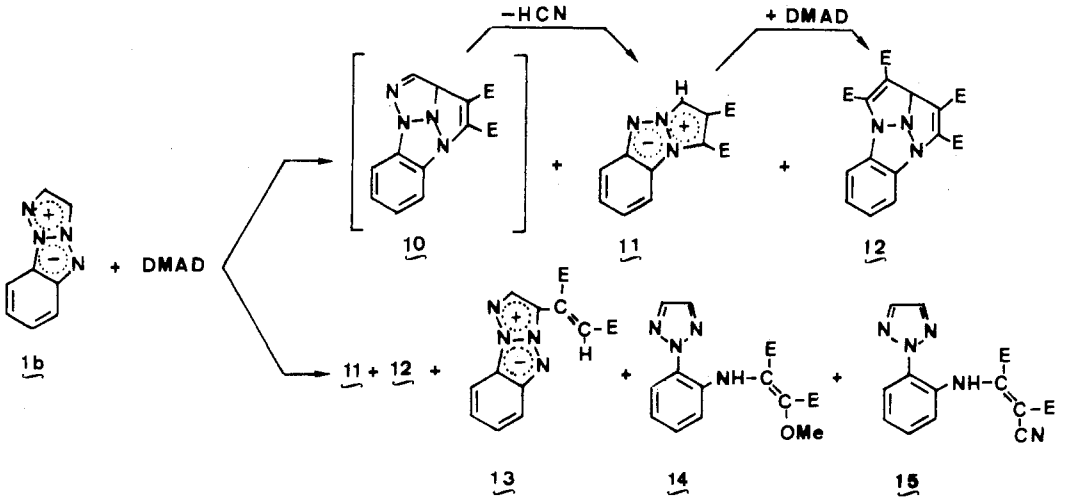
(6) Albini, A.; Bettinetti, G. F.; Minoli, G. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2941.

Table I. Chemical Yield from the Reaction of the Heteropentalenes 1a-c with ADC

no.	solvent	temp[a]	rxn time	% convern	product (% yield) from path A	from path B	from path D
1a	CCl_4	rt	4 h	100	2 (29)		3 (10), 4 (18)
1a	MeOH	rt	4 h	100	2 (3), 7 (18)	5 (10), 6 (10)	3 (3)
1b	CCl_4	rt	25 days	93	11 (30), 12 (6)		
1b	toluene	reflux	3 h	75	11 (39), 12 (7)[b]		
1b	MeOH	rt	2 days	47	11 (28), 12 (5) 14 (15), 15 (7)	13 (25)	
1c	CCl_4	reflux	2 days	87			16 (30), 17 (6), 18 (6)
1c	toluene	reflux	1.5 h	80			16 (37), 17 (4), 18 (4)
1c	MeOH	rt	2 days	33			16 (7), 17 (20), 18 (25), 19 (18)

[a] rt = room temperature. [b] Under these conditions compound 12 in part further reacts to a product of unknown structure.

Scheme III



Reactions of 1,2,3-Triazolo[2,1-*a*]benzotriazole (1b).[1b] As expected the introduction of a further nitrogen atom in the heterocyclic nucleus causes a remarkable enhancement of the ionization potential, and thus diminishes the rate of the reaction with DMAD, which now requires much longer times or higher temperatures. The slow reaction favors subsequent processes, so that products arising from sequential steps, rather than primary products, are obtained if the reaction is carried out to a reasonable conversion.

Thus in aprotic solvents the most abundant product is dimethyl pyrazolo[1,2-*a*]benzotriazole-1,2-dicarboxylate (11), formally arising from the addition of one molecule of DMAD and the loss of one molecule of HCN. Its formation is interpreted as involving the intermediacy of the cycloadduct 10, which undergoes retrocycloaddition with loss of HCN, although there is no direct evidence of the sequential steps leading to compound 11. The less abundant product 12 was shown in a separate experiment to be formed by the slow addition of DMAD to compound 11. The reaction of 1b to give 11 as well as the previously mentioned retrocycloaddition products from 2d (see Scheme II) represents another example of preparing new heteropentalenes by cycloaddition followed by retrocycloaddition. Another example of this approach has been described previously.[7]

The reaction in methanol gives a more complex mixture including, besides compounds 11 and 12, products which arise from different modes of attack, i.e., dimethyl 2-(1,2,3-triazolo[2,1-*a*]benzotriazol-3-yl)maleate (13) and the ring cleavage products dimethyl 2-methoxy-3-[(2-(1,2,3-triazol-2-yl)phenyl)amino]maleate (14) and dimethyl 2-cyano-3-[(2-(1,2,3-triazol-2-yl)phenyl)amino]maleate (15), the former having added methanol, the latter hydrogen cyanide besides DMAD. The source of the cyanide group incorporated in product 15 is apparently the hydrogen cyanide arising from the retrocycloaddition of 10 to 11 (see Scheme III).

The structure of products 10–15 was deduced on the basis of elemental analysis and comparison of their spectroscopic properties with those of the previously discussed

(7) Abe, N.; Nishiwaki, T.; Omori, T.; Harada, E. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 200.

Table II. Relevant Spectroscopic Data for New Compounds[a]

no.	mp, °C	formula	^{1}H NMR[b] heterocycl CH	vinyl CH	MeO	NH	IR[c]
2[d]	113–114[e]	$C_{13}H_{13}N_3O_4$	5.4 (2 H, m), 6.45 (t)		3.75, 3.95		1735, 1700, 1625
3[f]	131–132[g]	$C_{13}H_{13}N_3O_4$	6.85 (2 H, m), 7.55 (t)	6.4	3.8, 3.95		1730, 1705, 1600
4	139–140[g]	$C_{21}H_{19}N_3O_8$	5.3, 5.7	6.35	3.7, 3.75, 3.8, 3.9		1740, 1715, 1640, 1630
5[f]	195–197[e]	$C_{15}H_{13}N_3O_4$	6.8 d	7.7	3.85, 4.05		1735, 1700, 1600
6[f]	120–122[g]	$C_{15}H_{13}N_3O_4$	6.8 d	7.65	3.8, 4.0		1710, 1620
7	viscous oil	$C_{16}H_{17}N_3O_5$	6.5 (t), 7.8 (2 H, m)		3.7, 3.75, 3.8	9.3	3260 br, 1720, 1600
8[h]	84–85[e]	$C_{15}H_{15}N_3O_4$	6.75 (d), 7.6 (d)		3.75, 3.72		1725
9[i]	84–85[e]	$C_{15}H_{17}N_3O_4$	6.4 (d), 7.7 (d)		3.75, 3.7	3.5	3410, 3320, 1730
11	139–141[j]	$C_{13}H_{11}N_3O_4$	7.95		3.95, 4		1710, 1700
12	121–122[j]	$C_{19}H_{17}N_3O_8$	5.7		3.9, 4		1720, 1620
13[f]	179–181[j]	$C_{14}H_{12}N_4O_4$	8.4	7.05	3.65, 3.8		1735, 1700, 1600
14	91–93[j]	$C_{15}H_{16}N_4O_5$	7.85		3.75	10.4	3440, 1725, 1635
15	viscous oil	$C_{15}H_{13}N_5O_4$	7.9		3.8, 3.95	12.3	3200, 3140, 2210, 1745, 1690
16[m]	215–217[g]	$C_{14}H_{11}N_4O_4$					1725
17[f]	171–172[e]	$C_{14}H_{12}N_4O_4$	7.85	6.65	3.8, 3.95		1735, 1710, 1620
18[f]	130–131[e]	$C_{14}H_{12}N_4O_4$	8	7.3	3.65, 3.9		1720, 1595
19[k]	viscous oil	$C_{15}H_{16}N_4O_5$	7.3		3.52, 3.55, 3.3		1740
20[l]	134–135[e]	$C_{14}H_{14}N_4O_4$	7.65		3.75		1725

[a] Satisfactory analyses ±0.2% for C, H, N were reported for all compounds. [b] In $CDCl_3$ with chemical shift in ppm vs. internal Me_4Si. [c] In nujol mull, cm^{-1}. [d] Aromatic protons, AB system centered at 7.1 δ. [e] From benzene–cyclohexane. [f] All maleates show two carbonyl absorptions at ca. 1730 and 1700 cm^{-1}; the fumarates, which are not planar, due to steric hindrance, show only one band. [g] From benzene. [h] $CHECH_2E$, ABX system centered at 3.0–3.4 and 4.9 δ. [i] $CHECH_2E$, ABX system centered at 3.0–3.2 and 4.35 δ. [j] From cyclohexane. [k] Mixture of threo and erythro isomers. The signals of the two diastereoisomers are better distinguished in the ^{13}C NMR spectrum: the more abundant compoundat 132.2 (d), 126.5 (d), 119.9 (d), 115.9 (d), 111.9 (d), 81.2 (d), 59.8 (q), 52.5 (2 q), 49.5 (d) δ; the less abundant at 131.8 (d), 126.7 (d), 120.3 (d), 116 (d), 111.7 (d), 81.4 (d), 59.6 (q), 53.2 (2 q), 45.3 (d) δ. [l] $CHECH_2E$, ABX system centered at 2.75–3.2 and 4.6 δ. [m] Mass spectrum, M^+ 299.

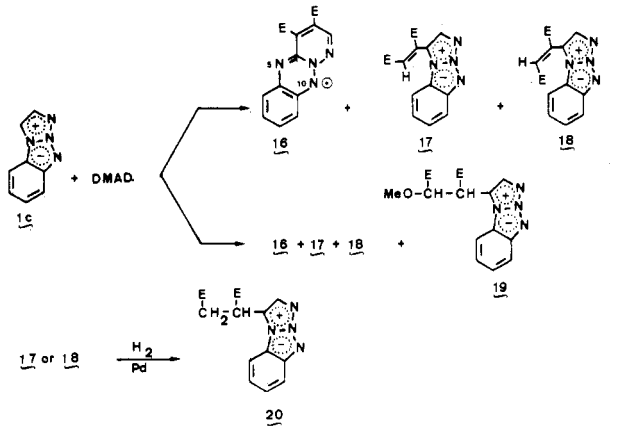
adducts from the heteropentalene **1a**. The stereochemistry of the double bond in compound **13** as well as the previously mentioned products **3**, **5**, and **6** can be derived from regularities observed in *E* and *Z* derivatives, respectively (see Table II, note).

Reactions of 1,2,3-Triazolo[1,2-*a*]benzotriazole (1c).[1b] The reaction of the heteropentalene **1c** with DMAD in aprotic solvents takes a different course. Thus dimethyl 2-(1,2,3-triazolo[1,2-*a*]benzotriazol-3-yl)maleate (**17**) and its geometric isomer **18**, identified from their spectroscopic properties and hydrogenation to the succinate **20**, are only minor products. The main product **16** is a deep blue crystalline material. Elemental analysis and mass spectrum show that it arises from the addition of one DMAD molecule and the loss of a hydrogen atom, and thus lead to the proposal that compound **16** is a new stable radical. This is supported by the deep color and the ESR signal (see Scheme IV).

Little information is obtained from spectroscopic data, as no fine structure NMR spectrum is obtained because of the paramagnetism, and the fragmentation pattern in the mass spectrum shows scarce features, as expected from an extensively conjugated molecule, besides hinting that initial attack has occurred at position 1. Fortunately, the structure of dimethyl pyridazino[2,3-*b*]benzo-1,2,4-triazine-3,4-dicarboxylate radical was ascertained on the basis of a crystallographic analysis.[8]

Owing to the strong spin–spin interaction, the ESR spectrum of the pure radical, when recorded at 25 °C in the solid state, consists of a structureless singlet centered at $g = 2.003$. In dilute, oxygen-free benzene solution (10^{-3} M), partially resolved complex patterns with average peak to peak separation of 0.4 G are obtained, which are being analyzed in terms of the magnetic interaction of seven nonequivalent nuclei (four nitrogen and three hydrogen atoms). The hyperfine features so far ascertained as well as the results of INDO and extended Hückel calculation are diagnostic of a structure of the radical with a major

Scheme IV



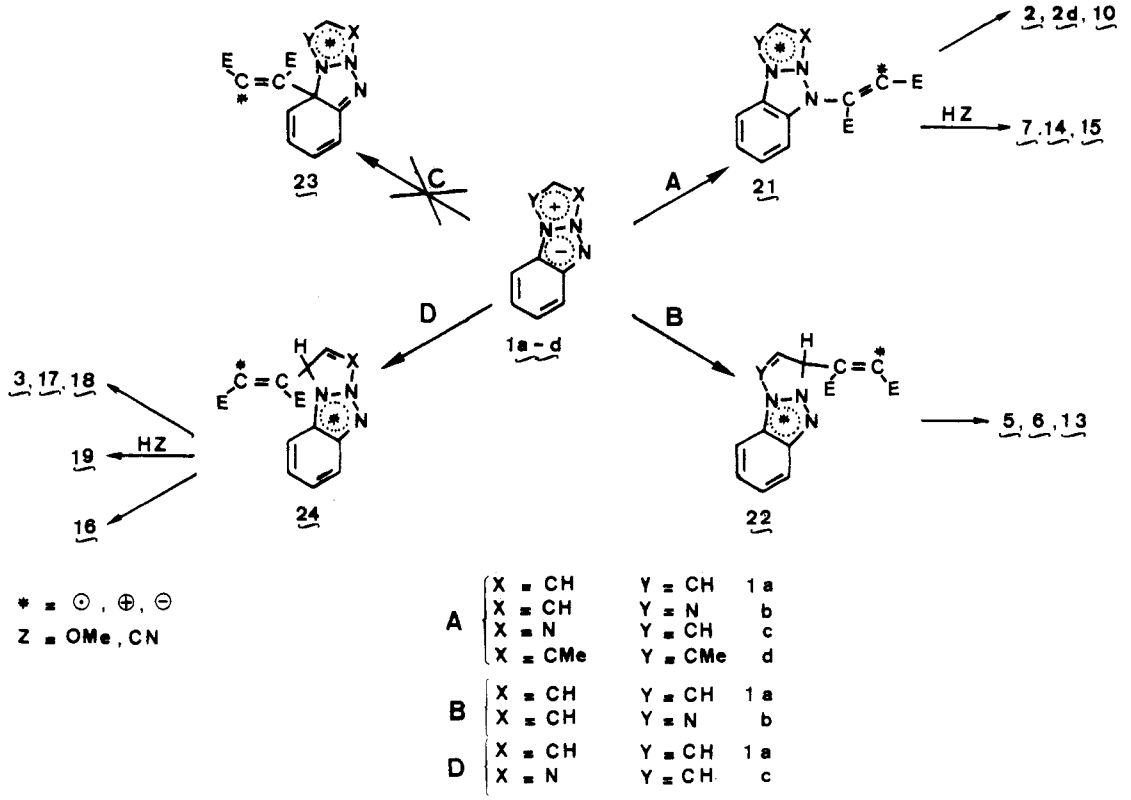
part of the unpaired spin density centered in the $2p_z$ orbitals of the nitrogen atoms in positions 5 and 10.[9] When the reaction is carried out in methanol, the radical **16** is only a minor component, while the two geometric isomers **17** and **18** are obtained in good yield. Furthermore compound **19**, again arising from attack of DMAD in position 1, but requiring also incorporation of methanol as well as hydrogen shift, is obtained.

Mechanistic Discussion. The order of reactivity of the heteropentalenes **1a–d** with DMAD (**1a** ≃ **1d** ≫ **1b** ≃ **1c**) is the same as the order of reactivity of the same compounds with singlet oxygen[1b] and is parallel to the variation we found in the ionization potential (**1a** = 6.5, **1b** = 7.56, **1c** = 7.58, **1d** = 6.5 eV, obtained from PES measurements) as is expected for these HOMO controlled reactions. A difference between **1a** and **1d**, the former being somewhat more reactive with DMAD, the latter with $^1O_2$, points to a greater influence of steric hindrance due to the methyl groups present in **1d** in the reaction with the more bulky molecule of DMAD.

(8) Crystallographic and molecular data on radical **16** are the subject of a separate paper submitted by Dr. B. Bovio (Pavia).

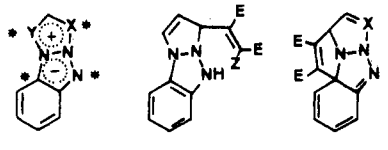
(9) Courtesy of Dr. A. Faucitano (Pavia). Full details of ESR measurement and MO calculation will be given in a separate paper.

Scheme V



The wealth of reactions discussed above can be rationalized in the general frame delineated in Scheme V. Thus, the addition of the heteropentalenes **1a–d** onto DMAD is a two-step reaction involving discrete zwitterionic or diradical intermediates. This mode of attack must be postulated to explain at least some of the ensuing processes and the effect of polar solvents, although there is no spectroscopic indication that any intermediate accumulates in detectable amount.

The first step can be envisaged as a Michael addition of the electron-rich heteropentalene onto the unsaturated ester, in all the possible modes, to give the intermediates **21**, **22**, **23**, and **24**. Intuitive considerations, as well as preliminary calculations,[10] show that the HOMO of these heteropentalenes has a substantial coefficient at the four atoms starred in formula **25**, and that these four coefficients are quite similar. Thus, reaction is expected to take place concurrently at these four positions. The mode of attack leading to the effective reaction product is determined by the stability of the developing intermediate and by the availability of pathways leading to stable products, otherwise the first step results only in reversible charge transfer complexation. Thus path C is precluded by the loss of aromaticity that is involved. Path A leads, through the intermediate **21**, which can be trapped by protic reagents such as alcohols, water, and hydrocyanic acid, to the cycloadducts **2**, **2d**, and **10**. These cycloadducts suffer a steric constraint. Thus only **2** has been actually isolated, whereas the formation of **2d** in solution has been shown to take place by spectroscopic analysis.[6] These products undergo spontaneous decomposition either involving retrocycloaddition from the other side to give new heteropentalenes or other processes involving radical cleavage (see Schemes II and III).



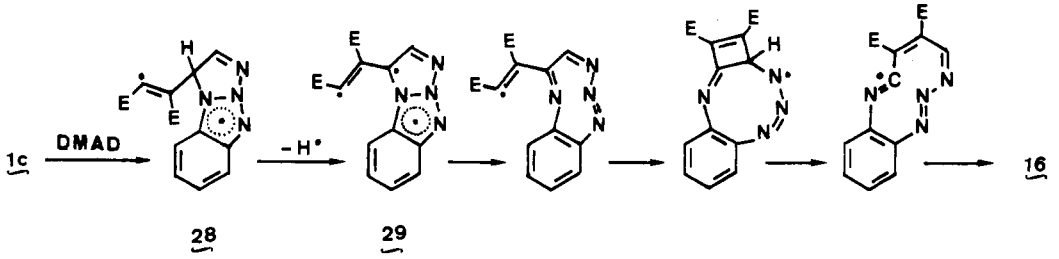
25 **26** **27**

There is no evidence that the alternative intermediate **22**, derived from path B, is involved in the formation of cycloadduct **2**. In fact in methanol, products arising from the solvent trapping of **21**, such as **7** and **14** are found with the exclusion of product **26**, which would arise from the trapping of **22**. The intermediate **24**, arising from path D can not close to the cycloadduct **27**, i.e., the formal cycloadduct on the azomethinylide site of the heteropentalene, as this would imply the loss of the aromaticity of the carbocyclic ring. In fact in the case of pyrazolo[1,2-*a*]triazole where there is no loss of aromaticity, the adduct on the azomethinylide site is reported to be the main product.[4e] The same holds for the cycloaddition of 5*H*-pyrazolo[1′,2′:1,2]-1,2,3-triazolo[5,4-*a*]phenazinyliumide,[11] in which the loss of conjugation is limited. Cycloaddition being excluded, the only processes taking place from intermediates **22** and **24**, and thus the practicable pathway from path B and D, is 1,3-hydrogen shift, to give the new heteropentalenes **3**, **5**, **6**, **13**, **17**, **18**, and **19**, provided that, of course X, or respectively Y, is a CH group. An intramolecular (suprafacially forbidden) shift is hardly a viable scheme. The available evidence, such as the favorable effect of protic solvents on the yields of these products, and the formation of mixtures of *E* and *Z* isomers, suggests an intermolecular solvent-mediated process.

A possibility to visualize the two-step process leading to hydrogen transfer is to consider a radical intermediate (e.g., **29**), which could attain some stabilization as the vinyl group is in plane. This hypothesis is useful in understanding the formation of radical **16** from **1c** and its solvent dependence. Thus, in aprotic solvents the radical **29**

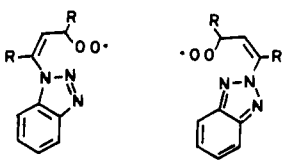
(10) Private communication by Dr. F. Mark (Mulheim/Ruhr).
(11) Albini, A.; Bettinetti, G. F.; Minoli, G.; Pietra, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2904.

Scheme VI



suffers N–N bond cleavage before picking up a hydrogen atom again. This corresponds to a skeletal rearrangement of the pentalene → cyclooctatetraene type. While the pentalene dianion and the heteropentalene isoelectronic with it are more stable than the corresponding monocyclic forms,[2] this need not to be true when an electron has been taken away from the HOMO and thus we are at the pentalene radical anion level. Subsequent cyclization and electrocyclic ring enlargement brings from the 8-membered to a 10-membered cyclic radical, which undergoes easy cyclization to two condensed 6-membered rings (Scheme VI). The extensive conjugation makes the radical **16** unusually stable. This interpretation is supported by the solvent effect. Thus in protic medium solvent-mediated hydrogen transfer takes place and the radical **29** has much less chance to undergo intramolecular reaction, so that the radical **16** is only a minor product and the "normal" products with the pendant vinyl group (**17** and **18**) are formed.

The intermediates **21**, **22**, and **24** are stable enough to show a dual chemistry. Thus trapping with methanol points to the presence of localized charges, making the carbon atom α to the ester group more prone to nucleophylic attack, whereas other properties, such as hydrogen transfer from **24** to form the radical **29**, points to the existence of localized radical centers. That compounds **1a** and **1d** both react in two modes with singlet oxygen[1] (the analogous of paths B and D), while with DMAD only one mode of reaction (path A) is observed for **1d** and three modes are followed, at least in protic solvents, for **1a** (paths A, B, and D), is explained by the fact that in the singlet oxygen reaction the intermediates from paths B and D undergo irreversible cleavage of the pyrazole ring to the corresponding carbonyl oxides **30** and **31** and path A is not



followed owing to the lesser energy gain in forming a N–O rather than a C–O bond. On the contrary with DMAD path B and D are fruitful only when, as it is the case with **1a**, a hydrogen atom is present in position 3 and respectively 1, particularly in protic solvent, which favors hydrogen transfer, whereas for the dimethyl derivative **1d** no such shift is possible and the only available path remains A, both in aprotic and protic solvents.

In conclusion the regioselectivity which is observed in some of these reactions is not due to a different electronic distribution in the reactant. Indeed, initial reversible complexation does take place in different modes. The availability of pathways, which lead to products without a loss of aromaticity or a symmetry barrier, then determines the course of the reaction.

Experimental Section

Apparatus. The UV–visible spectra were recorded on a Perkin-Elmer 200 spectrophotometer, the NMR spectra on a Perkin-Elmer R12 or a Brucker WP80 instrument with $(CH_3)_4Si$ as an internal standard, IR spectra on a Perkin-Elmer 197 spectrophotometer, and mass spectra on a Du Pont 492 spectrometer. Melting points are uncorrected.

Materials. Commercial (Merck and Carlo Erba) spectroscopic grade solvents were used after distillation and, in the case of chlorinated solvents, treatment with Na_2CO_3. Column chromatography was performed with silica gel 60HR (Merck). Dimethyl acetylenedicarboxylate (DMAD) (Fluka) was freshly distilled before use. Pyrazolo[1,2-*a*]benzotriazole (**1a**), 1,2,3-triazolo[2,1-*a*]benzotriazole (**1b**), and 1,2,3-triazolo[1,2-*a*]benzotriazole (**1c**) were prepared and purified as described elsewhere.[1b]

Thermal Addition of the Heteropentalenes 1a–c and DMAD. Reaction of 1a in CCl_4. 0.785 g (5 mmol) of **1a** was dissolved in 60 mL of carbon tetrachloride and the solution was dried by distilling away 30 mL of solvent. To the cooled solution was added 0.72 g (5.5 mmol) of DMAD. The colorless solution turned gradually to a red-brown color, and TLC (silica gel, benzene–ethyl acetate 9:1) revealed the formation of two spots at first, with R_f higher than the starting material, and later also of a third one, between the first two. The starting material being consumed after 4 h at room temperature (TLC, NMR evidence), the solution was evaporated and the residue dark-red oil was chromatographed eluting with a benzene–ethyl acetate (95:5) mixture to yield in this order 0.435 g (29%) of dimethyl pyrazolo[1,2-*a*]pyrazolo[1,2-*b*]benzotriazole-1,2-dicarboxylate (**2**), 0.396 g (18%) of the bis adduct dimethyl 2-(3,4-bis(methoxycarbonyl)pyrazolo[1,2-*a*]pyrazolo[1,2-*b*]benzotriazol-1-yl)maleate (**4**), and 0.15 g (10%) dimethyl 2-(pyrazolo[1,2-*a*]benzotriazol-1-yl)maleate (**3**). The three products were obtained as viscous oils, which were easily brought to crystallization. Analytically pure samples were obtained by recrystallization (see Table II).

Reaction of 1a in MeOH. 0.785 g (5 mmol) of **1a** was dissolved in 30 mL of methanol and 0.72 g (5.5 mmol) of DMAD was added. The colorless solution turned to orange and TLC showed the formation of a complex mixture of products. After the starting material was consumed (4 h at room temperature), the solution was evaporated and the residue red-orange oil was chromatographed, eluting with benzene–ethyl acetate (95:5) to yield in this order 0.045 g (3%) of product **2**, 0.15 g (10%) of dimethyl 2-(pyrazolo[1,2-*a*]benzotriazol-3-yl)maleate (**5**), 0.295 g (18%) of dimethyl 2-methoxy-3-[(2-pyrazol-1-ylphenyl)amino]maleate (**7**), 0.15 g (10%) of dimethyl 2-(pyrazolo[1,2-*a*]benzotriazol-3-yl)fumarate (**6**), and 0.045 g (3%) of product **3**.

Analytically pure products were obtained by recrystallization (see Table II). NMR analysis showed that at no stage of this reaction was compound **2** present in the mixture above the detection limit (5%). A pure sample of compound **2** dissolved in MeOH slowly degraded, and was completely consumed after 10 days. However no detectable amount of compound **7**, or of any other of the previously mentioned products was formed.

Reaction of 1b and 1c. The reaction of the heteropentalenes **1b** and **1c** were carried out in the conditions reported in Table I, checking the degree of the conversion by TLC and NMR spectroscopy. The workup was performed as above. In the case of the reaction of **1c** in aprotic solvent the blue spot of dimethyl pyridazino[2,3-*b*]benzo-1,2,4-triazine-3,4-dicarboxylate radical **16**

was already apparent in TLC after some minutes. This compound could be separated by chromatography, but a substantial amount could be recovered in pure state by cooling the reaction mixture overnight at 0 °C. The radical **16** slowly degrades in solution mainly yielding an unidentified brown material, but the decomposition was not complete even after 1 month at room temperature. Beside the experiments mentioned in Table I the reactions of the heteropentalenes **1a-c** were conducted in other conditions, viz., at different temperatures, in different solvents (chloroform or benzene), or quenching the reaction at a lower conversion, in the presence or in the absence of oxygen. In every case no large variation in the product distribution was observed.

Catalytic Hydrogenation of Compounds 3, 5, 6, 17, and 18. 0.050 g of compound **3** dissolved in 25 mL of ethanol was hydrogenated at room temperature and atmospheric pressure in the presence of Pd/C (10%). The solution turned from yellow to colorless while 1 mol equiv of hydrogen was absorbed. Evaporation of the solution afforded a pale yellow oil, which was crystallized from cyclohexane to yield 0.043 g (95%) of colorless needles of dimethyl 2-(pyrazolo[1,2-*a*]benzotriazol-1-yl)succinate (**8**).

The hydrogenation of compounds **5, 6, 17,** and **18** was similarly carried out to give (70-120 min, 80-90% yield) respectively compounds **9** and **20** (see Table II and Schemes I and IV).

1-(2-Aminophenyl)pyrazole. 0.285 g (15 mM) of 1-(2-nitrophenyl)pyrazole in 20 mL of ethanol was hydrogenated at room temperature and atmospheric pressure in the presence of Pd/C 10%. In 3 h the theoretical amount of hydrogen was absorbed. The solution was evaporated and the residue (0.23 g, 96%) was recrystallized from cyclohexane to yield pure 1-(2-aminophenyl)pyrazole, colorless crystals melting at 47-47.5 °C and correctly analyzing for $C_9H_9N_3$. NMR ($CDCl_3$) 6.45 (1 H, t), 7.72 (2 H, t), 4.6 (NH_2, br) δ.

Hydrolysis of Compound 7. A solution of 0.05 g of **7** in 2 mL of acetone containing 0.3 mL of 1:1 hydrochloric acid was refluxed for 10 min. After cooling and neutralization with solid sodium carbonate, the solution was filtered and evaporated. The usual workup of the residue and crystallization from cyclohexane afforded a quantitative yield of 1-(2-aminophenyl)pyrazole identical (admixed melting point and spectral properties) with the product obtained as reported above.

Addition of DMAD to Dimethyl 2-(Pyrazolo[1,2-*a*]-benzotriazol-1-yl)maleate (3). To a solution of 0.09 g (0.3 mM) of **3** in 5 mL of carbon tetrachloride was added 0.057 g (0.4 mmol) of DMAD. The gradual formation of compound **4** was monitored by TLC. After 5 days at room temperature the starting material was consumed and the solution was evaporated. Chromatography of the residue eluting with benzene-ethyl acetate (9:1) yielded 0.1 g (73%) of product **4**.

Addition of DMAD to Dimethyl Pyrazolo[1,2-*a*]benzotriazole-1,2-dicarboxylate (11). A solution of 0.055 g (0.2 mmol) of **11** and 0.142 g (1 mmol) of DMAD in 20 mL of carbon tetrachloride was refluxed for 2 days. TLC showed that a partial conversion to the bis adduct **12** had taken place. The solution was evaporated and the residue chromatographed, eluting with a benzene-ethyl acetate (9:1) mixture, to yield 0.025 g (30%) of compound **12**.

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Registry No. **1a**, 1738-57-4; **1b**, 15285-01-5; **1c**, 84681-22-1; **2**, 90460-12-1; **3**, 90460-13-2; **4**, 90460-14-3; **5**, 90481-23-5; **6**, 90460-15-4; **7**, 90460-16-5; **8**, 90460-17-6; **9**, 90460-18-7; **11**, 90460-19-8; **12**, 90460-20-1; **13**, 90460-21-2; **14**, 90460-22-3; **15**, 90460-23-4; **16**, 90460-24-5; **17**, 90460-25-6; **18**, 90460-26-7; **19** (isomer 1), 90460-27-8; **19** (isomer 2), 90460-28-9; **20**, 90460-29-0; DMAD, 762-42-5; 1-(2-nitrophenyl)-1*H*-pyrazole, 25688-17-9; 1-(2-aminophenyl)-1*H*-pyrazole, 54705-91-8.

Enamines from Iodine Oxidation of Trialkylamines. 1. Electrophilic Capture by Cationic Heterocyclic Rings

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Simple enamines derived from acetaldehyde, acetone, and propionaldehyde were generated in situ by iodine oxidation of triethylamine, *N,N*-diisopropylmethylamine, and tri-*n*-propylamine, respectively. The enamines were captured by a variety of cationic substrates including trityl, indolizinium, dithiolium, pyrylium, thiapyrylium, selenapyrylium, and tellurapyrylium cations. The use of a second equivalent of iodine (or excess) oxidized the initial products of enamine capture to various iminium dyes. These dyes were easily hydrolyzed to heterocyclylidene aldehydes and ketones. Cyclic amines such as *N*-methylpyrrolidine gave enamines derived from ring oxidation. 2-Cyano-*N,N*-dimethylethylamine generated a cyano-substituted enamine under the reaction conditions.

Tertiary amines have been oxidized to enamines or iminium salts by a variety of methods including photochemical transformations in the presence of suitable electron acceptors,[1] neutral permanganate,[2] iodine pentafluoride,[3] alkoxyaryltrifluoroperiodinanes,[4] trifluoroacetic anhydride,[5] hexachloroacetone,[6] and a variety of biochemical redox reagents.[7] Hydrolysis of the intermediate iminium salts or enamines to the corresponding aldehydes and ketones has been the major synthetic utility of such reactions.[8]

Capture of enamine species in the oxidation of tertiary amines has found limited success.[5,6] One example perti-

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