Electronic Substituent Effects on the Acid-Catalyzed [4⁺ + 2] Cycloaddition of Isopyrazoles with Cyclopentadiene and the Photochemical and Thermal Denitrogenation of the Resulting 1,4-Diaryl-7,7-dimethyl-2,3-diazabicyclo[2.2.1]hept-2-ene Azoalkanes to Bicyclo[2.1.0]pentanes

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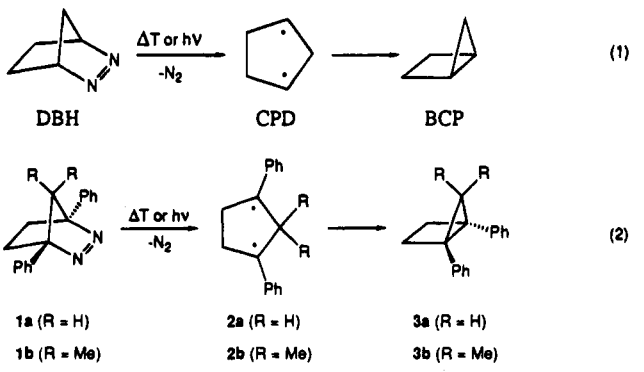
Eight symmetrically disubstituted 3,5-diaryl-4,4-dimethylisopyrazoles **6** with *para* and *meta* substituents (OMe, Me, H, F, Cl, Br, CN, NO_2) and two unsymmetrically *para*-substituted derivatives (OMe and NO_2; Me and CO_2Me) were synthesized from the corresponding 1,3-diaryl-2,2-dimethyl-1,3-propanediones **5**, which in turn were readily available by 2,2-dimethylation of the diones **4**. The acid-catalyzed cycloaddition of cyclopentadiene to the isopyrazoles **6**, a Diels–Alder reaction with inverse electron demand, afforded the 1,4-diaryl-substituted *gem*-dimethyl azoalkanes **7** of the diazabicyco[2.2.1]hept-2-ene (DBH) type. The cycloadduct yields were strongly dependent on the nature of the aryl substituents and highest for the electron-withdrawing substituents. In acidic solution, the azoalkanes showed cycloreversion to generate an equilibrium between isopyrazole **6**, cyclopentadiene, and azoalkane **7**. For the *p*-methoxy derivative, cycloreversion was essentially quantitative, whereas only 20% cycloreversion occurred for the *para* nitro compound. A positive Hammett ϱ value (ϱ = 3.24 for 2 equiv of CF_3COOH) was determined for the equilibrium constants of the acid-catalyzed [4⁺ + 2] cycloaddition. The unsymmetrically substituted isopyrazoles gave two regioisomeric cycloadducts with a slight excess of one isomer. The direct and triplet-sensitized photochemical and thermal denitrogenation of the azoalkanes **7** gave in quantitative yields the 1,4-diaryl-substituted bicyclo[2.1.0]pentanes (BCP) **8** with retention of configuration. The azoalkanes **7** and the housanes **8** are more persistent than the related 1,4-diaryl-substituted DBH and BCP derivatives. The stabilizing effect is rationalized in terms of less favorable benzylic conjugation in the transition states for C–N (azoalkanes) and C–C (housanes) bond cleavage due to steric interactions between the *geminal* methyl groups at the methano bridge and the diaryl substituents at the bridgehead sites.

Introduction

Thermally and photochemically, 2,3-diazabicyclo[2.2.1]-hept-2-ene (DBH) eliminates molecular nitrogen to yield bicyclo[2.1.0]pentane (BCP) through the corresponding 1,3-cyclopentanediyl (CPD) biradical (eq 1).[1] By analogy (eq 2), the 1,4-diaryl-substituted DBH derivatives **1** form the corresponding housanes **3** through the CPD biradicals **2**.[2] The parent CPD biradical and simple alkylated derivatives thereof have been subject to considerable mechanistic,[1] spectroscopic,[3] and theoretical[4] work. More recently, the 1,3-diphenyl-substituted biradicals **2**, which are much more persistent, have been studied by transient absorption,[2] EPR,[5] and ^1H NMR[6] spectroscopy, as well as by the oxygen-trapping method.[2a,7] Their exceptional persistence in liquid[2] and matrix[5] phases and the presence of the benzylic chromophore make 1,3-diaryl-



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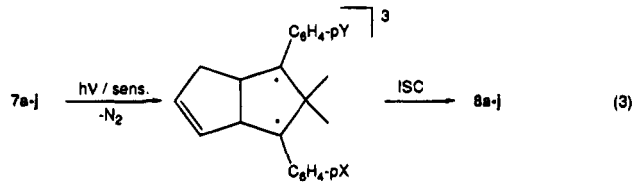
substituted CPD biradicals excellent models for the spectral examination of the structural dependence which governs the lifetimes and the zero-field splitting parameters of their triplet states.

To assess electronic effects in CPD biradicals, e.g., through *meta* and *para* substitution, efficient and convenient routes to suitable azoalkane precursors such as **1** with a wide range of aryl substituents are required. Work by us and others[8] showed that the introduction of aryl substituents in DBH derivatives through the classical route,[9,10] namely the addition of triazolinediones to substituted cyclopentadienes, catalytic hydrogenation of the resulting unsaturated adduct, hydrolysis, and final oxidation to yield the azoalkanes, suffers from serious disadvantages. These include the difficult synthesis of the substituted cyclopentadienes and their ease of isomerization, cycloreversion, and selective hydrogenation of the unsaturated adducts, as well as oxidation and isolation problems of the thermally labile azoalkanes. The alternative useful synthesis of DBH derivatives, namely the intramolecular cyclization of olefinic tosyl hydrazones under acidic conditions,[9,11] requires extensive heating in the last step and, thus, may not be applied to the thermally less persistent derivatives **1**.

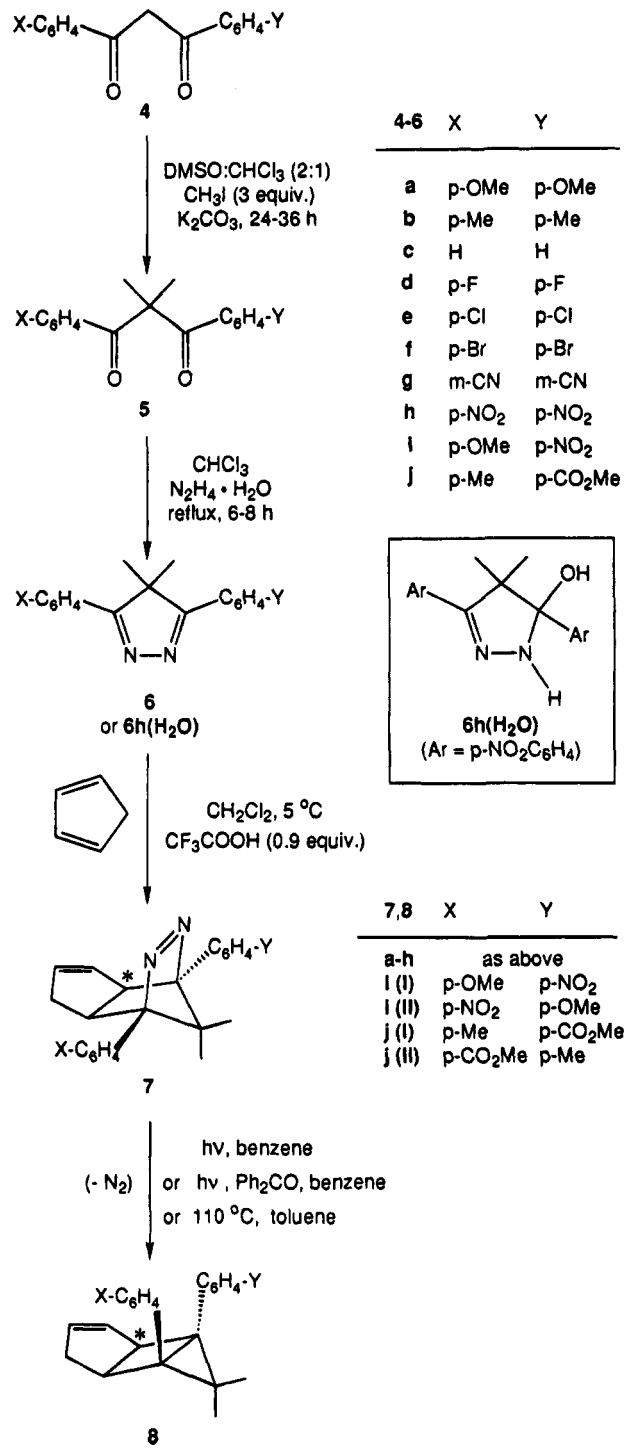
To bypass these problems, we have applied[12] the less common isopyrazole method for the synthesis of 1,4-diarylated DBH derivatives according to Scheme 1. This synthetic route involves the conversion of the 1,3-propanediones **4** to the 2,2-dimethylated derivatives **5**, and cyclization with hydrazine affords the 4,4-dimethyl-4*H*-pyrazoles (isopyrazoles) **6**, which undergo cycloaddition with cyclopentadiene to yield the azoalkanes **7**. This isopyrazole method is compatible with a large variety of aryl substituents, and we have prepared the 1,4-diaryl-substituted azoalkanes **7a–j**, which show excellent thermal stability in contrast to the parent molecule **1a**. The corresponding triplet CPD biradicals (eq 3), readily generated by direct and sensitized photolysis of the azoalkanes **7a–j**, are persistent at 77 K in matrix[12a] and relatively long-lived in solution;[12b] on intersystem crossing they afford the housanes **8**.



(3)

Isopyrazoles undergo Diels–Alder reactions with appropriate dienophiles (cyclobutadiene,[13] triazolinediones,[14] cyclopropenones[15] and norbornene[16]) to give DBH-type azoalkanes as cycloadducts.[9] Hünig *et al.*[17] have shown that even for electron-rich or strained olefins as dienophiles acid catalysis is necessary. Cyclopentadiene

Scheme 1



4-6	X	Y
a	p-OMe	p-OMe
b	p-Me	p-Me
c	H	H
d	p-F	p-F
e	p-Cl	p-Cl
f	p-Br	p-Br
g	m-CN	m-CN
h	p-NO_2	p-NO_2
i	p-OMe	p-NO_2
j	p-Me	p-CO_2Me

7,8	X	Y
a-h	as above	
i (I)	p-OMe	p-NO_2
i (II)	p-NO_2	p-OMe
j (I)	p-Me	p-CO_2Me
j (II)	p-CO_2Me	p-Me

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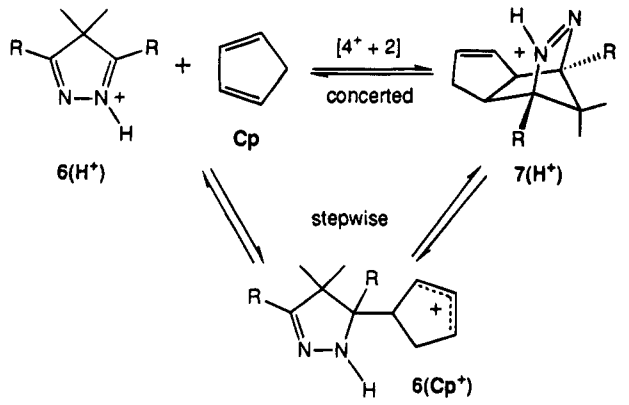
Scheme 2



(Scheme 2) is by far the most reactive, followed by norbornene and norbornadiene, which are still much more reactive than cyclopentene.[17a] The reactivity of the isopyrazole, as reflected by the yield of cycloadduct, reaction time, and required temperature, depends[17a-c] on the nature of the 3,5 substituents R, e.g., it decreases in the order H > Me > Ph. This experimental trend reflects the increasing steric demand of the bridgehead substituents R in the transition state for the cycloaddition. Moreover, the reactivity of the isopyrazole is much enhanced in the presence of acid.[17a] On the basis of the reactivity order with respect to the olefin[18] and the catalytic effect of acid, a [4⁺ + 2]-type[19] Diels–Alder reaction was suggested (Scheme 2) in which the protonated isopyrazole **6(H⁺)** functions as the electron-deficient diene and the olefin as electron-rich dienophile (inverse electron demand[18]).

The cycloaddition of isopyrazoles **6** (R = H, Me) and *trans*-cyclooctene[17c] was shown to proceed with retention of the *trans* configuration in the cyclooctene moiety. Although this result suggested a concerted reaction mechanism, a stepwise mechanism could not be rigorously excluded.[17a] Indeed, for cyclopentadiene as dienophile, control experiments and theoretical considerations implied a stepwise mechanism.[17d] The stepwise cycloaddition mechanism appears likely since a carbocationic intermediate like **6(Cp⁺)** is stabilized through allylic resonance (Scheme 2).

Fast acid-catalyzed cycloreversion has been observed[17a] for azoalkane **7** (R = Me), which led to an equilibrium mixture of azoalkane, isopyrazole, and cyclopentadiene. Slow cycloreversion occurred also for the bridgehead unsubstituted azoalkane **7** (R = H) at low acid concentration, while at high acid concentration Cope rearrangement with the loss of the azo chromophore took place.[17d] Thus, the cycloaddition of isopyrazoles and cyclopentadiene represents a typical equilibrium reaction (Scheme 2).

The impact of electronic effects on this acid-catalyzed Diels–Alder reaction (Scheme 2) remains to date still unexplored. Consequently, it would be of interest to assess how electron-donating and -accepting groups of the isopyrazole as diene partner affect the rates and the equilibrium of the [4⁺ + 2] cycloaddition with cyclopentadiene. For this purpose, an extensive set of 3,5-diaryl-substituted isopyrazoles **6** was required, and we now present the experimental details of our synthetic work displayed in Scheme 1. Since the azoalkanes **7a–j** have previously served[12] as precursors in the spectroscopic studies of the corresponding CPD biradicals (eq 3), we focus on the mechanistic implications of their mode of formation and on their photolysis and thermolysis behavior. The latter denitrogenations afford the corresponding housanes **8a–j**, whose structures and chemical reactivities have been examined as well.

Table 1. Yields of Isolated Diketones 5, Isopyrazoles 6, Azoalkanes 7, and Housanes 8 and Equilibrium Concentrations [6]:[7] for the Cycloaddition–Cycloreversion Process

			yields (%)				
	X	Y	**5**	**6**	**7**	**8**[b]	equilibrium mixture[a] [6]:[7]
a	*p*-OMe	*p*-OMe	58	81	38	97	99.5:0.5
b	*p*-Me	*p*-Me	23	62	40	96	96.3:3.7
c	H	H	64	82	47	96	91.7:8.3
d	*p*-F	*p*-F	43	80	53	97	89.3:10.7
e	*p*-Cl	*p*-Cl	22	76	56	96	83.4:16.6
f	*p*-Br	*p*-Br	27	87	66	97	75.8:24.2
g	*m*-CN	*m*-CN	40	64	77	96	24.7:75.3
h	*p*-NO_2	*p*-NO_2	34	87[c]	82	96	19.4:80.6
i	*p*-OMe	*p*-NO_2	49	81	15[d]	94[d]	86.3:13.7[e]
j	*p*-Me	*p*-CO_2Me	21	71	20[d]	93[d]	82.2:17.8

[a] Equilibrium mixtures determined by ^1H NMR spectroscopy and normalized to 100% (error ca. 3% of stated values). Conditions: 5×10^{-5} mol of azoalkane **7** with 2 equiv of CF_3COOH in 0.7 mL of $CDCl_3$ at 20 °C. [b] Obtained by direct photolysis in degassed benzene (**7a–f**) or thermolysis (**7g–j**). [c] Yield refers to isolated half-aminal **6h(H₂O)**. [d] Assignment of X and Y may be reversed; cf Table 2. [e] A precipitate formed on addition of acid; thus, the equilibrium constant may not be as reliable as determined for the other derivatives.

Results and Discussion

Synthesis. The synthetic route (Scheme 1) for the preparation of the 3,5-diarylisopyrazoles **6** started from the corresponding 1,3-diaryl-1,3-propanediones **4**, of which most are known and which exist in solution as their enols. Dimethylation of the diketones **4** gave the 1,3-diaryl-2,2-dimethyl-1,3-propanediones **5** in low to moderate yields (Table 1). Since even under identical conditions the double methylations gave variable yields (e.g., 13–34% for **4h**), no efforts for optimization were undertaken. The *E,Z* isomers of the C,O-dimethylated enol ethers constitute byproducts under these aprotic, polar reaction conditions, and in several cases significant amounts were observed by NMR spectroscopy of the crude material.

In contrast, the conversion of the dimethylated diketones **5** to the isopyrazoles **6** was easily accomplished throughout in high yields (Table 1). The diketone **5h** is particularly reactive, since complete conversion with hydrazine hydrate occurred even at 0 °C within 2 h in methylene chloride. The precipitate, however, was not the expected isopyrazole **6h**, but its hydrate in form of the half-aminal **6h(H₂O)**, cf. Scheme 1. The latter eliminated water readily on acid catalysis and slower on thermolysis (160 °C, 0.01 Torr, 5 h) to give the free isopyrazole **6h**. The formation of the intermediary half-aminal has not been observed for the other isopyrazoles.

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Table 2. Relative Yields[a] of the Regioisomers for Azoalkanes 7i,j and for Housanes 8i,j

X	Y	azoalkane	rel yields[b] (%)	housane	rel yields[c] (%)
p-OMe	*p*-NO_2	**7i(I)**	54	**8i(I)**	54
p-NO_2	*p*-OMe	**7i(II)**	46	**8i(II)**	46
p-Me	*p*-CO_2Me	**7j(I)**	52	**8j(I)**	51
p-CO_2Me	*p*-Me	**7j(II)**	48	**8j(II)**	49

[a] Normalized to 100%. [b] Determined by quantitative ^{13}C NMR analysis of the characteristic resonances at δ 43.2 and 57.3 for **7i(I)**, δ 43.7 and 56.7 for **7i(II)**, δ 43.1 and 56.9 for **7j(I)**, and δ 43.3 and 56.7 for **7j(II)**; error ±5% of the stated values. [c] Determined by quantitative ^1H NMR analysis of the characteristic resonances at δ 2.85, 3.41 and 5.52 for **8i(I)**, δ 2.96, 3.28 and 5.42 for **8i(II)**, δ 3.36 for **8j(I)**, and δ 3.29 for **8j(II)**; error ±3% of stated values.

The cycloadditions of the isopyrazoles **6** to afford the azoalkanes **7** (Table 1) were conveniently carried out overnight at 5 °C in methylene chloride with trifluoroacetic acid as catalyst. An excess of cyclopentadiene was used to drive the equilibrium (see below) toward the cycloadducts. Since cycloreversion occurred under the reaction conditions, the *endo* stereochemistry of the cycloadducts, which has been established elsewhere,[17] may also represent thermodynamic reaction control. Indeed, AM1 calculations[20] suggest that the *endo* stereoisomer is 10.0 kcal/mol more stable than its *exo* form.

The yields of isolated azoalkanes **7** strongly depended on the electronic nature of the aryl substituents; they were lower for the electron-donating substituents, e.g., for the *p*-methoxy and *p*-methyl derivatives **6a** and **6b**, and higher for the electron-accepting groups, e.g., for the *m*-cyano and *p*-nitro cases **6g** and **6h**. The exceptional reactivity of the nitropyrazole **6h** is noteworthy, since it underwent cycloaddition at 0 °C in 20 min, despite its very low solubility in methylene chloride. The yield of azoalkane **7h** was the highest observed under these reaction conditions. Such high yields were only reported for a few cases,[17c] when the reactions conditions were quite drastic, e.g., 7 kbar at 130 °C.

The cycloaddition of the unsymmetrically *p*-phenyl-substituted isopyrazoles **6i,j** with cyclopentadiene afforded the corresponding azoalkanes **7i,j** in quite low yields of isolated material. For the methyl/carbomethoxy derivative **7j**, the low yield derives from purification problems, since several chromatographic separations were necessary. For the nitro/methoxy derivative **7i**, however, the reduction in the yield was due to side reactions, since precipitation occurred on acid addition to a solution of **7i** (see below and Table 1). No efforts were expended to elucidate the structure of this precipitate.

For azoalkanes **7i,j**, the regioisomers **I** with the C=C double bond proximate to the electron-accepting aryl substituents were formed in slight excess (Table 2). The regiochemistry was established by comparison with the ^{13}C NMR spectral data of the symmetrically substituted derivatives. For example, the resonances at δ 57.4 for the dinitro derivative **7h** and at δ 56.7 for the dimethoxy derivative **7a** are assigned to the C-4a carbon atoms (asterisk in structure **7**, Scheme 1). For the unsymmetrical derivative **7i**, resonances occur at δ 57.3 and 56.7, which are assigned to the regioisomers **I** and **II**.

(20) For the AM1 method, cf. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. The VAMP program was used by employing a Silicon Graphics Iris Indigo workstation: Rauhut, G.; Chandrasekhar, J.; Clark, T., *VAMP 4.4* (Universität Erlangen, Erlangen, FRG, 1992).

The regioisomeric ratio was then determined by quantitative analysis of the ^{13}C integrals of the characteristic peaks. The relative yields of the azoalkane regioisomers do not change on prolonged storage in acidic solution. Since cycloreversion does occur under these conditions, the latter result indicates that the compositions of regioisomers represent their equilibrium concentrations. Thus, the approximate 1:1 ratios indicate very similar energies for the two regioisomers as confirmed by AM1 calculations, which give the small energy difference of ΔH_f = 0.04 kcal/mol in favor of the slightly more abundant isomer **7i(I)**. Identical relative yields of the regioisomeric housanes **8i,j** were obtained from the corresponding azoalkanes on thermolysis (Table 2).

The regiochemistry of the unsymmetrical housanes **8i,j** was determined in a similar manner by using for example the C-5 carbon atoms (asterisk in structure **8**, Scheme 1). Note, however, that for the housanes **8i,j** the assignments and isomeric ratios were also based on the characteristic ^1H NMR resonances (e.g., 5-H) of the regioisomers, which were sufficiently resolved for assignment, in contrast to the azoalkanes **7i,j**.

Substituent Effects on the Cycloaddition–Cycloreversion Equilibrium. When the azoalkanes **7** were dissolved in deuterated chloroform together with 2 equiv of trifluoroacetic acid, cycloreversion to the isopyrazoles **6** and cyclopentadiene took place, which was monitored by ^1H NMR spectroscopy until an equilibrium mixture of isopyrazoles **6** and azoalkanes **7** was reached at ambient temperature (Table 1). The samples were stored for a period of 3 d (at 0 °C to minimize dimerization of cyclopentadiene), and no side reactions or changes of the equilibrium concentrations (±5%) were observed by NMR spectroscopy, but for derivative **7i**, a precipitate formed. The rates of cycloreversion to attain the equilibrium mixture decreased in the order *p*-OMe (ca. 1 min) > *p*-Me > *p*-H > *p*-F > *p*-Cl > *p*-Br > *m*-CN > *p*-NO_2 (ca. 5 h), which follows the electron-accepting propensity of these substituents as measured by the Hammett σ values. Thus, the higher reactivity of the isopyrazoles **6** with electron-accepting substituents and the relative rates for cycloreversion corroborate the inverse electron demand for this Diels–Alder reaction.

More informative than the relative rates for cycloreversion are the absolute equilibrium concentrations of the azoalkanes **7**. The methoxy derivative **7a** undergoes essentially quantitative cycloreversion under the applied conditions. Thus, **7a** is extremely labile toward traces of acid, and some cycloreversion even occurs when this azoalkane is dissolved in commercial deuterated chloroform. To obtain the azoalkane **7a** in preparative amounts, it is imperative to use a large excess of cyclopentadiene as dienophilic partner and also larger amounts of acid to ensure efficient protonation of the isopyrazole. In contrast, the nitro derivative **7h**, which is stable toward acid traces, may be obtained in similar yield with much smaller amounts of acid and cyclopentadiene (cf. Experimental Section). Since the yields of the symmetrically substituted azoalkanes **7** follow the same dependence on the substituents as the equilibrium constants of this reversible cycloaddition (Table 1), knowledge of the electronic substituent effects should be helpful in the design of efficient conditions for the cycloaddition of isopyrazoles and dienes.

A quantitative treatment of the substituent effects on the equilibrium constants provides valuable information on the electronic factors which govern the stability of the

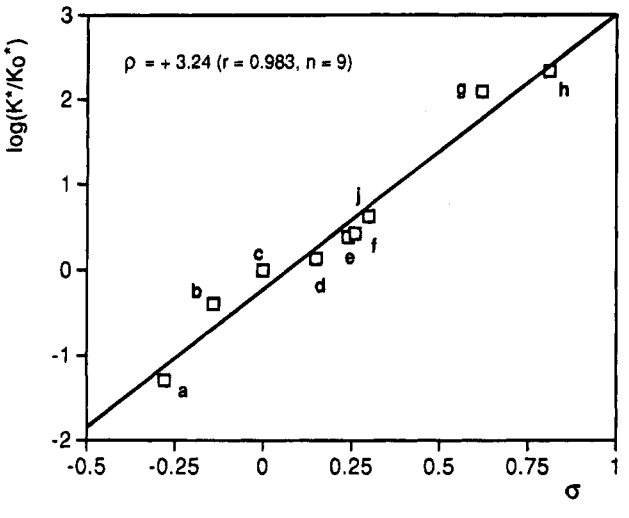


Figure 1. Hammett plot of the equilibrium constants (K^*) for the cycloaddition of the 3,5-diaryl-4,4-dimethylisopyrazoles **6** and cyclopentadiene.

cycloadducts. According to Scheme 2, acid catalysis requires that the protonated isopyrazole **6**(H^+) and the protonated azoalkane **7**(H^+) concentrations constitute the equilibrium constant K (eq 4). The concentrations of the

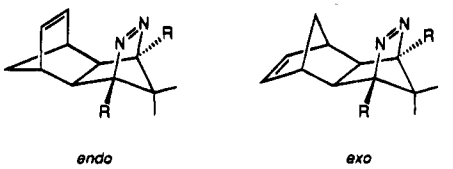
$$K = \frac{[\mathbf{7}(H^+)]}{[\mathbf{6}(H^+)][Cp]} = \frac{K_a^{\mathbf{6}}}{K_a^{\mathbf{7}}}\frac{[\mathbf{7}]}{[\mathbf{6}][Cp]} = \frac{K_a^{\mathbf{6}}}{K_a^{\mathbf{7}}}\frac{[\mathbf{7}]}{[\mathbf{6}]^2} = \frac{K_a^{\mathbf{6}}}{K_a^{\mathbf{7}}}K^* \quad \text{with } K^* = \frac{[\mathbf{7}]}{[\mathbf{6}]^2} \quad (4)$$

protonated forms, in turn, may be expressed by the relative concentration of isopyrazole and azoalkane, namely [**6**] and [**7**], and by the acid dissociation constants of these two components. Finally, the cyclopentadiene concentration [**Cp**] is equal to the isopyrazole concentration [**6**] since the dissociation produces 1 equiv of each and, thus, [Cp] = [**6**] in eq 4. The constants K^* for the various substituents may then be calculated by using the relative isopyrazole and azoalkane concentrations [**6**] and [**7**], which are directly obtained by ^{1}H NMR analysis of the equilibrium mixtures (Table 1).

To a first approximation, one may assume that the acid dissociation constants are equal for all isopyrazoles and equal for all azoalkanes.[21] Thus, with $K_a^{\mathbf{6}}/K_a^{\mathbf{7}}$ = constant, $K \propto K^*$ follows and a Hammett treatment was applied. A semilogarithmic plot (Figure 1) of the relative K^* values *versus* the Hammett σ constants[22] gave $\varrho = +3.24$ ($r = 0.983$, $n = 9$) for the cycloaddition/cycloreversion equilibrium. Thus, an appreciable dependence of the equilibrium constants on electronic substituent effects becomes evident, in which the positive ϱ value indicates that the cycloaddition is assisted by electron-accepting substituents. The methoxy/nitro derivatives **6i** and **7i** had to be excluded in the Hammett plot since a precipitate was formed, and thus, no reliable equilibrium concentrations could be determined.

The inverse electron demand of this Diels–Alder reaction implies that the more electron-deficient isopyrazoles show enhanced reactivity due to a smaller HOMO–LUMO gap. Indeed, this is manifested by the results of AM1 calculations.[20] The calculated LUMO energies of the isopyrazoles **6a–j** vary between −0.94 (X, Y = OMe) and −2.26 eV (X, Y = NO_2), and the HOMO energy of cyclopentadiene is placed at −9.1 eV, which is in good agreement with the experimental[23] ionization energy (9.0 eV). Thus, a calculated HOMO–LUMO gap of 7–8 eV results for the uncatalyzed cycloaddition, which is in the order expected for [4 + 2] cycloadditions.[24] Protonation of the isopyrazoles lowers their LUMO energies by 3–4 eV according to the semiempirical method.[20] This results in smaller HOMO–LUMO energy gaps and explains the observed acid catalysis for this cycloaddition/cycloreversion process.

Direct and Sensitized Photolysis of the Azoalkanes. The azoalkanes **7** exhibit n,π^* absorption maxima at ca. 360 nm, except derivatives **7h,i**, for which shoulder contours due to the overlapping n,π^* absorption of the nitrophenyl chromophore are observed. The direct photolyses of azoalkanes **7** were carried out in degassed benzene at room temperature by irradiation at the absorption maxima of the azo chromophore, i.e., at the 364-nm line of the CW argon ion laser. The azoalkanes, except **7h,i**, photodenitrogenate cleanly to the crystalline housanes **8** (Scheme 1, Table 1) like their unsubstituted parent DBH, which extrudes molecular nitrogen with unit quantum yield.[1e] Consequently, azoalkanes **7**, despite their higher degree of substitution, are normal DBH derivatives. Note, however, that other DBH-type azoalkanes obtained through the isopyrazole route, namely the azoalkanes derived from cycloaddition of norbornadiene and isopyrazoles, behave completely differently. Thus, the *endo* isomers show [2 + 2] photocycloadditions of the parallel C=C and N=N bonds,[17b] whereas the corresponding *exo* isomers display β C–C cleavage and unusually long triplet lifetimes.[25]



For a rigorous stereochemical assignment of the housanes **8**, an X-ray analysis of the chloro derivative **8e** was performed, which crystallizes as a racemic mixture[26] (Figure 2). Clearly, photochemical denitrogenation proceeded with retention of configuration, although normally DBH derivatives give on direct irradiation preferentially

(21) This approximation is reasonable for such azoalkanes since the phenyl substituents are not in direct resonance with the azo nitrogen atoms. For the isopyrazoles **6**, the acid dissociation constants are expected to be somewhat lower, i.e., $K_a^{\mathbf{6}}$ (X = OMe) < $K_a^{\mathbf{6}}$ (X = NO_2), for the electron-donating substituents, which should enhance the basicity of the isopyrazole nitrogen atoms through resonance interaction. As can be seen from eq 4, this would result in even smaller K values for the electron-donating substituents and, thus, would tend to give a ϱ value still larger than +3.24.

(22) Taken from: March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; p 244.

(23) Harrison, A. G.; Honnen, L. R.; Dauben, H. J., Jr.; Lossing, F. P. *J. Am. Chem. Soc.* **1960**, *82*, 5593.

(24) (a) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: Chichester, 1985. (b) Houk, K. N. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II, Chapter 4.

(25) Adam, W.; Nau, W. M.; Sendelbach, J.; Wirz, J. *J. Am. Chem. Soc.* **1993**, *115*, 12571.

(26) Atomic parameters, isotropic and anisotropic displacement coefficients, bond lengths, and bond and torsion angles of the X-ray determination for compound **8e** may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, FRG, on quoting the depository number CSD-400528, the names of the authors, and the journal citation; see also the Experimental Section.

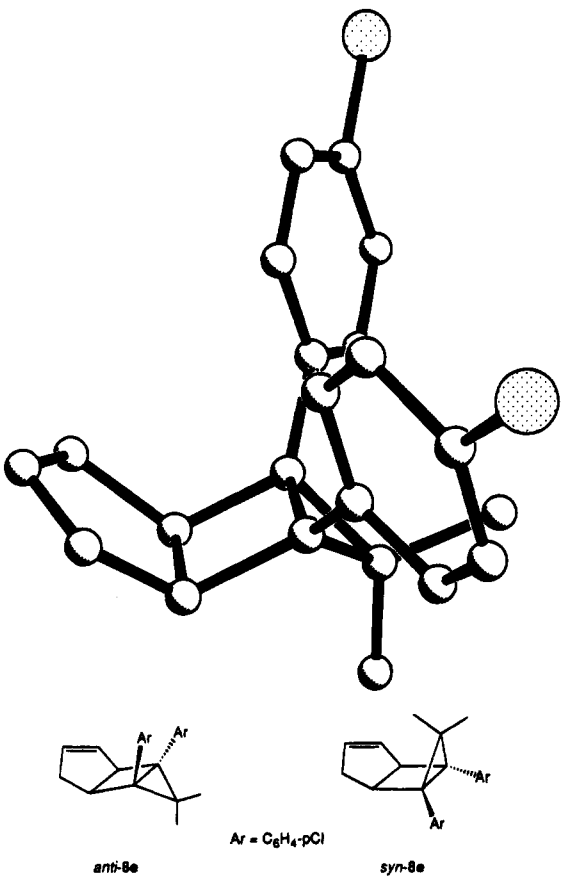


Figure 2. X-ray structure of the housane *anti*-**8e** and projections of the two possible stereoisomers.

housanes with double inversion.[1,4c-e] Inspection of molecular models reveals that the *syn*-**8** housanes with inverted geometry are strongly disfavored by steric repulsion between the cyclopentene and *geminal* methyl groups. In fact, AM1 calculations[20] suggest that such steric destabilization should be worth ca. 5.5 kcal/mol. Thus, the propensity for double inversion[1,4c-e] in the direct photodenitrogenation is overcompensated by steric constraints and retention prevails.

It should also be mentioned that no drastic changes of the central bond do occur in differently substituted housanes. Thus, the length of the central bond for the housane **8e** is 155.9 pm according to the X-ray analysis (Figure 2) and 153.6 pm for the unsubstituted parent BCP, for which a microwave spectroscopic study has been carried out.[27]

Direct irradiation of the azoalkanes **7h,i** did not produce the desired housanes **8h,i**, but rather complicated product mixtures, for which identification of the photoproducts was difficult. Presumably, secondary photolyses of the photoactive nitrophenyl groups[28a] in the resulting housanes **8h,i** are responsible for this complexity. Indeed, the photolability was confirmed by means of control experiments on the authentic housanes **8h,i**, which were prepared by thermolysis of the azoalkanes **7h,i** (see below). Since the nitrophenyl chromophore itself functions as an effective internal triplet sensitizer ($^3\Phi = 0.67$),[28b] triplet reactivity was expected in the direct photolysis of the housanes **8i,j** and also of the azoalkanes **7i,j**. Moreover, the triplet-sensitized photolysis with benzophenone gave also the expected housanes **8**, but was not carried out for the problematic nitrophenyl derivatives **7h,i**.

Thermolysis of the Azoalkanes. Thermal extrusion of molecular nitrogen from the azoalkanes **7** occurred at 110 °C, with substituent-dependent half-lives in the range 30–190 min; the unsubstituted derivative **7c** was the most persistent derivative in this series. Thus, the azoalkane **7c** is thermally much more persistent than the corresponding 1,4-diphenyl-substituted DBH derivative without the alkyl groups **1a**.[2a] The latter extrudes molecular nitrogen at ca. 20 °C with a half-life of 30 min, but is appreciably less persistent than the unsubstituted DBH, which undergoes thermal denitrogenation at a similar rate only at 160 °C.[1a,d] The activation parameters[1a] for the parent DBH are $\Delta H^{\ddagger} = 37$ kcal/mol and $\Delta S^{\ddagger} = 8.7$ eu, and if one assumes the same entropy of activation for all DBH derivatives, the enthalpies of activation for **1a** ($\Delta H^{\ddagger}$ ca. 25 kcal/mol) and azoalkane **7c** ($\Delta H^{\ddagger}$ ca. 33 kcal/mol) may be estimated. The lower thermal stability of azoalkane **1a** compared to the parent DBH derives from the decreased bond dissociation energy of the benzylic C–N bonds, apparently worth ca. 12 kcal/mol ($\Delta\Delta H^{\ddagger}$). Since the *gem*-dimethyl derivative[2b] **1b** (half-life ca. 30 min at 110 °C, this work) displays a thermal stability similar to the azoalkane **7c**, the increased persistence of these must be inherently related to dialkylation of the methylene bridge between the benzylic termini. The stabilizing influence of *gem*-dimethyl substitution in DBH derivatives is, therefore, unexpectedly large ($\Delta\Delta H^{\ddagger}$ ca. 8 kcal/mol for **1b** *versus* **1a**), an effect also exhibited by the respective housanes (see below).

Reactivity of the Housanes. The housanes **8** are exceptionally stable toward acid and also toward molecular oxygen; e.g., housane **8h** may be heated even at 200 °C in air without significant decomposition. In contrast, the 2,4-diphenyl-substituted housane **3a** readily rearranges on acid catalysis[2a] and reacts with molecular oxygen already at room temperature.[2a,7] This pronounced reactivity toward dioxygen is due to the low bond dissociation energy (ca. 12 kcal/mol) of the central bond in this BCP derivative,[6,7] which is responsible for an appreciable stationary concentration of the CPD biradical **2a** at room temperature and the latter is trapped by O_2. Thus, the higher thermal stability of the housanes **8** resembles that of the *gem*-dimethylated housane **3b**.[2b] For example, at up to 100 °C in deuterated toluene, **3b** does not show any ^{1}H NMR coalescence as does **3a**.[6]

These results reveal that *gem*-dimethyl substitution at the 5 position in housanes increases considerably the bond dissociation energy of the central bond or the activation energy for bond scission. Most likely,[6,7] the greater persistence of the *gem*-dimethylated housanes **8** and **3b** is due to steric inhibition (repulsion between the *gem*-dimethyl and the diaryl groups) of benzylic resonance in the radical-like transition state for C–C bond cleavage. Similarly, steric constraints of the *gem*-dimethyl group in the azoalkanes **7** and **1b** prevent full benzylic stabilization of the developing radical sites in the transition state for C–N bond cleavage and, thus, stabilize these azoalkanes toward thermal denitrogenation (see above).

Be this as it may, *gem*-dialkyl substitution is an effective means for the preparation of thermally persistent 1,4-diaryl-substituted DBH and BCP derivatives. A

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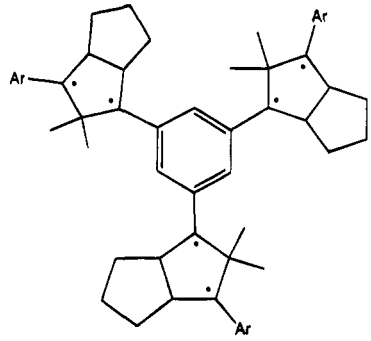
wide variety of the azoalkanes and housanes is conveniently available through [4⁺ + 2] cycloaddition of 4,4-dialkyl-substituted isopyrazoles and subsequent thermal or photochemical denitrogenation.

Conclusions

A set of 3,5-diarylisopyrazoles has been used for a comprehensive study of substituent effects on their acid-catalyzed cycloaddition with cyclopentadiene, which affords diaryl-substituted azoalkanes of the DBH-type. It has been shown that the reactivity of the isopyrazoles in this Diels–Alder reaction and the equilibrium constants are quite sensitive toward electronic substituent effects. Even though electron-donating substituents promote acid-catalyzed cycloreversion, this method provides access to sufficiently persistent 1,4-diaryl-substituted DBH-type azoalkanes for isolation, purification, and handling. Important to realize is that the seemingly innocuous *gem*-dimethyl substitution is responsible for the enhanced persistence.

The thermal and photochemical denitrogenation of DBH-type azoalkanes affords 1,3-cyclopentanediyl biradical intermediates, which are currently under intensive investigation.[1-12] The diaryl-substituted DBH-type azoalkanes, which are conveniently accessible through the isopyrazole cycloaddition methodology,[13-17] may be used as precursors for particularly long-lived triplet biradicals.[12] Such biradicals may serve as attractive spin carriers for potentially more persistent[2,5-8,12] high-spin polyradicals. For example, in view of the recent reports on high-spin systems[29] in which the non-Kekulé *m*-phenylene moiety functions as ferromagnetic coupling unit, it should be of interest to prepare the novel polyradical below and probe its magnetic properties.



Experimental Section

General Aspects. NMR spectra were recorded on a Bruker AC 200 with $CDCl_3$ as solvent and internal standard, unless stated differently. UV absorption spectra were recorded with a Hitachi U 3200 spectrophotometer, infrared spectra were measured on a Perkin-Elmer 1420 ratio recording infrared spectrophotometer (values in cm^{-1}), and melting points were taken on a Reichert Thermovar Kofler apparatus. Combustion analyses were performed by the Microanalytical Division of the Institute of Inorganic Chemistry, and mass spectra were carried out in the Institute of Organic Chemistry, both at the University Würzburg. The X-ray analysis was carried out with a Siemens R3m/V diffractometer by using Mo Kα radiation and a graphite monochromator; the Siemens SHELXTL PLUS program, run on a MicroVAX-II station, was used for the structural analysis. Solvents and commercially available chemicals were purified by standard procedures or used as bought. Column chromatography was carried out on silica gel (0.032–0.063 mm, Woelm). Irradiations were carried out with the 333-, 353-, and 364-nm UV lines (widened beam) of a CW argon ion laser (INNOVA 100, Coherent Company).

NMR assignments were made on the basis of known spectral data of the parent compounds.[17b] For the aromatic region, group increments[30] for *para* substituents were used as far as possible. The specific assignments of the NMR spectra of the regioisomers for **7i,j** and **8i,j** are based on the NMR data for the symmetrically substituted derivatives **7a,b,h** and **8a,b,h**. Coupling constants are given with an accuracy of 0.2 Hz (^1H NMR) and 1 Hz (^{13}C NMR). ^1H NMR coupling constants are J_{HH} values unless stated differently.

Preparation of the 1,3-Diaryl-1,3-propanediones 4. The 1,3-diaryl-1,3-propanediones were prepared according to literature procedures (**4a,b**,[31a] **4f**,[31b] **4h**,[31c] **4i**[31d,e]), except **4c**, which was bought from Aldrich Chemical Company, and **4d,e,g,j**, which were synthesized in analogy to the literature procedures[31a,b] and purified by column chromatography (**4g**) or recrystallization (**4d,e,j**). Although the melting points for compounds **4e,f** differed considerably from the previously reported data[31b,f] the comparison of the NMR spectral data with the other derivatives **4** established sample identity.

1,3-Bis(4′-methoxyphenyl)-1,3-propanedione (4a; X, Y = *p*-OMe): 39%, yellow powder, mp 115–116 °C (ethanol, lit.[31f] mp 116 °C).

1,3-Bis(4′-methylphenyl)-1,3-propanedione (4b; X, Y = *p*-Me): 80%, pale yellow powder, mp 125–126 °C (ethanol, lit.[31g] mp 126–127 °C).

1,3-Diphenyl-1,3-propanedione (4c; X, Y = H): commercial, mp 78–79 °C (lit.[31f] mp 78 °C).

1,3-Bis(4′-fluorophenyl)-1,3-propanedione (4d; X, Y = *p*-F): 22%, colorless powder, mp 112–113 °C (ethanol, lit.[31h] mp 109 °C).

1,3-Bis(4′-chlorophenyl)-1,3-propanedione (4e; X, Y = *p*-Cl): 29%, pale yellow powder, mp 195–196 °C (toluene, lit.[31f] mp 159 °C).

1,3-Bis(4′-bromophenyl)-1,3-propanedione (4f; X, Y = *p*-Br): 37%, yellow powder, mp 185–186 °C (toluene, lit.[31b] mp 197–198.5 °C).

1,3-Bis(3′-cyanophenyl)-1,3-propanedione (4g; X, Y = *m*-CN): 55%, pale yellow powder, mp 278–280 °C, $R_f = 0.42$ (SiO_2, methylene chloride). IR (KBr): ν = 3100, 2940, 2210, 1710, 1590, 1540, 1460, 1310, 1290, 1240, 1180, 1170, 1160, 1080, 1110, 990, 905, 780, 670. ^1H NMR ($CD_3S(O)CD_3$): δ = 7.56 (s, 1 H, 2-H of enol), 7.80 (t, ^3J = 7.9 Hz, 2 H, 5′-H), 8.13 (d, ^3J = 7.9 Hz, 2 H, 6′-H), 8.49 (d, ^3J = 7.9 Hz, 2 H, 4′-H), 8.70 (br s, 2 H, 2′-H). The ^1H NMR resonance of the enolic hydrogen is expected at ca. 16.5 ppm[31e] and has not been recorded. ^{13}C NMR ($CD_3S(O)CD_3$): δ = 94.2 (d, C-2), 112.0 (s, C-3′), 117.8 (s, CN), 129.9 (d, C-5′), 130.9 (d, C-6′), 131.4 (d, C-2′), 135.2 (s, C-1′), 135.9 (d, C-4′), 183.0 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{10}N_2O_2$ (274.3): C, 74.44; H, 3.68; N, 10.21. Found: C, 74.71; H, 3.78; N, 9.99.

1,3-Bis(4′-nitrophenyl)-1,3-propanedione (4h; X, Y = *p*-NO_2): 60%, yellow powder, mp 238–239 °C (lit.[31f] mp 241–242 °C).

(29) (a) Jacobs, S. J.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744. (b) Jacobs, S. J.; Dougherty, D. A. *Angew. Chem.* **1994**, *106*, 1155; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1104.

(30) ^{13}C NMR and ^1H NMR substituent increments taken from: Kalinowski, H. O.; Berger, S.; Braun S. In *^{13}C-NMR-Spectroscopy*; Thieme Verlag: Stuttgart, 1984. Jackman, L. M.; Sternhell, S. In *Applications of Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: Oxford, 1969. For the ^{13}C NMR data of the cyano derivatives **4g–8g** cf.: Exner, O.; Budesinski, M. *Magn. Reson. Chem.* **1989**, *27*, 27.

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1-(4′-Methoxyphenyl)-3-(4″-nitrophenyl)-1,3-propanedione (4i; X = *p*-OMe, Y = *p*-NO₂): 20%, yellow powder, mp 204–205 °C (lit.[31d,e] mp 180–181 °C).

1-(4′-Carbomethoxyphenyl)-3-(4″methylphenyl)-1,3-propanedione: **(4j; X = *p*-CO₂Me, Y = *p*-Me)**: 22%, pale yellow powder, mp 144–146 °C (methylene chloride/*n*-pentane). IR (KBr): ν = 2920, 1690, 1580, 1520, 1480, 1420, 1260, 1170, 1095, 1000, 959, 860, 820, 785, 755, 700. ^{1}H NMR ($CDCl_3$): δ = 2.44 (s, 3 H, *p*-CH_3), 3.96 (s, 3 H, OCH_3), 6.87 (s, 1 H, 2-H of enol), 7.29 (d, J = 8.5 Hz, 2 H, 3″-H), 7.91 (d, J = 8.5 Hz, 2 H, 2″-H), 8.03 (d, J = 9 Hz, 2 H, 2′-H), 8.15 (d, J = 9 Hz, 2 H, 3′-H). The ^{1}H NMR resonance of the enolic hydrogen is expected at ca. 16.5 ppm[31e] and has not been recorded. ^{13}C NMR ($CDCl_3$): δ = 21.7 (q, *p*-CH_3), 52.4 (q, OCH_3), 93.5 (d, C-2), 126.9 (d, C-2′), 127.4 (d, C-2″), 129.5 (d, C-3″), 129.8 (d, C-3′), 132.7 (s, C-1″), 133.1 (s, C-4′), 139.3 (s, C-1′), 143.7 (s, C-4″), 166.3 (s, CO_2Me), 182.8 (s, C-3), 187.3 (s, C-1). Anal. Calcd for $C_{18}H_{16}O_4$ (298.3): C, 72.96; H, 5.44. Found: C, 72.72; H, 5.29.

General Procedure for the Preparation of the 2,2-Dimethyl-1,3-diaryl-1,3-propanediones (5). The corresponding diketones **4a–j** (30.0 mmol) were dissolved in 80 mL of DMSO, and 40 mL of chloroform and 15.0 g of potassium carbonate powder were added. The mixture was chilled by means of an ice bath, and 12.8 g (90.0 mmol) of methyl iodide was added all at once. The mixture was stirred for 2 h at 0 °C and 12–14 h at ambient temperature, and 100 mL of methyl *tert*-butyl ether were added. After filtration, 45 mL of water and 5 mL of acetic acid were added to the filtrate, and the aqueous DMSO layer was separated. The methyl *tert*-butyl ether layer was washed with 50 mL of a saturated aqueous copper(II) acetate solution and dried over magnesium sulfate, and the solvent was evaporated (40 °C, 18 Torr). The crude product was recrystallized for purification; however, the dimethylated diketone **5a** crystallized only on prolonged standing. Also, for **5g–i** recrystallization was not always successful, and purification was then achieved by column chromatography on silica gel.

2,2-Dimethyl-1,3-bis(4′-methoxyphenyl)-1,3-propanedione (5a; X, Y = *p*-OMe): 5.40 g (58%), pale yellow powder, mp 88–89 °C (lit.[31i] mp 89 °C).

2,2-Dimethyl-1,3-bis(4′-methylphenyl)-1,3-propanedione (5b; X, Y = *p*-Me): 1.94 g (23%), colorless powder, mp 188–190 °C (methanol). IR (KBr): ν = 2970, 2910, 1640, 1590, 1560, 1450, 1400, 1380, 1250, 1170, 1120, 940, 825, 735. ^{1}H NMR ($CDCl_3$): δ = 1.63 (s, 6 H, 2-CH_3), 2.29 (s, 6 H, 4′-CH_3), 7.10 (d, J = 8.5 Hz, 4 H, 3′-H), 7.75 (d, J = 8.5 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 21.5 (q, 4′-CH_3), 25.4 (q, 2-CH_3), 59.2 (s, C-2), 133.0 (s, C-1′), 129.3 (d, C-2′), 129.3 (d, C-3′), 143.8 (s, C-4′), 200.0 (s, C-1 and C-3). Anal. Calcd for $C_{19}H_{20}O_2$ (280.4): C, 81.40; H, 7.19. Found: C, 81.16; H, 7.24.

2,2-Dimethyl-1,3-diphenyl-1,3-propanedione (5c; X, Y = H): 4.82 g (64%), colorless powder, mp 96–97 °C (methanol, lit.[31j] mp 97–98 °C).

2,2-Dimethyl-1,3-bis(4′-fluorophenyl)-1,3-propanedione (5d; X, Y = *p*-F): 3.75 g (43%), colorless powder, mp 127–128 °C (methanol). IR (KBr): ν = 3070, 2980, 2910, 1645, 1580, 1490, 1290, 1230, 1145, 935, 840, 735. ^{1}H NMR ($CDCl_3$): δ = 1.64 (s, 6 H, 2 CH_3), 6.98 (dd, J_{HH} = 9.0 Hz, J_{HF} = 8.5 Hz, 4 H, 3′-H), 7.86 (dd, J_{HH} = 9.0 Hz, J_{HF} = 5.5 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 25.3 (q, 2-CH_3), 59.3 (s, C-2), 115.9 (dd, J_{CF} = 22 Hz, C-3′), 131.7 (d, J_{CF} = 1 Hz, C-1′), 131.9 (dd, J_{CF} = 9 Hz, C-2′), 165.5 (d, J_{CF} = 255 Hz, C-4′), 198.6 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{14}F_2O_2$ (288.3): C, 70.83; H, 4.89. Found: C, 71.06; H, 4.93.

2,2-Dimethyl-1,3-bis(4′-chlorophenyl)-1,3-propanedione (5e; X, Y = *p*-Cl): 2.14 g (22%), colorless powder, mp 145–146 °C (methanol). IR (KBr): ν = 3060, 2980, 2960, 2920, 1645, 1575, 1555, 1475, 1450, 1390, 1270, 1230, 1115, 1035, 885, 790, 685. ^{1}H NMR ($CDCl_3$): δ = 1.64 (s, 6 H, 2-CH_3), 7.29 (d, J = 8.75 Hz, 4 H, 3′-H), 7.76 (d, J = 8.75 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 25.2 (q, 2-CH_3), 59.3 (s, C-2), 129.0 (d, C-3′), 130.5 (d, C-3′), 133.4 (s, C-1′), 139.8 (s, C-4′), 198.8 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{14}Cl_2O_2$ (321.2): C, 63.57; H, 4.39. Found: C, 63.44; H, 4.32.

2,2-Dimethyl-1,3-bis(4′-bromophenyl)-1,3-propanedione (5f; X, Y = *p*-Br): 3.29 g (27%), colorless powder, mp 146–147 °C (methanol). IR (KBr): ν = 3020, 2970, 1655, 1585, 1565, 1485, 1465, 1395, 1250, 1175, 1080, 950, 850, 740. ^{1}H NMR ($CDCl_3$): δ = 1.63 (s, 6 H, 2-CH_3), 7.46 (d, J = 8.75 Hz, 4 H, 3′-H), 7.68 (d, J = 8.75 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 25.2 (q, 2-CH_3), 59.4 (s, C-2), 128.6 (s, C-4′), 130.6 (s, C-2′), 132.1 (d, C-3′), 133.9 (d, C-1′), 199.0 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{14}Br_2O_2$ (410.1): C, 49.79; H, 3.44. Found: C, 49.65; H, 3.39.

2,2-Dimethyl-1,3-bis(3′-cyanophenyl)-1,3-propanedione (5g; X, Y = *m*-CN): 3.66 g (40%), pale yellow powder, mp 124–125 °C, R_f = 0.49 (SiO_2, methylene chloride). IR (CCl_4): ν = 3020, 2950, 2900, 2210, 1710, 1650, 1580, 1440, 1405, 1370, 1245, 1130, 1020, 990, 880, 700, 670. ^{1}H NMR ($CDCl_3$): δ = 1.67 (s, 6 H, 2-CH_3), 7.48 (dt, ^3J = 7.9 Hz, ^5J = 0.6 Hz, 2 H, 5′-H), 7.74 (dt, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 2 H, 6′-H), 7.94 (dt, ^3J = 8 Hz, ^4J = 1.5 Hz, 2 H, 4′-H), 8.14 (dt, ^4J = 1.5 Hz, ^5J = 0.6 Hz, 2 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 24.8 (q, 2-CH_3), 59.6 (s, C-2), 113.5 (s, C-3′), 117.4 (s, CN), 129.8 (d, C-5′), 132.63 (d, C-2′), 132.65 (d, C-6′), 135.9 (s, C-1′), 136.1 (d, C-4′), 197.6 (s, C-1 and C-3). Anal. Calcd for $C_{19}H_{14}N_2O_2$ (302.3): C, 75.48; H, 4.67; N, 9.27. Found: C, 75.33; H, 4.98, N, 9.03.

2,2-Dimethyl-1,3-bis(4′-nitrophenyl)-1,3-propanedione (5h; X, Y = *p*-NO₂): 3.46 g (34%), pale yellow powder, mp 129–130 °C (ethanol), R_f = 0.79 (SiO_2, methylene chloride). IR (KBr): ν = 3140, 3020, 2960, 1720, 1680, 1615, 1545, 1470, 1370, 1340, 1290, 1255, 1175, 1000, 985, 885, 745. ^{1}H NMR ($CDCl_3$): δ = 1.72 (s, 6 H, 2-CH_3), 7.97 (d, J = 9.0 Hz, 4 H, 2′-H), 8.19 (d, J = 9.0 Hz, 4 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 24.8 (q, 2-CH_3), 60.1 (s, C-2), 124.0 (d, C-3′), 130.0 (d, C-2′), 139.6 (s, C-1′), 150.1 (s, C-4′), 198.1 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{14}N_2O_6$ (342.3): C, 59.65; H, 4.12; N, 8.18. Found: C, 59.64; H, 4.02; N, 8.29.

2,2-Dimethyl-1-(4′-methoxyphenyl)-3-(4″-nitrophenyl)-1,3-propanedione (5i; X = *p*-OMe, Y = *p*-NO₂): 4.85 g (49%), pale yellow powder, mp 78–80 °C, R_f = 0.69 (SiO_2, methylene chloride). IR (KBr): ν = 2940, 2890, 1700, 1630, 1570, 1505, 1325, 1230, 1140, 995, 920, 830, 815, 700. ^{1}H NMR ($CDCl_3$): δ = 1.62 (s, 6 H, 2-CH_3), 3.72 (s, 3 H, OCH_3), 6.74 (d, J = 9.0 Hz, 2 H, 3′-H), 7.76 (d, J = 9.0 Hz, 2 H, 2′-H), 7.93 (d, J = 9.0 Hz, 2 H, 2″-H), 8.09 (d, J = 9.0 Hz, 2 H, 3″-H). ^{13}C NMR ($CDCl_3$): 25.0 (q, 2-CH_3), 55.3 (q, OCH_3), 59.3 (s, C-2), 113.9 (d, C-3′), 123.6 (d, C-3″), 128.0 (s, C-1′), 130.0 (d, C-2″), 131.4 (d, C-2′), 139.9 (s, C-1″), 149.7 (s, C-4″), 163.4 (s, C-4′), 197.5 (s, C-3), 199.2 (s, C-1). Anal. Calcd for $C_{18}H_{17}NO_5$ (327.3): C, 66.05; H, 5.24; N, 4.28. Found: C, 65.98; H, 5.31; N, 4.51.

2,2-Dimethyl-1-(4′-carbomethoxyphenyl)-3-(4″-methylphenyl)-1,3-propanedione (5j; X = *p*-CO₂Me, Y = *p*-Me): 2.04 g (21%), colorless powder, mp 155–156 °C (methanol/methylene chloride). IR (KBr): ν = 2940, 1720, 1640, 1590, 1420, 1275, 1230, 1105, 940, 825, 720. ^{1}H NMR ($CDCl_3$): δ = 1.66 (q, 6 H, 2-CH_3), 2.29 (q, 3 H, 4″-CH_3), 3.88 (q, 3 H, OCH_3), 7.10 (d, J = 8.5 Hz, 2 H, 3″-H), 7.72 (d, J = 8.5 Hz, 2 H, 2″-H), 7.86 (d, J = 9.0 Hz, 2 H, 2′-H), 7.96 (d, J = 9.0 Hz, 2 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 25.1 (q, 4″-CH_3), 21.4 (q, 2-CH_3), 52.3 (q, OCH_3), 59.4 (s, C-2), 128.9 (d, C-2′), 129.2 (d, C-2″), 129.3 (d, C-3″), 129.6 (d, C-3′), 132.8 (s, C-1″), 133.5 (s, C-4′), 138.7 (s, C-1′), 144.0 (s, C-4″), 165.9 (s, CO_2-Me), 199.2 (s, C-1), 200.0 (s, C-3). Anal. Calcd for $C_{20}H_{20}O_4$ (324.4): C, 74.06; H, 6.21. Found: C, 73.85; H, 6.01.

General Procedure for the Preparation of the 4,4-Dimethyl-3,5-diarylisopyrazoles (6). The corresponding dimethylated diketones **5a–j** (6.00 mmol) were dissolved in 30 mL of chloroform, and 310 mg of hydrazine hydrate (6.19 mmol) were added. The mixture was refluxed for 6 h and chilled, and 5 g of magnesium sulfate was added. After brief stirring, filtration, and evaporation of the solvent (40 °C, 18 Torr), the crystalline crude material was obtained, which was further purified by recrystallization (or column chromatography for **6g**) to give the isopyrazoles **6a–j**. The isopyrazole **6i** partly precipitates after reflux, and additional solvent had to be added before addition of magnesium sulfate. For the diketone **5h**, the half-aminal **6h(H₂O)** precipitated at 0 °C

within 2 h in methylene chloride. The crystalline hydrate was collected and washed with ethanol and *n*-pentane. The isopyrazole **6h** was obtained from the hydrate **6h(H$_2$O)** in quantitative yield by heating to 160 °C at 0.01 Torr for 5 h. This transformation occurred instantly on addition of trifluoroacetic acid to a $CDCl_3$ solution as monitored by NMR spectroscopy.

4,4-Dimethyl-3,5-bis(4′-methoxyphenyl)-4*H*-pyrazole (6a; X, Y = *p*-OMe): 1.50 g (81%), pale yellow needles, mp 196–198 °C (toluene). IR (KBr): ν = 3050, 2990, 2920, 1600, 1500, 1450, 1410, 1305, 1245, 1155, 1030, 850, 830, 640. ^{1}H NMR ($CDCl_3$): δ = 1.68 (s, 6 H, 4-CH_3), 3.87 (s, 6 H, OCH_3), 7.00 (d, J = 9.0 Hz, 4 H, 3′-H), 8.05 (d, J = 9.0 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 23.2 (q, 4-CH_3), 55.3 (q, OCH_3), 58.4 (s, C-4), 114.2 (d, C-3′), 122.7 (s, C-1′), 129.4 (d, C-2′), 161.5 (s, C-4′), 177.8 (s, C-3 and C-5). Anal. Calcd for $C_{19}H_{20}N_2O_2$ (308.4): C, 74.00; H, 6.54; N, 9.08. Found: C, 74.45; H, 6.82; N, 9.13.

4,4-Dimethyl-3,5-bis(4′-methylphenyl)-4*H*-pyrazole (6b; X, Y = *p*-Me): 1.03 g (62%), pale yellow needles, mp 208–209 °C (toluene/*n*-hexane). IR (KBr): ν = 2950, 1595, 1490, 1450, 1395, 1180, 1155, 1115, 850, 825, 730. ^{1}H NMR ($CDCl_3$): δ = 1.68 (s, 6 H, 4-CH_3), 2.42 (s, 6 H, 4′-CH_3), 7.29 (d, J = 8.0 Hz, 4 H, 3′-H), 7.98 (d, J = 8.0 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 21.5 (q, 4′-CH_3), 23.0 (q, 4-CH_3), 58.3 (s, C-4), 127.2 (s, C-1′), 127.8 (d, C-2′), 129.5 (d, C-3′), 141.1 (s, C-4′), 178.6 (s, C-3 and C-5). Anal. Calcd for $C_{19}H_{20}N_2$ (276.4): C, 82.57; H, 7.29; N, 10.14. Found: C, 82.94; H, 7.54; N, 10.10.

4,4-Dimethyl-3,5-diphenyl-4*H*-pyrazole (6c; X, Y = H): 1.22 g (82%), colorless needles, mp 125–126 °C (toluene/*n*-hexane, lit.[14c] mp 128 °C).

4,4-Dimethyl-3,5-bis(4′-fluorophenyl)-4*H*-pyrazole (6d; X, Y = *p*-F): 1.37 g (80%), colorless needles, mp 162–163 °C (toluene/cyclohexane). IR (KBr): ν = 3090, 3010, 2955, 1610, 1520, 1470, 1415, 1355, 1245, 1170, 1120, 880, 865, 830, 750. ^{1}H NMR ($CDCl_3$): δ = 1.66 (s, 6 H, 4-CH_3), 7.16 (dd, J_{HH} = 8.75 Hz, J_{HF} = 8.75 Hz, 4 H, 3′-H), 8.06 (dd, J_{HH} = 8.75 Hz, J_{HF} = 5.5 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 22.7 (q, 4-CH_3), 58.3 (s, C-4), 116.0 (dd, J_{CF} = 21 Hz, C-3′), 126.0 (d, J_{CF} = 1 Hz, C-1′), 129.5 (dd, J_{CF} = 8 Hz, C-2′), 164.2 (d, J_{CF} = 251 Hz, C-4′), 177.8 (s, C-3 and C-5). Anal. Calcd for $C_{17}H_{14}F_2N_2$ (284.3): C, 71.82; H, 4.96; N, 9.85. Found: C, 72.16; H, 5.18; N, 9.91.

4,4-Dimethyl-3,5-bis(4′-chlorophenyl)-4*H*-pyrazole (6e; X, Y = *p*-Cl): 1.45 g (76%), colorless needles, mp 202–203 °C (toluene/cyclohexane). IR (KBr): ν = 3100, 2990, 2940, 1600, 1525, 1500, 1470, 1405, 1345, 1275, 1105, 1010, 845, 755, 735. ^{1}H NMR ($CDCl_3$): δ = 1.66 (s, 6 H, 4-CH_3), 7.46 (d, J = 9.0 Hz, 4 H, 3′-H), 8.01 (d, J = 9.0 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 22.7 (q, 4-CH_3), 58.4 (s, C-4), 128.1 (s, C-1′), 129.1 (d, C-2′), 129.1 (d, C-3′), 137.1 (s, C-4′), 178.1 (s, C-3 and C-5). Anal. Calcd for $C_{17}H_{14}Cl_2N_2$ (317.2): C, 64.37; H, 4.45; N, 8.83. Found: C, 64.87; H, 4.41; N, 8.89.

4,4-Dimethyl-3,5-bis(4′-bromophenyl)-4*H*-pyrazole (6f; X, Y = *p*-Br): 2.11 g (87%), colorless needles, mp 235–236 °C (toluene). IR (KBr): ν = 3130, 3030, 2980, 1620, 1540, 1520, 1480, 1420, 1365, 1290, 1100, 1030, 860, 750, 690. ^{1}H NMR ($CDCl_3$): δ = 1.66 (s, 6 H, 4-CH_3), 7.62 (d, J = 8.5 Hz, 4 H, 3′-H), 7.93 (d, J = 8.5 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 22.6 (q, 4-CH_3), 58.4 (s, C-4), 125.6 (s, C-4′), 128.6 (s, C-1′), 129.3 (d, C-2′), 132.1 (d, C-3′), 178.2 (s, C-3 and C-5). Anal. Calcd for $C_{17}H_{14}Br_2N_2$ (406.1): C, 50.28; H, 3.47; N, 6.90. Found: C, 50.68; H, 3.50; N, 6.93.

4,4-Dimethyl-3,5-bis(3′-cyanophenyl)-4*H*-pyrazole (6g; X, Y = *m*-CN): 1.15 g (64%), pale yellow needles, mp 182–184 °C, R_f = 0.31 (SiO_2, methylene chloride:methanol = 20:1). IR (KBr): ν = 3040, 3010, 2980, 2910, 2210, 1580, 1560, 1510, 1490, 1460, 1330, 1160, 1090, 920, 895, 830, 805, 795, 710, 670. ^{1}H NMR ($CDCl_3$): δ = 1.71 (s, 6 H, 2-CH_3), 7.67 (t, ^3J = 7.8 Hz, 2 H, 5′-H), 7.83 (dt, 2 × ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2 H, 6′-H), 8.33 (t, ^4J = 1.2 Hz, 2 H, 2′-H), 8.36 (dt, 2 × ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2 H, 4′-H). ^{13}C NMR ($CDCl_3$): δ = 22.3 (q, 4-CH_3), 58.8 (s, C-4), 113.4 (s, C-3′), 117.9 (s, CN), 129.9 (d, C-5′), 130.7 (s, C-1′), 131.2 (d, C-2′), 132.0 (d, C-6′), 134.2 (d, C-4′), 177.8 (s, C-3 and C-5). Anal. Calcd for $C_{19}H_{14}N_4$ (298.4): C, 76.49; H, 4.73; N, 18.78. Found: C, 76.31; H, 4.73; N, 18.62.

4,5-Dihydro-5-hydroxy-4,4-dimethyl-3,5-bis(4′-nitrophenyl)pyrazole [6h(H$_2$O)]: 1.86 g (87%), bright yellow powder, mp 215–216 °C, dec. IR (KBr): ν = 3520, 3330, 2980, 2930, 1590, 1550, 1510, 1340, 1110, 1040, 1000, 860, 740, 705, 690. ^{1}H NMR ($CD_3C(O)CD_3$): δ = 0.85 (s, 3 H, 4-CH_3), 1.56 (s, 3 H, 4-CH_3), 5.69 (s, 1 H, OH or NH), 7.63 (s, 1 H, OH or NH), 8.04 and 8.05 (2 × d, J = 9.0 Hz, 4 H, 2′-H), 8.26 and 8.30 (2 × d, J = 9.0 Hz, 4 H, 3′-H). ^{13}C NMR ($CD_3C(O)CD_3$): δ = 17.5 (q, 4-CH_3), 24.0 (q, 4-CH_3), 53.9 (s, C-4), 99.7 (s, C-5), 123.6 and 124.3 (2 × d, C-3′), 128.0 and 129.6 (2 × d, C-2′), 140.5 and 147.9 (2 × s, C-1′), 148.0 and 148.8 (2 × s, C-4′), 154.1 (s, C-3). MS (70 eV): at the temperature of the MS analysis (170 °C) conversion to **3h** occurred. Anal. Calcd for $C_{17}H_{16}N_4O_5$ (356.3): C, 57.30; H, 4.53; N, 15.72. Found: C, 57.27; H, 4.53; N, 15.98.

4,4-Dimethyl-3,5-bis(4′-nitrophenyl)-4*H*-pyrazole (6h; X, Y = *p*-NO$_2$): pale yellow powder, mp 263–264 °C. IR (KBr): ν = 3080, 3050, 2960, 1585, 1515, 1500, 1445, 1330, 1300, 1270, 1090, 990, 850, 840, 745, 700. ^{1}H NMR ($CDCl_3$): δ = 1.76 (s, 6 H, 4-CH_3), 8.28 (d, J = 9.0 Hz, 4 H, 2′-H), 8.39 (d, J = 9.0 Hz, 4 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 22.3 (q, 4-CH_3), 59.1 (s, C-4), 124.2 (d, C-3′), 128.9 (d, C-2′), 135.2 (s, C-1′), 149.2 (s, C-4′), 178.1 (s, C-3 and C-5). MS (70 eV) *m/z*: 338 (100) [M$^+$], 293 (51), 264 (46), 263 (36), 203 (30), 202 (35), 190 (97), 189 (46), 175 (36), 149 (70), 42 (31). Anal. Calcd for $C_{17}H_{14}N_4O_4$ (338.3): C, 60.35; H, 4.17; N, 16.56. Found: C, 60.79; H, 4.26; N, 16.91.

4,4-Dimethyl-3-(4′-methoxyphenyl)-5-(4″-nitrophenyl)-4*H*-pyrazole (6i; X = *p*-OMe, Y = *p*-NO$_2$): 1.56 g (81%), yellow powder, mp 252–254 °C (ethanol). IR (KBr): ν = 3100, 2975, 2920, 1595, 1515, 1490, 1450, 1340, 1260, 1155, 1020, 855, 825, 700. ^{1}H NMR ($CDCl_3$): δ = 1.72 (s, 6 H, 4-CH_3), 3.90 (s, 3 H, OCH_3), 7.03 (d, J = 9.0 Hz, 2 H, 3′-H), 8.09 (d, J = 9.0 Hz, 2 H, 2′-H), 8.24 (d, J = 9.0 Hz, 2 H, 2″-H), 8.35 (d, J = 9.0 Hz, 2 H, 3″-H). ^{13}C NMR ($CDCl_3$): 22.9 (q, 4-CH_3), 55.5 (q, OCH_3), 58.3 (s, C-4), 114.4 (d, C-3′), 121.8 (s, C-1′), 124.0 (d, C-3″), 128.5 (d, C-2″), 129.9 (d, C-2′), 136.0 (s, C-1″), 148.7 (s, C-4″), 162.2 (s, C-4′), 176.4 (s, C-3), 179.5 (s, C-5). Anal. Calcd for $C_{18}H_{17}N_3O_3$ (323.4): C, 66.86; H, 5.30; N, 13.00. Found: C, 66.57; H, 4.98; N, 13.13.

4,4-Dimethyl-3-(4′-carbomethoxyphenyl)-5-(4″-methylphenyl)-4*H*-pyrazole (6j; X = *p*-CO$_2$Me, Y = *p*-Me): 1.35 g (71%), pale yellow powder, mp 221–222 °C (toluene/*n*-hexane). IR (KBr): ν = 2970, 2930, 1700, 1600, 1490, 1430, 1395, 1270, 1100, 1000, 815, 775, 705. ^{1}H NMR ($CDCl_3$): δ = 1.70 (q, 6 H, 4-CH_3), 2.43 (q, 3 H, 4″-CH_3), 3.96 (q, 3 H, OCH_3), 7.31 (d, J = 8.0 Hz, 2 H, 3″-H), 7.99 (d, J = 8.0 Hz, 2 H, 2″-H), 8.14 (s, 4 H, 2′-H and 3′-H). ^{13}C NMR ($CDCl_3$): δ = 21.5 (q, 4″-CH_3), 22.8 (q, 4-CH_3), 52.3 (q, OCH_3), 58.6 (s, C-4), 126.9 (s, C-1″), 127.7 (d, C-2″), 128.0 (d, C-2′), 129.6 (d, C-3″), 129.9 (d, C-3′), 131.7 (s, C-1′), 134.1 (s, C-4′), 141.6 (s, C-4″), 166.4 (s, CO_2Me), 177.9 (s, C-5), 179.4 (s, C-3). Anal. Calcd for $C_{20}H_{20}N_2O_2$ (320.4): C, 74.98; H, 6.29; N, 8.74. Found: C, 74.59; H, 6.49; N, 8.85.

General Procedure for the Preparation of the Azoalkanes 7. The corresponding isopyrazoles **6a–j** (3.00 mmol) and 308 mg (2.70 mmol) of trifluoroacetic acid were dissolved in 20 mL of methylene chloride, the mixture was chilled in an ice bath, and 15 mL of freshly recondensed cyclopentadiene was added. After the mixture was allowed to stand overnight at 5 °C, 4.0 g of potassium carbonate and 4.0 g of silica gel (0.2–0.5 mm), the latter not for **7j**, were added, and stirring was continued for 30 min at 0 °C. The mixture was filtered and the solvent removed (ca. 40 °C, 18 Torr) to afford the crude crystalline product. The analytical samples of azoalkanes **7** were obtained by column chromatography.

Azoalkane **7h** was also obtained by three modifications: (i) only 20 min stirring at 0 °C before workup, (ii) use of the hydrate **6h(H$_2$O)**, which is readily converted to **6h** under the acidic reaction conditions, and (iii) use of less cyclopentadiene (1 mL) and only 0.5 equiv (1.35 mmol) of acid. Since the yields of the isolated azoalkane **7h** were quite similar in all reactions

(74–82%), the *in situ* method ii is recommended for preparative purposes.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-bis(4′-methoxyphenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (7a; X, Y = *p*-OMe): 427 mg (38%), colorless powder, mp 167–168 °C, dec, R_f = 0.52 (SiO_2, 3:1 cyclohexane:ethyl acetate). IR (KBr): ν = 3000, 2960, 2930, 1610, 1520, 1460, 1310, 1250, 1185, 1020, 815, 740, 635. UV (benzene): λ_{max} (ϵ) = 331 nm (30), 352 (80), 362 (140). ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 3 H, *exo*-8-CH_3), 0.96 (s, 3 H, *endo*-8-CH_3), 2.20 (dd, J = 7.5 and 3.0 Hz, 2 H, 7-H), 3.57 (dd, J = 7.8 Hz, 1 H, 7a-H), 3.87 (2 × s, 6 H, OCH_3), 4.04 (m, 1 H, 4a-H), 5.50 (m, 2 H, 5-H and 6-H), 7.02 (2 × d, J = 9.0 Hz, 4 H, 3′-H), 7.69 (2 × d, J = 9.0 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 17.0 (q, *exo*-8-CH_3), 17.3 (q, *endo*-8-CH_3), 31.4 (t, C-7), 43.8 (d, C-7a), 55.3 (2 × q, OCH_3), 56.7 (d, C-4a), 63.9 (s, C-8), 96.5 (s, C-1), 97.6 (s, C-4), 113.8 (2 × d, C-3′), 127.3 (d, C-6), 128.0 (2 × s, C-1′), 128.3 and 128.7 (2 × d, C-2′), 133.5 (d, C-5), 159.2 (2 × s, C-4′). Anal. Calcd for $C_{24}H_{26}N_2O_2$ (374.5): C, 76.98; H, 7.00; N, 7.48. Found: C, 76.82; H, 6.88; N, 7.51.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-bis(4′-methylphenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (7b; X, Y = *p*-Me): 410 mg (40%) colorless powder, mp 177–178 °C, dec, R_f = 0.45 (SiO_2, 9:1 cyclohexane:ethyl acetate). IR (KBr): ν = 3030, 3000, 2940, 2880, 1500, 1450, 1425, 1355, 1290, 1175, 1000, 790, 720. UV (benzene): λ_{max} (ϵ) = 330 nm (40), 350 (100), 361 (170). ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 3 H, *exo*-8-CH_3), 0.99 (s, 3 H, *endo*-8-CH_3), 2.21 (dd, J = 7.5 and 3.0 Hz, 2 H, 7-H), 2.42 and 2.42 (2 × s, 6 H, 4′-CH_3), 3.61 (dd, ^3J = 7.9 Hz, 1 H, 7a-H), 4.07 (m, 1 H, 4a-H), 5.50 (m, 2 H, 5-H and 6-H), 7.30 (2 × d, J = 8.0 Hz, 4 H, 3′-H), 7.67 (2 × d, J = 8.0 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 17.0 (q, *exo*-8-CH_3), 17.3 (q, *endo*-8-CH_3), 21.2 (2 × q, 4′-CH_3), 31.7 (t, C-7), 43.1 (d, C-7a), 56.6 (d, C-4a), 63.9 (s, C-8), 96.7 (s, C-1), 97.8 (s,-C-4), 127.1 and 127.5 (2 × d, C-2′), 127.3 (d, C-6), 129.1 (2 × d, C-3′), 132.9 (2 × s, C-1′), 133.5 (d, C-5), 137.4 and 137.5 (2 × s, C-4′). Anal. Calcd for $C_{24}H_{26}N_2$ (342.5): C, 84.17; H, 7.65; N, 8.18. Found: C, 84.43; H, 7.90; N, 8.10.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-diphenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (7c; X, Y = H): 443 mg (47%), colorless powder, mp 167–168 °C (dec, lit.[17b] mp 138–140 °C), R_f = 0.40 (SiO_2, 9:1 cyclohexane: ethyl acetate). Despite the different melting point, the spectral data were identical to those reported.[17b]

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-bis(4′-fluorophenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (7d; X, Y = *p*-F): 557 mg (53%), colorless needles, mp 166–167 °C, dec, R_f = 0.55 (SiO_2, methylene chloride). IR (KBr): ν = 3060, 2950, 2920, 1595, 1510, 1460, 1300, 1225, 1160, 1010, 830, 820, 735. UV (benzene): λ_{max} (ϵ) = 329 nm (20), 350 (90), 360 (160). ^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 3 H, *exo*-8-CH_3), 0.99 (s, 3 H, *endo*-8-CH_3), 2.20 (m, 2 H, 7-H), 3.59 (ddd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 6.0 Hz, 1 H, 7a-H), 4.06 (m, 1 H, 4a-H), 5.50 (m, 2 H, 5-H and 6-H), 7.19 (2 × t (dd), J_{HH} and J_{HF} = 8.75 Hz, 4 H, 3′-H), 7.75 (2 × dd, J_{HH} = 8.75 Hz and J_{HF} = 3.5 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 16.8 (q, *exo*-8-CH_3), 17.2 (q, *endo*-8-CH_3), 31.5 (t, C-7), 43.3 (d, C-7a), 56.8 (d, C-4a), 64.0 (s, C-8), 96.3 (s, C-1), 97.4 (s, C-4), 115.4 (2 × dd, J_{CF} = 21 Hz, C-3′), 126.8 (d, C-6), 128.8 and 129.2 (2 × dd, J_{CF} = 8 Hz, C-2′), 131.4 and 131.5 (2 × s, C-1′), 133.7 (d, C-5), 162.5 (2 × d, J_{CF} = 245 Hz, C-4′). Anal. Calcd for $C_{22}H_{20}F_2N_2$ (350.4): C, 75.41; H, 5.75; N, 7.99. Found: C, 75.78; H, 5.89; N, 8.20.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-bis(4′-chlorophenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (7e; X, Y = *p*-Cl): 643 mg (56%), colorless powder, mp 172–173 °C, dec, R_f = 0.61 (SiO_2, methylene chloride). IR (KBr): ν = 3080, 2980, 2930, 1610, 1525, 1425, 1400, 1330, 1250, 1235, 1030, 850, 775, 740. UV (benzene): λ_{max} (ϵ) = 329 nm (30), 350 (100), 360 (190). ^{1}H NMR ($CDCl_3$): δ = 0.17 (s, 3 H, *exo*-8-CH_3), 0.99 (s, 3 H, *endo*-8-CH_3), 2.19 (m, 2 H, 7-H), 3.58 (ddd, ^3J = 8.4 Hz, ^3J = 6.0 Hz, 1 H, 7a-H), 4.03 (m, 1 H, 4a-H), 5.49 (m, 2 H, 5-H and 6-H), 7.47 (2 × d, J = 8.5 Hz, 4 H, 3′-H), 7.71 (2 × d, J = 8.5 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 16.8 (q, *exo*-8-CH_3), 17.3 (q, *endo*-8-CH_3), 31.5 (t, C-7), 43.3 (d, C-7a), 56.9 (d, C-4a), 64.2 (s, C-8), 96.4 (s, C-1), 97.5 (s, C-4), 126.7 (d, C-6), 128.5 and 128.9 (2 × d, C-2′), 128.7 (2 × d, C-3′), 133.8 (d, C-5), 133.9, 134.0, 134.1 and 134.2 (4 × s, C-1′ and C-4′). Anal. Calcd for $C_{22}H_{20}Cl_2N_2$ (383.3): C, 68.94; H, 5.26; N, 7.31. Found: C, 69.38; H, 5.34; N, 7.46.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-bis(4′-bromophenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (7f; X, Y = *p*-Br): 934 mg (66%), colorless powder, mp 181–182 °C, dec, R_f = 0.64 (SiO_2, methylene chloride). IR (KBr): ν = 3060, 2920, 2900, 1590, 1495, 1470, 1395, 1295, 1080, 1015, 815, 740, 710. UV (benzene): λ_{max} (ϵ) = 329 nm (20), 350 (70), 361 (140). ^{1}H NMR ($CDCl_3$): δ = 0.17 (s, 3 H, *exo*-8-CH_3), 0.99 (s, 3 H, *endo*-8-CH_3), 2.19 (m, 2 H, 7-H), 3.58 (ddd, 2 × $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 5.8 Hz, 1 H, 7a-H), 4.03 (m, 1 H, 4a-H), 5.49 (m, 2 H, 5-H and 6-H), 7.65 (s (m), 8H, 2′-H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 16.8 (q, *exo*-8-CH_3), 17.3 (q, *endo*-8-CH_3), 31.5 (t, C-7), 43.2 (d, C-7a), 56.8 (d, C-4a), 64.2 (s, C-8), 96.5 (s, C-1), 97.5 (s, C-4), 122.1 and 122.2 (2 × s, C-4′), 126.7 (d, C-6), 128.8 and 129.2 (2 × d, C-2′), 131.7 (2 × d, C-3′), 133.8 (d, C-5), 134.6 and 134.7 (2 × s, C-1′). Anal. Calcd for $C_{22}H_{20}Br_2N_2$ (472.2): C, 55.96; H, 4.27; N, 5.93. Found: C, 56.39; H, 4.30; N, 6.08.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-bis(3′-cyanophenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (7g; X, Y = *m*-CN): 841 mg (77%), colorless powder, mp 186–187 °C, dec, R_f = 0.27 (SiO_2, methylene chloride). IR (KBr): ν = 3040, 2960, 2880, 2880, 2210, 1585, 1540, 1495, 1470, 1455, 1365, 1295, 1175, 1110, 1020, 900, 835, 790, 720, 690. UV (benzene): λ_{max} (ϵ) = 327 (sh, 34), 349 (sh, 92), 360 nm (163). ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 3 H, *exo*-8-CH_3), 1.05 (s, 3 H, *endo*-8-CH_3), 2.21 (dddd, ^2J = 12.1 Hz, ^3J= 9.2 Hz, ^3J = 4.5 Hz, ^3J = 2.2 Hz, 2 H, 7-H), 3.63 (ddd, ^3J = 9.2 Hz, ^3J= 8.6 Hz, ^3J = 4.5 Hz, 1 H, 7a-H), 4.09 (ddd, ^3J = 8.6 Hz, ^3J = 2.0 Hz, 1 H, 4a-H), 5.45 (ddd, ^3J = 5.8 Hz, J = 4.0 Hz, ^4J = 2.2 Hz, 1 H, 5-H or 6-H), 5.54 (ddd, ^3J = 5.8 Hz, J = 4.0 Hz, ^4J = 2.0 Hz, 1 H, 5-H or 6-H), 7.64 (dt, ^3J = 7.7 and 7.4 Hz, 2 H, 5′-H), 7.73 (dt, 2 H, 6′-H), 7.77 (dt, 2 H, 2′-H), 8.05 (m, 2 H, 4′-H). ^{13}C NMR ($CDCl_3$): δ = 16.8 (q, *exo*-8-CH_3), 17.3 (q, *endo*-8-CH_3), 31.4 (t, C-7), 43.4 (d, C-7a), 57.0 (d, C-4a), 64.6 (s, C-8), 96.2 (s, C-1), 97.3 (s, C-4), 112.9 (2 × s, C-3′), 118.7 (2 × s, CN), 126.1 (d, C-6), 129.5 (2 × d, C-5′), 130.6 and 130.9 (2 × s, C-1′), 131.6 and 131.7 (2 × d, C-2′), 131.8 and 132.0 (2 × d, C-6′), 134.2 (d, C-5), 137.0 and 137.1 (2 × d, C-4′). Anal. Calcd for $C_{24}H_{20}N_4$ (364.5): C, 79.10; H, 5.53; N, 15.37. Found: C, 79.24; H, 5.43; N, 15.27.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-bis(4′-nitrophenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (7h; X, Y = *p*-NO_2): 992 mg (82%), pale yellow powder, mp 199–200 °C, dec, R_f = 0.39 (SiO_2, methylene chloride). IR (KBr): ν = 3040, 2970, 2880, 1580, 1500, 1335, 1285, 1100, 1000, 840, 830, 730, 685. UV (benzene): λ_{max} (ϵ) = 346 nm (sh, 1260), 360 (sh, 860). ^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 3 H, *exo*-8-CH_3), 1.11 (s, 3 H, *endo*-8-CH_3), 2.22 (m, 2 H, 7-H), 3.70 (ddd, 2 × ^3J = 8.5 Hz, ^3J = 4.0 Hz, 1 H, 7a-H), 4.17 (m, 1 H, 4a-H), 5.45 (ddd, ^3J = 5.8 Hz, 3 × ^3J or ^4J = 2.0 Hz, 1 H, 5-H or 6-H), 5.56 (ddd, ^3J = 5.8 Hz, 3 × ^3J or ^4J = 2.0 Hz, 1 H, 5-H or 6-H), 7.99 (2 × d, J = 9.0 Hz, 4 H, 2′-H), 8.38 (2 × d, J = 9.0 Hz, 4 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 16.8 (q, *exo*-8-CH_3), 17.4 (q, *endo*-8-CH_3), 31.4 (t, C-7), 43.8 (d, C-7a), 57.4 (d, C-4a), 65.2 (s, C-8), 96.6 (s, C-1), 97.7 (s, C-4), 123.8 (2 × d, C-3′), 126.1 (d, C-6), 128.1 and 128.4 (2 × d, C-2′), 134.3 (d, C-5), 142.6 (2 × s, C-1′), 147.7 and 147.8 (2 × s, C-4′). Anal. Calcd for $C_{22}H_{20}N_4O_4$ (404.4): C, 65.34; H, 4.98; N, 13.85. Found: C, 65.45; H, 5.02; N, 13.90.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1-(4′-methoxyphenyl)-4-(4″-nitrophenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine [7i(I); X = *p*-OMe, Y = *p*-NO_2] and (1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1-(4′-nitrophenyl)-4-(4″-methoxyphenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine [7i(II); X = *p*-NO_2, Y = *p*-OMe] were obtained as a mixture of isomers; cf. Table 2: 174 mg (15%), yellow powder, mp 165–166 °C, dec, R_f = 0.23 (SiO_2, methylene chloride). IR (KBr): ν = 3040, 2950, 1580, 1500, 1440, 1335, 1165, 1095, 1025, 1005, 840, 810, 720. UV (benzene): λ_{max} (ϵ) = 340 nm (sh, 690), 356 (sh 490), 361 (140).

Anal. Calcd for $C_{23}H_{23}N_3O_3$ (389.5): C, 70.93; H, 5.95; N, 10.79. Found: C, 71.31; H, 6.20; N, 10.96.

Isomer 7i(I). ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 3 H, *exo*-8-CH_3), 1.03 (s, 3 H, *endo*-8-CH_3), 2.21 (m, 2 H, 7-H), 3.64 (m, 1 H, 7a-H), 3.87 (s, OCH_3), 4.10 (m, 1 H, 4a-H), 5.48 (m, 2 H, 5-H and 6-H), 7.04 (d, J = 9.0 Hz, 2 H, 3′-H), 7.68 (d, J = 9.0 Hz, 2 H, 2′-H), 8.00 (d, J = 9.0 Hz, 2 H, 2″-H), 8.36 (d, J = 9.0 Hz, 2 H, 3″-H). ^{13}C NMR ($CDCl_3$): δ = 16.9 (q, *exo*-8-CH_3), 17.3 (q, *endo*-8-CH_3), 31.4 or 31.5 (t, C-7), 43.2 (d, C-7a), 55.2 (q, OCH_3), 57.3 (d, C-4a), 64.6 (s, C-8), 95.9 (s, C-1), 98.4 (s, C-4), 113.9 (d, C-3′), 123.6 (d, C-3″), 126.2 (d, C-6), 127.0 (s, C-1′), 128.0 or 128.4 (d, C-2″), 128.3 or 128.7 (d, C-2′), 134.3 (d, C-5), 143.6 or 143.7 (s, C-1″), 147.5 or 147.6 (s, C-4″), 159.4 (s, C-4′).

Isomer 7i(II). ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 3 H, *exo*-8-CH_3), 1.03 (s, 3 H, *endo*-8-CH_3), 2.21 (m, 2 H, 7-H), 3.64 (m, 1 H, 7a-H), 3.87 (s, OCH_3), 4.10 (m, 1 H, 4a-H), 5.48 (m, 2 H, 5-H and 6-H), 7.04 (d, J = 9.0 Hz, 2 H, 3″-H), 7.68 (d, J = 9.0 Hz, 2 H, 2″-H), 8.00 (d, J = 9.0 Hz, 2 H, 2′-H), 8.36 (d, J = 9.0 Hz, 2 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 16.9 (q, 8-*ex*OCH_3), 17.3 (q, *endo*-8-CH_3), 31.4 or 31.5 (t, C-7), 43.7 (d, C-7a), 55.2 (q, OCH_3), 56.7 (d, C-4a), 64.6 (s, C-8), 96.9 (s, C-1), 97.3 (s, C-4), 113.9 (d, C-3″), 123.6 (d, C-3′), 127.0 (d, C-6), 127.0 (s, C-1″), 128.0 or 128.4 (d, C-2′), 128.3 or 128.7 (d, C-2″), 133.2 (d, C-5), 143.6 or 143.7 (s, C-1′), 147.5 or 147.6 (s, C-4′), 159.4 (s, C-4″).

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1-(4′-methylphenyl)-4-(4″-carbomethoxyphenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine [7j(I); X = *p*-Me, Y = *p*-CO_2Me] and (1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1-(4′-carbomethoxyphenyl)-4-(4″-methylphenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine [7j(II); X = *p*-CO_2Me, Y = *p*-Me] were obtained as a mixture of isomers; cf. Table 2: 233 mg (20%), colorless powder, mp 153–154 °C, dec, R_f = 0.62 (SiO_2, 20:1 methylene chloride:methyl *tert*-butyl ether). IR (KBr): ν = 3020, 2900, 2870, 1695, 1585, 1490, 1415, 1340, 1260, 1170, 1090, 995, 750, 735. UV (benzene): λ_{max} (ϵ) = 329 nm (30), 349 (80), 361 (140). Anal. Calcd for $C_{25}H_{26}N_2O_2$ (386.5): C, 77.69; H, 6.78; N, 7.25. Found: C, 77.94; H, 7.09; N, 7.27.

Isomer 7j(I). ^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 3 H, *exo*-8-CH_3), 1.01 (s, 3 H, *endo*-8-CH_3), 2.21 (m, 2 H, 7-H), 2.42 (s, 3 H, 4′-CH_3), 3.65 (m, 1 H, 7a-H), 3.96 (s, 3 H, OCH_3), 4.10 (m, 1 H, 4a-H), 5.50 (m, 2 H, 5-H and 6-H), 7.31 (d, J = 8.0 Hz, 2 H, 3′-H), 7.65 (d, J = 8.0 Hz, 2 H, 2′-H), 7.87 (d, J = 8.5 Hz, 2 H, 2″-H), 8.16 (d, J = 8.5 Hz, 2 H, 3″-H). ^{13}C NMR ($CDCl_3$), δ = 17.0 (q, *exo*-8-CH_3), 17.4 (q, *endo*-8-CH_3), 21.2 (q, 4′-CH_3), 31.5 or 31.6 (t, C-7), 43.1 (d, C-7a), 52.1 (q, OCH_3), 56.9 (d, C-4a), 64.3 (s, C-8), 96.4 (s, C-1), 98.2 (s, C-4), 127.1 or 127.5 (d, C-2′), 126.7 (d, C-6), 127.6 or 127.7 (d, C-2″), 129.1 (d, C-3′), 129.6 (d, C-3″), 129.9 (s, C-4″), 132.3 or 133.4 (s, C-1′), 133.9 (d, C-5), 137.6 or 137.7 (s, C-4′), 141.2 (s, C-1″), 166.9 (s, CO_2-Me).

Isomer 7j(II). ^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 3 H, *exo*-8-CH_3), 1.01 (s, 3 H, *endo*-8-CH_3), 2.21 (m, 2 H, 7-H), 2.42 (s, 3 H, 4″-CH_3), 3.65 (m, 1 H, 7a-H), 3.96 (s, 3 H, OCH_3), 4.10 (m, 1 H, 4a-H), 5.50 (m, 2 H, 5-H and 6-H), 7.31 (d, J = 8.0 Hz, 2 H, 3″-H), 7.65 (d, J = 8.0 Hz, 2 H, 2″-H), 7.87 (d, J = 8.5 Hz, 2 H, 2′-H), 8.16 (d, J = 8.5 Hz, 2 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 17.0 (q, *exo*-8-CH_3), 17.4 (q, *endo*-8-CH_3), 21.2 (q, 4″-CH_3), 31.5 or 31.6 (t, C-7), 43.3 (d, C-7a), 52.1 (q, OCH_3), 56.7 (d, C-4a), 64.3 (s, C-8), 97.1 (s, C-1), 97.5 (s, C-4), 127.1 or 127.5 (d, C-2″), 127.2 (d, C-6), 127.6 or 127.7 (d, C-2′), 129.1 (d, C-3″), 129.6 (d, C-3′), 129.9 (s, C-4′), 132.3 or 133.4 (s, C-1″), 133.4 (d, C-5), 137.6 or 137.7 (s, C-4″), 141.2 (s, C-1′), 166.9 (s, CO_2-Me).

General Procedures for the Preparation of the Housanes (8). (i) Direct Photolyses. To obtain housanes **8a–g**, the azoalkanes **7a–g** (0.200 mmol) were dissolved in 1 mL of C_6D_6 and placed into an NMR tube. The solution was irradiated at 364 nm by means of a CW argon ion laser (0.6 W) until the NMR spectra showed complete conversion (ca. 10 min). The solvent was removed (ca. 50 °C, 18 Torr) to afford the analytically pure, crystalline products. **(ii) Triplet-Sensitized Photolyses.** The corresponding azoalkanes **7a–g** (0.040 mmol) and 39.0 mg of benzophenone (0.210 mmol) were dissolved in 1 mL of C_6D_6 to which 3 μL of acetonitrile was added as internal ^{1}H NMR standard. The solution was irradiated with the 333-, 351-, and 364-nm lines (2.0 W) of the CW argon ion laser for ca. 10 min. The yields of housanes **8a–g**, as determined by ^{1}H NMR analysis against the internal standard acetonitrile, were in all cases greater than 90%. **(iii) Thermolyses.** To obtain housanes **8g–j**, the azoalkanes **7g–j** (0.200 mmol) were dissolved in 20 mL of toluene and refluxed for 8 h. Evaporation of the solvent (ca. 60 °C, 18 Torr) and column chromatography afforded the crystalline materials. For azoalkanes **7a–f**, similar thermolyses were carried out on an NMR scale (0.050 mmol) in deuterated toluene without isolation of the housanes; ^{1}H NMR spectra showed only the housanes **8a–f** as products.

3,3-Dimethyl-2,4-bis(4′-methoxyphenyl)-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene (8a; X, Y = *p*-OMe): 67.1 mg (97%), colorless powder, mp 94–95 °C. IR (KBr): ν = 3050, 2930, 1610, 1525, 1465, 1290, 1255, 1180, 1030, 830, 800, 765. ^{1}H NMR ($CDCl_3$): δ = 0.78 (s, 3 H, *exo*-3-CH_3), 1.59 (s, 3 H, *endo*-3-CH_3), 2.43 (m, 2 H, 8-H), 2.86 (m, 1 H, 1-H), 3.31 (m, 1 H, 5-H), 3.83 (2 × s, 6 H, OCH_3), 5.55 (m, 1 H, 7-H), 5.85 (m, 1 H, 6-H), 6.86 (2 × d, J = 9.0 Hz, 4 H, 3′-H), 7.12 and 7.17 (2 × d, J = 9.0 Hz, 4 H, 2′-H). ^{13}C NMR ($CDCl_3$): δ = 15.3 (q, *exo*-3-CH_3), 22.7 (q, *endo*-3-CH_3), 30.9 (t, C-8), 34.3 (s, C-3), 40.1 (d, C-1), 45.8 (s, C-4), 50.3 (s, C-2), 51.1 (d, C-5), 55.1 (q, OCH_3), 112.9 (2 × d, C-3′), 129.6 and 130.5 (2 × s, C-1′), 130.9 (2 × d, C-2′), 131.5 and 131.8 (2 × d, C-6 and C-7), 157.6 (2 × s, C-4′). Anal. Calcd for $C_{24}H_{26}O_2$ (346.5): C, 83.20; H, 7.56. Found: C, 83.65; H, 7.77.

3,3-Dimethyl-2,4-bis(4′-methylphenyl)-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene (8b; X, Y = *p*-Me): 60.2 mg (96%), colorless powder, mp 95–96 °C. IR (KBr): ν = 2950, 2880, 1490, 1420, 1385, 1095, 1000, 800, 745, 690. ^{1}H NMR ($CDCl_3$): δ = 0.77 (s, 3 H, *exo*-3-CH_3), 1.58 (s, 3 H, *endo*-3-CH_3), 2.37 (2 × s, 6 H, 4′-CH_3), 2.41 (m, 2 H, 8-H), 2.86 (m, 1 H, 1-H), 3.32 (m, 1 H, 5-H), 5.54 (m, 1 H, 7-H), 5.82 (m, 1 H, 6-H), 7.11 (br s, 8 H, 2′-H, 2″-H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 15.3 (q, *exo*-3-CH_3), 21.1 (q, *p*-CH_3), 22.6 (q, *endo*-3-CH_3), 31.1 (t, C-8), 34.3 (s, C-3), 40.0 (d, C-1), 46.2 (s, C-4), 50.7 (s, C-2), 51.0 (d, C-5), 128.2 (2 × d, C-3′), 129.8 (2 × d, C-2′), 134.4, 135.0, 135.2 and 135.3 (4 × s, C-1′ and C-4′), 131.3 and 131.9 (2 × d, C-6 and C-7). Anal. Calcd for $C_{24}H_{26}$ (314.5): C, 91.67; H, 8.33. Found: C, 91.88; H, 8.00.

3,3-Dimethyl-2,4-diphenyl-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene (8c; X, Y = H): 55.1 mg (96%), colorless powder, mp 64–65 °C (lit.[31k] mp 63–64.5 °C).

3,3-Dimethyl-2,4-bis(4′-fluorophenyl)-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene (8d; X, Y = *p*-F): 62.2 mg (97%), colorless powder, mp 59–60 °C. IR (KBr): ν = 3050, 2930, 1600, 1520, 1230, 1160, 1095, 840, 825, 770. ^{1}H NMR ($CDCl_3$): δ = 0.73 (s, 3 H, *exo*-3-CH_3), 1.57 (s, 3 H, *endo*-3-CH_3), 2.30 and 2.48 (2 × m, 2 H, 8-H), 2.88 (m, 1 H, 1-H), 3.30 (m, 1 H, 5-H), 5.49 (m, 1 H, 7-H), 5.83 (m, 1 H, 6-H), 7.16 (2 × dd, J_{HH} = 9.0 Hz and J_{HF} = 5.5 Hz, 4 H, 2′-H), 7.75 (2 × t (dd), J_{HH} and J_{HF} = 9.0 Hz, 4 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 15.2 (q, *exo*-3-CH_3), 22.6 (q, *endo*-3-CH_3), 31.1 (t, C-8), 34.3 (s, C-3), 40.1 (d, C-1), 45.9 (s, C-4), 50.5 (s, C-2), 51.1 (d, C-5), 114.5 (2 × dd, J_{CF} = 21 Hz, C-3′), 131.3 (2 × dd, J_{CF} = 8 Hz, C-2′), 131.2 and 132.1 (2 × d, C-6 and C-7), 133.0 and 133.8 (2 × s, C-1′), 161.3 (2 × d, J_{CF} = 243 Hz, C-4′). Anal. Calcd for $C_{22}H_{20}F_2$ (322.4): C, 81.96; H, 6.25. Found: C, 81.80; H, 6.40.

3,3-Dimethyl-2,4-bis(4′-chlorophenyl)-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene (8e; X, Y = *p*-Cl): 68.5 mg (96%), colorless rhombic crystals, mp 125–126 °C. IR (KBr): ν = 3050, 2940, 2910, 1490, 1445, 1390, 1260, 1095, 1020, 825, 770, 745, 700. ^{1}H NMR ($CDCl_3$): δ = 0.74 (s, 3 H, *exo*-3-CH_3), 1.57 (s, 3 H, *endo*-3-CH_3), 2.29 and 2.49 (2 × m, 2 H, 8-H), 2.88 (m, 1 H, 1-H), 3.32 (m, 1 H, 5-H), 5.49 (m, 1 H, 7-H), 5.83 (m, 1 H, 6-H), 7.11 (2 × d, J = 8.5 Hz, 4 H, 2′-H), 7.27 (2 × d, J = 8.5 Hz, 4 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 15.2 (q, *exo*-3-CH_3), 22.4 (q, *endo*-3-CH_3), 31.6 (t, C-8), 34.2 (s, C-3), 40.0 (d, C-1), 46.0 (s, C-4), 50.6 (s, C-2), 51.0 (d, C-5), 127.8 (2 × d, C-3′), 130.9 and 132.2 (2 × d, C-6 and C-7), 131.2 (2 × d, C-2′), 131.7 and 131.8 (2 × s, C-4′), 135.7 and 136.4 (2 × s, C-1′). Anal. Calcd for $C_{22}H_{20}Cl_2$ (355.3): C, 74.37; H, 5.67. Found: C, 74.15; H, 5.76.

X-ray crystallographic data:[26] crystal size, 0.95 × 1.2 × 0.3 mm; number of reflections measured, 7217; number of reflections $F > 3\sigma(F)$, 5314; R, R_w, 0.055, 0.052; space group, $Pna2_1$; crystal system, orthorhombic; lattice constants (standard deviation), a = 702.1(1), b = 1484.0(3), c = 1735.1(4), in pm; V, 1808.0(6) × 10^6 pm^3; molecules/elemental cell, 4; d_{calcd}, 1.305 gcm^{-3}.

3,3-Dimethyl-2,4-bis(4′-bromophenyl)-*endo*-tricyclo-[3.3.0.0^{2,4}]oct-6-ene (8f; X, Y = *p*-Br): 86.4 mg (97%), colorless needles, mp 159–160 °C. IR (KBr): ν = 3060, 2960, 2920, 1610, 1495, 1450, 1395, 1270, 1080, 1020, 830, 775, 735, 700. ^{1}H NMR ($CDCl_3$): δ = 0.74 (s, 3 H, *exo*-3-CH_3), 1.57 (s, 3 H, *endo*-3-CH_3), 2.28 and 2.49 (2 × m, 2 H, 8-H), 2.87 (m, 1 H, 1-H), 3.32 (m, 1 H, 5-H), 5.48 (m, 1 H, 7-H), 5.83 (m, 1 H, 6-H), 7.05 (2 × d, J = 8.5 Hz, 4 H, 2′-H), 7.42 (2 × d, J = 8.5 Hz, 4 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 15.3 (q, *exo*-3-CH_3), 22.4 (q, *endo*-3-CH_3), 31.6 (t, C-8), 34.2 (s, C-3), 39.9 (d, C-1), 46.1 (s, C-4), 50.7 (s, C-2), 50.9 (d, C-5), 119.9 (2 × s, C-4′), 130.7 (2 × d, C-3′), 130.9 and 132.2 (2 × d, C-6 and C-7), 131.5 (2 × d, C-2′), 136.2 and 136.9 (2 × s, C-1′). Anal. Calcd for $C_{22}H_{20}Br_2$ (444.2): C, 59.49; H, 4.54. Found: C, 59.00; H, 4.58.

3,3-Dimethyl-2,4-bis(3′-cyanophenyl)-*endo*-tricyclo-[3.3.0.0^{2,4}]oct-6-ene (8g; X, Y = *m*-CN): 64.7 mg (96%), colorless powder, mp 77–78 °C, R_f = 0.58 (SiO_2, 1:1 *n*-pentane: methylene chloride). IR (KBr): ν = 3020, 2960, 2890, 2210, 1580, 1520, 1470, 1375, 1340, 1250, 1160, 1130, 910, 890, 795, 750, 690. ^{1}H NMR ($CDCl_3$): δ = 0.70 (s, 3 H, *exo*-3-CH_3), 1.59 (s, 3 H, *endo*-3-CH_3), 2.19 (ddd, ^2J= 17.7 Hz, ^3J= 7.7 Hz, ^3J = 2.5 Hz, 1 H, 8-H), 2.50 (ddd, ^2J = 17.7 Hz, ^3J = 7.7 Hz, ^3J = 1.8 Hz, 1 H, 8-H), 2.91 (dd, ^3J = 7.7 Hz, ^3J = 1.8 Hz, 1 H, 1-H), 3.32 (m, 1 H, 5-H), 5.41 (dd, ^3J = 5.7 Hz, ^3J = 2.5 Hz, 1 H, 7-H), 5.85 (d, ^3J = 5.7 Hz, 1 H, 6-H), 7.28–7.47 (m, 8 H, arom.). ^{13}C NMR ($CDCl_3$): δ = 15.2 (q, *exo*-3-CH_3), 22.4 (q, *endo*-3-CH_3), 32.1 (t, C-8), 34.3 (s, C-3), 40.0 (d, C-1), 46.4 (s, C-4), 51.0 (d, C-5), 51.1 (s, C-2), 112.1 (2 × s, C-3′), 118.8 and 118.9 (2 × s, CN), 128.6 (2 × d, C-5′), 129.9 (2 × d, C-4′), 130.3 and 132.8 (2 × d, C-6 and C-7), 133.2 (2 × d, C-2′), 134.3 and 134.5 (2 × d, C-6′), 138.6 and 139.0 (2 × s, C-1′). Anal. Calcd for $C_{24}H_{20}N_2$ (336.4): C, 85.68; H, 5.99; N, 8.33. Found: C, 85.80; H, 6.31; N, 7.95.

3,3-Dimethyl-2,4-bis(4′-nitrophenyl)-*endo*-tricyclo-[3.3.0.0^{2,4}]oct-6-ene (8h; X, Y = *p*-NO_2): 72.3 mg (96%), yellow powder, mp 172–173 °C, R_f = 0.76 (SiO_2, methylene chloride). IR (KBr): ν = 3080, 2980, 2960, 1610, 1530, 1370, 1330, 1270, 1190, 1125, 880, 770, 745, 720. UV (benzene): λ_{max} = 306 nm. ^{1}H NMR ($CDCl_3$): δ = 0.76 (s, 3 H, *exo*-3-CH_3), 1.63 (s, 3 H, *endo*-3-CH_3), 2.21 and 2.55 (2 × m, 2 H, 8-H), 2.99 (m, 1 H, 1-H), 3.41 (m, 1 H, 5-H), 5.44 (m, 1 H, 7-H), 5.85 (m, 1 H, 6-H), 7.29 (2 × d, J = 9.0 Hz, 4 H, 2′-H), 8.15 (2 × d, J = 9.0 Hz, 4 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 15.4 (q, *exo*-3-CH_3), 22.1 (q, *endo*-3-CH_3), 33.6 (t, C-8), 34.3 (s, C-3), 40.2 (d, C-1), 47.3 (s, C-4), 51.1 (d, C-5), 52.0 (s, C-2), 123.0 (2 × d, C-3′), 130.1 and 132.9 (2 × d, C-6 and C-7), 130.4 and 130.7 (2 × d, C-2′), 145.0 and 145.4 (2 × s, C-1′), 146.3 (2 × s, C-4′). Anal. Calcd for $C_{22}H_{20}N_2O_4$ (376.4): C, 70.20; H, 5.36; N, 7.44. Found: C, 69.84; H, 5.44; N, 7.30.

3,3-Dimethyl-2-(4′-methoxyphenyl)-4-(4′-nitrophenyl)-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene [8i(I); X = *p*-OMe, Y = *p*-NO_2] and 3,3-Dimethyl-2-(4′-nitrophenyl)-4-(4′-methoxyphenyl)-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene [8i(II); X = *p*-NO_2, Y = *p*-OMe] were obtained as a mixture of isomers; cf. Table 2: 68.0 mg (94%), yellow oil, R_f = 0.76 (SiO_2, methylene chloride). IR (film): ν = 3020, 2900, 1575, 1500, 1330, 1230, 1165, 1095, 1015, 840, 730. UV (benzene): λ_{max} = 312 nm. Anal. Calcd for $C_{23}H_{23}NO_3$ (361.4): C, 76.43; H, 6.41; N, 3.88. Found: C, 76.26; H, 6.02; N, 3.42.

Isomer 8i(I). ^{1}H NMR ($CDCl_3$): δ = 0.75 (s, 3 H, *exo*-3-CH_3), 1.58 (s, 3 H, *endo*-3-CH_3), 2.33 (m, 2 H, 8-H), 2.85 (m, 1 H, 1-H), 3.41 (m, 1 H, 5-H), 3.82 (s, 3 H, OCH_3), 5.52 (m, 1 H, 7-H), 5.81 (m, 1 H, 6-H), 6.85 (d, J = 9.0 Hz, 2 H, 3′-H), 7.14 (d, J = 9.0 Hz, 2 H, 2′-H), 7.22 (d, J = 9.0 Hz, 2 H, 2″-H), 8.09 (d, J = 9.0 Hz, 2 H, 3″-H). ^{13}C NMR ($CDCl_3$): δ = 15.6 (q, *exo*-3-CH_3), 22.3 (q, *endo*-3-CH_3), 33.0 (t, C-8), 34.1 (s, C-3), 40.3 (d, C-1), 46.1 (s, C-2), 50.6 (d, C-5), 52.4 (s, C-4), 55.2 (q, OCH_3), 113.3 (d, C-3′), 122.6 or 122.8 (d, C-3″), 127.6 or 128.5 (s, C-1′), 129.7 or 130.1 (d, C-2″), 130.5 or 131.0 and 132.0 or 132.7 (2 × d, C-6 and C-7), 131.6 (d, C-2′), 145.6 (s, C-4″), 147.5 or 148.0 (s, C-1″), 158.3 (s, C-4′).

Isomer 8i(II). ^{1}H NMR ($CDCl_3$): δ = 0.75 (s, 3 H, *exo*-3-CH_3), 1.58 (s, 3 H, *endo*-3-CH_3), 2.33 and 2.52 (2 × m, 2 H, 8-H), 2.96 (m, 1 H, 1-H), 3.28 (m, 1 H, 5-H), 3.82 (s, 3 H, OCH_3), 5.42 (m, 1 H, 7-H), 5.81 (m, 1 H, 6-H), 6.85 (d, J = 9.0 Hz, 2 H, 3″-H), 7.14 (d, J = 9.0 Hz, 2 H, 2″-H), 7.22 (d, J = 9.0 Hz, 2 H, 2′-H), 8.09 (d, J = 9.0 Hz, 2 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 15.4 (q, *exo*-3-CH_3), 22.2 (q, *endo*-3-CH_3), 33.2 (t, C-8), 34.6 (s, C-3), 39.9 (d, C-1), 47.8 (s, C-2), 50.6 (s, C-4), 51.6 (d, C-5), 55.2 (q, OCH_3), 113.3 (d, C-3″), 122.6 or 122.8 (d, C-3′), 127.6 or 128.5 (s, C-1″), 129.7 or 130.1 (d, C-2′), 130.5 or 131.0 and 132.0 or 132.7 (2 × d, C-6 and C-7), 131.6 (d, C-2″), 145.6 (s, C-4′), 147.5 or 148.0 (s, C-1′), 158.3 (s, C-4″).

3,3-Dimethyl-2-(4′-methylphenyl)-4-(4′-carbomethoxyphenyl)-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene [8j(I); X = *p*-Me, Y = *p*-CO_2Me)] and 3,3-Dimethyl-2-(4′-carbomethoxyphenyl)-4-(4′-methylphenyl)-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene [8j(II); X = *p*-CO_2Me, Y = *p*-Me] were obtained as a mixture of isomers; cf. Table 2: 66.9 mg (93%), colorless powder, mp 49–51 °C. IR (KBr): ν = 2940, 2870, 1690, 1580, 1405, 1250, 1155, 1090, 1000, 795, 730, 690. Anal. Calcd for $C_{25}H_{26}O_2$ (358.5): C, 83.76; H, 7.31. Found: C, 82.99; H, 7.62.

Isomer 8j(I). ^{1}H NMR ($CDCl_3$): δ = 0.73 (s, 3 H, *exo*-3-CH_3), 1.57 (s, 3 H, *endo*-3-CH_3), 2.36 (s, 3 H, 4′-CH_3), 2.40 (br m, 2 H, 8-H), 2.88 (m, 1 H, 1-H), 3.36 (m, 1 H, 5-H), 3.90 (s, 3 H, OCH_3), 5.48 (m, 1 H, 7-H), 5.79 (m, 1 H, 6-H), 7.09 (br s, 4 H, 2′-H and 3′-H), 7.20 (d, J = 8.5 Hz, 2 H, 2″-H), 7.92 (d, J = 8.5 Hz, 2 H, 3″-H). ^{13}C NMR ($CDCl_3$): δ = 15.4 (q, *exo*-3-CH_3), 21.1 (q, 4′-CH_3), 22.3 (q, *endo*-3-CH_3), 32.1 (t, C-8), 34.2 or 34.4 (s, C-3), 40.0 or 40.2 (d, C-1), 46.3 (s, C-2), 50.8 or 51.3 (d, C-5), 51.7 (s, C-4), 51.9 (q, OCH_3), 127.2 or 127.3 (s, C-4″), 128.3, 128.7, 128.8, 129.5, 130.0 or 130.1 (4 × d, C-2′, C-3′, C-2″ and C-3″), 130.8 or 131.1 and 132.0 or 132.3 (2 × d, C-6 and C-7), 133.3 or 134.3 (s, C-1′), 135.6 or 135.7 (s, C-4′), 144.1 or 144.8 (s, C-1″), 167.2 (s, CO_2Me).

Isomer 8j(II). ^{1}H NMR ($CDCl_3$): δ = 0.73 (s, 3 H, *exo*-CH_3), 1.57 (s, 3 H, *endo*-3-CH_3), 2.36 (s, 3 H, 4″-CH_3), 2.40 (br m, 2 H, 8-H), 2.88 (m, 1 H, 1-H), 3.29 (m, 1 H, 5-H), 3.90 (s, 3 H, OCH_3), 5.48 (m, 1 H, 7-H), 5.79 (m, 1 H, 6-H), 7.09 (br s, 4 H, 2″-H and 3″-H), 7.20 (d, J = 8.5 Hz, 2 H, 2′-H), 7.92 (d, J = 8.5 Hz, 2 H, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 15.4 (q, *exo*-3-CH_3), 21.1 (q, 4″-CH_3), 22.3 (q, *endo*-3-CH_3), 32.1 (t, C-8), 34.2 or 34.4 (s, C-3), 40.0 or 40.2 (d, C-1), 47.2 (s, C-2), 50.8 or 51.3 (d, C-5), 51.7 (s, C-4), 51.9 (q, OCH_3), 127.2 or 127.3 (s, C-4′), 128.3, 128.7, 128.8, 129.5, 130.0 or 130.1 (4 × d, C-2′, C-3′, C-2″ and C-3″), 130.8 or 131.1 and 132.0 or 132.3 (2 × d, C-6 and C-7), 133.3 or 134.3 (s, C-1″), 135.6 or 135.7 (s, C-4″), 144.1 or 144.8 (s, C-1′), 167.2 (s, CO_2Me).

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