Radical Stabilization and Ground State Polar Substituent Effects in the Thermal Decomposition of Azoalkanes[†]

Werner M. Nau,* Heinrich M. Harrer, and Waldemar Adam

Contribution from the Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, FRG

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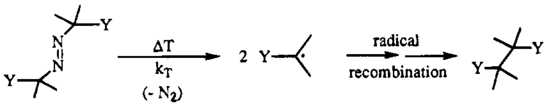
Abstract: The thermolysis rates of a series of the 1,4-diaryl-2,3-diaza[2.2.1]bicyclohept-2-ene derivatives **1** with a large variety of aryl substituents (p-NH$_2$, p-OMe, p-Me, H, p-F, p-Cl, p-Br, m-I, p-I, m-CN, p-CN, m-NO$_2$, p-NO$_2$, and p-CO$_2$Me) have been determined to probe the electronic substituent effects in the thermal decomposition of azoalkanes. The correlation of the logarithmic relative rate constants *versus* the Creary substituent constants for radical stabilization (cf. Creary, X.; *et al. J. Org. Chem.* **1987**, *52*, 3254) improved considerably when polar effects (positive ϱ value) were included in the form of a two-parameter Hammett treatment. The importance of polar effects was also established in the reported thermolysis rate data for aryl-substituted azopropanes **2**, azoethanes **3**, azomethanes **4**, azoneopentanes **5**, and 3,5-diaryl-1-pyrazolines **6**. The two-parameter analysis reveals that the thermal decomposition rates of azoalkanes are enhanced by radical- as well as anion-stabilizing substituents. On one hand, the ratio of the radical and polar reaction constants ($\varrho_{rad}/\varrho_{pol}$) serves as useful parameter to diagnose the radical nature in the decompositions of azoalkanes; thus, in general, radical effects dominate within the azoalkane **1–6** series. On the other hand, the overall sensitivity of the thermal decompositions toward substituent effects is reflected by the sum of the reaction constants ($\varrho_{rad} + \varrho_{pol}$). The polar effect is attributed to polar destabilization in the ground states of the azoalkanes, for which the polarized C–N bond is weakened by aryl substituents with electron acceptors at the positively charged benzylic carbon atom. Semiempirical (AM1) calculations corroborate such polar effects for the azoalkanes **1–6** *versus* their corresponding diaryl-substituted alkanes **7–12**.

Introduction

Quantification of substituent effects in radical reactions presents an experimental and theoretical challenge.[1] It is well established that azoalkanes cleanly produce carbon-centered radicals and molecular nitrogen on thermolysis through a radical-like transition state.[2] Thus, the rates for thermal decomposition show a strong dependence on the stability of the incipient radical and provide a direct measure of the stabilization by the substituents.[2] For example, Timberlake's radical stabilization scale[3] for substituted propyl radicals is based on the thermolysis rates (k_T) of substituted azopropanes (eq 1), amongst them the



(1)

Y = H, Me, Pr, t-Bu, CH$_2$tBu, CH$_2$Ph, c-C$_3$H$_5$, CH$_2$OCOMe, CH$_2$COMe, COMe, COPh, CO$_2$Me, CO$_2$Et, CONH$_2$, CN, Ph, CH=CH$_2$, C≡CH, CH=C=CH$_2$, OMe, OCOMe, NCO, SMe, SPh, SCOMe, SO$_2$Me, PO(OEt)$_2$, Cl

well-known initiator for radical chain reactions azobis(isobutyronitrile) (AIBN, Y = CN). It was argued[3d] that the mechanism for C–N bond cleavage "should not involve polar transition states and should, therefore, mimic true radical character". Indeed, a polar contribution in the transition state for such azoalkane derivatives appears to be minor since solvent polarity changes gave only small variations in the thermolysis rates.[3] Correlations between Timberlake's scale and more recent theoretical[4] and experimental[5–7] scales on radical stabilization are satisfactory.[3d] They provide support for the overall suitability of the thermal decomposition of azopropanes (eq 1) as a tool for the assessment of substituent effects in radical chemistry.

In addition to Timberlake's fundamental study,[3] the thermolysis rates of a number of more or less extensive sets of aryl-substituted azoalkanes have become available over the years. These include our polycyclic azoalkanes[8] **1**, the symmetrical azopropanes[9a,b] **2**, azoethanes[9c,d] **3**, azomethanes[3c] **4**, azoneopentanes[10] **5**, and 3,5-diaryl-1-pyrazolines[3b,c] **6**. The derivatives **2–5** all possess *trans* stereochemistry. Also a few unsym-

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[†] Dedicated to Professor Christoph Rüchardt on the occasion of his 65th birthday.

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(1) *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; NATO ASI Series, Series C; Reidel: Dordrecht, The Netherlands, 1986; Vol. 189.

(2) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

(3) (a) Timberlake, J. W.; Hodges, M. L. *Tetrahedron Lett.* **1970**, *11*, 4147. (b) Timberlake, J. W.; Bandlish, B. K. *Tetrahedron Lett.* **1971**, *12*, 1393. (c) Bandlish, B. K.; Garner, A. W.; Hodges, M. L.; Timberlake, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 5856. (d) Timberlake, J. W. Reference 1, pp 271–281. (e) Luedtke, A.; Meng, K.; Timberlake, J. W. *Tetrahedron Lett.* **1987**, *28*, 4255.

(4) Pasto, D. J.; Krasnansky, R.; Zercher, C. *J. Org. Chem.* **1987**, *52*, 3062.

(5) (a) Rüchardt, C.; Beckhaus, H. D. *Topics Curr. Chem.* **1985**, *130*, 1. (b) Birkhofer, H.; Beckhaus, H. D.; Rückhardt, C. Reference 1, pp 199–218.

(6) (a) Creary, X. *J. Org. Chem.* **1980**, *45*, 280. (b) Creary, X.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* **1986**, *51*, 1110. (c) Creary, X. Reference 1, pp 245–262. (d) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1987**, *52*, 3254.

(7) (a) Dust, J. M.; Arnold, D. R. *J . Am. Chem. Soc.* **1983**, *105*, 1221, 6531. (b) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1167. (c) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 2378. (d) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1986**, *64*, 270. (e) Arnold, D. R. Reference 1, pp 171–188. (f) Note that an experimental σ_α value for the p-phenyl group has recently been reported, cf.: Neumann, W. P.; Penenory, A.; Stewen, U.; Lehnig, M. *J. Am. Chem. Soc.* **1989**, *111*, 5845.

(8) (a) Adam, W.; Harrer, H. M.; Nau, W. M. *J. Org. Chem.* **1994**, *59*, 3786. (b) Adam, W.; Nau, W. M.; Wirz, J. Unpublished results. (c) For the synthesis of the unsubstituted azoalkane **1**, see: Beck, K.; Hünig, S. *Chem. Ber.* **1987**, *120*, 477.

(9) (a) Shelton, J. R.; Liang, C. K.; Kovacic, P. *J. Am. Chem. Soc.* **1968**, *90*, 354. (b) Kovacic, P.; Flynn, R. R.; Gormish, J. F.; Kappelman, A. H.; Shelton, J. R. *J. Org. Chem.* **1969**, *34*, 3312. (c) Shelton, J. R.; Liang, C. K. *Synthesis* **1971**, *90*, 204. (d) Shelton, J. R.; Liang, C. K. *J. Org. Chem.* **1973**, *38*, 2301.

(10) Peyman, A.; Hickl, E.; Beckhaus, H.-D. *Chem. Ber.* **1987**, *120*, 713.

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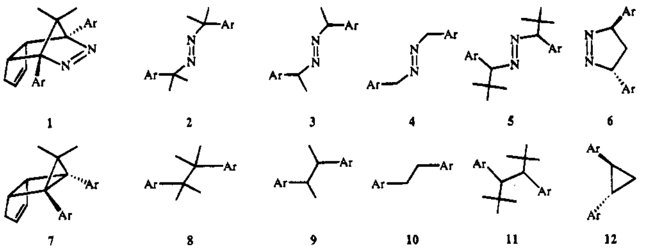
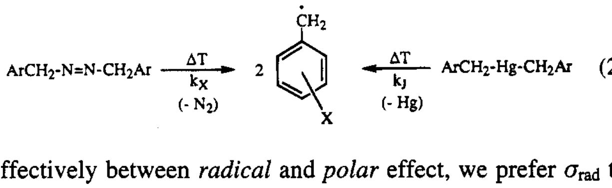


Ar = C_6H_4-X for all derivatives

metrical sets, but only with two or three substituents, have been reported.[11] Nevertheless, despite this large body of existing experimental data, it is astonishing that the decomposition rates of such aryl-substituted azoalkanes have not been utilized[2] to develop a definitive radical stabilization scale based on the rate constants k_X in eq 2. Such a σ_{rad} scale (to differentiate more effectively between *radical* and *polar* effect, we prefer σ_{rad} to σ^* for the former and σ_{pol} to σ for the latter), which was first proposed by Streitwieser,[12] constitutes a straightforward and instructive approach for the differentiation of steric from electronic and resonance from inductive effects in radical reactions, which is analogous to the Hammett treatment in polar reactions. Instead, the more problematic (polar effects, induced decomposition, etc.) thermolysis of dibenzylmercury compounds (rate constants k_J in eq 2) has been employed by Jackson[13] to define a σ_{rad} scale.



(2)

To date, four other σ_{rad} scales are available: (a) the Fisher scale[14] based on the hydrogen abstraction from aryl-substituted *m*-cyanotoluenes by bromine atoms generated from *N*-bromosuccinimide (NBS), (b) the Creary scale[6] derived from the rates of rearrangement of 2-aryl-3,3-dimethylmethylenecyclopropanes (rate constants k_C in eq 3), (c) the most recent scale by Jiang,[15] defined by the rates for dimerization of substituted trifluorostyrenes, and (d) the σ_α scale by Arnold,[7] which makes use of the α hydrogen hyperfine coupling constants of substituted benzyl radicals. The former three, like the Timberlake[3] and Jackson[13] scales, are kinetic scales founded on chemical reactivity; the latter is based on EPR spectroscopy. Recently we have introduced[16] another spectroscopic scale, namely the ΔD scale. It measures the relative changes of the zero-field splitting parameter *D* of substituted 1,3-diaryl-1,3-cyclopentanediyl triplet biradicals which were obtained by direct photolytic denitrogenation of the azoalkanes **1** at 77 K in MTHF (2-methyltetrahydrofuran) glass (eq 4).

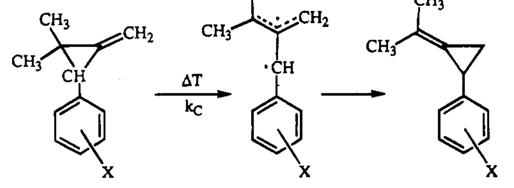


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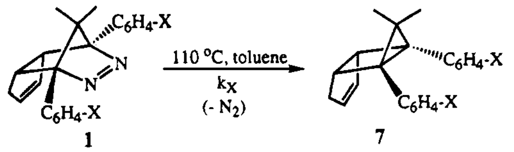
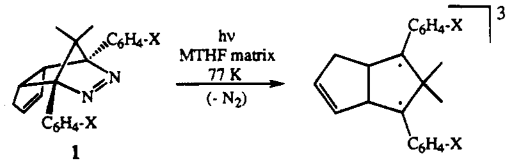
Table 1. Rate Constants for the Thermal Denitrogenation of Azoalkanes **1** and the Creary and Hammett Substituent Constants for Radical (σ_{rad}) and Polar (σ_{pol}) Effects



1 **7**

X	$k_X \times 10^5$ [a] (s^{-1})	k_{rel}[b]	σ_{rad}[c]	σ_{pol}[d]
p-NH_2	*e*	1.51	0.90[f]	−0.66
p-OMe	8.28	1.34	0.24	−0.268
p-Me	7.83	1.27	0.11	−0.170
***p*-H**	**6.19**	**1.00**	**0.00**	**0.000**
p-F	6.14	0.99	−0.08	0.062
p-Cl	10.3	1.67	0.12	0.227
p-Br	11.1	1.79	0.13	0.232
m-I	10.2	1.65	[0.10 ± 0.15][g]	0.352
p-I	13.4	2.17	[0.41 ± 0.15][g]	0.278
m-CN	11.2	1.80	−0.12	0.56
p-CN	24.9	4.02	0.46	0.66
m-NO_2	15.1	2.43	−0.11	0.710
p-NO_2	31.4	5.07	0.57	0.778
p-OMe/*p*-NO_2[h]	29.2	4.72	0.24/0.57	−0.268/0.778
p-Me/*p*-CO_2Me[h]	14.0	2.26	0.11/0.35	−0.170/0.39

[a] Thermolysis temperature = 110.0 ± 0.5 °C. Average values determined from duplicate runs in toluene, error ca. ±3%. [b] $k_{rel} = k_X/k_H$. [c] Creary's radical substituent constants taken from ref 6. [d] Hammett's σ_{pol} values taken from ref 20. [e] See text. [f] Value given for *p*-NMe_2; see also text. [g] No experimental value available, calculated according to eq 6 by using the ϱ_{pol} and ϱ_{rad} values for azoalkane **1** from Table 2. [h] Unsymmetrical derivatives (different aryl X substituents).



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(4)

All scales,[6,7,14,16] except the one by Jackson,[13] predict radical *destabilization* by essentially all *meta* substituents and by the *p*-fluoro group and *stabilization* by all resonance-active electron-accepting *para* substituents. These results establish clear-cut trends in substituent effects on radical species. The excellent agreement between the Creary[6] and Arnold[7] scales suggests that the Jackson[13] and Fisher[14] scales reflect also steric and/or polar effects.[14b]

With this background, it appeared imperative to assess the *meta* and *para* substituent effects on the rates for thermal decomposition (k_X) of the diaryl-substituted azoalkanes **1** (Table 1) and to compare the results with now established σ_{rad} scales.[6,7] In line with Timberlake's arguments,[3] we expected pure radical character in the transition state for these homolytic diazetations, but we observed rather large discrepancies in that the azoalkane

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(11) (a) Overberger, C. G.; Stoddard, J. W.; Yaroslavsky, C.; Katz, H.; Anselme, J.-P. *J. Am. Chem. Soc.* **1969**, *91*, 3226. (b) McGreer, D. E.; Wigfield, Y. Y. *Can. J. Chem.* **1969**, *47*, 3965. (c) Deleux, J. P.; Leroy, G.; Weiler, J. *Tetrahedron* **1973**, *29*, 1135.

(12) Streitwieser, A., Jr.; Perrin, C. *J. Am. Chem. Soc.* **1964**, *86*, 4938.

(13) (a) Dinçtürk, S.; Jackson, R. A.; Townson, M. *J. Chem. Soc., Chem. Commun.* **1979**, 172. (b) Dinçtürk, S.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1127. (c) Agirbas, H.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 739. (d) Jackson, R. A. reference 1, pp 325−328. (e) Jackson, R. A.; Moosavi, R. *J. Chem. Soc., Perkin Trans. 2* **1992**, 885. (f) Jackson, R. A. *J. Organomet. Chem.* **1992**, *437*, 77.

(14) (a) Fisher, T. H.; Meierhoefer, A. W. *J. Org. Chem.* **1978**, *43*, 224. (b) Fisher, T. H.; Dershem, S. M.; Prewitt, M. L. *J. Org. Chem.* **1990**, *55*, 1040.

(15) (a) Jiang, X.-K.; Ji, G.-Z.; Yu, C.-X. *Acta Chim. Sin. (Engl. Ed.)* **1984**, 82. (b) Jiang, X.-K.; Li, X.-Y.; Zhao, C.-X.; Ji, G.-Z. *Rev. Chem. Intermed.* **1986**, *7*, 195. (c) Jiang, X.-K.; Liu, W. W.-Z.; Wu, S.-H. *Tetrahedron* **1994**, *50*, 7503.

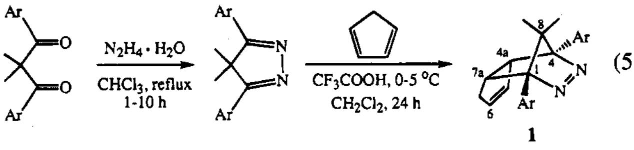
(16) (a) Adam, W.; Fröhlich, L.; Nau, W. M.; Korth, H.-G.; Sustmann, R. *Angew. Chem.* **1993**, *105*, 1383; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1339. (b) Adam, W.; Harrer, H. M.; Nau, W. M.; Korth, H.-G.; Sustmann, R. Unpublished results.

decomposition rates did not correlate well with the established[6,7] radical substituent parameters (σ_{rad}). In fact, even a cursory examination of the earlier, independently obtained rate data for azoalkanes **2**−**6**[3b,c,9,10] provided compelling evidence that substituents exercise polar effects in such homolytic decompositions.

Clearly, a revision appeared essential, and to this end, we undertook the present study. Indeed, a two-parameter Hammett treatment[17] of our rate data for the thermolysis of the cyclic azoalkanes **1** and of the reported derivatives **2**−**6** gave excellent quantitative correlations, provided radical as well as polar substituent effects (with positive Hammett ϱ_{pol} value) are explicitly considered. The polar contributions are interpreted in terms of ground state effects of the substituents[18] on the polarized C−N bonds in azoalkanes. This interpretation is corroborated by semiempirical MO calculations (AM1) on the changes in the ground state energies in azoalkanes **1**−**6** relative to alkanes **7**−**12** as a function of *para* substituents.

Results

Azoalkanes **1** were prepared according to established methods,[8a] which entailed the preparation of 2,2-dimethylated dibenzoylmethanes, cyclization to the isopyrazoles with hydrazine, and acid-catalyzed cycloaddition with cyclopentadiene (eq 5). The



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(5)

thermolysis of the azoalkanes **1** was carried out in boiling toluene ($T = 110.0 \pm 0.5$ °C) for a comprehensive set of symmetrical derivatives with X = *p*-OMe, *p*-Me, H, *p*-F, *p*-Cl, *p*-Br, *m*-I, *p*-I, *m*-NO_2, *p*-NO_2, *m*-CN, and *p*-CN and for two unsymmetrical ones, namely X = *p*-OMe/X′ = *p*-NO_2 and X = *p*-Me/X′ = *p*-CO_2Me. The bicyclo[2.1.0]pentanes **7** (Table 1) were obtained exclusively on thermal denitrogenation (>95%).[8]

The absolute and relative rate constants k_X and k_{rel} for the thermal decomposition of azoalkanes **1** were conveniently measured by ^1H NMR spectroscopy in deuterated toluene (Table 1) and correspond to half-lives between 0.5 and 3 h at 110 °C. As expected,[2] the thermolyses followed first-order kinetics, which was rigorously established for the parent compound (X = H). Since the *p*-amino-disubstituted azoalkane **1** was not available, the very closely related derivatives[8b] with the hydrogenated C=C double bond in the cyclopentene moiety were employed to determine its relative thermolysis rate constant (k_{NH_2}), which is included for the sake of completeness. Also listed in Table 1 are Creary's[6,19] σ_{rad} values and the polar Hammett σ_{pol} parameters.[20] Instead of the σ_{rad} parameter for *p*-amino, we have used the value for *p*-dimethylamino, since these two amino substituents exhibit very similar benzyl radical stabilization.[21] Since positive ϱ_{rad} values are characteristic for radical-type decompositions,[6,7,13,14] positive σ_{rad} values, which are synonymous with better radical stabilization by the substituent, suggest an acceleration in the thermolysis rates of azoalkanes.[22]

Except for the *p*-fluoro group, all substituents accelerate the thermal decomposition. Small rate enhancements were measured for *p*-methyl, *p*-methoxy, and *p*-amino, moderate enhancements for *p*-chloro, *p*-bromo, *m*-iodo, and *m*-cyano, and the largest for the derivatives with *p*-nitro, *m*-nitro, *p*-carbomethoxy, *p*-cyano, and *p*-iodo substituents. In contrast to the previous series of azoalkanes **2**−**6**,[3b,c,9,10] we feature also the strong electron acceptors nitro, cyano, and carbomethoxy in our series of azoalkanes **1** as well as the strongest electron donor *p*-amino. Since these substituents in the *para* position are at the same time the most powerful radical-stabilizing groups (cf. σ_{rad} in Table 1), such a wide range of substituents covers the possible extremes from *p*-NO_2 and *p*-NH_2, i.e. almost 1.5 σ_{pol} units and ca. 1.0 σ_{rad} units. This should, therefore, provide better mechanistic insight on radical stabilization and polar effects in such homolytic decompositions. For comparison, the range for the most comprehensive previous study[9c,d] of aryl-substituted azoethanes **3** covers 0.7 units on the σ_{pol} scale and only 0.32 units on the σ_{rad} scale.

A comparison (Table 1) of the relative rate constant for the unsymmetrical *p*-nitro/*p*-methoxy derivative ($k_{NO_2/OMe} = 29.2$) with those for the symmetrically substituted *p*-methoxy ($k_{OMe} = 8.28$) and *p*-nitro ($k_{NO_2} = 31.4$) ones shows that the unsymmetrical azoalkane decomposes nearly as readily as the less stable symmetrical derivative (with two *p*-nitro groups). Similar observations have been made for other unsymmetrical azoalkanes,[2] but our finding constitutes the first example of an aryl-substituted case. The rate constant measured for the *p*-nitro/*p*-methoxy derivative may be taken as additional support[2] for one-bond breakage rather than simultaneous two-bond rupture for the thermal denitrogenation of *unsymmetrical* azoalkanes.

Discussion

The relative rate constants in Table 1 reveal clearly that the influence of *meta* and *para* substituents on the thermolysis rates of azoalkanes **1** is significant. However, even a qualitative comparison with Creary's[6] σ_{rad} values displays considerable deviations which do not follow the radical-stabilizing properties of the substituents. With the premise that stabilization of the incipient radical site enhances the rate of azoalkane thermolysis, we note that the *p*-amino group, which is known to be one of the most powerful radical-stabilizing groups[6,20] (σ_{rad} ca. 0.90), causes only a small acceleration (ca. 50%). Yet, the *meta* substituents cyano and nitro, which are now generally accepted to destabilize benzyl radicals,[6,7,14b,16] show as well appreciable rate enhancements. Moreover, fluorine, which is certainly a benzyl radical destabilizing group in the *para* position,[6,7,14a,16] exhibits a decomposition rate comparable to that of the parent azoalkane. Thus, a plot (Figure 1a) of log k_{rel} *versus* the Creary σ_{rad} substituent constants[6] for radical stabilization in benzyl radicals gave a typical shotgun-type scatter of points, a dramatic display of the lack of a correlation ($r^2 = 0.165$).

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[17] (a) Yamamoto, T.; Otsu, T. *Chem. Ind. (London)* **1967**, 787. (b) Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

[18] (a) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1850, 1860. (b) Clark, K. B.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1991**, *113*, 9363. (c) Wayner, D. D. M.; Sim, B. A.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 4853. (d) Bordwell, F. G.; Zhang, X.-M.; Satish, A. V.; Cheng, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 6605.

[19] Our ΔD[16] as well as Arnold's σ_α scale[7] for radical stabilization are not based on kinetic data, such that their use in linear free energy relationships is questionable. For this reason, the ΔD scale was not employed in the Hammett treatment of the kinetic data for the azoalkane **1**−**6** decompositions. Note also that Arnold's scale[7] does not provide experimental σ_α values for the *p*-bromo, *p*-amino, and *p*-nitro substituents. Since the latter substituents were important for our analysis and since the Creary σ_{rad} scale[6] is the most comprehensive kinetic scale known to date, it was used in the present analysis.

[20] Hammett σ values were taken from McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420, except for *p*-I, cf. Sjöström, M.; Wold, S. *Acta Chem. Scand., Ser. B* **1976**, *30*, 167. See also: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

[21] (a) Merényi, R.; Daffe, V.; Klein, J.; Masamba, W.; Viehe, H. G. *Bull. Soc. Chim. Belg.* **1982**, *91*, 456. (b) Merényi, R.; Janousek, Z.; Viehe, H. G. Reference 1, pp 301−324. (c) Viehe, H. G.; Merényi, R.; Janousek, Z. *Pure Appl. Chem.* **1988**, *60*, 1635.

[22] Negative ϱ_{rad} values are expected to apply for radical recombinations, but no experimental data appear to be yet available.[13b]

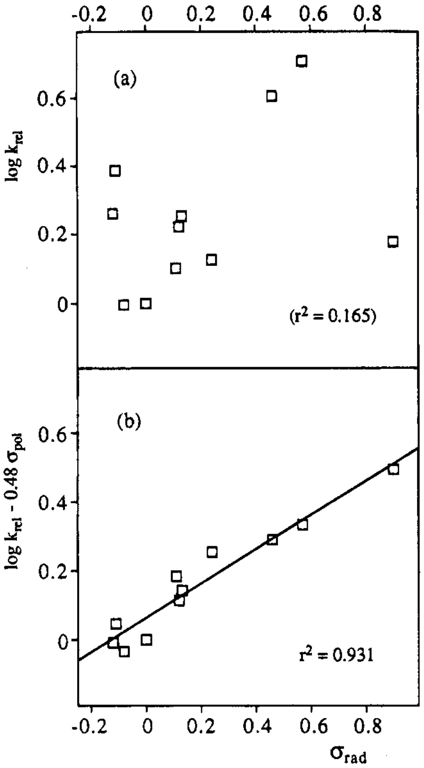

Figure 1. Semilogarithmic plot of the relative thermolysis rate constants (k_{rel}) for azoalkane **1** *versus* the Creary σ_{rad} values (both taken from Table 1): (a) one-parameter plot without inclusion of polar contribution and (b) two-parameter plot with polar contributions ($0.48\sigma_{pol}$) included according to eq 6. The σ_{pol} values were taken from ref 20.

We suspected that superimposed polar effects obscured the radical nature in these homolytic decompositions. However, since the typical order of increasing electron donation (e.g., p-NH$_2$ > p-OMe > p-Me > H > p-NO$_2$, cf. σ_{pol}) is not in line with the observed rate constants, polar effects must be much less dominant than for the radical-type hydrogen abstractions from toluenes, which are adequately described by a polar parameter only.[23] Consequently, we have employed the two-parameter Hammett equation[17] of eq 6 to assess the relative

$$\log k_{rel} = \rho_{rad}\sigma_{rad} + \rho_{pol}\sigma_{pol} \qquad (6)$$

importance of polar (σ_{pol}) and radical (σ_{rad}) effects of the substituents. The polar term (ρ_{pol}) was fitted by iteration to achieve the best correlation and subtracted from log k_{rel}. As can be seen from Figure 1b, the inclusion of polar effects gives now a good correlation ($r^2 = 0.931$) with σ_{rad}. The relative radical and polar contributions for the thermal decomposition of azoalkanes **1**, as measured by the reaction constants ρ, are $\rho_{rad} = 0.50$ and $\rho_{pol} = 0.48$.

In view of this successful correlation of our rate data for azoalkanes **1**, we felt encouraged to analyze the reported experimental data on the thermal decompositions for other sets of diaryl-substituted azoalkanes (Table 2) in terms of the two-parameter Hammett equation (eq 6). Indeed, in every case, considerable improvement was obtained when the polar contributions were included (Figure 2). Most impressively, the correlation coefficients (r^2) for the decomposition rates of azopropanes[9a,b] **2** and azoethanes[9c,d] **3** improve from 0.120 and 0.038 to 0.824 and 0.896. Furthermore, the correlation for the azoethane **3** series improves significantly ($r^2 = 0.974$) when the m-OMe derivative, which might be in error, is excluded. Most importantly, the ρ_{pol} values for the best correlation coefficients are positive for all six sets of data. Moreover, the correlation for the azomethane[3c] **4** series, which is already quite satisfactory ($r^2 = 0.904$) without consideration of polar effects, improves further ($r^2 = 0.991$) by inclusion of even a relatively small polar contribution ($\rho_{pol} = 0.16$ *versus* $\rho_{rad} = 0.59$). Since the literature thermolysis data[3b,c,9,10] for azoalkanes **2**–**6** have

Table 2. Two-Parameter Hammett Treatment of Radical and Polar Substituent Effects on the Thermolysis Rates of Azoalkanes **1**–**6**

azo-alkane[a]	T (°C)[b]	ρ_{rad}[c]	ρ_{pol}[d]	r^2 [e]	ρ_{rad}/ρ_{pol}	$\rho_{rad} + \rho_{pol}$	θ[f]	ρ_{pol}^{calc} [g]
1[h]	110	0.50	0.48	0.931 (0.165)	1.04	0.98	174	0.66
2[i,j]	42.8	1.55	0.83	0.824 (0.120)	1.86	2.39	107	0.53
3[j,k]	105	1.42	0.71	0.896 (0.038)	2.00	2.12	108	0.51
4[l]	150	0.59	0.16	0.991 (0.904)	3.60	0.75	113	0.26
5[m]	150	0.79	0.56	0.866 (0.512)	1.40	1.35	121	0.33
6[n]	80	1.13	0.46	0.918 (0.327)	2.44	1.59	119	1.07

[a] All substituents, for which σ_{rad} values from Creary (ref 6) were available, have been included. [b] Thermolysis temperature. [c] Obtained by linear regression analysis according to eq 6 for the given ρ_{pol} value and the Creary σ_{rad} values. [d] Fitted to achieve the best correlation (largest r^2) between log(k_{rel}) and σ_{rad} according to eq 6. [e] Correlation coefficient of eq 6 for the ρ_{pol} values given in column 4. The values given in parentheses refer to the correlation coefficients without polar terms included, i.e. $\rho_{pol} = 0$. [f] Dihedral angle between the C–N bond and the phenyl plane calculated by the AM1 method. [g] Calculated from the relationship PSE = $2.30RT\rho_{pol}^{calc}\Delta\sigma_{pol}$; PSE values taken from Table 3 with $\Delta\sigma_{pol} = \sigma_{pol}(NO_2) - \sigma_{pol}(NH_2) = 1.438$. [h] Thermolysis rate data taken from Table 1; the iodo and the unsymmetrical derivatives were not included; the Creary value for p-NMe$_2$ has been used for p-NH$_2$ (cf. Table 1 and text). [i] Thermolysis rate data for X = H, p-OMe, p-Me, p-Et, p-iPr, p-tBu, p-F, m-Cl, p-Cl, and p-Br taken from ref 9a,b; the p-iPr derivative was not included. [j] The Creary value employed for the p-Et substituent ($\sigma_{rad} = 0.085$) has not been experimentally determined but was calculated from the relationship[7e] with Arnold's σ_α values. [k] Thermolysis rate data for H, m-OMe, p-OMe, m-Me, p-Me, p-Et, m-F, p-F, m-Cl, p-Cl, and m-CF$_3$ taken from ref 9 c,d; the o-OMe derivative was not included. The correlation improves significantly ($r^2 = 0.974$) when the thermolysis rate constant for the m-OMe derivative is omitted, i.e. $\rho_{rad} = 1.17$, $\rho_{pol} = 0.61$, $\rho_{rad}/\rho_{pol} = 1.94$, $\rho_{rad} + \rho_{pol} = 1.78$. [l] Thermolysis rate data for H, p-OMe, p-Me, p-Ph, and p-Cl taken from ref 3c. [m] Thermolysis rate data H, p-OMe, p-tBu, p-Ph, and p-Cl taken from ref 10. [n] Thermolysis rate data for H, p-OMe, p-Me, and p-Cl taken from ref 3b,c.

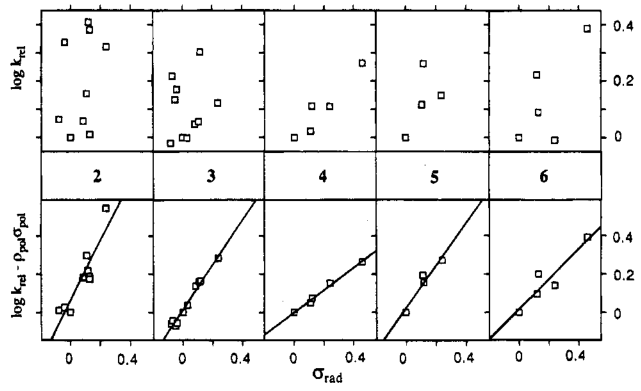

Figure 2. Semilogarithmic plots of the relative thermolysis rate constants (k_{rel}) for azoalkanes **2**–**6**, taken from the literature,[3c,9,10] *versus* the Creary σ_{rad} values.[6] The upper row contains the one-parameter plots without inclusion of polar contributions, and the lower row shows the two-parameter plots with polar contributions ($\rho_{pol}\sigma_{pol}$) included according to eq 6. The ρ_{pol} values were taken from Table 2 and the σ_{pol} values from ref 20. Note that the plots for azoalkane **3** do not contain the value for m-OMe, which might be in error (see footnote k in Table 2 and text). For correlation coefficients and slopes (ρ_{rad}), see Table 2.

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(23) (a) Russell, G. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, p 295. (b) Henderson, R. W. *J. Am. Chem. Soc.* **1975**, *97*, 213. (c) Reference 3c. (d) Héberger, K. *J. Phys. Org. Chem.* **1994**, *7*, 244.

been obtained in different laboratories at different temperature ranges and by employing different analytical techniques, these correlations are indeed impressive.

From the two-parameter correlation obtained for azoalkanes **1** (Figure 1; log $k_{rel} = 0.50\sigma_{rad} + 0.48\sigma_{pol}$), the unknown Creary σ_{rad} values[6] for the *p*-iodo (0.41 ± 0.15) and *m*-iodo (0.10 ± 0.15) groups were estimated by using the rate data and σ_{pol} values in Table 1. Even though these estimates are subject to a rather large error, the *p*-iodo substituent acts apparently as quite a strong radical-stabilizing group, significantly stronger than *p*-bromo. In contrast, Fisher[14a] suggested a slightly weaker radical-stabilizing effect for the *p*-iodo relative to *p*-bromo substituent.

Our findings provide convincing evidence for the existence of a polar effect in the decomposition of azoalkanes, which is well-described by the Hammett σ_{pol} values.[24] Thus, the thermal decomposition of azoalkanes is accelerated not only by radical-stabilizing substituents but also by electron acceptors ($\sigma_{pol} > 0$), as indicated by the positive ϱ_{pol} values. It is now no longer surprising that the azoalkanes **1** with *meta* substituents, which possess large positive σ_{pol} values, e.g. *m*-CN and *m*-NO_2, decompose thermally faster (Table 1), although on the basis of their small negative σ_{rad} values, radical destabilization and, thus, a lower decomposition rate would have been expected. Furthermore, substitution with the *p*-amino group, which should stabilize the incipient radical most effectively, enhances the thermolysis rate only nominally (Table 1) because radical stabilization is nearly counterbalanced by the strong electron-donating nature of this group. Moreover, the same rate of thermolysis (Table 1) for the *p*-fluoro-substituted derivative as the parent azoalkane **1** (X = H) can now be understood in that the small electron-accepting effect of the *p*-fluoro substituent ($\sigma_{pol} = 0.062$) is exactly counterbalanced by its small radical-destabilizing nature ($\sigma_{rad} = -0.08$). Finally, for the majority of the substituents, e.g. *p*-Cl, *p*-Br, *p*-CN, and *p*-NO_2, both radical and polar σ parameters predict a faster denitrogenation and the measured thermolysis rates (Table 1) should be somewhat higher than expected on the basis of their radical-stabilizing effects alone. The same principal trends are revealed by the rate data for the decompositions of the other azoalkanes **2**–**6**.[3b,c,9,10] However, in contrast to azoalkanes **1**, the particularly instructive probes for polar effects, i.e. the substituents *p*-NH_2, *m*-CN, and *m*-NO_2, whose polar and radical σ parameters show opposite signs (Table 1), have not been included in the azoalkane **2**–**6** series. The use of these probes in the series of azoalkanes **1** has significantly contributed to the detection of the polar effect.

The reaction constants ϱ_{rad} and ϱ_{pol} obtained from the two-parameter Hammett treatment of the azoalkanes **1**–**6** (Table 2) provide valuable information on the relative contributions of polar and radical effects, given by the $\varrho_{rad}/\varrho_{pol}$ parameter, and on the overall sensitivity of the reaction toward substituent effects, given by the $\varrho_{rad} + \varrho_{pol}$ parameter. For example, the $\varrho_{rad}/\varrho_{pol}$ parameter for our azoalkane **1** is close to unity and the lowest of the azoalkanes **1**–**6**. This means that polar effects are particularly important for this system and that they contribute as much to the thermal decomposition as radical effects.[25] It should be no longer surprising that azoalkane **1** was instrumental in pinpointing polar effects in the homolytic decompositions of azoalkanes. On the other end, azomethane **4** possesses the highest radical contribution (ca. 80%) of the azoalkanes **1**–**6**, namely $\varrho_{rad}/\varrho_{pol} = 3.6$. The other azoalkanes fall within the range $1 \leq \varrho_{rad}/\varrho_{pol} \leq 3.6$ spanned by azoalkanes **1** and **4**, which confirms that radical contributions dominate in the thermal decomposition rates of azoalkanes. For this reason, the thermolysis of azoalkanes is much more suitable for assessing radical effects than many other radical processes, e.g. the hydrogen abstractions from toluenes.[23]

As to the $\varrho_{rad} + \varrho_{pol}$ parameter, which is a direct measure for the susceptibility of the reaction toward substituent effects, the values range between 0.75 (azomethane **4**) and 2.4 (azocumene **2**) for the azoalkanes examined here (Table 2). Since all azoalkanes bear aryl groups at the incipient radical sites, optimal alignment between the benzylic center and the aryl π system in the transition state should result in higher values for the $\varrho_{rad} + \varrho_{pol}$ parameter due to more effective interaction with substituents. To probe this supposition, we have calculated the dihedral angle θ between the aryl planes and the C–N bonds in azoalkanes **1**–**6** and assumed that the (steric) restraints governing this angle in the azoalkanes would be retained to a certain degree in the transition states. The θ values range between 107° and 174° (Table 2). Since a θ angle of 90° would ensure maximum interaction, the θ angle of 174° calculated[26] for azoalkanes **1** is most unfavorable and may thus explain the relatively low value of the $\varrho_{rad} + \varrho_{pol}$ parameter for this system. The enhanced influence of substituents on the thermolysis of azocumenes **2** compared to diarylazomethanes **4** has been addressed by different authors[3,9] and is quantified herein by means of the $\varrho_{rad} + \varrho_{pol}$ parameter. However, the changes in the calculated angles θ for the open-chain azoalkanes **2**–**5** (107–121°) are too small to allow unambiguous statements to be made about the origin of the large variations of the $\varrho_{rad} + \varrho_{pol}$ values. It is noteworthy, nonetheless, that the decrease of the $\varrho_{rad} + \varrho_{pol}$ values on going from **2** to **3** to **5** to **4** is not due to the change of only one of the two ϱ values, since they both show the same trend.

The polar effects in azopropanes (eq 1),[3] as assessed through the relatively low $\varrho_{rad}/\varrho_{pol}$ parameter in their diaryl derivatives[9a,b] **2**, are also quite substantial. As a consequence, the Timberlake[3] scale (eq 1) measures not only the effects of incipient radical stabilization but polar effects as well. The question arises whether the *direct* attachment of substituents enhances their radical-stabilizing effects to a higher degree than their polar effects, such that the latter contribute only little to the measured rate constants of Timberlake's set of azopropanes (eq 1). The answer to this question requires knowledge about the nature of the polar effect.

The Origin of the Polar Effect. The mechanistic details of the denitrogenation of azoalkanes are still subject to controversial debate,[27–33] and detailed discussions are provided elsewhere.[2,27] Thus, the concerted extrusion of nitrogen on

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(24) Other polar substituent constants such as σ^+, σ^-, σ_R, and σ_I, which have been used to describe polar effects in radical reactions,[7a,23] are less appropriate for the description of polar effects in the thermal decompositions of azoalkanes.

(25) Note that the definition of the "relative contributions of radical and polar effects", even though highly desirable for ease of understanding and argumentation, may be somewhat arbitrary, since the two effects are essentially independent. The comparison appears most meaningful if the σ scales for polar and radical effects span a similar range such that the radical and polar contributions to the free enthalpy of activation (given as $\Delta\Delta G^{\ddagger} = 2.30RT\varrho\sigma$) cover a similar energy range for the most common substituents. This is the case for the Hammett and Creary scales employed herein, which cover ca. 1.5 units for σ_{pol} (from −0.66 for *p*-NH_2 to +0.778 for *p*-NO_2) and ca. 1 unit for σ_{rad} (from +0.90 for *p*-NMe_2 to −0.12 for *m*-CN). Arnold has used a similar definition ($\varrho_\alpha/\varrho_{pol}$) for his σ_α values,[7] which span a range from −0.026 to +0.063. Since the σ_α values are of a different order of magnitude from that of the common Hammett σ_{pol} values (from −0.66 to +0.78), similar values for ϱ_α and ϱ_{pol}, i.e. a $\varrho_\alpha/\varrho_{pol}$ parameter approaching unity, do *not* indicate comparable radical and polar effects. When Arnold's σ_α values are used, the value for the $\varrho_\alpha/\varrho_{pol}$ parameter must be ca. 10–15 to reflect equally large contributions.

(26) The calculated θ angle (174°) is very close to the experimental angle (150/160°) determined by X-ray analysis for a closely related derivative, in which the *geminal* methyl groups are substituted by chlorine: Adam, W; Ammon, H.; Nau, W. M. Unpublished results.

thermolysis has been experimentally supported[2] also for the arylazoalkanes considered herein (**2** and **3** with X = H),[28] but experiments[29] and theoretical predictions[30] for other symmetrical azoalkanes are more in line with a stepwise nitrogen extrusion through intermediate diazenyl radicals, originally proposed by Pryor.[32] The intermediacy of diazenyl biradicals is more and more becoming an established fact for the thermolysis and photolysis of cyclic azoalkanes,[27,29-31] in particular for the bicyclic azoalkane 2,3-diazabicyclo[2.2.1]hept-2-ene,[33] which is the parent compound for the azoalkanes **1** studied herein.

Timberlake has pointed out that his radical stabilization scale (eq 1)[3] is not dependent on the mechanistic knowledge of concerted *versus* stepwise nitrogen extrusion as long as the mechanism remains the same for all azopropanes. Also, our conclusions for the thermolyses of the azoalkanes **1**−**6** hold for both mechanistic alternatives. In any case, it is accepted that the transition state for C−N bond cleavage is radical-like and reflects the stabilization of the incipient radical sites, albeit the stabilization in the transition state will be necessarily smaller than in the radicals because of diminished spin density in the transition state.

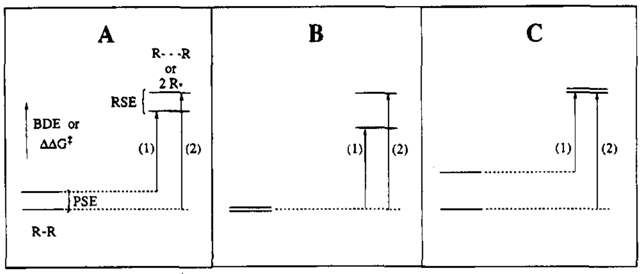

Figure 3. Possible contributions of ground state polar stabilization energy (PSE) and radical stabilization energy (RSE) to the bond dissociation energy (BDE) in a radical reaction ($R-R \rightarrow 2R^{\bullet}$) or to the free energy of activation ($\Delta\Delta G^{\ddagger}$) for a bond homolysis with radical-like transition state ($R^{\delta\bullet}$- - -$^{\delta\bullet}R$). In all cases A−C, the BDE and $\Delta\Delta G^{\ddagger}$ are lower for reaction 1 relative to reaction 2. In case A, both PSE and RSE contribute, but in the limiting cases, only RSE (case B) or PSE (case C) contributes.

A possible origin of the polar effect may be sought in a polarized transition state. For the present azoalkane decompositions with positive ϱ_{pol} values, the transition state would be required to be diazonium-like, i.e. $Ar-C^{\delta-}$---$N^{\delta+}=N-R$, to allow stabilization by electron-accepting substituents and, thus, an acceleration of the thermal decomposition. Such a polarized transition state has been proposed by Firestone[34] on the basis of the Linnett bonding theory. Thus, he attributed the high thermolysis rates of azopropanes with electron-accepting groups[3] to derive partly from such transition state polarization, whereas Timberlake argued[3d] that good anion-stabilizing groups also significantly stabilize radical sites. Despite Firestone's arguments, it would be quite astounding if the polarization of the transition state were inverse to that in the ground state of the azoalkane, which is unambiguously $Ar-C^{\delta+}-N^{\delta-}=N-R$, due to the higher electronegativity of nitrogen. Moreover, since polar transition states should be sensitive toward solvent effects, it is difficult to understand why the changes of the decomposition rates of azoalkanes in different solvents are small and show no clear dependence on solvent polarity.[3d,e] An alternative, and in our opinion more likely, origin for the polar effects observed in azoalkane thermolyses should be sought in the ground state properties, especially in view of the inherent polarization of the C−N bond. Not only is this interpretation in agreement with the postulated[2,3] radical-like transition state but, in contrast to transition states, ground state properties can be more reliably and conveniently assessed by semiempirical MO calculations.

The experimental detection of such ground state polar effects and the quantification of their polar stabilization energies (PSE) represents an area of current interest in radical chemistry.[18,35] It essentially constitutes an extension of Benson's concept[36] (Figure 3, case B), according to which relative bond dissociation energies (BDE) are a direct measure of radical stabilization energies (RSE). For a homolytic bond cleavage, a radical-stabilizing substituent will lower the energy of the resulting radical and, as a direct consequence, lower the BDE of the molecule (Figure 3, case B). Not surprisingly, since Benson's pioneering work has provided principal understanding of the interplay between structure and reactivity in radical reactions, measurements of BDE have become common denominators in numerous studies of substituent effects in radical chemistry.[1]

Despite the success of this concept for radical reactions, polar contributions to BDE as caused by substituent effects on the intact bond in the ground state molecule (Figure 3, case A) need not be negligible, i.e. BDE = f(RSE,PSE).[18] An extreme prototype for such a ground state polar effect is depicted in case C in Figure 3; even though the reaction is characterized by a radical-type transition state, the substituent acts principally on the polarized *intact* bond, which senses a stabilization or destabilization. As can be seen, the net effect is lowering of the BDE for all three situations (A, B, and C) in Figure 3, as given by the energy difference for reaction 1. From a conceptual point of view, it is important to realize that the polar effect of substituents on the ground state of the molecule (case C) contrasts the radical effect on the transition state (case B), in that the ground state *destabilizing* group becomes a radical-*stabilizing* substituent.

Arnold has suggested that the strength of a polar bond is subject to polar substituent effects, which change the ground state energy and, in turn, the BDE.[18a] Consequently, ground state polar effects on the BDE may become important for polar bonds such as the C−Br bond in benzyl bromides and the C−N bond in azoalkanes. For example, recently Clark and Wayner[18b] have studied the BDEs of *para*-substituted benzyl bromides *versus* toluenes by photoacoustic calorimetry and have concluded dominant ground state effects. If ground state polar effects are important, measurements of BDE provide no longer an accurate means for assessing the radical-stabilizing properties

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[27] (a) Koenig, T. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, p 113. (b) Drewer, R. J. *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Wiley: New York, 1975; p 936. (c) Adam, W.; Oppenländer, T.; Zang, G. *J. Org. Chem.* **1985**, *50*, 3303.

[28] (a) Seltzer, S. *J. Am. Chem. Soc.* **1961**, *83*, 2625; **1963**, *85*, 14. (b) Seltzer, S.; Hamilton, E. *J. Am. Chem. Soc.* **1966**, *88*, 3775−3781. (c) Neumann, R. C., Jr.; Amrich, M. J. *J. Org. Chem.* **1980**, *45*, 4629.

[29] (a) Neumann, R. C., Jr.; Binegar, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 134. (b) Engel, P. S.; Gerth, D. B. *Ibid.* **1983**, *105*, 6849. (c) Engel, P. S.; Nalepa, C. J.; Horsey, D. W.; Keys, D. E.; Grow, R. T. *Ibid.* **1983**, *105*, 7102.

[30] (a) Hiberty, P. C.; Jean, Y. *J. Am. Chem. Soc.* **1979**, *101*, 2538. (b) Dannenberg, J. J.; Rocklin, D. *J. Org. Chem.* **1982**, *47*, 4529.

[31] It has been proposed that the diazenyl radical derived from the *photolysis* of azocumene **2** (X = H) has a lifetime of ca. 9 μs (Sumiyoshi, T.; Kamachi, M.; Kuwae, Y.; Schnabel, W. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 77). This result has been reexamined, and the lifetime of this diazenyl radical has been determined to be too short-lived for detection, i.e. <20 ns (Boate, D. R.; Scaiano, J. C. *Tetrahedron Lett.* **1989**, *30*, 4633).

[32] (a) Pryor, W. A.; Smith, K. *J. Am. Chem. Soc.* **1967**, *89*, 1741. (b) Pryor, W. A.; Smith, K. *J. Am. Chem. Soc.* **1970**, *92*, 5403.

[33] (a) Adams, J. S.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 9115. (b) Simpson, C. J. S. M.; Wilson, G. J.; Adam, W. *J. Am. Chem. Soc.* **1991**, *113*, 4728.

[34] Firestone, R. A. *J. Org. Chem.* **1980**, *45*, 3604.

[35] Rüchardt, C. *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 830. See also: Leroy, G.; Sana, M.; Wilante, C. Reference 1, pp 1−48. Leroy, G.; Sana, M.; Wilante, C. *J. Mol. Struct. (THEOCHEM)* **1990**, *205*, 97.

[36] O'Neal, H. E.; Benson, S. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. III.

of substituents. Consequently, significant contributions of ground state polar effects to the BDE will also influence the activation energy for bond homolysis (Figure 3, case A). Thus, for azoalkanes, electron acceptors weaken the polarized $ArC^{\delta+}—N^{\delta-}$ bond, i.e. they raise the relative energy of the ground state molecules, and this should lower the activation energy for bond homolysis and ultimately result in a faster thermolysis rate. Therefore, ground state polar effects will become more important the more polarization is lost in the transition state since this will increase the relative importance of the polar stabilization by substituents in the ground state. Thus, Timberlake's postulate[3] of a radical-type transition state for the azopropane thermolysis in eq 1 is not in conflict with the established polar effects as long as the polar contribution of the substituent manifests itself in the ground state molecules. Moreover, since solvent effects on the ground state molecules should be much less pronounced than on the transition states due to their much lower polarizability, the small effect of solvent polarity on azoalkane thermolyses[3d,e] is in line with this argument.

For radical reactions involving polar bonds, it is expected that a composite situation applies (Figure 3, case A), for which the trends in the experimental BDE will reflect transition state radical as well as ground state polar effects. In limiting cases, the radical contribution, i.e. the effects in the transition state (Figure 3, case B), will dominate. Thus, the contribution of ground state polar effects should be negligible for the homolysis of symmetrical alkanes[5] since the nonpolar C—C bond to be broken is much less sensitive to polar substituents than, for example, a polar C—N bond. However, for the general case A (Figure 3), it is *a priori* difficult to know whether RSE or PSE effects dominate. Such a situation applies to the azoalkanes **1—6** under consideration, and the two-parameter Hammett treatment (eq 6) is necessary to gain mechanistic insight on the nature of the action by the substituent. If one accepts the premise that ground state polar effects are operative in the thermal denitrogenation of azoalkanes and that they act in concert with radical-stabilizing effects (Figure 3, case A), their relative contributions are determined by the ϱ_{rad} and ϱ_{pol} values (Table 2).

Semiempirical Calculations. To corroborate the involvement of ground state polar effects in the thermal decompositions of azoalkanes, we have carried out semiempirical (AM1) calculations.[37] Since we assumed, as proposed previously by Arnold,[18a] that these effects derive from the stabilization (destabilization) of a polar bond by the reduction (increase) of the partial charges, computation of this effect requires a reliable reference for which polar effects are negligible. For the *p*-nitro- and *p*-amino-substituted azoalkanes **1—6**, we have selected as reference substances the corresponding *p*-amino- and *p*-nitro-substituted alkanes **7—12**, i.e. the respective nitrogen-free products of the azoalkanes.[38] The two *para* substituents, namely *p*-nitro (strongest electron acceptor) and *p*-amino (strongest electron donor), were chosen to provide the greatest possible spread in polar substituent properties. In contrast to the C—N bonds in the corresponding azoalkanes, the C—C bonds in such symmetrical alkanes are not polarized and should not be subject to ground state polar effects. Therefore, the difference in the calculated heats of formation $\Delta\Delta H_f$ (alkane) for the amino- and nitro-substituted alkanes **7—12** should solely represent the inherent energy change as caused by the different *para* substituents in the absence of polar effects (Table 3). The difference in the calculated heats of formation for the amino- and nitro-substituted azoalkanes **1—6** ($\Delta\Delta H_f$(azo)) is consistently larger than $\Delta\Delta H_f$(alkane), which indicates that an additional, supposedly polar, substituent effect on the azoalkanes operates.

Table 3. Calculated Heats of Formation[a] of the *p*-Nitro- and *p*-Amino-Substituted Azoalkanes **1—6** and the Corresponding Alkanes **7—12** and Calculated Ground State Polar Stabilization Energies (PSE)

AM1 Results[a]

	1	**2**[b]	**3**	**4**	**5**	**6**
$\Delta H_f(X = p\text{-}NO_2)$	151.93	90.37	88.27	94.17	68.22	101.76
$\Delta H_f(X = p\text{-}NH_2)$	142.56	81.89	79.40	85.52	60.26	91.07
$\Delta\Delta H_f$(azo)	9.37	8.48	8.87	8.65	7.96	10.69
	7	**8**[c]	**9**	**10**	**11**	**12**
$\Delta H_f(X = p\text{-}NO_2)$	126.24	41.73	36.26	41.63	25.86	77.84
$\Delta H_f(X = p\text{-}NH_2)$	118.53	34.38	28.67	33.71	18.81	69.64
$\Delta\Delta H_f$(alkane)	7.71	7.35	7.59	7.92	7.05	8.20
PSE[d]	1.66	1.13	1.28	0.73	0.91	2.49

[a] All given in kcal/mol; the amino hydrogens were kept in the plane of the phenyl ring to ensure identical conformations for all derivatives. [b] Other calculated ΔH_f values are 7.38 for X = *p*-OMe, 67.98 for X = *p*-Me, 83.46 for X = H, 68.97 for X = *p*-Cl, and 146.29 for X = *p*-CN. [c] Other calculated ΔH_f values are −40.36 for X = *p*-OMe, 20.03 for X = *p*-Me, 35.32 for X = H, 20.67 for X = *p*-Cl, and 97.82 for X = *p*-CN. [d] Ground state polar stabilization energies (PSE) for the azoalkanes calculated as PSE = $\Delta\Delta H_f$(azo) − $\Delta\Delta H_f$(alkane).

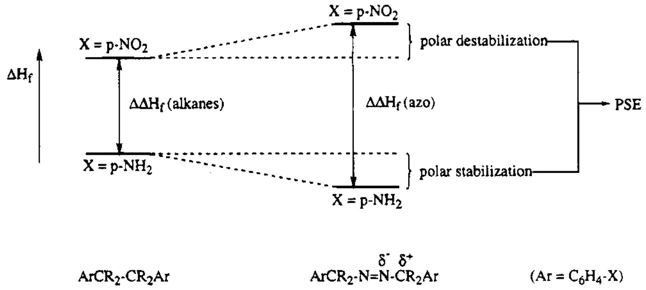

Figure 4. Schematic representation of ground state polar substituent effects on the heats of formation (ΔH_f) of *p*-amino- and *p*-nitro-substituted alkanes (e.g., **7—12**) and azoalkanes (e.g., **1—6**). The polarized C—N bond in the azoalkanes is stabilized (for *p*-amino) or destabilized (for *p*-nitro) relative to the alkanes. The enhanced difference between the heats of formation ($\Delta\Delta H_f$) for the azoalkanes is reproduced by semiempirical (AM1) calculations (Table 3).

If the values for $\Delta\Delta H_f$(alkane) are subtracted from $\Delta\Delta H_f$(azo), i.e. $\Delta\Delta H_f$(azo) − $\Delta\Delta H_f$(alkanes), one obtains values for the polar stabilization energy (PSE) in the ground states of the azoalkanes, which represent the maximum effects promoted by the extreme electron-accepting (*p*-NO_2) and electron-donating (*p*-NH_2) groups. The results are collected in Table 3, which for the set of azoalkanes **1—6** *versus* the corresponding alkanes **7—12** covers a range of 0.7—2.5 kcal/mol in PSE values (for two C—N bonds).

The qualitative trends of our model calculation are visualized in Figure 4. The increase in the $\Delta\Delta H_f$ values for the azoalkanes relative to the alkanes is attributed to the polar substituent effect on the positively charged benzylic carbon atom, which enhances (for *p*-nitro) or reduces (for *p*-amino) the charge. For *p*-nitro,

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[37] 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 4.4 program (Rauhut, G.; Chandrasekhar, J.; Clark, T. University of Erlangen, FRG, 1992) was used by employing a Silicon Graphics Iris Indigo workstation.

[38] Strictly speaking, the value for $\Delta\Delta H_f$(alkanes) should remain constant in the alkane series since the absence of ground state polar effects is postulated for all alkanes **7—12**. Thus, one alkane should be sufficient as the reference, but one finds that $\Delta\Delta H_f$ (alkanes) varies from 7.0 to 8.2 kcal/mol. We propose that increasing substitution (e.g., by alkyl groups for **8—11**) or through-bond interactions (e.g., through the methylene bridge in **12**) might alter the electronic effects of the aryl groups, which is ultimately reflected in the $\Delta\Delta H_f$ (alkane) values. We anticipated that such secondary effects (alkylation in **2—5** and through-bond interactions in **6**) are present in the azoalkanes **1—6** as well and, thus, have chosen the alkanes **7—12** as reference molecules.

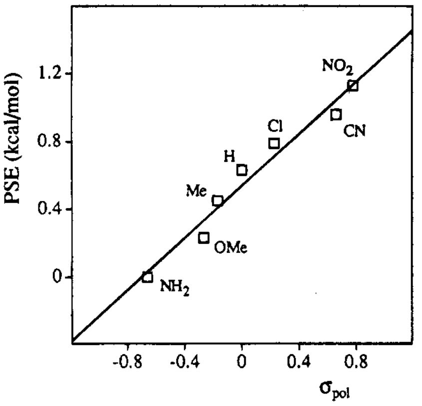

Figure 5. Plot of the calculated (AM1) ground state polar stabilization energies (PSE) for azocumene **2** relative to the alkane **8** for different *para* substituents X *versus* the Hammett σ_{pol} values.[20] Calculated data taken from Table 3 with PSE = $[\Delta H_f(\text{azo-X}) - \Delta H_f(\text{azo-NH}_2)] - [\Delta H_f(\text{alkane-X}) - \Delta H_f(\text{alkane-NH}_2)]$.

this corresponds to a relative destabilization of the C−N bond and, thus, of the molecule as a whole. *Vice versa*, a relative stabilization is predicted for *p*-amino.

Most gratifying is a plot of the calculated PSE values *versus* the Hammett σ_{pol} values, e.g. for azocumenes **2** (Figure 5). The PSE values for the various substituents were arbitrarily defined relative to that for the *p*-amino substituent, i.e. PSE = $[\Delta H_f(\text{azo-X}) - \Delta H_f(\text{azo-NH}_2)] - [\Delta H_f(\text{alkane-X}) - \Delta H_f(\text{alkane-NH}_2)]$. A good linear Hammett correlation (PSE = $0.767\sigma_{pol} + 0.536$; $r^2 = 0.964$; $n = 7$) was obtained which establishes unequivocally that polar effects on the ground state azoalkanes are significant in that they follow a linear free energy relationship.

The polar substituent effects on the ground state change merely the C−N bond strength. It is thus a justifiable assumption that the relative entropy contributions ($\Delta\Delta S$) to ground state polar effects are constant, such that the calculated PSE ($\Delta\Delta H$) values may be used as a measure for $\Delta\Delta G$ in the ground state azoalkanes. Due to the postulated origin of the polar effect (Figure 3, case C), the free enthalpy difference of the ground states ($\Delta\Delta G$) should be identical with the difference in the free enthalpy of activation ($\Delta\Delta G^{\ddagger}$). Hence, the expected polar contributions to $\Delta\Delta G^{\ddagger}$ can be directly estimated by using the calculated PSE values.

By making use of the relationship PSE $\approx \Delta\Delta G^{\ddagger}$, the slope of the Hammett plot for the PSE (Figure 5) can be employed for the calculation of a ϱ_{pol}^{calcd} value according to PSE = $2.30RT\varrho_{pol}^{calcd}\sigma_{pol}$ (cf. $\Delta\Delta G^{\ddagger} = 2.30RT\varrho_{pol}\sigma_{pol}$). Such analysis was performed for all azoalkanes **1−6** by using the theoretical data in Table 3 to yield the ϱ_{pol}^{calcd} values in Table 2, which represent the ground state polar effects for *two* C−N bonds. These values should be diagnostic for the polar contributions in those azoalkane decompositions[28] for which both C−N bonds are broken more or less simultaneously such that the polar (de)-stabilization of *both* C−N bonds will contribute to the activation energy. Consequently, if the mechanism for denitrogenation is stepwise,[29,33] i.e. cleavage of only one C−N bond in the rate-determining step, the ϱ_{pol}^{calcd} values in Table 2 need to be corrected for the statistical factor by division by 2 to reflect the actual experimental trends (thermolysis rates) on the activation energy.

The ϱ_{pol}^{calcd} values provide a quantitative measure of the substrate sensitivity to polar effects in the thermal decomposition of azoalkanes **1−6**. Comparison of these theoretical values with the experimental ϱ_{pol} values obtained from the two-parameter Hammett treatment provides a good agreement since the experimental ϱ_{pol} values range between 0.1 and 0.9 and the calculated ϱ_{pol}^{calcd} values between 0.2 and 1.1. It is also interesting to note that the order of the relative experimental and theoretical ϱ_{pol} values for the open-chain azoalkanes **2−5** is the same, i.e. **2** > **3** > **5** > **4**. The fact that the calculated and experimental ϱ_{pol} values are of the same order of magnitude and the finding that the simple semiempirical calculations (AM1) pick up such subtle electronic substituent effects imply that polar contributions in the thermal decomposition of azoalkanes are attributable to variations of the ground state energies. Since ground state polar effects may constitute a general phenomenon in homolytic reactions which involve polar bonds, the computational approach introduced herein presents a convenient tool for their detection.

In view of our success in assessing the polar contributions by substituents on the thermal decomposition rates of azoalkanes **1−6** in terms of the calculated polar stabilization energies in the ground state molecules (Table 3), an attempt was made to apply this method to estimate the polar character in the Timberlake azoalkane rate data[3] (eq 1). For this purpose, and by analogy to the azoalkanes **1−6** *versus* the alkanes **7−12**, the corresponding 2,3-disubstituted 2,3-dimethylbutanes (eq 1) were taken as reference systems. Unfortunately, steric effects dominate because the substituents are directly attached to the incipient carbon radical site and preclude any regular trends in the polar nature of this azoalkane homolysis. We contend that polar effects also play a role in Timberlake's system but radical effects dominate.

Conclusions

The present work has shown the advantages of employing substituted benzyl-type azoalkanes **1−6** to probe polar substituent effects rather than attaching the substituents directly at the incipient radical site as in Timberlake's case (eq 1).[3] It must be emphasized, however, that the availability of appropriate σ_{rad} scales like Creary's[6] and Arnold's[7] has made possible the present two-parameter Hammett treatment of polar effects in the thermolysis of azoalkanes **1−6**. In view of the successful analysis of azoalkane decompositions, it is quite astounding that literature examples for two-parameter Hammett treatments of polar effects in radical reactions are rare.[6a,d,7a,g,13b,15c,23d] Jackson has brought forward the pertinent argument[13b] that only few radical reactions are known, for which polar effects do *not* dominate, and the few reactions for which radical effects are particularly large have been employed themselves for the definition of radical stabilization scales.

The polar contributions in azoalkane decompositions were attributed to polar ground state effects in the azoalkanes. The key questions regarding such polar effects are (a) how effectively do they contribute compared to radical stabilization and (b) how can they be reliably diagnosed. In polar reactions, for example, the small ground state effects may not be differentiated from the much larger ones on the transition state; besides, since both effects are polar in nature, the same trends apply and these are described by the same set of Hammett substituent constants (σ_{pol}). In radical reactions, polar effects on the ground state are more easily detected and can be assessed by means of the two-parameter Hammett treatment (eq 6). Thereby, the quantification of polar contributions in azoalkane decompositions has been made possible and, interestingly, simple semiempirical calculations have proven to be a powerful predictor for such polar ground state effects.

Experimental Section

General Aspects. NMR spectra were recorded on a Bruker AC 200 or AC 250 instrument with $CDCl_3$ as the solvent and internal standard, unless stated differently. Infrared spectra were measured on a Perkin-Elmer Infrared Ratio Recording Spectrometer 1420, and UV spectra were run on a Hitachi U 3200 spectrophotometer. Melting points were taken on a Büchi SMP-535 apparatus, and the combustion analyses were performed by the Microanalytical Division of the Institute of Inorganic Chemistry (University of Wuerzburg). 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) with an adsorbent:substrate ratio of ca. 100:1. Thin layer chromatography (TLC) was performed on Polygram Sil G/UV$_{254}$ (40 × 80 mm) from Macherey & Nagel. Irradiations were carried out with the 333-, 353-, and 364-nm UV lines (widened beam) of a CW argon ion laser (INNOVA 100, Coherent Co.). The NMR assignments were made on the basis of known spectral data[8] of related compounds. ^{1}H NMR coupling constants are J_{HH} values, given in an accuracy of 0.2−1 Hz.

Syntheses. The preparation of the symmetrically substituted azoalkanes **1** with X = *p*-OMe, *p*-Me, H, *p*-F, *p*-Cl, *p*-Br, *m*-CN, and *p*-NO$_2$ and also of the unsymmetrically substituted azoalkanes **1** with X = *p*-OMe/*p*-NO$_2$ and *p*-Me/*p*-CO$_2$Me has been recently reported by us.[8] Below we present the synthesis of the *p*-CN, *m*-NO$_2$, *m*-I, and *p*-I derivatives.

Preparation of 2,2-Dimethyl-1,3-propanediones. The *m*-nitro- and *p*-cyano-substituted 1,3-diaryl-2,2-dimethyl-1,3-propanediones were prepared by the known procedure[8] through dimethylation of the corresponding 1,3-diaryl-1,3-propanediones and purified by column chromatography. The *m*-nitro- and *p*-cyano-substituted 1,3-diaryl-1,3-propanediones were prepared in analogy to literature known procedures[39] and purified by recrystallization. The *m*-iodo- and *p*-iodo-substituted 1,3-diaryl-2,2-dimethyl-1,3-propanediones were obtained through Sandmeyer reaction of the corresponding amino-substituted 1,3-diaryl-2,2-dimethyl-1,3-propanediones. The latter were prepared by catalytic reduction of their nitro-substituted derivatives.

1,3-Bis(4′-cyanophenyl)-1,3-propanedione:[39a] 59%, yellow plates, mp 220−222 °C, R_f = 0.30 (SiO$_2$, methylene chloride); IR (KBr) ν 3040, 2210, 1700, 1590, 1560, 1540, 1480, 1120, 1020, 850, 780; ^{1}H NMR (CDCl$_3$) δ 6.87 (s, 1 H, 2-H of enol), 7.81 (d, ^3J = 8.4 Hz, 4 H, 3′-H), 8.09 (d, ^3J = 8.4 Hz, 4 H, 2′-H); ^{13}C NMR (CDCl$_3$) δ 94.5 (d, C-2), 116.1 (s, C-4′), 117.9 (s, CN), 127.7 (d, C-2′), 132.6 (d, C-3′), 138.8 (s, C-1′), 184.1 (s, C-1 and C-3).

1,3-Bis(3′-nitrophenyl)-1,3-propanedione:[39b] 60%, yellow powder, mp 235−237 °C (ethanol); IR (KBr) ν 3060, 1680, 1600, 1580, 1530, 1420, 1340, 1070, 780, 710; ^{1}H NMR (CD$_3$S(O)CD$_3$) δ 7.69 (s, 1 H, 2-H of enol), 7.89 (t, ^3J = 8 Hz, 2 H, 5′-H), 8.50 (d, ^3J = 8 Hz, 2 H, 6′-H), 8.67 (d, ^3J = 8 Hz, 2 H, 4′-H), 8.91 (s, 2 H, 2′-H); ^{13}C NMR [CD$_3$S(O)CD$_3$] δ 94.6 (d, C-2), 123.3 (d, C-2′), 127.3 (d, C-4′), 130.2 (d, C-5′), 133.8 (s, C-1′), 135.0 (d, C-6′), 147.7 (s, C-3′), 184.5 (s, C-1 and C-3).

1,3-Bis(4′-cyanophenyl)-2,2-dimethyl-1,3-propanedione: 30%, colorless needles, mp 181−182 °C, R_f = 0.39 (SiO$_2$, methylene chloride); IR (KBr) ν 3080, 2980, 2220, 1710, 1730, 1700, 1390, 1330, 1250, 990; ^{1}H NMR (CDCl$_3$) δ 1.68 (s, 6 H, 2-CH$_3$), 7.65 (dd, ^3J = 8.8 Hz, ^4J = 4.8 Hz, 4 H, 3′-H), 7.89 (dd, ^3J = 8.8 Hz, ^4J = 4.8 Hz, 4 H, 2′-H); ^{13}C NMR (CDCl$_3$) δ 24.8 (q, 2-CH$_3$), 59.9 (s, C-2), 116.7 (s, C-4′), 117.4 (s, CN), 129.4 (d, C-2′), 132.6 (d, C-3′), 138.1 (s, C-1′), 198.3 (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, 75.00; H, 4.83; N, 9.19.

1,3-Bis(3′-nitrophenyl)-2,2-dimethyl-1,3-propanedione: 24%, slightly yellow powder, mp 134−135 °C, R_f = 0.63 (SiO$_2$, methylene chloride); IR (KBr) ν 3060, 2980, 2910, 1645, 1600, 1515, 1420, 1375, 1340, 1230, 1075, 990, 930, 810; ^{1}H NMR (CDCl$_3$) δ 1.74 (s, 6 H, 2-CH$_3$), 7.57 (dt, ^3J = 7.9 Hz, ^3J = 8.2 Hz, ^5J = 0.4 Hz, 2 H, 5′-H), 8.07 (ddd, ^3J = 7.9 Hz, ^4J = 2 Hz, ^4J = 1.0 Hz, 2 H, 6′-H), 8.31 (ddd, ^3J = 8.2 Hz, ^4J = 2 Hz, ^4J = 1.0 Hz, 2 H, 4′-H), 8.72 (dt, ^4J = 2 Hz, ^5J = 0.4 Hz, 2 H, 2′-H); ^{13}C NMR (CDCl$_3$) δ 24.9 (q, 2-CH$_3$), 58.8 (s, C-2), 124.0 (d, C-2′), 127.6 (d, C-4′), 130.2 (d, C-5′), 134.2 (d, C-6′), 136.4 (s, C-1′), 148.5 (s, C-3′), 197.5 (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, 59.90; H, 4.14; N, 7.95.

Preparation of the 1,3-Bis(aminophenyl)-2,2-dimethyl-1,3-propanediones by Catalytic Reduction. A sample of 5.00 mmol of *meta* or *para* derivatives of the appropriate 1,3-bis(nitrophenyl)-2,2-dimethyl-1,3-propanedione was dissolved in 20 mL of ethanol and 40 mL of ethyl acetate. The reduction was carried out under a hydrogen gas atmosphere with 0.5 g of Pd on charcoal catalyst within 10 h at ambient temperature. After filtration and solvent evaporation (40 °C, 30 Torr), the crude product was purified by recrystallization or by column chromatography on silica gel.

1,3-Bis(3′-aminophenyl)-2,2-dimethyl-1,3-propanedione: 97%, pale yellow powder, mp 169−170 °C (ethanol); IR (KBr) ν 3440, 3340, 2980, 2930, 1635, 1610, 1580, 1480, 1445, 1370, 1310, 1280; ^{1}H NMR (CDCl$_3$) δ 1.61 (s, 6 H, 2-CH$_3$), 3.55 (br s, 4 H, NH$_2$), 6.74 (dt, ^3J = 7.7 Hz, ^4J = 1.2 Hz, ^4J = 1 Hz, 2 H, 4′-H), 7.06 (t, ^3J = 7.7 Hz, 2 H, 5′-H), 7.13 (t, ^4J = 1 Hz, 2 H, 2′-H), 7.19 (dd, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 2 H, 6′-H); ^{13}C NMR (CDCl$_3$) δ 24.9 (q, 2-CH$_3$), 59.6 (s, C-2), 115.0 (d, C-2′), 119.5 (d, C-4′ and C-6′), 129.4 (d, C-5′), 136.7 (s, C-1′), 146.6 (s, C-3′), 200.5 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{18}N_2O_2$ (282.3): C, 72.32; H, 6.43; N, 9.92. Found: C, 72.41; H, 6.86; N, 9.78.

1,3-Bis(4′-aminophenyl)-2,2-dimethyl-1,3-propanedione: 96%, pale yellow powder, mp 214−215 °C, R_f = 0.45 (methylene chloride/methanol, 20:1); IR (KBr) ν 3450, 3330, 2980, 1650, 1580, 1520, 1460, 1435, 1380, 1310, 1280; ^{1}H NMR (CDCl$_3$) δ 1.59 (s, 6 H, 2-CH$_3$), 4.03 (br s, 4 H, NH$_2$), 6.48 (dd, ^3J = 8.8 Hz, ^4J = 5.0 Hz, 4 H, 3′-H), 7.70 (dd, ^3J = 8.8 Hz, ^4J = 5.0 Hz, 4 H, 2′-H); ^{13}C NMR (CDCl$_3$) δ 25.8 (q, 2-CH$_3$), 58.4 (s, C-2), 113.7 (d, C-3′), 126.0 (s, C-1′), 131.8 (d, C-2′), 150.7 (s, C-4′), 199.1 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{18}N_2O_2$ (282.3): C, 72.32; H, 6.43; N, 9.92. Found: C, 72.58; H, 6.77; N, 9.88.

Preparation of the 1,3-Bis(iodophenyl)-2,2-dimethyl-1,3-propanediones by Sandmeyer Iodination.[40] A sample of 4.00 mmol of the corresponding 1,3-bis(aminophenyl)-2,2-dimethyl-1,3-propanedione was dissolved in dilute sulfuric acid and the solution chilled by means of an ice bath. The diazotation was carried out at 0−5 °C with 607 mg (8.80 mmol) of sodium nitrite. The resulting diazonium salt solution was added dropwise to a chilled solution which contained 3.33 g (20.0 mmol) of potassium iodide in 25 mL of H$_2$O. The reaction mixture was stirred for 2 h at ambient temperature and afterward warmed up for 30 min to 80 °C. The precipitate was collected by means of filtration, dissolved in 20 mL of methylene chloride, and washed with saturated sodium thiosulfate solution (50 mL) and with H$_2$O (100 mL). The organic layer was dried over magnesium sulfate, and evaporation of the solvent (40 °C, 30 Torr) afforded the crude product, which was purified by column chromatography on silica gel.

1,3-Bis(3′-iodophenyl)-2,2-dimethyl-1,3-propanedione: 50%, colorless needles, mp 125−126 °C dec, R_f = 0.85 (SiO$_2$, methylene chloride); IR (KBr) ν 2980, 2900, 1660, 1640, 1540, 1390, 1370, 1230, 1210, 950; ^{1}H NMR (CDCl$_3$) δ 1.63 (s, 6 H, 2-CH$_3$), 7.03 (t, ^3J = 7.9 Hz, 2 H, 5′-H), 7.64 (ddd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, ^4J = 0.9 Hz, 2 H, 4′-H), 7.77 (ddd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, ^4J = 0.9 Hz, 2 H, 6′-H), 8.28 (t, ^4J = 1.8 Hz, 2 H, 2′-H); ^{13}C NMR (CDCl$_3$) δ 25.1 (q, 2-CH$_3$), 59.5 (s, C-2), 94.7 (s, C-3′), 127.9 (d, C-6′), 130.2 (d, C-5′), 137.0 (s, C-1′), 138.1 (d, C-2′), 141.9 (d, C-4′), 198.5 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{14}I_2O_2$ (504.1): C, 40.50; H, 2.80. Found: C, 40.39; H, 2.72.

1,3-Bis(4′-iodophenyl)-2,2-dimethyl-1,3-propanedione: 41%, colorless needles, mp 178−179 °C dec, R_f = 0.90 (SiO$_2$, methylene chloride); IR (KBr) ν 2980, 2900, 1650, 1630, 1560, 1540, 1465, 1445, 1375, 1250, 1230, 1160, 1050; ^{1}H NMR (CDCl$_3$) δ 1.63 (s, 6 H, 2-CH$_3$), 7.51 (dd, ^3J = 8.8 Hz, ^4J = 4.7 Hz, 4 H, 2′-H), 7.69 (dd, ^3J = 8.8 Hz, ^4J = 4.7 Hz, 4 H, 3′-H); ^{13}C NMR (CDCl$_3$) δ 25.1 (q, 2-CH$_3$), 59.3 (s, C-2), 101.6 (s, C-4′), 130.4 (d, C-2′), 134.5 (s, C-1′), 138.1 (d, C-3′), 199.1 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{14}I_2O_2$ (504.1): C, 40.50; H, 2.80. Found: C, 40.26; H, 2.74.

Preparation of the 3,5-Diaryl-4,4-dimethylisopyrazoles. The cyclizations of the 2,2-dimethyl-1,3-diones with hydrazine hydrate to the isopyrazoles were carried out according to the published procedure.[8] Only for the 3,5-bis(4′-cyanophenyl)-4,4-dimethyl-4*H*-pyrazole was the reaction completed within 1.5 h, which precipitated after cooling down of the reaction mixture. The crystalline precipitate was collected and washed with cold chloroform (10 mL) and methanol (20 mL).

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(39) (a) Anselme, J.-P. *J. Org. Chem.* **1967**, *32*, 3716. (b) Dayer, F.; Dao, H. L.; Gold, H; Rodé-Gowal, H.; Dahn, H. *Helv. Chim. Acta* **1974**, *57*, 2201.

(40) Lucas, H. J.; Kennedy, E. R. *Org. Synth. Collect. Vol. II*, **1948**, 351.

3,5-Bis(4′-cyanophenyl)-4,4-dimethyl-4*H*-pyrazole: 84%, colorless needles, mp 264−265 °C (methanol) dec; IR (KBr) ν 3040, 2980, 2210, 1590, 1485, 1450, 1390, 1340, 1270, 850; ^{1}H NMR (CD$_3$C(O)CD$_3$) δ 1.78 (s, 6 H, 4-CH$_3$), 7.98 (dd, ^{3}J = 8.8 Hz, ^{4}J = 4.8 Hz, 4 H, 2′-H), 8.37 (dd, ^{3}J = 8.8 Hz, ^{4}J = 4.8 Hz, 4 H, 3′-H); ^{13}C NMR (CD$_3$C(O)CD$_3$) δ 22.2 (q, 4-CH$_3$), 59.9 (s, C-4), 115.1 (s, C-4′), 118.9 (s, CN), 129.6 (d, C-2′), 133.6 (d, C-3′), 134.8 (s, C-1′), 179.4 (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, 76.25; H, 4.80; N, 18.78.

3,5-Bis(3′-nitrophenyl)-4,4-dimethyl-4*H*-pyrazole: 80%, colorless powder, mp 230−231 °C (benzene/cyclohexane); IR (KBr) ν 3040, 2980, 1565, 1520, 1450, 1420, 1340, 1085, 750, 700; ^{1}H NMR (CDCl$_3$) δ 1.79 (s, 6 H, 4-CH$_3$), 7.75 (t, ^{3}J = 8.0 Hz, 2 H, 5′-H), 8.40 (ddd, ^{3}J = 8.0 Hz, ^{4}J = 2 Hz, ^{4}J = 1.1 Hz, 2 H, 6′-H), 8.51 (ddd, ^{3}J = 8.0 Hz, ^{4}J = 2 Hz, ^{4}J = 1.1 Hz, 2 H, 4′-H), 8.88 (t, ^{4}J = 2 Hz, 2 H, 2′-H); ^{13}C NMR (CDCl$_3$) δ 22.4 (q, 4-CH$_3$), 59.0 (s, C-4), 122.5 (d, C-2′), 125.8 (d, C-4′), 130.3 (d, C-5′), 131.1 (s, C-1′), 133.7 (d, C-6′), 148.6 (s, C-3′), 177.8 (s, C-3 and C-5). Anal. Calcd for $C_{17}H_{14}N_4O_4$ (338.3): C, 60.35; H, 4.17; N, 16.56. Found: C, 60.20; H, 4.29; N, 16.88.

3,5-Bis(3′-iodophenyl)-4,4-dimethyl-4*H*-pyrazole: 86%, colorless needles, mp 157−158 °C dec, R_f = 0.32 (SiO$_2$, methylene chloride/methanol, 40:1); IR (KBr) ν 3040, 2960, 1540, 1495, 1440, 1395, 1320, 1150, 985, 790; ^{1}H NMR (CDCl$_3$) δ 1.66 (s, 6 H, 4-CH$_3$), 7.24 (t, ^{3}J = 7.9 Hz, 2 H, 5′-H), 7.84 (ddd, ^{3}J = 7.9 Hz, ^{4}J = 1.6 Hz, ^{4}J = 1.1 Hz, 2 H, 4′-H), 7.99 (ddd, ^{3}J = 7.9 Hz, ^{4}J = 1.6 Hz, ^{4}J = 1.1 Hz, 2 H, 6′-H), 9.13 (t, ^{4}J = 1.6 Hz, 2 H, 2′-H); ^{13}C NMR (CDCl$_3$) δ 22.5 (q, 4-CH$_3$), 58.7 (s, C-4), 94.6 (s, C-3′), 126.9 (d, C-6′), 130.4 (d, C-5′), 131.7 (d, C-1′), 136.7 (s, C-2′), 139.8 (d, C-4′), 177.9 (s, C-3 and C-5). Anal. Calcd for $C_{17}H_{14}I_2N_4$ (500.1): C, 40.83; H, 2.82; N, 5.60. Found: C, 41.19; H, 2.92; N, 5.64.

3,5-Bis(4′-iodophenyl)-4,4-dimethyl-4*H*-pyrazole: 57%, pale yellow needles, mp 255−256 °C dec, R_f = 0.70 (SiO$_2$, methylene chloride/methanol, 20:1); IR (KBr) ν 3060, 2975, 1580, 1505, 1470, 1445, 1380, 1050, 990, 820; ^{1}H NMR (CDCl$_3$) δ 1.66 (s, 6 H, 4-CH$_3$), 7.83 (mc, 8 H, 2′-H and 3′-H); ^{13}C NMR (CDCl$_3$) δ 22.7 (q, 4-CH$_3$), 58.5 (s, C-4), 98.0 (s, C-4′), 129.0 (s, C-1′), 129.3 (d, C-2′), 138.2 (d, C-3′), 178.5 (s, C-3 and C-5). Anal. Calcd for $C_{17}H_{14}I_2N_4$ (500.1): C, 40.83; H, 2.82; N, 5.60. Found: C, 41.05; H, 2.98; N, 5.52.

Preparation of the Azoalkanes 1. The syntheses of the azoalkanes **1** with X = *p*-CN, *m*-NO$_2$, *m*-I, and *p*-I substituents were carried out under the same conditions as described.[8] Analytically pure samples were obtained by column chromatography on silica gel. The atom numbering for the NMR assignments of azoalkanes **1** is shown in eq 5.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-1,4-bis(4′-cyanophenyl)-8,8-dimethyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1, X = *p*-CN): 78%, colorless powder, mp 182−182 °C dec, R_f = 0.57 (SiO$_2$, methylene chloride/methanol, 40:1); IR (KBr) ν 3040, 2960, 2880, 2820, 2205, 1590, 1490, 1450, 1380, 1360, 810; UV (C$_6$H$_6$) λ_{max} (log ϵ) 360 nm (2.269), 347 (2.007, sh), 327 (1.531, sh); ^{1}H NMR (CDCl$_3$) δ 0.17 (s, 3 H, *exo*-8-CH$_3$), 1.06 (s, 3 H, *endo*-8-CH$_3$), 2.21 (mc, ^{2}J = 12.5 Hz, 2 H, 7-H), 3.65 (ddd, ^{3}J = 9.6 Hz, ^{3}J = 8.9 Hz, ^{3}J = 5.1 Hz, 1 H, 7a-H), 4.11 (ddd, ^{3}J = 8.9 Hz, ^{3}J = 3.6 Hz, ^{4}J = 2.1 Hz, 1 H, 4a-H), 5.44 (ddd, ^{3}J = 6.9 Hz, ^{3}J = 4.0 Hz, ^{4}J = 2.1 Hz, 1 H, 5-H), 5.54 (ddd, ^{3}J = 6.9 Hz, ^{3}J = 4.0 Hz, ^{4}J = 2.1 Hz, 1 H, 6-H), 7.81 (mc, 4 H, 3′-H), 7.91 (mc, 4 H, 2′-H); ^{13}C NMR (CDCl$_3$) δ 16.8 (q, C-9), 17.4 (q, C-10), 31.4 (t, C-7), 43.5 (d, C-7a), 57.1 (d, C-4a), 65.0 (s, C-8), 96.6 (s, C-1), 97.7 (s, C-4), 112.1 (s, C-4′), 118.6 (s, CN), 126.1 (d, C-6), 127.9 and 128.2 (2 × d, C-2′), 132.4 (d, C-3′), 134.2 (d, C-5), 140.6 and 140.7 (2 × s, C-1′). Anal. Calcd for $C_{24}H_{20}N_4$ (364.5): C, 79.10; H, 5.53; N, 15.37. Found: C, 79.53; H, 5.75; N, 14.89.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-bis(3′-nitrophenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1, X = *m*-NO$_2$): 71%, pale yellow powder, mp 175−176 °C dec, R_f = 0.36 (SiO$_2$, methylene chloride); IR (KBr) ν 3060, 2970, 2900, 2820, 1520, 1540, 1470, 1420, 1380, 1365, 1335; UV (C$_6$H$_6$) λ_{max} (log ϵ) 359 nm (2.813); ^{1}H NMR (CDCl$_3$) δ 0.23 (s, 3 H, *exo*-8-CH$_3$), 1.11 (s, 3 H, *endo*-8-CH$_3$), 2.21 (mc, ^{2}J = 12.3 Hz, ^{3}J = 9.8 Hz, 2 H, 7-H), 3.72 (ddd, ^{3}J = 9.8 Hz, ^{3}J = 8.5 Hz, ^{3}J = 4.9 Hz, 1 H, 7a-H), 4.19 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 4.0 Hz, 1 H, 4a-H), 5.47 (ddd, ^{3}J = 6.1 Hz, ^{3}J = 4.0 Hz, 1 H, 5-H), 5.57 (ddd, ^{3}J = 6.1 Hz, ^{3}J = 4.0 Hz, 1 H, 6-H), 7.64 (mc, 2 H, 5′-H), 7.73 (mc, 2 H, 6′-H), 7.77 (mc, 2 H, 4′-H), 8.05 (mc, 2 H, 2′-H); ^{13}C NMR (CDCl$_3$) δ 16.8 (q, C-9), 17.4 (q, C-10), 31.4 (t, C-7), 43.7 (d, C-7a), 57.2 (d, C-4a), 64.8 (s, C-8), 96.4 (s, C-1), 97.5 (s, C-4), 121.8 and 122.2 (2 × d, C-2′), 123.2 and 123.3 (2 × d, C-4′), 126.1 (d, C-6), 129.7 (d, C-5′), 133.5 and 133.9 (2 × d, C-6′), 134.3 (d, C-5), 137.5 and 137.6 (2 × s, C-1′), 148.5 (s, C-3′). Anal. Calcd for $C_{22}H_{20}N_4O_4$ (404.4): C, 65.34; H, 4.98; N, 13.85. Found: C, 65.19; H, 5.13; N, 13.86.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-1,4-bis(3′-iodophenyl)-8,8-dimethyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1, X = *m*-I): 62%, colorless needles, mp 180−181 °C dec, R_f = 0.46 (SiO$_2$, methylene chloride); IR (KBr) ν 3020, 2890, 2820, 1570, 1490, 1460, 1390, 1360, 1270, 990; UV (C$_6$H$_6$) λ_{max} (log ϵ) 360 nm (2.415), 349 (2.161, sh), 327 (1.777, sh); ^{1}H NMR (CDCl$_3$) δ 0.19 (s, 3 H, *exo*-8-CH$_3$), 1.01 (s, 3 H, *endo*-8-CH$_3$), 2.20 (mc, ^{2}J = 9.1 Hz, 2 H, 7-H), 3.56 (ddd, ^{3}J = 8.9 Hz, ^{3}J = 5.5 Hz, 1 H, 7a-H), 4.03 (mc, ^{3}J = 8.9 Hz, 1 H, 4a-H), 5.49 (mc, 2 H, 5-H and 6-H), 7.23 (dt, ^{3}J = 7.9 Hz, 2 H, 5′-H), 7.74 (m, 4 H, 4′-H and 6′-H), 8.13 (mc, 2 H, 2′-H); ^{13}C NMR (CDCl$_3$) δ 16.9 (q, C-9), 17.3 (q, C-10), 31.5 (t, C-7), 43.2 (d, C-7a), 56.8 (d, C-4a), 64.4 (s, C-8), 94.7 (s, C-3′), 96.2 (s, C-1), 97.3 (s, C-4), 126.4 and 126.6 (2 × d, C-6′), 126.8 (d, C-6), 130.2 (d, C-5′), 133.9 (d, C-5), 136.1 (d, C-4′), 136.4 and 137.0 (2 × s, C-1′), 137.1 and 138.0 (2 × d, C-2′). Anal. Calcd for $C_{22}H_{20}I_2N_2$ (566.2): C, 46.67; H, 3.56; N, 4.95. Found: C, 46.72; H, 3.38; N, 4.78.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-1,4-bis(4′-iodophenyl)-8,8-dimethyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1, X = *p*-I): 64% colorless needles, mp 183−184 °C dec, R_f = 0.42 (SiO$_2$, methylene chloride); IR (KBr) ν 3030, 2920, 1570, 1470, 1450, 1380, 1360, 1340, 1290, 1160, 1090, 1000; UV (C$_6$H$_6$) λ_{max} (log ϵ) 356 nm (2.596), 346 (2.448), 326 (2.415); ^{1}H NMR (CDCl$_3$) δ 0.16 (s, 3 H, *exo*-8-CH$_3$), 0.98 (s, 3 H, *endo*-8-CH$_3$), 2.18 (mc, ^{2}J = 8.3 Hz, 2 H, 7-H), 3.57 (ddd, ^{3}J = 8.6 Hz, ^{3}J = 6.2 Hz, 1 H, 7a-H), 4.03 (mc, ^{3}J = 8.6 Hz, 1 H, 4a-H), 5.48 (mc, 2 H, 5-H and 6-H), 7.52 (mc, 4 H, 2′-H), 7.83 (mc, 4 H, 3′-H); ^{13}C NMR (CDCl$_3$) δ 16.8 (q, C-9), 17.3 (q, C-10), 31.5 (t, C-7), 43.2 (d, C-7a), 56.7 (d, C-4a), 64.2 (s, C-8), 93.8 and 93.9 (2 × s, C-4′), 96.5 (s, C-1), 97.6 (s, C-4), 126.7 (d, C-6), 129.1 and 129.5 (2 × d, C-2′), 133.8 (d, C-5), 135.2 and 135.3 (2 × s, C-1′), 137.6 (d, C-3′). Anal. Calcd for $C_{22}H_{20}I_2N_2$ (566.2): C, 46.67; H, 3.56; N, 4.95. Found: C, 46.65; H, 3.46; N, 4.95.

Preparation of the Housanes 7. (i) Direct photolyses: Irradiation of the particular azoalkane **1** (0.200 mmol with X = *p*-CN, *m*-NO$_2$, *m*-I, and *p*-I substituents) in 3 mL of degassed C$_6$H$_6$ with the 333-, 351-, and 364-nm (2.0 W) lines of a CW argon ion laser afforded the corresponding housanes **7**.[8] (ii) Thermolyses: The above housanes **7** were also obtained by refluxing the corresponding azoalkanes **1** (0.200 mmol) dissolved in 20 mL of toluene for 8 h.[8] Purification was accomplished by column chromatography on silica gel.

2,4-Bis(4′-cyanophenyl)-3,3-dimethyl-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene (7, X = *p*-CN): 96%, colorless microcrystalline powder, mp 198−200 °C, R_f = 0.47 (SiO$_2$, methylene chloride); IR (KBr) ν 3040, 2910, 2880, 2820, 2200, 1580, 1480, 1390, 820, 710; ^{1}H NMR (CDCl$_3$) δ 0.71 (s, 3 H, *exo*-3-CH$_3$), 1.58 (s, 3 H, *endo*-3-CH$_3$), 2.19 (ddd, ^{2}J = 17.1 Hz, ^{3}J = 4.4 Hz, ^{3}J = 2.4 Hz, 1 H, 8-H), 2.51 (dddd, ^{2}J = 17.1 Hz, ^{3}J = 9.2 Hz, ^{3}J = 4.0 Hz, 1 H, 8-H), 2.94 (ddd, ^{3}J = 9.2 Hz, ^{3}J = 4.4 Hz, ^{3}J = 1.6 Hz, 1 H, 1-H), 3.36 (mc, 1 H, 5-H), 5.42 (dt, ^{3}J = 5.6 Hz, ^{3}J = 2.4 Hz, 1 H, 7-H), 5.82 (mc, ^{3}J = 5.6 Hz, 1 H, 6-H), 7.45 (dd, ^{3}J = 8.3 Hz, ^{4}J = 4.8 Hz, 4 H, 2′-H), 7.57 (dd, ^{3}J = 8.3 Hz, ^{4}J = 4.8 Hz, 4 H, 3′-H); ^{13}C NMR (CDCl$_3$) δ 15.4 (q, C-9), 22.1 (q, C-10), 33.1 (d, C-3), 34.3 (t, C-8), 40.1 (d, C-1), 47.2 (s, C-2), 51.0 (d, C-5), 51.9 (s, C-4), 109.9 (s, C-4′), 118.9 and 119.0 (2 × s, CN), 130.2 (d, C-6), 130.4 and 130.7 (2 × d, C-2′), 131.5 and 131.7 (2 × d, C-3′), 132.7 (d, C-7), 142.8 and 143.2 (2 × s, C-1′). Anal. Calcd for $C_{24}H_{20}N_4$ (336.4): C, 85.68; H, 5.99; N, 8.33. Found: C, 85.78; H, 6.05; N, 7.92.

2,4-Bis(3′-nitrophenyl)-3,3-dimethyl-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene (7, X = *m*-NO$_2$): 97%, pale yellow powder, mp 79−80 °C, R_f = 0.85 (SiO$_2$, methylene chloride); IR (KBr) ν 3100, 2890, 2820, 1560, 1520, 1380, 1090, 800, 730, 685; ^{1}H NMR (CDCl$_3$) δ 0.75 (s, 3 H, *exo*-3-CH$_3$), 1.63 (s, 3 H, *endo*-3-CH$_3$), 2.21 (ddt, ^{2}J = 17.8 Hz, ^{3}J = 5.4 Hz, ^{3}J= 2.4 Hz, 1 H, 8-H), 2.53 (dddd, ^{2}J = 17.8 Hz, ^{3}J = 9.2 Hz, ^{3}J = 4.0 Hz, ^{3}J = 2.2 Hz, 1 H, 8-H), 2.97 (ddd, ^{3}J = 9.2 Hz, ^{3}J = 4.4 Hz, ^{3}J = 1.6 Hz, 1 H, 1-H), 3.39 (mc, 1 H, 5-H), 5.43 (dt, ^{3}J = 5.7 Hz, ^{3}J = 2.4 Hz, 1 H, 7-H), 5.87 (mc, ^{3}J = 5.7 Hz, 1 H, 6-H), 7.46 (mc, 4 H, 5′-H and 6′-H), 8.01 (mc, 2 H, 2′-H), 8.08 (mc, 2 H, 4′-H); ^{13}C NMR (CDCl$_3$) δ 15.2 (q, C-9), 22.3 (q, C-10), 32.4 (s, C-3), 34.3 (t, C-8), 40.0 (d, C-1), 46.5 (s, C-2), 51.1 (d, C-5), 51.3 (s, C-4), 121.4 (d, C-2′), 124.4 and 124.6 (2 × d, C-4′), 128.7 and 128.9 (2 × d, C-5′), 130.2 (d, C-6), 132.9 (d, C-7), 136.0 and 136.2 (2 × d, C-6′), 139.0 (s, C-1′), 148.0 (s, C-3′). Anal. Calcd for $C_{22}H_{20}N_2O_4$ (376.4): C, 70.20; H, 5.36; N, 7.44. Found: C, 69.91; H, 5.53; N, 7.19.

2,4-Bis(3′-iodophenyl)-3,3-dimethyl-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene (7, X = *m*-I): 96%, colorless needles, mp 80−81 °C, $R_f = 0.90$ (SiO$_2$, methylene chloride/*n*-pentane, 1:1); IR (KBr) ν 3020, 2900, 2820, 1570, 1460, 1440, 990, 800, 780, 690; ^{1}H NMR (CDCl$_3$) δ 0.72 (s, 3 H, *exo*-3-CH$_3$), 1.55 (s, 3 H, *endo*-3-CH$_3$), 2.26 (dddd, $^2J = 17.6$ Hz, $^3J = 4.5$ Hz, $^3J = 3.3$ Hz, $J = 2.4$ Hz, 1 H, 8-H), 2.45 (dddd, $^2J =$ 17.6 Hz, $^3J = 9.0$ Hz, $^3J = 4.0$ Hz, $J = 2.1$ Hz, 1 H, 8-H), 2.84 (ddd, $^3J = 9.0$ Hz, $^3J = 4.5$ Hz, $^3J = 1.8$ Hz, 1 H, 1-H), 3.27 (mc, 1 H, 5-H), 5.46 (dt, $^3J = 5.7$ Hz, $^3J = 2.4$ Hz, 1 H, 7-H), 5.81 (mc, $^3J = 5.7$ Hz, 1 H, 6-H), 6.96−7.13 (m, 4 H, arom), 7.51−7.57 (m, 4 H, arom); ^{13}C NMR (CDCl$_3$) δ 15.2 (q, C-9), 22.4 (q, C-10), 31.9 (s, C-3), 34.3 (t, C-8), 40.0 (d, C-1), 46.3 (s, C-2), 50.8 (d, C-5), 51.0 (s, C-4), 93.7 (s, C-3′), 129.2 and 129.3 (2 × d, C-5′), 130.7 (d, C-6, C-6′), 132.4 (d, C-7), 134.96 and 135.00 (d, C-2′), 138.6 (d, C-4′), 139.7 (s, C-1′). Anal. Calcd for $C_{22}H_{20}I_2$ (538.2): C, 49.10; H, 3.75. Found: C, 48.89; H, 3.92.

2,4-Bis(4′-iodophenyl)-3,3-dimethyl-*endo*-tricyclo[3.3.0.0^{2,4}]oct-6-ene (7, X = *p*-I): 97%, colorless needles, mp 151−152 °C, $R_f = 0.85$ (SiO$_2$, methylene chloride/*n*-pentane, 1:1); IR (KBr) ν 3020, 2900, 2880, 2800, 1465, 1420, 1370, 990, 800, 750; ^{1}H NMR (CDCl$_3$) δ 0.70 (s, 3 H, *exo*-3-CH$_3$), 1.53 (s, 3 H, *endo*-3-CH$_3$), 2.24 (dq, $^2J = 17.6$ Hz, $^3J = 3.3$ Hz, $^3J = 2.3$ Hz, 1 H, 8-H), 2.44 (ddq, $^2J = 17.6$ Hz, $^3J = 8.9$ Hz, $^3J = 2.2$ Hz, 1 H, 8-H), 2.83 (ddd, $^3J = 8.9$ Hz, $^3J = 4.5$ Hz, $^3J = 2.2$ Hz, 1 H, 1-H), 3.27 (mc, 1 H, 5-H), 5.44 (dt, $^3J = 5.7$ Hz, $^3J =$ 2.3 Hz, 1 H, 7-H), 5.78 (mc, $^3J = 5.7$ Hz, 1 H, 6-H), 6.88 (mc, 4 H, 2′-H), 7.58 (mc, 4 H, 3′-H); ^{13}C NMR (CDCl$_3$) δ 15.3 (q, C-9), 22.3 (q, C-10), 31.7 (s, C-3), 34.3 (t, C-8), 39.9 (d, C-1), 46.2 (s, C-2), 50.8 (d, C-5), 50.9 (s, C-4), 91.3 (s, C-4′), 130.8 (d, C-6), 131.9 (d, C-2′), 132.3 (d, C-7), 136.7 (d, C-3′), 136.9 and 137.6 (2 × s, C-1′). Anal. Calcd for $C_{22}H_{20}I_2$ (538.2): C, 49.10; H, 3.75. Found: C, 48.80; H, 3.82.

Kinetics. A sample of 150 mg (0.48 mmol) of the unsubstituted azoalkane **1** (X = H) was dissolved in 7 mL deuteriotoluene and refluxed ($T = 110.0 \pm 0.5$ °C). The disappearance of **1** was determined at regular time intervals up to 90% conversion by removal of aliquots (0.7 mL). The relative amounts of the remaining azoalkane were directly determined by quantitative ^{1}H NMR spectroscopy of the *gem* dimethyl proton signals of the azoalkanes (δ 0.21 and 1.02) and housanes (δ 0.79 and 1.62). A first-order plot gave a good linear correlation ($r^2 = 0.996$, $n = 9$). From the slope of this plot, the absolute thermolysis rate constant for the unsubstituted azoalkane **1** (X = H) was determined to be $(6.19 \pm 0.12) \times 10^{-5}$ s^{-1}.

For the other derivatives, 15-mM stock solutions of each azoalkane **1** were prepared in toluene (the solvent was passed through basic aluminum oxide to remove acid traces which could lead to cycloreversion[8]). A 3.0-mL aliquot was placed into a 5-mL round-bottomed flask, equipped with a reflux condenser, and heated at reflux for 90 min ($T = 110.0 \pm 0.5$ °C), except for the *p*-CN and *p*-NO$_2$ derivatives (50 min). The disappearance of the azoalkanes **1** and the formation of the housanes **7** was measured by quantitative ^{1}H NMR spectroscopy by using the characteristic resonances of the *gem* dimethyl groups of the azoalkanes **1** ($\delta \approx 0.2$ and 1.0) and of the housanes **7** ($\delta \approx 0.7$ and 1.6). The rate constants k_X (Table 1) were calculated from the ^{1}H NMR data by first-order kinetics; the error in the rate data is ca. ±3%.

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