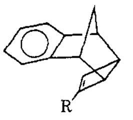
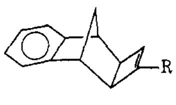
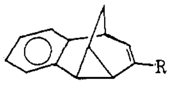
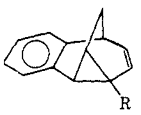
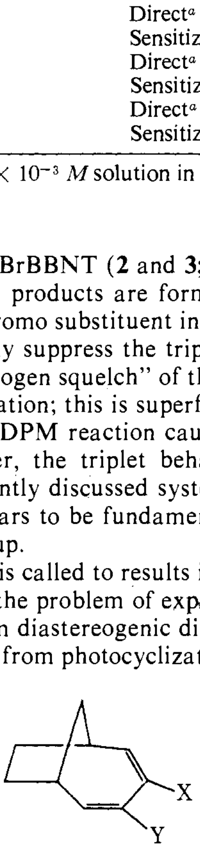
Table I. Product Distributions from Irradiations of 3-Substituted Benzo[7,8]bicyclo[4.2.1]nona-2,4,7-trienes

Triene	Irradiation mode	Products (%)			
					
1	Direct[a]	23	17	60	
(R = H)	Sensitized[b]	0	0	100[c]	
2	Direct[a]	48	52	~0	~0
(R = Cl)	Sensitized[b]	68	32	0	0
3	Direct[a]	64	36	~0	~0
(R = Br)	Sensitized[b]	61	39	0	0
4	Direct[a]	70	20	7.8	~2.2
(R = CH_3)	Sensitized[b]	0	0	21	79

[a] Corex filter, *ca.* 5 × 10^{-3} *M* solution in pentane or ether. [b] Acetone or Michler's ketone. [c] Some dimer was isolated, but no other monomers.

istry of 3-Cl- and 3-BrBBNT (**2** and **3**; Table I) is striking; essentially *no* DPM products are formed. Thus, introduction of a chloro or bromo substituent into the 3-position of **1** suffices to completely suppress the triplet DPM rearrangement. A similar "halogen squelch" of the DPM reaction occurs on direct irradiation; this is superficially similar to the reduction in singlet DPM reaction caused by the 3-methyl substituent. However, the triplet behavior of **2** and **3** is unique among presently discussed systems; the halogen effect, therefore, appears to be fundamentally different from that of a methyl group.

Finally, attention is called to results in Table I which add a new dimension to the problem of explaining exo–endo cyclobutene ratios from diastereogenic dienes (*e.g.*, **13–15**).[14] The exo–endo ratios from photocyclization of **13–15** (30:70, 53:47, and 60:40, respectively) led Jefford and Delay to suggest that the two-carbon bridge of **13** offers less hindrance than the one-carbon bridge to the cyclobutene "nascent double bond." The ratios observed for **1** and **10** (42:58 and 27:73[8c,11]) support this analysis, and further indicate that an unsaturated two-carbon bridge creates about the same steric effect as a saturated two-carbon bridge. In this context, the decrease in the ratio for 3-MeBBNT (**4**) (22:78) is not unexpected.



13, X = Y = H
14, X = Cl; Y = H
15, X = Y = Cl

However, the behavior of the chlorotrienes (**2**, **14**, and **15**) is anomalous; enhanced exo formation occurs. Jefford and Delay ascribed this to attraction between polarizable chlorine(s) and the methylene bridge. Yet this second factor still is insufficient; sensitization of chlorotriene **2** causes a remarkable change in the cyclobutene ratio in favor of the endo isomer (32:68). We conclude that steric, polar, and multiplicity effects all must be among the factors considered. In this light, it is pertinent to note the *small* change in exo–endo ratio on direct *vs.* sensitized irradiation of 3-BrBBNT (**3**). This is consistent with a heavy-atom effect;[15] *i.e.*, the bromine may so facilitate $S_1 \rightarrow T_1$ intersystem crossing that reaction of **3** occurs almost completely from T_1, regardless of the identity of the initial excited state.

Further study of these highly reactive compounds and related structures is in progress.

References and Notes

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(9) The photodimer has mp 203–205°; mass spec (70 eV) *m/e* 336 ($M\cdot^+$, 0.23% of base; mol wt calcd for $C_{26}H_{24}$ = 336), 337 (M + 1, ~30% of M; M + 1 calcd for $C_{26}H_{24}$ = 28% of M), 168 (base peak), pattern at lower *m/e* values very similar to mass spectra of 1; pmr ($CDCl_3$) τ 6.02 (2 H, dd, J = 10, 9 Hz, vinyl H's) and 6.70 (2 H, dd, J = 10, 4 Hz, vinyl H's). Presence of only two types of vinyl protons indicates a [2 + 2] adduct; discussion of stereoisomeric possibilities and reasons for the apparently high stereoselectivity is deferred to our full paper.
(10) At the quencher concentrations cited, both singlet and triplet quenching almost certainly occur. However, for the product distribution to remain unchanged, both quenching modes would have to be equally efficient for both quenchers. We regard this as unlikely.
(11) The triplet selectivity of **4** is attributable to formation of the more stable of two possible triplet diradicals *via* 2,8-bridging; rationalization of the reversed singlet selectivity is more elusive.
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(16) National Science Foundation Trainee, 1973.

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Polar Effects in Radical Reactions. IV. Nucleophilic Character of the 3-Heptyl Radical[1]

Sir:

Hammett $\sigma\rho$ correlations for hydrogen abstraction from the side chain of ring-substituted toluenes (eq 1) have been reported for a number of radicals.[2] Polar effects arguments

$$R\cdot + CH_3C_6H_4X \xrightarrow{k_H} RH + \cdot CH_2C_6H_4X \qquad (1)$$

Table I. Ionization Potentials, Electron Affinities, and ΔH for Abstract of Hydrogen from Toluene for Various Alkyl Radicals

Radical	Ionization potential[a]	Electron affinity[a]	ΔH[a,b]	Temp, °C	ρ[c]
$CH_3\cdot$	227[d]	26[e]	−17	100	-0.17 ± 0.06[f]
$RCH_2\cdot$	200[d,g]	16[h]	−13	80	0.47 ± 0.07[i]
				81	0.50 ± 0.02[j]
$R_2CH\cdot$	180[d,k]	11[l]	−9	80	0.70 ± 0.09[m]
$R_3C\cdot$	167[d,n]		−6	30	0.99 ± 0.06[o]

[a] In kcal/mol. [b] Bond strength data were taken from J. A. Kerr, *Chem. Rev.*, **66,** 465 (1966). [c] For hydrogen abstraction from a series of substituted toluenes. [d] J. L. Franklin in "Carbonium Ions," Vol. I, G. A. Olah and P. v. R. Schleyer, ed., Interscience, New York, N. Y., 1968, pp 85–88. [e] R. S. Neale, *J. Phys. Chem.*, **68,** 143 (1964). [f] W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34,** 2018 (1969). [g] Value for 1-propyl and 1-butyl radicals. [h] F. M. Page, *Advan. Chem. Ser.*, **No. 36,** 68 (1962); value for 1-propyl and 1-butyl radicals. [i] R. W. Henderson and R. D. Ward, Jr., *J. Amer. Chem. Soc.*, in press; value for the 1-undecyl radical. [j] W. A. Pryor and W. H. Davis, Jr., *ibid.*, in press; value for the 1-undecyl radical. [k] An average of values for these radicals: 2-propyl, 182; 2-butyl, 182; 2-pentyl, 178; 3-pentyl, 181; cyclohexyl, 177. [l] H. O. Pritchard, *Chem. Rev.*, **52,** 529 (1953); value for 2-propyl radical. [m] This work; value for the 3-heptyl radical. [n] An average of values for these radicals: *tert*-butyl, 171; *tert*-amyl, 164. [o] W. A. Pryor, W. H. Davis, Jr., and J. P. Stanley, *J. Amer. Chem. Soc.*, **95,** 4754 (1973); value for the *tert*-butyl radical.

have commonly been invoked to rationalize these and other substituent effects in radical reactions.[3-8] According to this model, resonance structures such as II and III stabilize free

$$\left[\underset{\text{I}}{R\cdot\dot{H}\cdot CH_2Ar} \longleftrightarrow \underset{\text{II}}{R{:}^{-}\dot{H}\,{}^{+}CH_2Ar} \longleftrightarrow \underset{\text{III}}{R^{+}\dot{H}^{-}{:}CH_2Ar}\right] \quad (2)$$

radical transition states. Radicals for which form II is more important would be electrophilic, while those for which form III is more important would be nucleophilic. The magnitude of the effect in either case would be governed by the reactivity of the radical involved (Hammond postulate[9]).

In recent publications Zavitsas[10] concluded that the assumption of such resonance forms is unnecessary. He proposed that ρ merely reflects differences in the bond dissociation energies of the benzylic hydrogens in the substituted toluenes, and that the magnitude of ρ is nothing more than a measure of the sensitivity of the abstracting radical to these variations. Since substituents which weaken the C–H bond have negative σ values and those which strengthen the bond have positive σ values,[11] this treatment leads to the prediction that radicals are limited to negative (or zero) ρ values.

As the data in Table I indicate, a basis for assessing the relative importance of each effect is provided by the following series of alkyl radicals: methyl, primary, secondary, and tertiary. With respect to the polar effects model, the ρ value for each type of radical in the series would be dependent on three factors: the ionization potential and electron affinity of the radical and ΔH for the reaction of the radical with the toluenes. In going from the methyl radical to a tertiary alkyl radical, resonance form III (the form related to nucleophilic character) becomes progressively more important compared to form II (which is related to electrophilic character). Also, since the exothermicity decreases down the series, form III should be able to exert itself to a greater extent in the same order. Thus, a trend toward more positive ρ values on going toward more highly substituted radicals would be expected.

Application of bond dissociation energy arguments to this system leads to these predictions: (1) radicals are limited to negative (or zero) ρ values and (2) the more exothermic the reaction of a radical with the toluenes, the less sensitive that radical will be to differences in the bond dissociation energies of the benzylic hydrogens (*i.e.*, the closer its ρ value will be to zero). Since the exothermicity of the reaction of R· with the toluenes decreases as R· becomes more highly substituted with alkyl groups, a trend toward more negative ρ values would be expected in going down the series.

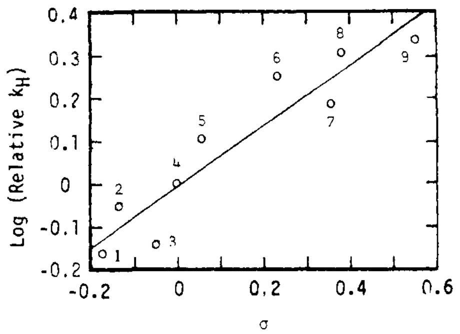

Figure 1. A Hammett plot of relative k_H values (eq 4) for the 3-heptyl radical *vs.* σ substituent constants. The code is as follows: 1, *p*-xylene; 2, mesitylene; 3, *m*-xylene; 4, toluene; 5, *p*-fluorotoluene; 6, *p*-chlorotoluene; 7, *m*-fluorotoluene; 8, *m*-chlorotoluene; 9, *m*-tolunitrile. The values for mesitylene and the xylenes have been statistically corrected.

ρ values for the methyl,[12] undecyl,[1a,b,13] and *tert*-butyl[14] radicals have been reported. We here report the ρ value for the 3-heptyl radical, completing the data for the series.

3-Heptyl radicals (R·) were generated by the thermolysis of *tert*-butyl 2-ethylperhexanoate at 80° in a mixture of a toluene (QH) and carbon tetrachloride.[15a] The equations for the reactions are as follows.

$$\text{perester} \longrightarrow R\cdot \text{ and other products} \quad (3)$$

$$R\cdot + QH \xrightarrow{k_H} RH + Q\cdot \quad (4)$$

$$R\cdot + CCl_4 \xrightarrow{k_{Cl}} RCl + CCl_3\cdot \quad (5)$$

Kinetic analysis of eq 3–5 leads to eq 6.[16] Values of k_H/k_{Cl}

$$\frac{[RH]}{[RCl]} = \frac{k_H}{k_{Cl}}\,\frac{[QH]}{[CCl_4]} \quad (6)$$

were obtained from a plot of [RH]/[RCl] *vs.* [QH]/[CCl$_4$].[17] A Hammett $\sigma\rho$ plot of the data (see Figure 1) gives $\rho = 0.70 \pm 0.09$ ($r = 0.94$)

The ρ values for the various alkyl radicals are included in Table I.[18] If bond dissociation energy effects alone were operating in this series, a trend toward more negative ρ values would be expected in going from the methyl radical to a tertiary radical. Since the ρ values become more positive, evidently the importance of resonance form III in the transition state increases sufficiently to overshadow completely the greater sensitivity of each succeeding radical to differences in the bond dissociation energies of the benzylic hydrogens.

Acknowledgments. The author wishes to thank Professor W. A. Pryor and W. H. Davis, Jr., for many helpful discussions. This work was supported by a Faculty Research Grant from Francis Marion College.

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(16) It is assumed in this derivation that the only sources of RH and RCl are the reactions given in eq 4-5. Control experiments showed that no more than a few per cent of the RH or RCl arose from sources other than QH and CCl$_4$. Also, it was found by comparison of the k_H/k_{Cl} values for the various substituted benzenes and toluenes that the ring contribution to the overall reactivity of the toluenes is no more than ~5%. The problem of extraneous sources of RH and RCl in this system has been discussed in an earlier paper.[1b]
(17) Analyses were performed on a Hewlett-Packard Model 5712A gas chromatograph equipped with a Disc Integrator.
(18) For the intercomparison of ρ values to be meaningful, it is necessary that these reactions be related isoentropically. Otherwise, not only the magnitude of ρ but also its sign might be temperature dependent. Available evidence suggests that atom transfer reactions in general (and hydrogen abstraction from toluenes in particular) are isoentropic (see discussion in ref 14). Ideally the ρ values to be compared should be measured at the same temperature. Except for *tert*-butyl radical, the radicals given in Table I were studied at approximately the same temperature. Generally, ρ decreases with an increase in temperature.[19] If the ρ value for the *tert*-butyl radical follows this trend, the corrected ρ would be smaller than 1.
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Temperature Dependent Relaxation Processes of an Electronically Excited Nitrosamide

Sir:

Irradiation of *N*-nitroso-*N*-methylacetamide (**1**) in benzene or methanol with a >400-nm light source caused homolysis of the N-NO bond to give the amido radical (**3**) and nitric oxide;[1] the homolysis occurs in spite of the fact that the ground state has partial double bond character due to contributions of other polar resonance forms. Flash excitation studies[1b] have indicated that the photoreaction occurs from the lowest singlet excited state of **1**. In contrast thermolysis[3] of **1** at <100° causes the exclusive intramolecular rearrangement to methyldiazo acetate (**5**) *via* rotamer **4**.

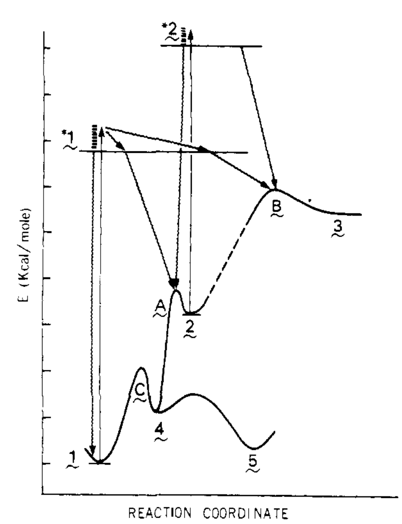
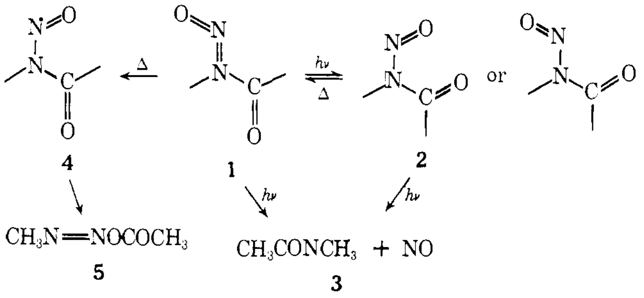


Figure 1. Schematic potential energy diagram for nitrosamide photoreaction. The numbers with asterisks represent the lowest singlet excited states.



Photochemical reactions in which the chemical process occurs within a singlet excited manifold are known but rather rare.[4,5] For the majority of photochemical reactions, the details of the chemical events following the electronic excitation are buried in the radiationless transition (electronic and vibrational relaxations), particularly that of an internal conversion during which the energy is converted into some form of nuclear motions.[6,7] Chemical intuition[8] as well as the mathematical model[7] based on a resonance interaction have predicted that a radiationless transition is biased in favor of the nearest potential energy hypersurface of the lower electronic state provided the two states are not far apart along the reaction coordinate. With reference to the energy profile, Figure 1, this is seen as the transitions of ***1** → A and ***2** → B are more favored than those of ***1** → C and ***2** → A, respectively. Implicit in this argument is that a higher energy surface of a ground state pathway (*e.g.*, **1** → **A** → **2**),[9] which is not accessible by thermolysis, may be reached *via* a radiationless transition from ***1**. At a low temperature such a high energy ground state vibronic species may be stabilized in a nearby minimum,[10] and the reaction pathway may be altered depending on temperature levels.

Irradiation of **1** in EtOH-MeOH (9:1) solution kept at −150° with a monochromatic light[11,12] at 405 nm caused decreases in the n → π* bands of **1** and concurrent emergence of a new set of absorptions at 454, 432, 414, and 396 nm as in Figure 2. On warming to −90°, the absorptions of the intermediates disappeared restoring the original intensity of **1**. However, on subsequent irradiation at −150° of the intermediate with a >430-nm light source, more than 70% of the intermediate was irreversibly decomposed and the balance of the percentage was restored to **1** as calculated from the spectral data. The consecutive biphotonic process of the decomposition of **1** at −150° was further substantiat-