Free Radical Additions.[1] Kinetics of Free Radical Additions of Bromomalononitrile to Alkenes and PMO Treatment of the Reactivity and Regioselectivity[2]

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The addition rate of dicyanomethyl (DCM) radicals to 2-methyl-1-pentene (**2**) was found to be $k_4 = (1.6 \pm 0.4) \times 10^6$ L·mol^{-1}·s^{-1}. Relative rates (k_{rel}) of additions to 11 alkenes were measured. Obviously steric effects do not influence the addition rates with *n*-alkyl-substituted alkenes. The ln k_{rel} values correlate linearly (r = 0.98) with the superdelocalizabilities, $S_r^{(R)}$, a measure for binding molecular orbital interactions between the reactants (Fukui). The $S_r^{(R)}$ values for the DCM radical attack at the two sp^2 C atoms of unsymmetrically substituted alkenes show significant differences. On the basis of the $S_r^{(R)}$ values, i.e., polar effects, a prediction of regioselectivities is made. The found regioselectivities are in accord with the predicted ones within the limits of error. A more accurate experimental verification seems to be of considerable interest because up to now only steric effects have been considered to be the reason for the anti-Markovnikov orientation in free radical additions to *n*-alkyl-substituted alkenes.

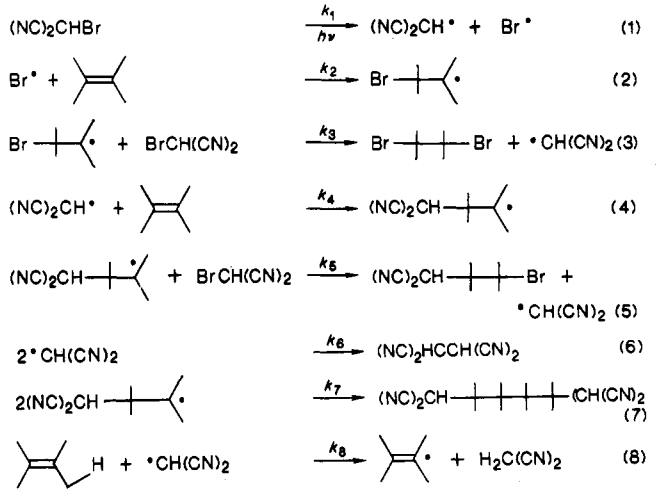
The synthetic use and the stereochemistry of the light-induced free radical addition of bromomalononitrile (BMN) to alkenes has been well investigated.[1,3-7] This free radical addition reaction seems to be outstanding insofar as it proceeds very cleanly and nearly quantitatively.[3,5] Therefore it should also be especially suitable for examinations of structure–reactivity relationships in free radical additions. We investigated the kinetics and regioselectivities of the BMN additions to the alkenes **1–11** (Table I).

Kinetic Measurements. The probable mechanism of the reaction is shown in Scheme I. The chain length was measured to be 3400 ± 10% in the case of cyclopentene.[5] The addition step in eq 4 has been proved to be irreversible.[6] The reactions in Scheme I are now further substantiated by the GLC/MS detection of the dibromides that should be formed in reaction 3. In the case of 1-pentene (**5**) the yield was 1.7% compared to the addition product and should be lower in additions to the more reactive alkenes due to greater chain lengths. Only traces of tetracyanoethane, the product of the termination reaction 6, could be detected by GLC.

Further byproducts, e.g., from the abstraction reaction 8, could not be detected. The ratio k_4/k_8 in the case of cyclohexene was found to be 2500 (40 °C).[5]

In order to guarantee that reaction 4 is rate controlling[9] we used an excess of BMN (molar ratio BMN/alkene ≥ 3.5:1. Experiments with molar ratios ≥10:1 showed the same results).

Scheme I



The following expressions are obtained from the kinetic treatment of the reaction scheme:[9]

$$\frac{d[\text{alkene}]}{dt} = -k_4(R_i/2k_6)^{0.5}[\text{alkene}] \quad (9)$$

and after integration,

$$\frac{\ln [\text{alkene}] - \ln [\text{alkene}]_0}{t - t_0} = -k_4(R_i/2k_6)^{0.5} = -k_4' \quad (10)$$

Thus k_4 can be determined by measuring R_i (=rate of initiation), k_6 and k_4'. R_i can be obtained by using the inhibitor method,[10] but unfortunately the "inhibitors" used (e.g., *p*-benzoquinone and 2,6-di-*tert*-butyl-4-methylphenol) acted only as retarders or even as initiators depending on the alkene (see Figures 1 and 2).

Using 2,6-di-tert-butyl-4-methylphenol instead of *p*-benzoquinone we found inhibition, retardation, or even initiation for the addition reaction to 2-methyl-1-pentene (**2**) depending on the phenol concentration (0.1–148 mmol/l). We are unable to explain these findings.

To avoid this complication we tried to make use of the relationship $R_i = (2k_6\tau^2)^{-1}$,[11] τ being the average lifetime

(1) This is Part 11 of the series "Free Radical Additions". For Part 10, see: Bartels, H. M.; Boldt, P.; Schomburg, D. *Chem. Ber.* **1981**, *100*, 3997.

(2) Partially published as short communications: (a) Riemenschneider, K.; Drechsel-Grau, E.; Boldt, P. *Tetrahedron Lett.* **1979**, *20*, 185–188. (b) Riemenschneider, K.; Bartels, H.; Eichel, W.; Boldt, P. *Tetrahedron Lett.* **1979**, *20*, 189–192.

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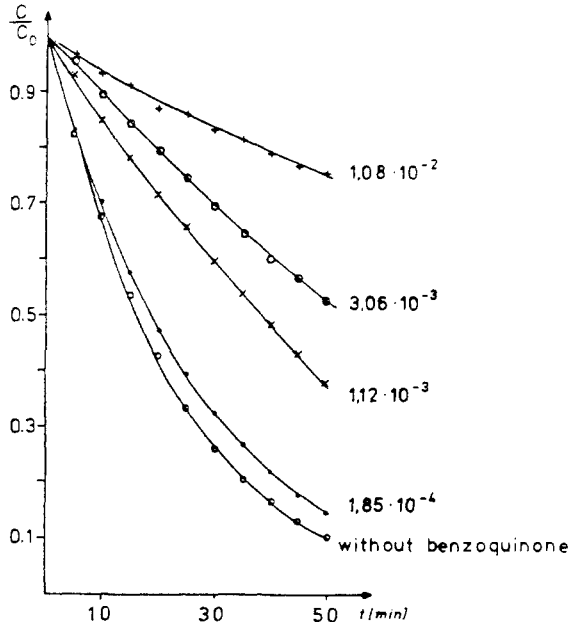

Figure 1. Plot of the alkene concentration c/c_0 ($c_0 \sim 0.1$ mol/L) vs. time (t) for the addition of BMN to 2-methyl-2-hexene (**4**) without and in the presence of various amounts of *p*-benzoquinone (concentrations in mol/L).

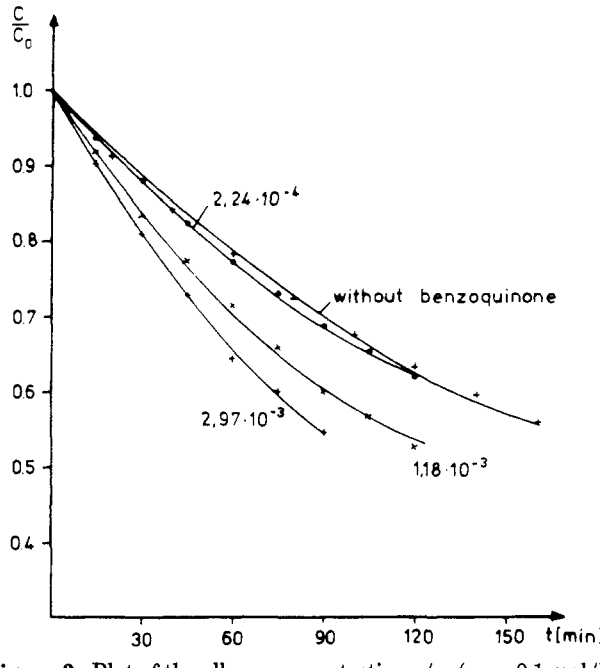

Figure 2. Plot of the alkene concentration c/c_0 ($c_0 \sim 0.1$ mol/L) vs. time (t) for the addition of BMN to (*E*)-2-hexene [(*E*)-**6**] without and in the presence of various amounts of *p*-benzoquinone (concentrations in mol/L).

of the radical chain which can be measured by the rotating sector method.[11,12]

The dimerization rate constant for DCM radicals k_6 was determined by Kaba and Ingold[13] as 1.2×10^9 L·mol^{-1}·s^{-1} at 20 °C. This value should be valid also at 28 °C, the temperature of our measurements, because activation energies of radical dimerizations are generally very small.

For the addition to 2-methyl-1-pentene (**2**) we found $\tau = (4.5 \pm 1.1) \times 10^{-2}$ s. Using eq 10 we got a k_4 value of $(1.6 \pm 0.4) \times 10^{-6}$ L·mol^{-1}·s^{-1}. Unfortunately the attainable accuracy of these measurements was not adequate with respect to the differences in reactivity of the alkenes. Relative addition rate constants (k_{rel}) can be derived from the k_4' values (eq 10), if R_i is independent of the nature of the alkene. This could be proved to be the case by measuring k_4' for the additions to the relative unreactive 1-pentene (**5**) without and in presence of various amounts of the much more reactive 2-methyl-1-pentene (**2**) (see Table I); k_4' of **5** was unaffected.

The k_4' values were always determined graphically according to eq 10; the pseudo-first-order kinetics proved to be valid in each case at least up to 75% conversion of the alkene. The standard deviation was in the range of 2.5–7.5%.

The results of our kinetic measurements (k_4' and the relative addition rate constants, $k_{rel} = 1$ for the addition to (*E*)-2-hexene [(*E*)-**6**]) are compiled in Table I. The regioselectivities (see Table I) were determined from the ^{1}H NMR spectra of the reaction mixtures after evaporation of the solvent. GLC could not be used due to the partial thermal conversion of the reaction products to cyclopropane-1,1-dicarbonitriles on the columns. The addition products were characterized by the ^{1}H NMR and IR spectra and the elementary analyses of the cyclization products obtained by reaction with triethylamine giving cyclopropane-1,1-dicarbonitriles in nearly quantitative yields.[3,5,14]

According to eq 10 k_4' should be proportional to $R_i^{0.5}$. Since $R_i = 2k_1[\text{BMN}]$[11] we tried to prove this relationship by measuring k_4' varying the concentration of BMN from 0.46 (standard condition) to at least 51 mmol/L, the molar ratio of BMN/alkene (≥10:1) being maintained. With the fast reacting 2-methyl-1-pentene (**2**) we found the relationship $k_4' \sim \text{BMN}^{0.65}$. This deviation may be due to traces of inhibitors (oxygen): The reaction should be influenced by inhibitors the more the quasi-stationary radical concentration decreases, i.e., the k_4' values measured at very low concentration of BMN may be probably a little to small. In general all addition reactions proved to be highly sensitive toward oxygen. So we excluded oxygen by using purified nitrogen (maximum oxygen concentration: 2×10^{-4} vol %) as inert gas. Most of our k_{rel} values were obtained directly from competition experiments, i.e., irradiation of BMN in the presence of two or even three alkenes. In these cases the effect of traces of oxygen possibly still present in the reaction mixture of the k_{rel} values can be excluded. In addition, k_{rel} values which were obtained from k_4' values from experiments with only one alkene did not deviate from the k_{rel} values obtained in competition experiments. This is a useful proof for the good constancy of our experimental conditions.

Interpretation and PMO Treatment of Addition Rates. The addition rate of free radicals to alkenes has been connected with polar effects of the substituents. Stefani et al. found for the additions of CF_3, cyclopropyl, and difluoroamino radicals a linear relationship between log k_{rel} (k_{rel} = relative addition rate constant) and the ionization potentials (IP) of alkenes.[15] Tedder[16] summarized the results of the then known investigations in the statement that polarity can have a major effect on the

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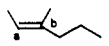
Table I. Relative Reaction Rates (k_{rel}), Superdelocalizabilities ($S_r^{(R)}$), Measured and Calculated Regioselectivities of the Free Radical Addition of BMN (0.46 mol/L) to Various Alkenes (~0.05 mol/L)

			$[-S_r^{(R)}(10/\beta)]$		orientation a:b[a]	
	k_4'	k_{rel}	C_a	C_b	obsd	calcd[b]
 1	3.25×10^{-2}	273	1.799	1.591	>95:5	99.99:0.01
 2	2.19×10^{-3}	18.4	1.765	1.611	>95:5	99.8:0.02
 3[c]	1.78×10^{-3}	15.0	1.757	1.697	>95:5	93:7
 4	1.65×10^{-3}	13.9	1.754	1.683	>95:5	96:4
 5	1.38×10^{-4}	1.16	1.684	1.600	99:1	99:1
 (E)-6	1.19×10^{-4}	1.00	1.671	1.683	~50:50	38:62
 (Z)-6	1.49×10^{-4}	1.25	1.680	1.679	~50:50	50:50
 (Z)-7	1.46×10^{-4}	1.23	1.681	1.680	~50:50	51:49
 8	1.62×10^{-4}	1.36	1.735	1.592	~95:5	93:7
 9	2.02×10^{-3}	17.0	1.764	1.7705	~50:50	43:57
 (Z)-10	0.52×10^{-4}	0.44	1.673	1.689	~80:20	34:66
 (Z)-11	0.31×10^{-4}	0.26	1.672	1.693	>99:1	29:75

[a] Attack of DCM radicals to C_a and C_b. [b] Calculated with eq 11. [c] Mixture of Z/E isomers.

overall rate of addition. Giese[8] found for the additions of cyclohexyl radicals to 1-mono- and 1,1-disubstituted alkenes a linear relationship between log k and the Hammett σ^-- or σ-values. He stated, that substituents at the nonattacked alkene C atom (C_β) influence the addition rates by polar effects (β-effect). Bayes et al.[17] found that log k for the reaction of alkyl radicals with oxygen and ozone increases nearly linearly with decreasing IP–EA gaps (IP of the alkyl radicals and electron affinities (EA) of O_2 or O_3). For the addition of the nucleophilic *tert*-butyl radicals to 1-mono- and 1,1-disubstituted alkenes Fischer et al.[18] found in a thorough and excellent investigation a linear relationship between log k_{300} and the EA of the alkene. For *tert*-butyl radical additions to chloroethenes he got a log k_{300} vs. EA plot with ethene and 1-chloro- and 1,1-dichloroethene on one line. The two 1,2-dichloroethenes and trichloroethene lie also on a line with the same slope but shifted by 1.4 units to lower values. Finally the point of tetrachloroethene deviates from the line of the 1,2-di- and trichloroethenes by −1.7 units. A plot of the activation energies vs. EA yield a similar picture.

The authors interpret their results on the basis of the common theory[8,16] that addition rates are governed by polar effects (i.e., in this case the EA's[19a]). They conclude therefore that the shifts of 1.5 units for the alkenes, where the *tert*-butyl radical attack takes place at the CHCl end, and of 1.7 units, in the case of the attack at the CCl_2 end, are due to steric effects of the chlorine. Assuming that the frequency factors are equal the authors estimated the increase of E_a by steric effects for one chlorine at E_a^1 = +8.5 kJ/mol and for the second at E_a^2 = +10 kJ/mol. For methyl-substituted ethenes (also implying equal frequency factors) they assumed similar but smaller steric effects (E_a^1 = +4 kJ/mol, E_a^2 = +2.5 kJ/mol).

As shown in Figure 3 we got—as Fischer[18]—two nearly parallel straight lines: Curve a with the alkenes, where attack of the DCM radical takes place at a CH_2 end, and—shifted by about 2.8 units to lower values—curve b with the alkenes, where attack takes place at a CHR (R = CH_3 or *n*-alkyl) end. The point for **9**, where the attack takes lace at a CCH_3R end (R = CH_3 or *n*-propyl), again is shifted by about 2.8 units to lower values. The negative

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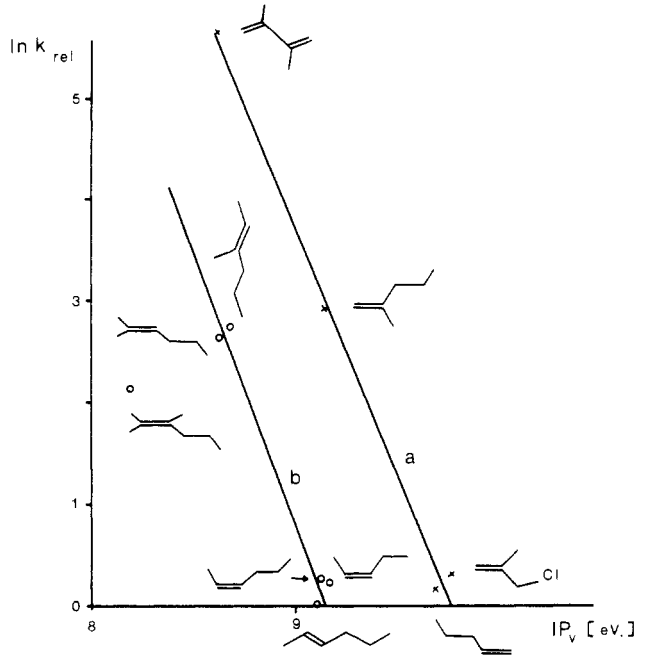

Figure 3. ln of the relative rate constants for the addition of DCM radicals to alkenes versus the ionization potential (IP) of the alkenes.

slope of the lines confirms the electrophilic character of the DCM radicals. In log the shifts are 1.2 units and lie between the values for the chloroethenes (−1.5 and −1.7, respectively) and methyl groups (−0.8 and −0.5, respectively) in the case of attack of the nucleophilic *tert*-butyl radicals.[18]

Following the common theories[8,16] and the conception of Fischer[18] again the results of Figure 3 should be interpreted as follows: the addition rate is governed in principle by the polar factor (in this case, with the electrophilic DCM radicals, represented by the IP[19a]) and will be slowed down by an additional steric effect if the alkyl group is attached to the attacked C atom (C_α, α-effect[8]) but not if the alkyl substituent is placed in β-position to the attacked C atom (β-effect). This could explain that two alkenes with the same IP [e.g., (*Z*)-7 and 2] show a difference of Δ ln k_{rel} = 5.4 (Δ log k_{rel} = 2.3).

Two major objections may be raised to this explanation.

(1) Substituents at the attacked alkene C atom may exert a steric influence (a) by hindering the approach of the attacking free radical and/or by raising the steric compression energy between the substituents at the attacked sp^2 C atom (C_α) which gets partly sp^3 character in the transition state. But free radical additions to alkenes are mostly exothermic and fast, and by reason of the Hammond principle it seems generally accepted[8,16] that the transition state lies rather early on the reaction coordinate with little bond formation and deformation of the reactants. This view is supported by calculations of the transition states for the methyl radical addition to ethene[20] and propene.[21] The distances between the radical C atom and the attacked alkene C atom (C_α) was found to be 240 pm for ethene and 239.4 or 229.6 pm for terminal or central attack to propene. The angles between the two hydrogens (H_α) at the attacked C atom of ethene and 1.3-butadiene are the same in the ground and transition states. With propene the deviation of the $C_\alpha H_\alpha$ or the $C_\alpha CH_3$ bonds from the plane of the molecule in the transition state is

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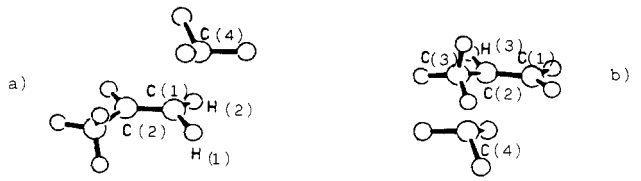

Figure 4. Geometries of the transition states for (a) terminal and (b) central attack of CF_3 radicals to propene as calculated with MNDO.[25]

Table II. MNDO Calculated Bond Lengths (*R*, pm), Angles (*A*, deg), and Heats of Formation (ΔH, kcal/mol) for the Approach of CF_3 Radicals to Propene (Notation as in Figure 4)

(a) Terminal Attack				
R(C1C4)	*R*(C1C2)	*A*(H1C1C2)	*A*(H1C1H2)	ΔH
162	148	109.5	106.0	−146.6
220	139	119.4	113.9	−109.5
500	134	122.3	114.1	−132.1

(b) Central Attack					
R(C2C4)	*R*(C1C2)	*A*(C1-C2H3)	*A*(C1-C2C3)	*A*(C3-C2H3)	ΔH
163	148	107.7	113.2	106.1	−136.1
220	139	117.8	122.2	113.8	−105.1
500	134	119.5	126.0	114.2	−132.1

10° (terminal attack) and 12–16° (central attack). From these and the other values given for bond lengths and bond angles it may be expected that only minor steric interactions between the attacking free radical and the alkene and no important strain between the α-substituents will arise in the transition state. Furthermore the amount of the steric strain at an sp^3 C atom seemed to have been overestimated. The differences of bond dissociation energy (*D*) for primary, secondary, and tertiary hydrogens in hydrocarbons were regarded as a measure for this strain energy.[22] But especially the value $D(C_2H_5\text{–H}) - D(i\text{-}C_3H_7\text{–H}) = 16.7$ kJ/mol possibly was too great. A new estimation is $D(n\text{-}C_3H_7\text{–H}) - D(i\text{-}C_3H_7\text{–H}) = 7.2$ kJ/mol.[23]

Alkyl radicals have nucleophilic character. Houk stressed the fact that the structures of the transition states for nucleophilic and electrophilic free radical attack to alkenes may differ considerably.[24] But similar results have been obtained by MNDO calculations of the electrophilic CF_3 radical for the addition reaction to propene (see Figure 4 and Table II) and 1,1-difluoropropene.[25]

The first row in both sections (a and b) of Table II give the optimized values for the addition product, the second for the transition states, and the third for the reactants. As can be seen the geometries of the transition states are much more reactant than product like.

The calculations were started with the two products of the CF_3 radical addition to propene. The new formed bond was then arbitrarily stretched in steps of 10 pm up to R = 300 pm and in steps of 50 pm from R = 300 to 500 pm. For each bond length the energy was minimized with respect to all other geometric variables. In each case, i.e., for central and terminal attack, the states with the largest energy were found for a bond distance of R = 220 pm. Stretching the bond length beyond R = 500 pm gave no significant energy change. Therefore the values for R =

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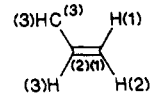
(24) Houk, K. N. In *Frontiers of Free Radical Chemistry*; Pryor, W. A., Ed.; Academic: New York, 1980; pp 43–72.
(25) Eichel, W. Dissertation, Technische Universität Braunschweig, Braunschweig, FRG, 1982.

Table III. MNDO Calculated Angles (A, deg) for the Approach of DCM Radicals to Propene, Depending on the Distance (R, pm) between the Attacking C Atom and the Attacked Alkene C Atom



R	A(C3C2H3)	A(H1C1H2)
	(a) Terminal Attack	
157	106.1	117.5
220	113.6	113.7
500	114.2	113.9
	(b) Central Attack	
156	117.5	106.0
220	113.9	114.1
500	113.7	113.5

500 pm should represent the parameters of the reactants.

For the reaction of DCM radicals with propene the calculations were performed only for the two addition products and for R = 220 and 500 pm. The bond angles of the alkene C atoms as sensitive measure for structure changes during the reaction are given in Table III. Again the angles for R = 220 ppm are very similar to those for the alkene (R = 500 pm) and not to those for the product (R = 157 and 156 pm, respectively).

From this it may be concluded that also for the electrophilic CF_3 and DCM radicals the reactants and not the products are good models for the transition states, and it seems therefore not reasonable to assume special steric interactions worth mentioning between the attacking free radical and the alkene or between the substituents at the attacked alkene C atom in the transition state.

(2) A still graver objection arises from the fact, that polar effects were related only to the IP[15] and EA[18] of the alkenes or the Hammett parameters of the substituents.[8] This

$$S_r^{(R)} = \sum_r^{occ.} \frac{c_{ra}^2}{E_{SOMO} - E_r}(-\beta) + \sum_r^{unocc.} \frac{c_{ra}^2}{E_r - E_{SOMO}}(-\beta) \quad (11)$$

implies an oversimplification of eq 11 for estimating relative reactivities of free radicals toward various but similar alkenes on the basis of perturbation molecular orbital theory (PMO).[19,26,27] $S_r^{(R)}$ is a reactivity index called superdelocalizability.[27] The greater the (negative) value of $S_r^{(R)}$ the faster the reaction of the free radical should be. It is a quantitative measure for binding MO interactions between the alkenes and the approaching free radical. These interactions depend on the energy of the singly occupied MO of the free radical (E_{SOMO}), the energy of the rth MO of the alkene (occ. = occupied, unocc. = unoccupied), on the value of the AO factor c of the rth MO at the atom a (c_{ra}) and on the value of the resonance integral β. β is assumed to be constant, or nearly so, for all reactions of the DCM radical with the alkenes used in this investigation.[28]

The IP can be regarded as an approximation to the energy of the HOMO. But with only the IP for correlations with the addition rates all interactions between the SOMO of the radical and all other occ. E_r and unocc. E_r are neglected as well as the AO coefficients at the attacked alkene C atom. The arguments against correlations with the EA's or the Hammett parameters are similar.

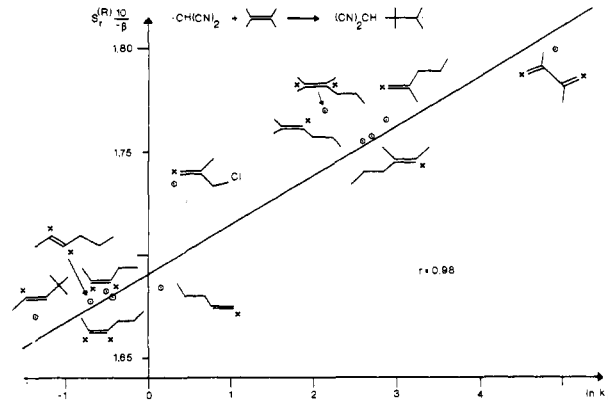


Figure 5. Plot of the superdelocalizabilities, $S_r^{(R)}$, vs. ln of the relative addition rates of DCM radicals, ln k_{rel}, to various alkenes. The position of attack is marked with an asterisk. The resonance integral β is assumed to be constant (r without the point for methallyl chloride (8)).

In this connection it is important that the values of the Hammett constants seem to be directly connected with the energy level of the frontier molecular orbitals (FMO).[19a] We[29] ascertained a linear correlation between the sum of the (inductive) σ^*[30] and the (mesomeric) σ^+[31] parameters of the alkyl substituents of the alkenes in Figure 3 and the IP (r = 0.98 and r = 0.99, respectively).

To our knowledge we were the first who showed that there exists a linear correlation between the superdelocalizability and the ln of the addition rates or the activation energies for the addition of DCM radicals and trifluoromethyl radicals, respectively, to various alkenes.[2b] Later on Giese[8] used a frontier orbital scheme of Fleming[19b] for a discussion of polar effects in free radical additions to alkenes in a qualitative way taking into consideration only the SOMO interaction with the HOMO or LUMO of the alkene. Fischer neglected the possible influence of the AO coefficients.[18]

Indeed as an inspection of the AO coefficients at the attacked C atom (C_α) of the alkenes in Figure 3 shows, a possible reason for the appearance of two curves a and b in the k_{rel}/IP plot may be found not in steric but in polar factors, i.e., MO interactions. Considering the electrophilic character of the DCM radicals the AO coefficient in the HOMO should be the most important one. The values for the alkenes of curve a (Figure 3) are as follows: **2** and **5**, $c_{HOMO,\alpha}$ = 0.44; **8**, $c_{HOMO,\alpha}$ = 0.41 (the value of the diene **1**, $c_{HOMO,\alpha}$ = 0.30, is not comparable with that of the monoenes). The values for all alkenes of curve b lie between $c_{HOMO,\alpha}$ = 0.37 and 0.38. The value for **9** is $c_{HOMO,\alpha}$ = 0.35. Furthermore the ln k_{rel} values (Table I) give an excellent linear correlation with the superdelocalizabilities $S_r^{(R)}$ at the position of attack [Figure 5 and eq 12, r = 0.98, without the value for 3-chloro-2-methylpropene (8)]. In the case of equal or nearly equal $S_r^{(R)}$ values at both alkene C atoms, the ln k_{rel} values are statistically corrected.

$$\ln k_{rel} = 424 S_r^{(R)}/\beta - 71.8 \quad (12)$$

The deviation of the k_{rel} value of methallyl chloride (8) from the expected one, may be explained plausibly by additional polar forces arising from dipole–dipole repulsion between the reactants. These Coulomb interactions are not taken into account in eq 11. Therefore we renounced kinetic measurements of the additions of BMN to allyl

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(29) Riemenschneider, K. Dissertation, Technische Universität Braunschweig, Braunschweig, FRG, 1977.
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chloride and 3-methoxy-2-methylpropene performed in a preparative scale (see Experimental Section). The good correlation of the $S_r^{(R)}$ values and ln k_{rel} of the other alkenes suggests that the overall addition rate is governed by polar effects (i.e., MO interactions[8]) and that a steric α-effect[8] can be neglected for one CH_3, C_2H_5, or n-C_3H_7 substituent: The addition rates to the one disubstituted and two trisubstituted alkenes in the middle of the diagram (with $S_r^{(R)}$ $(10/-\beta) \sim 1.76$) are simialr regardless of the fact that the attack takes place in one case at the CH_2 end of the alkene and in the other two cases at an C atom bearing one methyl or n-propyl group. The same is valid for the four alkenes in the range of $S_r^{(R)}(10/-\beta) = 1.68$.

Only with two alkyl groups at the attacked C atom or with a branched alkyl group as isopropyl or *tert*-butyl the steric α-effect may carry weight. So the attack to the tetrasubstituted alkene **9** is slower by the factor 3 than expected from the $S_r^{(R)}$ value, and the k_{rel} value of the *tert*-butyl-substituted **11** correlates with the $S_r^{(R)}$ value (eq 12, Figure 5) only, if the k_{rel} value is not statistically corrected, i.e., under the assumption that in spite of the somewhat higher $S_r^{(R)}$ value at C_b (see Table I) and in accordance with the measured regioselectivity the steric α-effect of the *tert*-butyl group prevents an attack at C_b. In this case even the attack in β-position to the *tert*-butyl group is slowed down by a factor of about 0.5, obviously by steric reasons. Giese et al. observed the same small β-effect of *tert*-butyl groups at the nucleophilic additions of cyclohexyl radicals to acryl esters.[32] For the nucleophilic additions of *tert*-butyl radicals to the alkenes CH_2=CHR, Fischer found that the frequency factor, reflecting the degree of order in the transition state, drops from the value of log $A \sim 7.5$ M^{-1} s^{-1} with R = CH_2, C_2H_5, and for the most other alkenes in his investigation to a value of log $A = 6.8 \pm 0.2$ M^{-1} s^{-1} for R = i-C_3H_7 and 6.1 $\pm$ 0.4 for R = t-C_4H_9, whereas the activation energies remain the same for these alkenes within the limit of error ($E_a \sim 24$ kJ/mol). Therefore the somewhat slower addition with the last two alkenes should be due also to a small steric β-effect of the isopropyl and *tert*-butyl group.

Interpretation of Regioselectivities. From the onset of the elucidation of the anti-Markovnikov addition to alkenes as free radical reaction,[33,34] the reasons for this regioselectivity were discussed controversially. Lately Koutecky et al.[35] have used a simple valence bond treatment with a three-center electron model and found that the regioselectivity is determined by the electronegativity difference between the radical and the attacked site of the alkene. Tedder[16] states for monosubstituted alkenes that the attack to the unsubstituted end of the alkene, always observed with free radicals, is due to steric strain, which arises at the substituted end in the course of addition. He postulates that this steric effect outweighs all other influences on regioselectivity. Also with polysubstituted alkenes he assumes that the regioselectivity is essentially determined by steric effects: only its magnitude can be influenced by polarity, especially when the steric effects on both sites of the alkene cancel each other. This view was supported by results of an ab initio study of the hydrogen atom addition to 1,1-difluoroethene.[36] Giese[8] postulates also that regioselectivity is mainly determined by steric effects. Canadell et al.[37] suggest for methyl radical additions to the alkenes CH_2=CHX (X = H, CH_3, F, Cl) and CH_2=CF_2 on the basis of MNDO, MINDO/3, and STO-3G calculations that the addition at the less substituted end of the alkene has an electronic origin. Ponec et al.[38] conclude from their MNDO calculations of the transition states for additions to fluoro alkenes that the directive effects with CF_3 radicals are primarily determined by charge-transfer contributions whereas the additions of CH_3 radicals are influenced predominantly by steric effects.

Lefour et al.[39] were able to predict the absolute rate constants for the hydrogen atom additions to ethylene, vinylamine, and vinylborane by UHF 3-StG and CIPSI calculations. They state that despite the importance of steric effects the preferential site of attack is not necessarily the site with the smaller steric repulsion.

As shown above obviously only polar and not steric factors determine the addition rates of DCM radicals to various alkenes, bearing CH_3 or n-alkyl substituents. The same should be true of the addition rates to both alkene C atoms of the same alkene. Therefore using eq 11 and 12 it should be possible to predict the regioselectivity of the additions. The results of our calculations are shown in Table I. Unfortunately up to now no exact measurements of the regioselectivities have been possible due to partly cyclization of the addition products during GCL analysis. The values in the table are taken from the ^1H NMR spectra of the product mixtures. This evaluation suffers not only from the inherent inaccuracy of this method but in some cases, e.g., with (*E*)-**6**, also from the formation of the threo and erythro isomers of both regioisomers. With this reservation all calculated orientations lie within the measured values. Only (*Z*)-**10** and (*Z*)-**11** show inverse ratios. Again, this strongly suggests a dominating steric influence of the branched isopropyl and *tert*-butyl group on addition rates, i.e., regioselectivity, which overrides the polar effects. Also in the case of CF_3 radical additions to alkenes we could show that only branched alkyl groups exert considerable steric effects.[40] We hope to overcome the experimental difficulties in determining more accurately the regioselectivities of this reaction and to be able to compare exact experimental data with the predicted ones.

Calculations. The MO data of Table I were calculated with MINDO/3.[41] The calculations were started with the data set of the thermodynamically most stable conformation of the alkenes. Because of the limited capacity of the computer (ICL 1906 S) only the C–C, C=C, and C=C—H bonds were optimized. For the other C–H bonds the optimized values for primary, secondary, and tertiary C–H bonds of simple alkanes were used. The complete set of datas is available on request.

The calculated E_{HOMO} values of 14 alkenes showed an excellent linear correlation ($r = 0.99$) with the measured first ionization potentials.[29] The SOMO energy of the DCM radical (–4.69 eV) was calculated[42] with the half-

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electron method of Dewar et al.[43]

Concluding Remarks. The generally accepted hypothesis stresses steric factors as reason for the always observed attack of free radicals toward the less substituted end of simple alkenes.[8,16,22] We found a linear correlation (r = 0.98) between the calculated PMO reactivity index $S_r^{(R)}$ and the ln of the addition rates of DCM radicals to various alkenes. The surprising result was that steric effects obviously do not influence the addition rates sensibly, i.e., the addition rate depends only on the value of $S_r^{(R)}$ independent of the fact whether the radical attack takes place at the CH_2 end of the alkene or a CHR end (R = CH_3 or n-alkyl). Hence no steric α-effect could be observed for these groups. Only with R = isopropyl or *tert*-butyl and for attack at a disubstituted C atom should a steric effect carry weight. This finding is important with respect to the common hypothesis on the steric orgin of the regioselectivity for free radical additions to alkenes: The found regioselectivities for the DCM radical addition to most alkenes of this investigation could be predicted by the aid of the calculated $S_r^{(R)}$ values, i.e., on the basis of ultimately *polar* and not *steric* effects.

This finding is supported by MNDO calculations of the transition states for CF_3 and DCM radical additions to propene. The geometry of propene is nearly unchanged, i.e., reactant-like, and the distance between the radical C atom and the attacked alkene C atom about 220 pm. This should exclude also steric interactions as the dominating factor in determining regioselectivity with alkenes bearing only up to three CH_3 or n-alkyl groups.

Experimental Section

General. Instrumentation and methods were as follows: ^{1}H NMR spectra, solvent deuteriochloroform, Varian T 60; IR spectra, Beckman Model Acculab IV; analytical GLC, Hewlett-Packard Model 5700 A (FID) with an integrator Model Minigrator (Spectra Physics); preparative GLC, APG 402, Dr. Hupe Apparatebau, Karlsruhe, West Germany.

Irradiation Equipment. For the kinetic measurements we used a thermostated Duran glass cell with quartz windows (length: 39.5 mm, diameter: 38.8 mm). Air-free samplings were made with a microliter syringe through a silicon rubber septum. The constancy of the light intensity was controlled by photocells measuring the scattered light at right angles to the light beam.

The lifetime measurements were performed with the rotating sector method.[11] We used a balanced metal disk with a segment of 90° giving a ratio of dark to light time period of r = 3:1. The flash time was calculated from the speed of rotation of the sector disk which was determined by means of a stroboscopic unit connected with a digital frequency counter (DP 100 from Hickol). The sector disk was driven by an electric motor (Dunkermotoren, Bonndorf/Schwarzwald, West Germany), giving a very constant (±2%) speed of rotation. The flash times in our experiments reached from 2.03×10^{-2} to 8.72×10^{-2} s.

To ensure absorption of light in the whole cell the BMN concentration was kept sufficiently low. The extinction coefficient of BMN was measured at 366 nm as ϵ = 0.047 L·mol^{-1}·cm^{-1} in 1,2-dichloroethane. The concentration of BMN was in all experiments 0.46 mol/L giving an absorption of about 18% in the irradiation cell. Only with the experiments for the determination of the dependence of k_4' on the concentration of BMN the concentration of BMN was varied from 0.46 mol/L down to 51 mmol/L. Light with a wavelength of 365–366 nm was produced with a glass filter with 46% transmission at 365 nm. The high-pressure mercury lamp used exhibits in this region a strong emission line at 365.0–366.33 nm (relative intensity 32). The next line to shorter wavelengths (334.2 nm, relative intensity 11.5) is totally absorbed by the glass filter. At the next lines to longer wavelengths (404.7, relative intensity 17; 434.8 nm, relative intensity 24) BMN does not absorb. To diminish the light intensity in the experiments with the high reactive alkenes two additional filters were used: (a) an interference filter (20% transmission at 366 nm and (b) filter GG 375 from Jenaer Glaswerk, Schott & Gen., Mainz, West Germany (transmission not measured).

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Table IV. Alkenes and Standards Used for GLC Alkene Measurements

standard[a]	alkenes
n-heptane	2 + 4; 1 + 2; 4; 2 + 3; 5 + (*E*)-6; 3 + 5 + (*E*)-6
cyclohexane	2; 5; (*E*)-6; 2 + 5; 5 + 8

[a] The linearity of the FID indication of the quotient alkene/alkane was proven for the whole scope of concentrations.

Kinetic Measurements. A mixture of about 3 mmol of the alkene (distilled from sodium wire with the exception of 2,3-dimethylbutadiene and 3-chloro-2-methylpropene), about 100 mg of the alkane (internal standard for CLC analysis), and 65 mL of 1,2-dichloroethane (dried over molecular sieves, Zeolit S 124, Bayer) was flushed with dry nitrogene for 2 h and afterwards distillated completely into a dropping funnel. After an additional hour under nitrogen the distillate was placed (also under nitrogen) into the reaction cell containing 4.33 g (29.9 mmol) of BMN (freshly sublimated at 0.1 mbar at 30 °C). The BMN was dissolved by stirring (magnetic stirrer). The stopcock at the outlet of the cell was closed to obtain a slight overpressure of nitrogen, which was necessary to avoid permation of traces of oxygen when taking probes. After a few minutes all other stopcocks were also closed. In order to detect a possible dark reaction two probes were taken through a gas-tight syringe in an interval of 30 min. The dark reaction was found to be less than 1% and was therefore neglected in all cases. After irradiation was started (the lamp was burned in before for 1 h) probes were taken at certain time intervals. The probes were always immediately shaken in microtubes with an aqueous solution containing 0.8 mL of 0.4 M $Na_2S_2O_3$ and 0.5 mL of 0.5 M KI to remove unreacted BMN. Before GLC analysis the probes were stored in a refrigerator. During the irradation the constancy of light intensity was controlled by a photocell in all experiments.

GLC Analysis. The GLC analyses were performed in all cases with a 2-m glass column (20% Carbowax 20 M on Chromosorb P) at 60 °C using nitrogen as the carrier gas. The alkenes and alkene mixtures (used for competition experiments) together with the internal standards for GLC analysis (k_4, k_4' measurements) are listed in Table IV.

Addition Products. The addition products of the reactions of BMN with the alkenes **1**, **2**, **5**–**7**, **10**, and **11** were described earlier.[3,5]

Addition of BMN to 2-Methyl-2-hexene (4) (General Procedure). The addition was performed as described for the kinetic experiments. Instead of 1,2-dichloroethane dichloromethane was used as solvent. After the irradiation of 2.82 g (19.45 mmol) of BMN and 2.64 g (26.8 mmol) of **4** for 24 h, the reaction mixture was washed twice with aqueous sodium bisulfite and then with water. After drying (Na_2SO_4) and evaporating the solvent, we got 4.1 g (86%) of 2-(1-bromo-1-methylethyl)pentane-1,1-dicarbonitrile (**4a**): ^{1}H NMR δ 4.63 (d, J = 2 Hz, 1 H), 2.26–2.60 (m, 1 H), 1.85–1.50, 1.87, 1.73 (m, 2 s, total 10 H), 1.16–0.77 (m, 3 H).

Cyclization of the Addition Product 4a (General Procedure). To a stirred solution of 4.1 g (16.9 mmol) **4a** in 10 mL of dichloromethane was added 1.9 g (21.3 mmol) of triethylamine in 5 mL of dichloromethane dropwise at 0 °C. After the mixture was stirred for 20 min, washed with 2 N HCl, saturated aqueous $NaHCO_3$, and water, and dried over anhydrous Na_2SO_4, the solvent was evaporated. Vacuum distillation of the remainder yielded 2.56 g (94%) of 2,2-dimethyl-3-propylcyclopropane-1,1-dicarbonitrile: bp 65 °C (0.02 mbar); ^{1}H NMR δ 1.87–1.23, 1.47, 1.37 (m, 2 s, total 11 H), 1.18–0.90 (m, 3 H); IR (film) 2247 cm^{-1} (CN). Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.27. Found: C, 74.25; H, 8.71; N, 17.17.

Addition of BMN to 3-Methyl-2-hexene (3). Irradiation of 7.2 g (50 mmol) of BMN and 5.5 g (56 mmol) of **3** in 25 mL of dichloromethane for 4 h gave after workup 11.4 g (94%) of 3-bromo-2,3-dimethylhexane-1,1-dicarbonitrile (**3a**) as a mixture of diastereoisomers: ^{1}H NMR δ 4.55, 4.35 (2 d, J = 2 Hz, 1 H),

2.5 (m, 1 H), 1.8 (m, 5 H), 1.4 (m, 5 H), 1.0 (m, 3 H). Anal. Calcd for $C_{10}H_{16}N_2Br$: Br, 30.05. Found: Br, 30.28.

Cyclization of 3a. Dehydrobromination of 11.4 g (46.9 mmol) of **3a** with 5.7 g (56.3 mmol) of triethylamine in 20 mL of dichloromethane gave after workup and distillation (Kugelrohr apparatus, 0.02 mbar) 7.1 g (93%) of 2,3-dimethyl-2-propylcyclopropane-1,1-dicarbonitrile: ^{1}H NMR δ 1.6, 1.5, 1.35 (3 m). Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.04; H, 8.70; N, 17.27. Found: C, 73.87; H, 8.70; N, 17.11.

Addition of BMN to 3-Chloro-2-methylpropene (8). Irradiation of 7.25 g (50 mmol) of BMN and 4.34 g (48 mmol) of 8 in 60 mL of dichloromethane for 24 h gave after workup 9.94 g (88%) of 3-bromo-4-chloro-3-methylbutane-1,1-dicarbonitrile (**8a**): ^{1}H NMR δ 4.27 (t, J = 7 Hz, 1 H), 3.97 (s, 2 H), 2.68 (d, J = 7 Hz, 2 H), 1.97 (s, 3 H).

Cyclization of 8a. Dehydrobromination of 4.9 g (20.8 mmol) of **8a** with 2.11 g (23.7 mmol) of triethylamine in 10 mL of dichloromethane gave after workup and distillation 2.95 g (91%) of 2-(chloromethyl)-2-methylcyclopropane-1,1-dicarbonitrile: bp 110 °C (0.2 mbar); ^{1}H NMR δ 3.76, 3.59 (dd, J = 12 Hz, 2 H), 1.88 (s, 2 H), 1.62 (s, 3 H); IR (film) 2245 cm^{-1} (CN). Anal. Calcd for $C_7H_7N_2Cl$: C, 54.38; H, 4.56; N, 18.12; Cl, 22.93. Found: C, 54.34; H, 4.58; N, 18.07; Cl, 23.04.

Addition of BMN to 2,3-Dimethyl-2-hexene (9). Irradiation of 3.5 g (24.1 mmol) of BMN and 1.2 g (10.7 mmol) of **9** in 35 mL of dichloromethane for 3 h gave after workup 2.6 g (94%) of addition product as a 1:1 mixture of regioisomers 3-bromo-2,2,3-trimethylhexane-1,1-dicarbonitrile (**9a**) and 2-(1-bromo-1-methylethyl)-2-methylpentane-1,1-dicarbonitrile (**9b**): ^{1}H NMR δ 4.51 (s, 1 H), 4.4 (s, 1 H), 1.92, 1.86, 1.76 (3 s, 9 H), 1.70 (m, 4 H), 1.45 (m, 4 H), 1.43 (s, 9 H), 1.01 (m, 6 H).

Cyclization of 9a/b. Dehydrobromination of a mixture of 2.6 g (10.1 mmol) of **9a** and **9b** with 1.2 g (11.8 mmol) of triethylamine in 20 mL of dichloromethane gave after workup quantitatively 2,2,3-trimethyl-3-propyl-cyclopropane-1,1-dicarbonitrile: mp 66 °C (benzene); ^{1}H NMR δ 1.58, 1.51, 1.40, 1.36, 1.33 (2 m, 3 s, total 13 H), 1.01 (m, 3 H). Anal. Calcd for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15; N, 15.90. Found: C, 74.95; H, 9.05; N, 15.85.

2-(Chloromethyl)cyclopropane-1,1-dicarbonitrile. Irradiation of 7.25 g (50 mmol) of BMN and 3.93 (50 mmol) of allyl chloride in 60 mL of dichloromethane for 3 days at 28 °C yielded after workup 8.52 g (77%) of the crude addition product, which after dehydrobromination with 4.9 g (55 mmol) of triethylamine in 10 mL of dichloromethane and distillation yielded 4.3 g (60%) of 2-(chloromethyl)cyclopropane-1,1-dicarbonitrile: bp 136 °C (2 mbar); ^{1}H NMR δ 1.67-2.78 (m, 3 H, cyclopropane H), 3.38-4.06 (m, AB part of ABX spectrum, J_{AB} = 12.5 Hz, 2 H, CH_2Cl); IR (film) 2240 cm^{-1} (CN). Anal. Calcd. for $C_6H_5N_2Cl$: C, 51.26; H, 3.59; N, 19.93; Cl, 25.22. Found: C, 51.25; H, 3.64; N, 19.79; Cl, 25.05.

A fraction with a bp 76 °C (2 mbar) was identified as 1-chloro-2,3-dibromopropane (0.6 g, 5%).

Addition of BMN to 2-Methyl-3-methoxypropene. Irradiation of 4.34 g (29.9 mmol) of BMN and 2.57 g (29.9 mmol) of 2-methyl-3-methoxypropene in 60 mL of dichloromethane for 24 h at 28 °C yielded after workup 6.4 g (93%) of 3-methyl-4-methoxy-3-bromobutane-1,1-dicarbonitrile: ^{1}H NMR δ 1.87 (s, 3 H, CH_3), 2.47 and 2.73 (2 m, AB part of ABX spectrum, J_{AB} = 15 Hz, 2 H, CH_2), 3.43 (s, 3 H, OCH_3), 3.62 (dd, AB spectrum, J_{AB} = 10 Hz, CH_2O), 4.30 (t, X part of ABX spectrum, $J_{AB} = J_{BX}$ = 6 Hz, 1 H, $CH(CN)_2$).

Cyclization of the Addition Product. The addition product (4.4 g, 19.1 mmol) yielded on dehydrobromination with 2.01 g (22.6 mmol) of triethylamine in 10 mL of dichloromethane 2.5 g (81%) of 2-methyl-2-(methoxymethyl)-cyclopropane-1,1-dicarbonitrile: bp 55-57 °C (0.01 mbar); ^{1}H NMR δ 1.46 (s, 3 H, CH_3), 1.65 and 1.87 (dd, AB spectrum, J_{AB} = 6 Hz, 2 H, cyclopropane H), 3.34 and 3.60 (dd, AB spectrum, J_{AB} = 11 Hz, 3 H, CH_2O), 3.83 (s, 3 H, OCH_3); IR (film) 2240 cm^{-1} (CN). Anal. Calcd for $C_8H_{10}N_2O$: C, 64.01; H, 6.67; N, 18.67; O, 10.66. Found: C, 64.17; H, 6.70; N, 18.74; O, 10.81.

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Registry No. 1, 513-81-5; 2, 763-29-1; 3, 17618-77-8; **3a**, 105694-96-0; 4, 2738-19-4; **4a**, 105694-94-8; 5, 109-67-1; (*E*)-6, 4050-45-7; (*Z*)-6, 7688-21-3; (*Z*)-7, 627-20-3; 8, 563-47-3; **8a**, 105694-98-2; 9, 7145-20-2; **9a**, 105695-00-9; **9b**, 105695-01-0; (*Z*)-10, 691-38-3; (*Z*)-11, 762-63-0; BMN, 1885-22-9; DCM, 58821-77-5; H_2C=$CHCH_2Cl$, 107-05-1; $BrCH_2CHBrCH_2Cl$, 96-12-8; H_2C=$C(CH_3)CH_2OCH_3$, 22418-49-1; $H_3COCH_2C(Br)(CH_3)CH_2CH(CN)_2$, 105695-04-3; 2,2-dimethyl-3-propylcyclopropane-1,1-dicarbonitrile, 105694-95-9; 2,3-dimethyl-2-propylcyclopropane-1,1-dicarbonitrile, 105694-97-1; 2-(chloromethyl)-2-methylcyclopropane-1,1-dicarbonitrile, 105694-99-3; 2,2,3-trimethyl-3-propylcyclopropane-1,1-dicarbonitrile, 105695-02-1; 2-(chloromethyl)cyclopropane-1,1-dicarbonitrile, 105695-03-2; 2-methyl-2-(methoxymethyl)cyclopropanedicarbonitrile, 105695-05-4.

New Synthetic Methods via Free Radicals. Free-Radical Generation via Photolytic Homolysis of Alkyl-Cobaloxime C-Co Bonds. Efficient Radical Trapping with Useful Functional Groups

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Visible-light photolyses of primary and secondary (pyridine)alkylcobalt(III) cobaloximes, R-$Co^{III}(dmgH)_2py$ (**2-7**), generate free radicals that can be trapped in good to excellent yield (75% to nearly quantitative) with radical-trapping agents PhSSPh (to produce R-SPh), PhSeSePh (to produce R-SePh), or $BrCCl_3$ (to produce R-Br). Studies with CH_2=$CH(CH_2)_4$-$Co^{III}(dmgH)_2py$ (**6**) demonstrate that a 5-hexenyl intramolecular radical-olefin cyclization can intervene between radical generation and radical trapping. At the dilute concentrations required to suppress premature radical trapping prior to 5-hexenyl cyclization, competing side reactions limit the yields of cyclized, trapped product to about 60%. Studies of *n*-decyl-$Co^{III}(dmgH)_2py$ (**2**) and *n*-pentyl-$Co^{III}(dmgH)_2py$ (**9**) photolyses in the presence of PhSSPh at various concentrations demonstrate that β-hydride elimination (4%) was the major side reaction at high concentrations (18-22 mM) and that at low concentrations (1 mM) β-hydride elimination (17-31%) and as yet uncharacterized radical-cobaloxime ligand reactions (14-26%) were the major side reactions.

Organic synthesis is the focus of a recent renaissance of radical chemistry.[1] To realize the full potential of radical-mediated organic synthesis, new methods are still needed to generate free radicals and exploit them in syn-

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