Experimental Section

Materials. Methyl α,α'-azobis(isobutyrate) (MAIB) was synthesized by the method reported by Thiele:[7] mp 26 °C; NMR (CCl_4) δ 3.70 (s, 3 H), 1.50 (s, 6 H); IR (liquid film) 2970, 2935, 1735, 1452 cm^{-1}. Methyl α-chloroisobutyrate was obtained by esterification of α-chloroisobutyric acid with CH_2N_2: NMR($CDCl_3$) δ 3.79 (s, 3 H), 1.79 (s, 6 H). AIBN was of commercial guaranteed grade and was used without further purification. α-*p*-Tolylisobutyronitrile (**1a**) was prepared by cyanation of 2-*p*-tolylisopropyl bromide [bp 109–110 °C (3 mm Hg)]: IR (liquid film) 2205 cm^{-1}; bp 78–80 °C (2 mmHg); NMR (CCl_4) δ 7.18 (s, 4 H), 2.39 (s, 6 H), 2.15 (s, 3 H). α-*m*-Tolylisobutyronitrile was obtained from *m*-cymene according to the procedure similar to that of the para isomer: IR (liquid film) 2200 cm^{-1}; NMR δ 7.2 (m, 4 H), 2.38 (s, 3 H), 1.69 (s, 6 H).

General Procedure. Halos high-pressure 100 and 300 W Hg lamps with a water-cooling quartz jacket were used as light sources. The reactant mixture was placed in a cylindrical quartz vessel (30 × 300 mm) and nitrogen gas was bubbled into the mixture. The vessel along with the lamp was immersed in a water bath and the distance between the vessel and the lamp was kept at approximately 5 cm.

Analyses of Products. The analyses and identifications of products were done by means of GLC employing a Yanagimoto Model GCG-550F operated with columns (1.2m × 4 mm) of both PEG 20M (10 wt %) on Chromosorb WAN and Silicon OV 17 (5 wt %) on Shimalite WAN.

Thermolysis of AIBN in Toluene. A solution of 0.096 M AIBN (2.35 g) in toluene (150 mL) was heated at 100–120 °C for 18 h. The reaction mixture, after separation from **3** (1.65 g, 84%) by filtration, was chromatographed on silica gel (Malinckrodt, 100 mesh) and on eluting with benzene–*n*-hexane (6:1) afforded an oil (10 mg, 0.5%) which was characterized as β-phenylpivalonitrile (**2a**): NMR ($CDCl_3$) δ 7.29 (s, 5 H), 2.82 (s, 2 H), 1.35 (s, 6 H); *m/e* (rel intensity) 159 (M^+) (50), 136 (100), 132 (38), 91 (25), 80 (50), 79 (63). The structure of **3** was determined from GLC–MS analysis: *m/e* (rel intensity) 138 (M^+) (3), 121 (20), 69 (100), 68 (91), 54 (55), 42 (34).

Photolysis of AIBN in Toluene. A solution of 0.096 M AIBN (2.35 g) in toluene (150 mL) was photolyzed with a 300-W high-pressure Hg lamp. After irradiating for 4 h, the reaction mixture was filtered to remove **3** (1.71 g, 90%) and the filtrate was chromatographed to give an oil (3%). It was found to be a mixture of α-*p*-tolylisobutyronitrile (**1a**) and β-phenylpivalonitrile (**2a**) in the ratio of 1.3, respectively. The compounds were identified by means of GLC and GLC–MS and comparing with the authentic samples synthesized independently. For **1a**, *m/e* (rel intensity) 159 (M^+) (73), 91 (100). Independently, the above toluene solution of AIBN was photolyzed by a Pyrex-filtered light from the same 300-W lamp. The GLC analysis of the mixture after 59% decomposition of AIBN indicates the formation of **3** (89%) and a mixture (0.5%) of **1a** and **2a** (the ratio of **1a/2a** equals 1.2).

Photolysis of MAIB in Toluene. A solution of 0.06 M MAIB (2.2 g) in toluene (170 mL) was photolyzed with the UV light. The disappearance of MAIB was observed after 5.5 h of irradiation. Chromatography of the reaction mixture on SiO_2 with benzene–ethyl acetate afforded bibenzyl (0.28 g) and an oil (0.36 g, 37%), which was characterized as a mixture of methyl α-*p*-tolylisobutyrate (**1b**) and methyl β-phenylpivalate (**2b**) in the ratio of 1:15, respectively. For **2b**: NMR δ 7.2 (m, 5 H), 3.65 (s, 3 H, OMe), 2.86 (s, 2 H), 1.20 (s, 6 H). For **1b**: NMR δ 7.2 (m, 4 H), 3.65 (s, 3 H), 2.35 (s, 3 H), 1.58 (s, 6 H).

Photolysis of Methyl α-Chloroisobutyrate in Toluene. A solution of 0.09 M methyl α-chloroisobutyrate (2.0 g) in toluene (150 mL) was photolyzed with UV light. After irradiation for 36 h, a 15% conversion of the isobutyrate was observed. Similar workup of the reaction mixture using silica gel chromatography gave bibenzyl (0.17 g) and a mixture of **1b** and **2b** (0.12 g, 57.7%) in the ratio of 6:11, respectively.

Registry No.—**3**, 3333-52-6; α-chloroisobutyric acid, 594-58-1; bibenzyl, 103-29-7; 2-*p*-tolylisopropyl bromide, 68682-49-5; α-*m*-tolylisobutyronitrile, 30568-27-5; *m*-cymene, 535-77-3; toluene, 108-88-3.

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(1) Contribution No. 249.

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Electronic Factors Governing the Direction of Hydrogen Migration in Substituted Isoindenes

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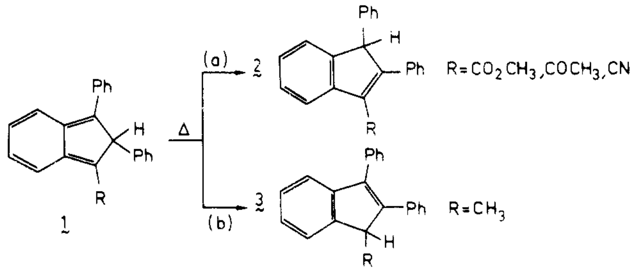
In a recent paper,[1] Pettit and Wilson correlated the direction of hydrogen migration in substituted isoindenes 1 (Scheme I) with the symmetry of the nonbonding orbital in the indenyl radical. In the unsubstituted radical, this orbital has a node at the C_2 carbon. In the substituted cases, the node is either between C_2 and C_1 or between C_2 and C_3, depending on R (Scheme II). The concerted suprafacial hydrogen migration is allowed when it occurs between two neighboring carbon atoms with the *same sign* in the nonbonding orbital. Simple Hückel molecular calculations allow predictions in remarkable agreement with the experimental results[1] (except for R = H). The purpose of this note is to show how the position of the node, and thus the direction of hydrogen migration, is related to the electronic properties of the substituent R.

As a model we study, by means of perturbation theory, the asymmetry induced by substitution in the nonbonding orbital of the allyl radical. This asymmetry arises from second-order mixings between the antisymmetric nonbonding orbital (φ_2^0) and the symmetric orbitals (φ_1^0 and φ_3^0) of the parent unsubstituted radical. The sign of the nonzero coefficient which appears on the central carbon C_2 depends on the signs of the mixing coefficients between the molecular orbitals.

Let us first assume that the substituent is a single orbital perturber (R = F, OH, NH_2, BH_2), whose p orbital energy is $x\beta$. In Figure 1 are drawn the Hückel orbitals prior to interaction. The orbitals are so oriented that all of the overlap integrals are positive. The mixing coefficients between φ_2^0 and φ_1^0, and between φ_2^0 and φ_3^0, are respectively:[2]

Scheme I



Scheme II

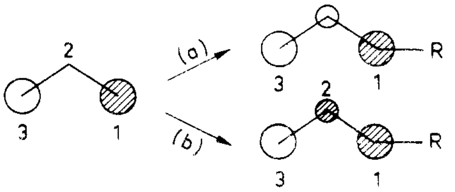


Table I. Coefficients in the Nonbonding Orbital of R-Substituted Allyl Radicals (C_1, C_2, C_3) and Mixing Coefficients between the Unperturbed Molecular Orbitals

R	registry no.	C_1[a]	C_2[b]	C_3	C_{21}[b]	C_{23}[b]
F	68408-53-7	0.710	(+) +0.105	−0.722	(+) +0.078	(−) −0.067
OH	15338-29-1	0.694	(+) +0.128	−0.712	(+) +0.092	(−) −0.083
NH_2	65332-07-2	0.642	(+) +0.218	−0.694	(+) +0.145	(−) −0.149
BH_2	68408-54-8	0.625	(−) −0.105	−0.667	(−) −0.110	(+) +0.045
CH_3	16520-21-1	0.714	(+) +0.066	−0.714	(+) +0.053	(−) −0.039
CN	62528-89-6	0.553	(−) −0.162	−0.614	(−) −0.167	(+) +0.071
COH	68408-55-9	0.623	(−) −0.091	−0.650	(−) −0.090	(+) +0.043
CO_2H	62393-36-6	0.605	(−) −0.120	−0.642	(−) −0.119	(+) +0.056

[a] Substituted center. [b] The sign in parentheses is that predicted by the qualitative analysis of the perturbation (see text).

$$C_{21} = \frac{K^2}{E_{\varphi_2{}^0} - E_{\varphi_1{}^0}} \frac{\langle \varphi_1{}^0 | p \rangle \langle p | \varphi_2{}^0 \rangle}{E_{\varphi_2{}^0} - E_{\mathrm{p}}} \tag{1}$$

and

$$C_{23} = \frac{K^2}{E_{\varphi_2{}^0} - E_{\varphi_3{}^0}} \frac{\langle \varphi_3{}^0 | p \rangle \langle p | \varphi_2{}^0 \rangle}{E_{\varphi_2{}^0} - E_{\mathrm{p}}} \tag{2}$$

Taking into account the sign of overlaps (all positive) and energy differences $(E_{\phi_2}{}^0 - E_{\phi_1}{}^0) > 0$, $(E_{\phi_2}{}^0 - E_{\phi_3}{}^0) < 0$, it follows that the two coefficients are of opposite signs. If $x > 0$ (R = F, OH, NH_2), C_{21} is positive and C_{23} is negative. Therefore the lobe on the central carbon in the perturbed ϕ_2 orbital is in phase with the lobe carried by the substituted carbon atom C_1 ((b) in Scheme II). For $x < 0$ (R = BH_2) the inverse situation will occur ((a) in Scheme II), the coefficients of C_1 and C_2 being out-of-phase.[4] These qualitative predictions are confirmed by the full perturbation calculation performed within the framework of extended Hückel method[5] (Table I).

The situation is a little bit more complex when the substituent carries more than one orbital which can interact with the π system of the allyl radical. If there are two orbitals (one bonding π_0 and one antibonding $\pi_0{}^*$), each mixing coefficient is now the sum of two terms of opposite signs. Two cases can be distinguished:

$$C_{21} = \frac{K^2}{E_{\varphi_2{}^0} - E_{\varphi_1{}^0}} \left[\frac{\langle \varphi_1{}^0 | \pi_0 \rangle \langle \pi_0 | \varphi_2{}^0 \rangle}{E_{\varphi_2{}^0} - E_{\pi_0}} + \frac{\langle \varphi_1{}^0 | \pi_0{}^* \rangle \langle \pi_0{}^* | \varphi_2{}^0 \rangle}{E_{\varphi_2{}^0} - E_{\pi_0{}^*}} \right] \tag{3}$$

and

$$C_{23} = \frac{K^2}{E_{\varphi_2{}^0} - E_{\varphi_3{}^0}} \left[\frac{\langle \varphi_3{}^0 | \pi_0 \rangle \langle \pi_0 | \varphi_2{}^0 \rangle}{E_{\varphi_2{}^0} - E_{\pi_0}} + \frac{\langle \varphi_3{}^0 | \pi_0{}^* \rangle \langle \pi_0{}^* | \varphi_2{}^0 \rangle}{E_{\varphi_2{}^0} - E_{\pi_0{}^*}} \right] \tag{4}$$

(1) **R is a π Donor (R = CH_3.)**[6] Then we have $|E_{\varphi_2{}^0} - E_{\pi_0}| \ll |E_{\varphi_2{}^0} - E_{\pi_0{}^*}|$. In each bracket, the first term is expected to dominate the second one and to impose the sign of the mixing coefficient: $C_{21} > 0$ and $C_{23} < 0$. In the perturbed nonbonding orbital φ_2, the coefficients on C_2 and the substituted carbon C_1 are in phase ((b) in Scheme II).

(2) **R is a π Acceptor (R = CN, COH, CO_2H).** Now we have $|E_{\varphi_2{}^0} - E_{\pi_0}| \gg |E_{\varphi_2{}^0} - E_{\pi_0{}^*}|$. In each bracket, the second term imposes the sign of the mixing coefficient: $C_{21} < 0$ and $C_{23} > 0$. In the nonbonding orbital φ_2, C_2 is in phase with the unsubstituted carbon C_3 ((a) in Scheme II). These qualitative conclusions are confirmed by the full perturbation calculations displayed in Table I.

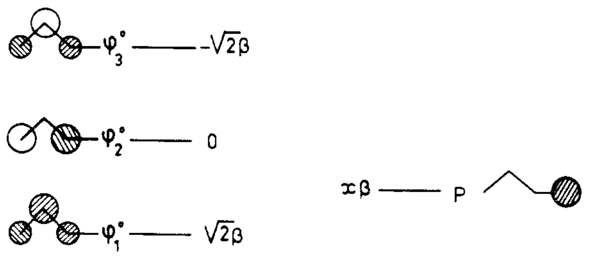


Figure 1.

In conclusion, we have shown that the asymmetry induced in the nonbonding orbital of the allyl radical by substitution at carbon C_1 depends on the electronic properties of the substituent R. If R is a donor (R = F, OH, NH_2, CH_3), the lobe on the central carbon C_2 is in phase with the lobe on the substituted center C_1. If R is a π acceptor (R = BH_2, CN, COH, CO_2H), the lobe on the central carbon is in phase with the lobe on the unsubstituted center C_3. This result allows a more complete understanding of the thermal rearrangement of substituted indenes **1**. In **1**, both carbons 1 and 3 are substituted, respectively, by R and Ph. Calculations on the allyl radical substituted by a phenyl group indicate that the phenyl acts as a weak π donor. Therefore, if an allyl radical is substituted by R at carbon C_1 and by Ph at carbon C_3, the perturbing effects of the two substituents on the asymmetry of the molecular orbital φ_2 add if R is a π acceptor, and are of opposite signs if R is a π donor. The most ambiguous case is the substitution at C_1 by a methyl group, which is the weakest π donor of the studied series of substituents R (Table I). Calculations on 1-methyl-3-phenylallyl radical indicates that the π donor character of the phenyl group is weaker than that of the methyl group. The node in φ_2 still remains between C_2 and C_3 ($C_1 = 0.620$, $C_2 = 0.027$, $C_3 = -0.631$). Therefore, the presence of a phenyl group at the carbon C_3 does not modify the established relation between the asymmetry of the nonbonding orbital and the electronic properties of R. Consequently, the product of hydrogen migration in substituted indenes **1** is **2** if R is a π acceptor and **3** if R is a π donor.

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References and Notes

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(2) These formulas are derived from the perturbation theory which neglects overlap. Furthermore, the approximation $H_{ij} = KS_{ij}$ has been made. It has been shown that these formulas are sufficient for a qualitative description of the orbital mixings.[3]

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(4) One can note that, for $x > 0$, φ_2 is the third π orbital of a four-atom skeleton. If we take into account the first-order mixing between $\varphi_2{}^0$ and p, φ_2 indeed looks like the $\pi_3{}^*$ of butadiene. For $x < 0$, φ_2 is the second π orbital built on four centers and looks like the π_2 orbital of butadiene.

(5) We are grateful to Professor R. Hoffmann for giving us the opportunity to use the Fragment Molecular Orbital (FMO) program.

(6) For a discussion of donor or acceptor properties of substituents, see ref 3.