washed successively with 2% hydrochloric acid, a saturated sodium bicarbonate solution, and water and dried over anhydrous calcium chloride. Concentration of the solution gave 59 g (98% yield) of the residue which was analyzed on conventional VPC to contain 9.0% of fraction A. This fraction was separated on the preparative VPC: retention time, 7.5 min; column, $^3/_8$ in. $\phi \times 10$ ft, packed with 30% Carbowax 20M on Chromosorb W-AW, at 150 °C; He pressure, 22 lb/in.^{2}; injection port temp, 200 °C; detector temp, 240 °C; 300 μL of the sample being injected every time.

A part (4.5 g, 0.03 mol) of the fraction thus obtained was then heated under reflux with 18.0 g (0.12 mol) of trifluoromethanesulfonic acid in 225 mL of methylene chloride for 16 h. The reaction was quenched by being poured onto 200 mL of ice–water and treated similarly as above to give a dry methylene chloride solution. Concentration of the solution afforded 4.5 g (quantitative yield) of the residue comprising the isomerization products. The residue was fractionated on the preparative VPC, and the first-eluted fraction (fraction A) was recovered to give 0.72 g of crude [3.3.3]propellane (**2**). Purification with slow sublimation in vacuo (~200 mm) yielded 0.58 g (0.97% yield based on **1**) of **2** with 94% purity: mp 116–117 °C; IR (neat) 2920, 2850, 1460, 1440, 1290, 1230, 1200, 1160, 1100, 990, 970, 900 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.40 (s). The mass spectrum[1] and the ^{13}C NMR chemical shifts (Table I) were in good agreement with those[3] of an authentic specimen.

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.9; H, 12.1.

4-Methylbicyclo[5.2.1]decan-10-one (10). To a solution of 24.0 g (0.21 mol) of 4-methylcyclohexanone (**8**) in 200 mL of a 50:50 v/v mixture of tetrahydrofuran and methanol kept at 2–5 °C was added 2.0 g of anhydrous potassium carbonate and then dropwise with efficient stirring in a period of 7 h a solution of 59.7 g (0.23 mol) of dimethyl *N,N'*-dinitroso-*N,N'*-tetramethylenedicarbamate (**9**) in 1 L of the THF–methanol mixture. The reaction was stirred at the same temperature for an additional 5 h and set aside overnight at ambient temperature. Solid matters were filtered off and the filtrate was concentrated. The residue was extracted with petroleum ether and the solvent was evaporated off. Fractional distillation of the residue gave 7.9 g (21% yield) of a mixture of isomeric 4-methylbicyclo[5.2.1]decan-10-one (**10**), bp 68–70 °C (0.5 mm).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.3; H, 11.0.

The mixture was analyzed on Golay GC–MS to comprise two major constituents (95% of the combined peak areas) in a 58:42 ratio, which were separable also on the preparative VPC. The earlier-eluted, more-abundant component: IR (neat) 2960, 2920, 2860, 1730, 1450, 1370, 1310, 1190, 1140 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ_C 24.20 (t, 2), 28.18 (d, 1), 32.49 (q, 1), 34.44 (t, 2), 35.98 (t, 2), 45.88 (d, 2), 232.04 (s, 0.3); mass spectrum (*m/e*, rel intensity) 166 (43, M$^+$), 151 (32), 112 (53), 110 (32), 109 (33), 97 (37), 96 (37), 95 (43), 84 (34), 83 (33), 82 (32), 81 (50), 68 (32), 67 (43), 55 (100), 54 (32), 41 (55). The later-eluted component: IR (neat) 2960, 2940, 2890, 1740, 1480, 1460, 1440, 1380, 1320, 1140 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ_C 18.03 (q, 1), 24.77 (t, 2), 29.64 (t, 2), 30.62 (d, 1), 31.43 (t, 2), 45.56 (d, 2), 230.09 (s, 0.4); mass spectrum (*m/e*, rel intensity) 166 (44, M$^+$), 123 (38), 112 (60), 110 (38), 109 (38), 96 (40), 95 (47), 84 (37), 83 (40), 82 (38), 81 (62), 68 (37), 67 (50), 55 (100), 54 (34), 41 (61).

4-Methylbicyclo[5.2.1]decan-10-one Tosylhydrazone (11). A solution of 4.3 g (0.026 mol) of the mixture of isomeric 4-methylbicyclo[5.2.1]decan-10-ones prepared above, 5.3 g (0.028 mol) of *p*-toluenesulfonylhydrazine, and 1.0 mL of 35% hydrochloric acid in 200 mL of absolute ethanol was heated under reflux for 3 h, and the reaction was set aside overnight at ambient temperature. Concentration of the solution and recrystallization of the residue from an ethanol–ether (50:50) mixture gave 3.2 g (37% yield) of 4-methylbicyclo[5.2.1]decan-10-one tosylhydrazone (**11**): mp 171–172 °C; IR (Nujol) 3200 (br), 1600, 1170 cm^{-1}.

Anal. Calcd for $C_{18}H_{26}O_2N_2S$: C, 64.65; H, 7.84; N, 8.38; S, 9.57. Found: C, 64.4; H, 7.7; N, 8.6; S, 9.8.

1-Methylperhydrotriquinacene (4). To 66 g of molten acetamide kept at 90–95 °C was added 1.6 g (0.070 mol) of sodium in small portions. After dissolution of the sodium, 5.5 g (0.017 mol) of 4-methylbicyclo[5.2.1]decan-10-one tosylhydrazone (**11**) was added to the solution with efficient stirring, and the reaction temperature was raised to 175 °C in a period of 30 min. The reaction was stirred for 5 min at the same temperature and then cooled down to 90 °C.

To the reaction mixture was added dropwise 55 mL of water, and the resulting mixture was set aside to cool at ambient temperature. The reaction mixture was extracted with three 50-mL portions of *n*-pentane, and the combined pentane extracts were washed with water and dried over anhydrous calcium chloride. Evaporation of the solvent and purification of the residue with the preparative VPC gave 1.7 g (67% yield) of a pure sample of 1-methylperhydrotriquinacene (**4**): mp 33–34 °C; ^{1}H NMR (CDCl$_3$) δ 1.05 (s, -CH$_3$), 0.9–2.2 (complex m); mass spectrum (*m/e*, rel intensity) 150 (22, M$^+$), 135 (15), 107 (30), 95 (15), 94 (100), 81 (44), 80 (21), 79 (22), 67 (14), 41 (14).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.7; H, 12.2.

Acknowledgment. The authors thank Professor Roger Alder, University of Bristol School of Chemistry, for the information of the ^{13}C NMR and the mass spectra of [3.3.3]-propellane prior to publication.

Registry No.—**1**, 32789-29-0; **8**, 589-92-4; **9**, 40002-44-6; **10**, *exo*-Me, 23109-52-6; **10**, *endo*-Me, 23109-50-4; **11**, 68796-73-6.

References and Notes

(1) N. Takaishi, Y. Inamoto, K. Tsuchihashi, K. Yashima, and K. Aigami, *J. Org. Chem.*, **40**, 2929 (1975).
(2) Furthermore, a 5 molar catalyst in 24 h reaction also caused practically no reaction, and only 16.5% **2** disappeared with as much as 25 molar catalyst in 6 h.
(3) R. Alder, private communication.
(4) E. Osawa, K. Aigami, N. Takaishi, Y. Inamoto, Y. Fujikura, Z. Majerski, P. v. R. Schleyer, E. M. Engler, and M. Farcasiu, *J. Am. Chem. Soc.*, **99**, 5361 (1977).
(5) D. Ginsburg, *Acc. Chem. Res.*, **2**, 121 (1969); **5**, 249 (1972); **7**, 286 (1974); *Tetrahedron*, **30**, 1487 (1974); R. L. Cargill, T. E. Jackson, N. T. Peet, and C. M. Pond, *Acc. Chem. Res.*, **7**, 106 (1974).
(6) (a) H. W. Whitlock, Jr., and M. W. Siefken, *J. Am. Chem. Soc.*, **90**, 4929 (1968); (b) E. M. Engler, M. Farcasiu, A. Sevin, J. M. Cense, and P. v. R. Schleyer, *ibid.*, **95**, 5769 (1973).
(7) R. C. Bingham and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 3189 (1971).
(8) L. A. Paquette, G. V. Meehan, and S. J. Marshall, *J. Am. Chem. Soc.*, **91**, 6779 (1969); T. Jacobson, *Acta Chim. Scand.*, **21**, 2235 (1967); J. W. Baum and C. D. Gutsche, *J. Org. Chem.*, **33**, 4312 (1968).
(9) C. M. Samour and J. P. Mason, *J. Am. Chem. Soc.*, **76**, 441 (1954).
(10) C. D. Gutsche and J. W. Baum, *Org. Prep. Proc.*, **1**, 35 (1969); *Chem. Abstr.*, **71**, 49373d (1969).
(11) J. K. Whitesell and R. S. Matthews, *J. Org. Chem.*, **42**, 3878 (1977).
(12) N. Takaishi, Y. Inamoto, and K. Aigami, *Chem. Lett.*, 1185 (1973); *J. Org. Chem.*, **40**, 276 (1975).

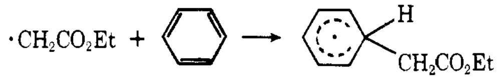
Photochemical Reaction of Radical ·CMe$_2$X with Toluene[1]

Yoshiro Ogata,* Katsuhiko Takagi, and Eiji Hayashi

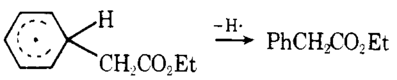
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464 Japan

Received May 22, 1978

In our previous paper,[2] photodecomposition of ethyl chloroacetate in benzene was found to give a ring substitution product, ethyl phenylacetate, suggesting a radical substitution reaction.



(1)



(2)

These types of ring-substituted products were not observed in the thermolysis of azo compounds.[3] To our knowledge, there is only one available report on the photoinduced decomposition of azo compounds in aromatic solvents.[4]

Herein, we report the photodecomposition of AIBN and MAIB in toluene showing a parallelism between the photochemical behavior of MAIB, AIBN, and α-chloroisobutyrate in toluene.

Results and Discussion

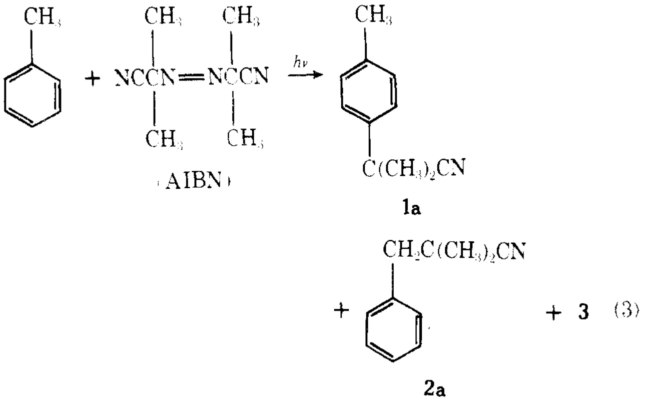
Photodecomposition of α,α'-Azobis(isobutyronitrile) (AIBN) in Toluene. Irradiation of 0.10 M AIBN in toluene under N$_2$ for 4 h gave a mixture (~3%) of α-*p*-tolyliso-

Table I. The Effect of Initial Concentration of AIBN on the Ratio of 1a/2a in the Photolysis of AIBN in Toluene[a]

$[AIBN]_0$, M	1a/2a	$[AIBN]_0$, M	1a/2a
0.015	0.18	0.10	0.57
0.025	0.21	0.20	0.63
0.05	0.42		

[a] The reaction mixture was irradiated for 13 h by a 100-W high-pressure Hg lamp.

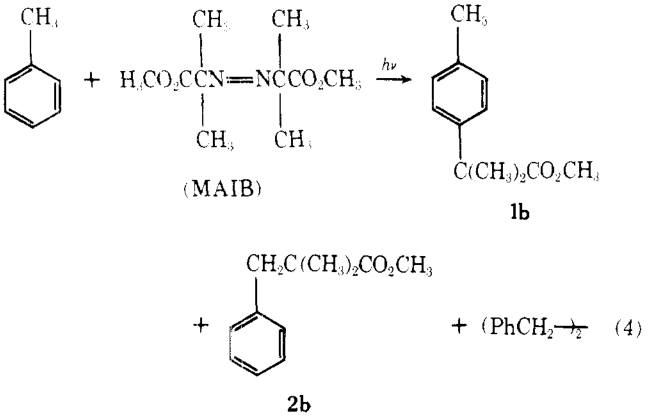
butyronitrile (1a) and β-phenylpivalonitrile (2a) along with a dimer, 1,1′,2,2′-tetramethylsuccinodinitrile (3) (90%). The ratio of 1a to 2a increased with an increase of the initial concentration of AIBN as shown in Table I.



The increase of light intensity raises the ratio of 1a/2a from 0.57 to 1.31. In a control experiment, where UV light shorter than 300 nm was cut off by a Pyrex filter, the similar tendency as above was also observed, that is, the ratio of 1a/2a equals 1.2 which is comparable to the ratio (1.3) without the filter.

Thermolysis of 0.10 M AIBN in toluene at 100–120 °C for 18 h gave **2a** (0.5%) along with dimer **3** (84%), but no **1a** was detected.

Photodecomposition of Methyl Azobis(isobutyrate)



(MAIB) in Toluene. A solution of 0.06 M methyl azobis(isobutyrate) (MAIB) in toluene on irradiation under N_2 for 5.5 h completely decomposed to yield a mixture (37%) of methyl α-p-tolylisobutyrate (**1b**, 2.3%) and methyl β-phenylpivalate (**2b**, 34.7%) along with bibenzyl (32%).

Photodecomposition of Methyl α-Chloroisobutyrate in Toluene. A solution of 0.09 M methyl α-chloroisobutyrate in toluene on irradiation under N_2 for 36 h led to the decomposition of the isobutyrate in a 15% conversion. The analogous workup gave a mixture of **1b** (20.4%) and **2b** (37.3%).

Effect of Radical Sources on Product Distribution. Reactivities and product distributions on decomposition of AIBN, MAIB, and methyl α-chloroisobutyrate in toluene are compiled in Table II.

It is of interest to note that no ring substitution occurred in thermal decomposition of AIBN and MAIB, although the thermal decomposition of them should afford the corresponding radicals, $\cdot CMe_2X$, which subsequently collapse into a dimer (e.g., **3**) or a disproportionation product (e.g., isobutyronitrile),[5] while the α-chloroisobutyrate is thermally stable, giving no detectable product on refluxing in toluene.

As mentioned above, there is observed no difference between the ratios of 1a/2a on photolyses of AIBN with and without a Pyrex filter, suggesting the reaction is initiated by UV light over 300 nm which was exclusively absorbed by AIBN. The ratio of 1a/2a increases with an increase in both $[AIBN]_0$ and light intensity used, which suggests the acceleration of ring substitution by a large excess of radical, $\cdot CMe_2CN$, and implies an attack of the radical on the ring. However, no ring substitution occurs in the thermolysis of AIBN in toluene to give the radical. Therefore, it may be insufficient to explain the reaction by means of a simple radical substitution as shown in eq 1.

No new UV and visible absorbing species were observed on addition of AIBN to toluene, indicating that they cannot form any ground state CT complex.

The following explanation would be reasonable. Excited AIBN may form an exciplex with toluene, which then collapses to nitrogen and the precursor to the ring-substitution product. Alternatively, another pathway via excitation of toluene by UV light shorter than 300 nm may be plausible because the substitution product (**1b**) was observed on photolysis of methyl α-chloroisobutyrate in toluene in which α-chloroisobutyrate was transparent in the range of UV light over 230 nm. In this case, the excited toluene may transfer its energy to α-chloroisobutyrate followed by the collapse to radicals, or it may form an exciplex, which is a transient intermediate similar to that from toluene and the excited AIBN.

Finally, in our present photolysis of AIBN and MAIB, ring substitution occurred at the para position of toluene. The other ortho and meta isomers were formed in small amounts. The result does not parallel with corresponding ortho and meta isomers in significant yields along with the para isomer.[2b,6]

Table II. Reactivities and Product Distributions Found in the Decompositions of AIBN, MAIB, and $ClCMe_2CO_2Me$ in Toluene[a]

substrate	condition	conv, %	time, h	temp, °C	CH_3Ph-p-CMe_2X 1,%	$PhCH_2CMe_2X$ 2,%
$(NCC(CH_3)_2N{=})_2$	$h\nu$	100	4	RT	1.5[e]	1.5[f]
(AIBN)[b]	Δ	100	18	100–120		0.5
$(H_3CO_2C(CH_3)_2N{=})_2$ (MAIB)[c]	$h\nu$	100	5.5	RT	3[g]	34[h]
$ClC(CH_3)_2CO_2Me$[d]	$h\nu$	15	36	RT	20	37

[a] A 300-W high-pressure Hg lamp with a quartz filter was used as light source. 0.05–0.1 M of the substrate in toluene was used in each run. [b] Registry no., 78-67-1. [c] Registry no., 2589-57-3. [d] Registry no., 22421-97-2. [e] Registry no., 40119-34-4. [f] Registry no., 35863-45-7. [f] Registry no., 68682-48-4. [g] Registry no., 14248-22-7.

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.

References and Notes

(1) Contribution No. 249.

(2) (a) Y. Ogata, T. Itoh, and Y. Izawa, *Bull. Chem. Soc. Jpn.*, **42**, 794 (1969); (b) Y. Ogata and E. Hayashi, *ibid.*, **50**, 323 (1977).

(3) (a) A. L. J. Beckwith and R. J. Leydon, *Tetrahedron Lett.*, 385 (1968); (b) M. Talat-Erben and S. Bywater, *J. Am. Chem. Soc.*, **77**, 3712 (1955); (c) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949); (d) A. F. Bickel and W. A. Waters, *Recl. Trav. Chim. Pays-Bas*, **69**, 312 (1950); (e) A. F. Bickel and W. A. Waters, *ibid.*, **69**, 1490 (1950); (f) C. G. Overberger and M. B. Berenbaum, *J. Am. Chem. Soc.*, **74**, 3293 (1952).

(4) J. C. Roy, J. R. Nash, R. R. Williams, and W. H. Hamill, *J. Am. Chem. Soc.*, **78**, 519 (1956).

(5) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961).

(6) Y. Ogata, E. Hayashi, and H. Kato, *Bull. Chem. Soc. Jpn.*, **51**, 3657 (1978).

(7) J. Thiele, *Justus Liebigs Ann. Chem.*, **290**, 32 (1896); "Methoden der Organishen Chemie, Stickstoff Verbindung 1", Part 2, Georg Thime Verlag, Stuttgart, 1967, p 785.

Electronic Factors Governing the Direction of Hydrogen Migration in Substituted Isoindenes

Yves Jean

Laboratoire de Chimie Théorique (490), Université Paris-Sud, 91405 Orsay Cedex, France

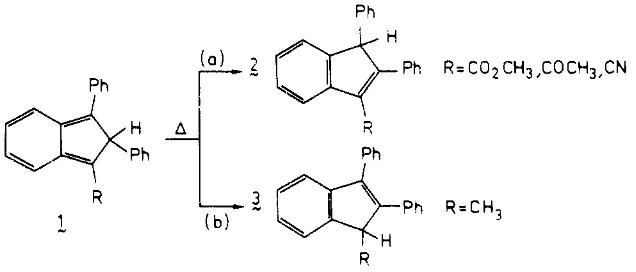
Received September 21, 1978

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