the several minor bands from the PLC plates amounted to more than 5% of the reaction product.

Reaction of *p*-(1,2-Dimethyl-1-nitropropyl)nitrobenzene (31) with the Salt 27. The nitro compound **31** (596 mg, 2.5 mmol) was allowed to react with the salt **27** (1.72 g, 5.0 mmol) in Me_2SO (10 mL) at 50 °C for 30 min. The reaction mixture was acidified with hydroxylamine hydrochloride and then worked up in the usual manner. The ^1H NMR spectrum of the crude reaction product revealed that there was one major component, whose NMR parameters strongly suggested the oxime ether **33**: δ 0.74 (d, 3 H, **MeCHMe**, $J = 6.8$ Hz), 1.02 (d, 3 H, MeCH**Me**, $J = 6.8$ Hz), 1.07 (d, 6 H, **Me_2CH**, $J = 6.8$ Hz), 1.80 (s, 3 H, Me), 2.10 (m, 1 H, MeCHMe), 2.65 (m, 1 H, Me_2CH), 6.06 (d, 1 H, N=CH, $J = 7.6$ Hz), AA′XX′ pattern 7.56 (m, 2 H), 8.18 (m, 2 H), $J_{AX} + J_{AX'} = 9.0$ Hz. The only other identifiable compound in the crude reaction product (ca. 10%) was the alcohol **32**. Attempted purification of **33** by PLC lead to decomposition and gave 50% (262 mg) **3-methyl-2-(*p*-nitrophenyl)-2-butanol (32)**: mp 48–49 °C; ^1H NMR δ 0.76 (d, 3 H, **MeCHMe**, $J = 6.7$ Hz), 0.94 (d, 3 H, MeCH**Me**, $J = 6.7$ Hz), 1.56 (s, 3 H, Me), 1.76 (s, 1 H, OH), 2.04 (sept, 1 H, Me_2**CH**, $J = 6.7$ Hz), AA′XX′ pattern 7.59 (m, 2 H), 8.18 (m, 2 H), $J_{AX} + J_{AX'} = 9.1$ Hz; IR ($CHCl_3$) 3605, 1600, 1510, 1350, 1170, 1070, 1010, 850 cm^{-1}; UV (MeOH) 274 nm (ϵ 1.02×10^4); mass spectrum, m/e 209 (M^+, 0.6%), 194 (1), 167 (19), 166 (100), 150 (9), 120 (13), 105 (12), 77 (15), 43 (100), 41 (13).

Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.13; H, 7.25; N, 7.02.

Reaction of *p*-(1-Methyl-1-nitropropyl)nitrobenzene (36) with Tetrabutylammonium 2-Nitro-2-propanide (34). Reaction of the nitro compound **36** (560 mg, 2.5 mmol) with the salt **34** (1.65 g, 5.0 mmol) in Me_2SO (10 mL) at 25 °C for 30 min gave, after workup, purification by PLC, and recrystallization from ethanol, *p*-(1-ethyl-1,2-dimethyl-2-nitropropyl)nitrobenzene (**38**; 518 mg, 78%), mp 96–97 °C (lit.[20] mp 94–95.5 °C). The use of the tetrabutylammonium salt **34** rather than the lithium salt **7** does not affect the yield of **38** but reduces the reaction time from 3 h (in HMPA).[20]

Reaction of *p*-(1,3,3-Trimethyl-1-nitrobutyl)nitrobenzene (37) with Tetrabutylammonium 2-Nitro-2-propanide (34). Reaction of the nitro compound **37** (532 mg, 2.0 mmol) with salt **34** (1.32 g, 4.0 mmol) in Me_2SO (8 mL) at 50 °C for 30 min gave, after workup, PLC, and recrystallization from light petroleum, ***p*-[1,3,3-trimethyl-1-(1-methyl-1-nitroethyl)butyl]nitrobenzene** (**39**; 468 mg, 76%): mp 117–118 °C; ^1H NMR δ 0.77 (s, 9 H, CMe_3), 1.40 (q, 3 H, **Me**C(NO_2)Me, $J = 0.7$ Hz), 1.57 (q, 3 H, MeC(NO_2)**Me**, $J = 0.7$ Hz), 1.64 (d, 3 H, Me, $J = 1.0$ Hz), 1.97 (d, 1 H, **H**CH, $J = 14.9$ Hz), 2.34 (dq, 1 H, HC**H**, $J = 14.9$, 1.0 Hz), AA′XX′ pattern 7.55 (m, 2 H), 8.17 (m, 2 H), $J_{AX} + J_{AX'} = 9.1$ Hz; IR ($CHCl_3$) 1605, 1595, 1530, 1520, 1370, 860, 855 cm^{-1}; UV (hexane) 264 nm (ϵ 1.24×10^4); mass spectrum, m/e 262 ($M^+ - NO_2$, 0.03%), 246 (1), 220 (3), 206 (6), 164 (64), 89 (18), 57 (100), 43 (24), 41 (37).

Anal. Calcd for $C_{16}H_{24}N_2O_4$: C, 62.31; H, 7.85; N, 9.09. Found: C, 62.57; H, 7.87; N, 8.91.

Reaction of *p*-(1,2-Dimethyl-1-nitropropyl)nitrobenzene (31) with Tetrabutylammonium 2-Nitro-2-propanide (34). Reaction of the nitro compound **31** (600 mg, 2.5 mmol) with the salt **34** (1.65 g, 5.0 mmol) in Me_2SO (10 mL) at 50 °C for 5 h gave no detectable amounts of C-alkylation products. The only isolable products after PLC were the reduction product *p*-(1,2-dimethylpropyl)nitrobenzene (92 mg, 19%), identical by TLC, IR, and ^1H NMR with an authentic sample,[29] and the alcohol **32** (44%, 221 mg), identical with the sample isolated above.

Reaction of *p*-Nitrocumyl Chloride (21) with Lithium 3-Methyl-2-nitro-2-butanide (42). Reaction of the chloride **21** (500 mg, 2.5 mmol) with the salt **42** (1.8 g, 5.0 mmol) in Me_2SO (10 mL) at 50 °C for 18 h gave after PLC, α,*p*-dinitrocumene (**35**; 68 mg, 13%) and *p*-nitrocumyl alcohol (**29**; 81 mg, 18%) as the only identifiable products. No C-alkylate could be detected.

Reaction of *p*-(1-Methyl-1-nitropropyl)nitrobenzene (36) with Tetrabutylammonium 2-Nitro-2-butanide (45). Reaction of the nitro compound **36** (448 mg, 2.0 mmol) with the salt **45** (1.38 g, 4.0 mmol) in Me_2SO (8 mL) at 50 °C for 15 min followed by workup and PLC gave the two diastereoisomers of ***p*-(1-ethyl-1,2-dimethyl-2-nitrobutyl)nitrobenzene** (**46**; 433 mg, 77%), which were formed in almost equal amounts. The diastereoisomers were inseparable and so the following spectroscopic and analytical data were obtained for the oily mixture: ^1H NMR δ 0.69 (t, CH_2CH_3, $J = 7.4$ Hz), 0.71 (t, CH_2CH_3, $J = 7.4$ Hz), 0.80 (t, 2 CH_2CH_3, $J = 7.4$ Hz), 1.40 (d, Me, $J = 0.9$ Hz), 1.46 (d, Me, $J = 0.9$ Hz), 1.50 (d, 2 Me, $J = 0.9$ Hz), 1.3–2.1 (m, **CH_2**CH_3), 2.1–2.6 (m, **CH_2**CH_3), AA′XX′ systems 7.41 (m, 2 H), 7.44 (m, 2 H), 8.17 (m, 4 H), $J_{AX} + J_{AX'} = 9.2$ Hz (both diastereoisomers); IR (liquid film) 1610, 1600, 1530, 1365, 860 cm^{-1}; mass spectrum, m/e 280 (M^+, 0.03%), 179 (24), 178 (100), 164 (27), 150 (41), 136 (47), 132 (35), 117 (28), 103 (67), 91 (20), 43 (31).

Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.19, N, 9.99. Found: C, 60.04; H, 7.17; N, 9.75.

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Registry No. 7, 3958-63-2; **21**, 14500-58-4; **23**, 14851-03-7; **27**, 80516-30-9; **29**, 22357-57-9; **30**, 80516-31-0; **31**, 65398-92-7; **32**, 80532-34-9; **33**, 80516-32-1; **34**, 65398-95-0; **35**, 3276-35-5; **36**, 58324-83-7; **37**, 74021-66-2; **38**, 65253-46-5; **39**, 80516-33-2; **41**, 35818-95-2; **42**, 65398-99-4; **43**, 65253-43-2; **45**, 65398-98-3; **46** (isomer 1), 80516-34-3; **46** (isomer 2), 80516-35-4; *p*-(1,2-dimethylpropyl)nitrobenzene, 80516-36-5.

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[29] Glattfeld, J. W. E.; Milligan, C. H. *J. Am. Chem. Soc.* **1920**, *42*, 2322.

Photoinduced Skeletal Rearrangement of Alkylindenes[1,2]

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The indene phototransposition reaction, a skeletal rearrangement of certain alkylindenes involving an interchange of carbons 1 and 2 (eq 2), is described. The postulated mechanism (Scheme II) involves a [2 + 2] closure followed by a [1,3] sigmatropic shift, opening to an isoindene and 1,5 hydrogen shifts to re-form the indene system. Results of experiments with indenes containing different alkyl groups at C_1 and C_2 and with 1,1-dimethylindene lend support to the proposed scheme. Experiments with (+)-1,2-dimethylindene indicate that the net migration of C_1 to C_3, necessary for transposition, occurs with clean inversion at C_1 (as would be expected for a ground-state, four-electron, electrocyclic reaction). The reaction derives from the excited singlet state, and partial movement along the initial [2 + 2] reaction surface appears to provide an efficient path for S_1 radiationless decay.

Until recently, most photochemical studies of indene and its simple alkyl derivatives have dealt with sensitized cycloadditions and dimerization.[3] This is in contrast with 1,1-diarylindenes where facile, unimolecular, 1,5 aryl shifts

0022-3263/82/1947-1051$01.25/0

Table I. Products and Quantum Efficiencies for the Photorearrangement of Alkylindenes[a]

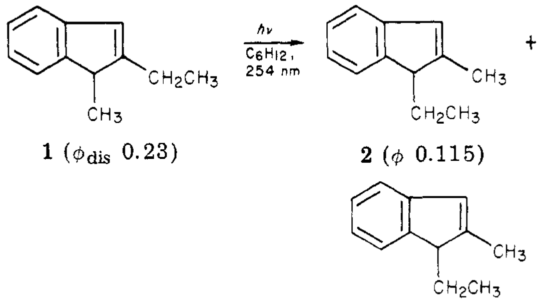
starting indene	ϕ_{dis}	product indene(s)	ϕ_{pdt}
1-methyl	0.16	2-methyl	0.029
2-methyl	0.13	1-methyl	0.025
		3-methyl	0.023
3-methyl			b
1,2-dimethyl	0.13	2,3-dimethyl	0.13
1-methyl-2-trideuteriomethyl		1-(trideuteriomethyl)-2-methyl	0.12
		2-methyl-3-trideuteriomethyl	0.13
1-methyl-2-ethyl	0.23	1-ethyl-2-methyl	0.11_5
		3-ethyl-2-methyl	0.098
1-ethyl-2-methyl	0.04	2-ethyl-1-methyl	0.0087
		2-ethyl-3-methyl	0.0096
		3-ethyl-2-methyl	0.0045
1,3-dimethyl			b
2,3-dimethyl	0.092	1,3-dimethyl	0.0033
		1,2-dimethyl	0.0038
2-ethyl-3-methyl	0.13	1-ethyl-3-methyl 3-ethyl-1-methyl	0.021
3-ethyl-2-methyl	0.06	3-ethyl-1-methyl 1-ethyl-3-methyl 1-ethyl-2-methyl	0.0087

[a] Photolysis in hexane solution at room temperature with 254-nm light. [b] No product detected.

have been extensively investigated.[4] During the course of our photochemical program involving bichromophoric molecules,[5] we noted some hitherto unobserved photoinduced alkylindene rearrangements in hydrocarbon media and have since been exploring the details of this new reaction; this paper summarizes these observations.[6,7] The following report[8] presents another new and mechanistically related reaction, a photochemical, acid-catalyzed, endocyclic to exocyclic double bond migration in 2-alkylindenes.[9] The interrelationship of the two reactions will be discussed in this companion paper.

Results

Photorearrangement of 2-Ethyl-1-methylindene (1). This reaction serves well as a prototype of the alkylindene rearrangement. An argon-degassed 1×10^{-2} M cyclohexane solution of 1 was irradiated with 254-nm light to provide a reaction mixture containing equal amounts (by VPC) of two products. Separation by preparative VPC and comparison with authentic samples demonstrated the products to be 1-ethyl-2-methylindene (2) and 3-ethyl-2-methylindene (3). Quantum efficiencies were determined by using 1-phenyl-2-butene actinometry,[10] and the results are presented in eq 1.



1 (ϕ_{dis} 0.23)

2 (ϕ 0.115)

3 (ϕ 0.098)

Photorearrangement of Other Alkylindenes. The rearrangements of other substrates we have studied are summarized in Table I. All the data are with hexane as the solvent; in one run, acetonitrile was used with 2-methylindene without significant effect ($\phi_{1\text{-methyl}} = 0.034$; $\phi_{3\text{-methyl}} = 0.020$).

Photolysis of (+)-1,2-Dimethylindene. The optically active indene was synthesized by known procedures and obtained with $[\alpha]^{27}_{D}$ +109° (1.7 g/100 mL, benzene) [lit.[11] $[\alpha]^{25}_{D}$ +115° (2.0 g/100 mL, benzene)]. Hexane solutions, 8×10^{-3} M in the substrate, were photolyzed and the amount of 2,3-dimethylindene was assayed by VPC. The 1,2-dimethylindene was isolated by VPC and analyzed by ORD to determine the extent of racemization. The results of several trials were as follows: (1) 9.97% conversion (to 2,3-dimethylindene) gave an average drop in specific rotations at 13 wavelengths for 1,2-dimethylindene of 0.06 ± 0.58%; (2) 11.8% conversion, 9 monitored wavelengths, average drop of 0.52 ± 0.28%; (3) 28.2% conversion, 9 monitored wavelengths, average drop of 1.16 ± 0.13%.

Triplet-Sensitized Photolysis of 2-Methylindene. Irradiation with 3000-Å lamps (Rayonet) of a 0.015 M solution of the indene in hexane containing 0.24 M acetophenone resulted in the loss of starting material but no

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(1) Organic Photochemistry. 50. Part 49: Morrison, H.; Miller, A., *Tetrahedron* **1981**, *37*, 3405.

(2) Abstracted from the Doctoral Dissertations of (a) F.P., Purdue University, 1977, and (b) D.G., Purdue University, 1980.

(3) (a) Schenk, G. O.; Hartman, W.; Mannsfeld, S.; Metzner, W.; Krauch, C. H. *Chem. Ber.* **1962**, *95*, 1642. (b) Krauch, C. H.; Metzner, W.; Schenck, G. O. *Naturwissenschaften* **1963**, *50*, 710. (c) Bowyer, J.; Porter, Q. N. *Aust. J. Chem.* **1966**, *19*, 1455. (d) McCullough, J. J.; Huang, C. W. *J. Chem. Soc., Chem. Commun.* **1967**, 815. (e) McCullough, J. J. *Can. J. Chem.* **1968**, *46*, 43. (f) Bowman, R. M.; McCullough, J. J.; Swenton, J. S. *Ibid.* **1969**, *47*, 4503. (g) Farid, S.; Hartman, S. E.; Evans, T. R. In "The Exciplex"; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975. (h) Dekker, J.; Martins, F. J. C.; Dekker, T. G., *S. Afr. J. Chem.* **1977**, 30. (i) Mizuno, K.; Kaji, R.; Okada, H.; Otsuji, Y. *J. Chem. Soc., Chem Commun.* **1978**, 594. (j) Padwa, A.; Pulwer, M. *J. Am. Chem. Soc.* **1980**, *102*, 6386.

(4) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270 and references therein.

(5) Morrison, H. *Acc. Chem. Res.* **1979**, *12*, 383.

(6) Portions of this research have been presented in preliminary form. Cf.: Palensky, F. J.; Morrison, H. *J. Am. Chem. Soc.* **1977**, *99*, 3507. Giacherio, D.; Morrison, H. *Ibid.* **1978**, *100*, 7109.

(7) A concomitant, but complementary, series of studies have been described for 1-arylindenes by Padwa and co-workers. Cf: (a) Padwa, A.; Loza, R.; Getman, D. *Tetrahedron Lett.* **1977**, 2847. (b) Padwa, A.; Loza, R.; Getman, D. *J. Org. Chem.* **1977**, *43*, 1481. (c) Padwa, A.; Goldstein, S.; Loza, R.; Pulwer, M. *Tetrahedron Lett.* **1979**, 4895. (d) Padwa, A.; Goldstein, S.; Loza, R.; Pulwer, M. *J. Org. Chem.* **1981**, *46*, 1858.

(8) Morrison, H.; Giacherio, D. *J. Org. Chem.*, following paper in this issue.

(9) Morrison, H.; Giacherio, D. *J. Chem. Soc., Chem. Commun.* **1980**, 1080.

(10) Morrison, H.; Pajak, J.; Peiffer, R. *J. Am. Chem. Soc.* **1971**, *93*, 3978.

(11) Meurling, L., *Acta Chem. Scand., Ser. B* **1974**, *B28*, 399.

Scheme I. Formation and Trapping of 2,2-Dimethylisoindene

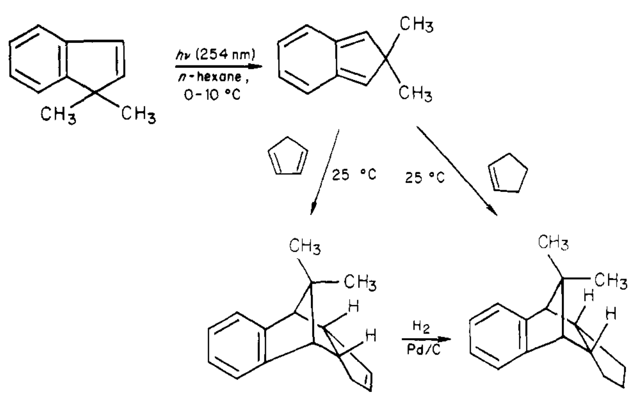


Table II. Fluorescence Quantum Efficiencies and Singlet-State Lifetimes of Alkylindenes^a

indene	ϕ_f	$^1\tau$	10^6k_f, s^{-1}	10^7k_s,^{b} s^{-1}
indene	0.072^c	16.9	4.3	5.9
1-methyl	0.031	7.2	4.3	14.0
2-methyl	0.024	2.3	10.0	43.0
2-ethyl	0.025	2.5	10.0	40.0
3-methyl	0.077	13.9	5.5	7.2
1,3-dimethyl	0.021	3.8	5.5	26.0
1,1-dimethyl	0.013	2.2	5.9	45.0
1,2-dimethyl	0.010	1.1	9.1	91.0
2,3-dimethyl	0.108	14.0	7.7	7.1
2-ethyl-1-methyl	0.007	0.9	8.0	110.0
1-ethyl-2-methyl	0.014	1.7	8.2	59.0
3-ethyl-2-methyl	0.086	13.2	6.5	7.6

^{a} Hexane solution at room temperature. ^{b} From $k_s = 1/^1\tau$. ^{c} Used as the reference value[13] for calculating the others ϕ_f's.

evidence for transposition. Four products with long retention times were detected by VPC; one was isolated and identified as a 2-methylindene dimer (see Experimental Section for details).

Photochemistry of 1,1-Dimethylindene. Photolysis of ~10^{-2} M pentane solutions of this indene at 0–10 °C results in a yellowing of the solution and the appearance of one photoproduct by VPC analysis. Addition of cyclopentadiene or cyclopentene to the photolyzed solution caused the disappearance of the photoproduct and the appearance of new products which were isolated by preparative VPC. The cyclopentadiene product could be hydrogenated to form the cyclopentene product, and the spectral and analytical data confirm that in both cases the added olefins have trapped 2,2-dimethylisoindene via Diels–Alder addition (see Experimental Section for details of the structure assignment). The overall transformations are outlined in Scheme I.

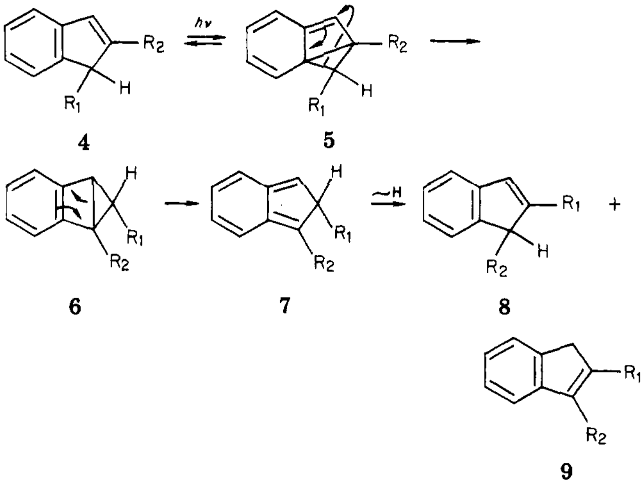
In a separate experiment, a 5.6×10^{-3} M hexane solution of 1,1-dimethylindene was sealed in a square quartz cell and irradiated with a 254-nm pen lamp until the solution had developed a pale yellow color. The UV absorption spectrum showed new maxima at 370, 398, and 422 nm. Excitation at 400 ± 10 nm in a fluorimeter gave mirror image related emission with a maximum at 455 nm and shoulders at 435 and 485 nm. The isoindene has been generated independently[12] by irradiation of an azoxy precursor in an EPA glass at 77 K and reported to have structured absorption with λ_{max} 405 nm and structured fluorescence with λ_{max} 467 nm.

Table III. Fluorescence Quantum Efficiencies and Singlet-State Lifetimes at Reduced Temperatures

indene	temp, °C	ϕ_f,^{a}	$^1\tau$^{b}	10^7k_s,^{c} s^{-1}
1,2-dimethyl	−18	0.027	3.0	33.0
1,1-dimethyl	−20	0.042	7.1	14.0
3-methyl	−18	0.13	20.7	4.8

^{a} Calculated by using $\phi_f^{T_1}/\phi_f^{T_2} = \text{area}^{T_1}/\text{area}^{T_2}$. ^{b} Calculated by assuming k_f to be temperature independent; i.e., $^1\tau^{T_1}/^1\tau^{T_2} = \text{area}^{T_1}/\text{area}^{T_2}$. ^{c} $k_s = 1/^1\tau$.

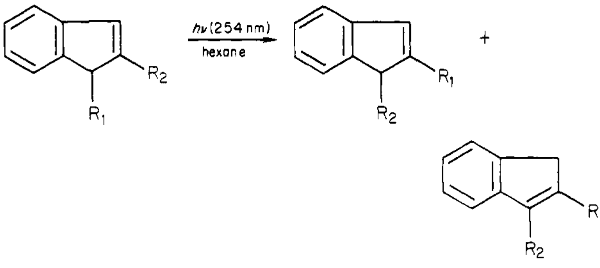
Scheme II. Mechanism for the Alkylindene Transposition



Fluorescence Efficiencies (ϕ_f) and Singlet-State Lifetimes ($^1\tau$). These data are summarized in Table II. Also included in the Table are k_f ($=\phi_f/^1\tau$) and k_s ($=1/^1\tau$). The latter represents the sum of all processes contributing to depletion of the excited singlet state. In Table III, we present the results of several experiments done at ca. −20 °C.

Discussion

(A) Photorearrangement. It is evident from these results that there exists a general, photoinduced, skeletal rearrangement of alkylindenes which interchanges C_1 and C_2 (eq 2).[14] Our observations (Table I) are corroborated



(2)

by those of Padwa and co-workers,[7] who have noted such a rearrangement for a number of 1-arylindenes. Our data suggest the reaction is cleanest when there are alkyl groups at C_1 and C_2 (for example, for 1-methyl-2-ethylindene, ϕ_{dis}

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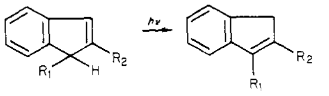
(12) (a) Dolbier, W. R., Jr.; Matsui, K.; Michl, J.; Horák, D. V. *J. Am. Chem. Soc.* **1977**, *99*, 3876. (b) Dolbier, W. R., Jr.; Matsui, K.; Dewey, H. J.; Horák, D. V.; Michl, J. *Ibid.* **1979**, *101*, 2136.

(13) Lyons, A. L., Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1978**, *97*, 3177.

(14) A careful examination of Table I will reveal the occasional appearance of a second reaction which corresponds to a net 1,3 hydrogen shift, i.e., eq 3. Note the formation of 3-ethyl-2-methylindene from 1-ethyl-2-methylindene and 1-ethyl-2-methylindene from 3-ethyl-2-methylindene. This reaction is currently under study.

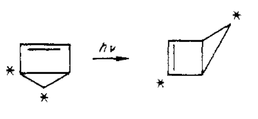


(3)

= 0.23 and ϕ_{pdt} = 0.21), is considerably less efficient with monoalkylindenes, and is inhibited by an alkyl group at C_3. The reported lack of deuterium scrambling upon irradiation of 1,1,3-trideuterioindene[3e] suggests the parent hydrocarbon is also resistant to rearrangement.

A mechanism which accounts for the transformation in eq 2, and which has ample precedent in heterocycle photochemistry,[15] is given in Scheme II. The intermediacy of an isoindene (**7**) has been confirmed by the detection and trapping of 2,2-dimethylisoindene from the photolysis of 1,1-dimethylindene (cf. Scheme I).[16] Others have shown[12b] that the bicyclic precursor (analogous to **6**) of 2,2-dimethylisoindene, (i.e., 5,5-dimethylbenzobicyclo[2.1.0]pent-2-ene) readily opens to the isoindene at room temperature (E_a = 18.9 kcal/mol). The final step, a [1,5] hydrogen shift in **7** to restore aromaticity, has been studied by McCullough for several isoindenes and shown to proceed with E_a's of ca. 13–14 kcal/mol.[4] It is worth noting that the mechanism in Scheme II is quite distinct from the [1,5] alkyl shifts observed in the thermolysis of alkylindenes[17] or the [1,5] aryl shifts observed in the photolysis of 1,1-diarylindenes[4] and certain 1-arylindenes.[7,18]

(B) Stereochemistry of the 1 to 3 Transformation. The transformation of **5** to **6** involves a [1,3] sigmatropic shift of C_1. The stereochemistry at this center during rearrangement is therefore of considerable interest, for it provides information about the reaction surface occupied at the time of the shift. Orbital symmetry considerations dictate that the four-electron process shown in Scheme II (**5** to **6**) should proceed with inversion at C_1 if it is a ground-state reaction, while reaction via an excited-state surface should go with retention. The question takes on added interest because of the reported[20] *photochemical* transposition of bicyclo[2.1.0]pentene (eq 4).

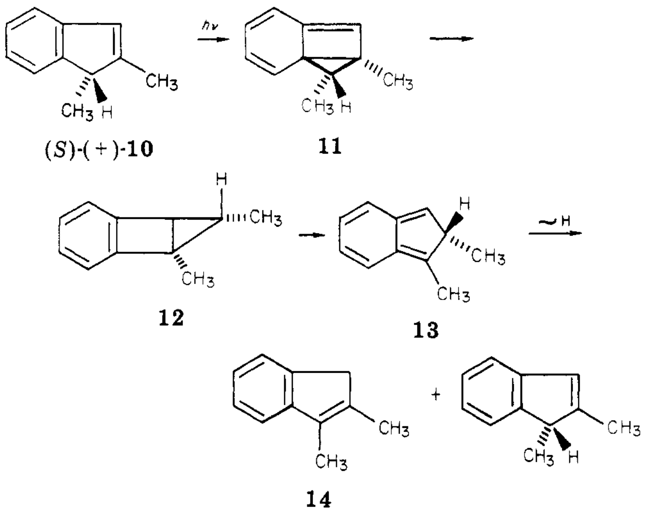


(4)

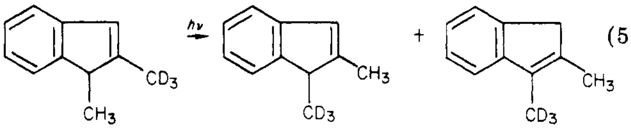
$* = {}^{13}C$

Our approach employed the partially degenerate rearrangement of optically active 1,2-dimethylindene. Scheme III outlines the anticipated result of this photolysis[21] with the assumption of a ground-state conversion of **11** to **12** (i.e., with inversion at C_1). It is evident that the stereochemistry at C_1 associated with the conversion of **11** to **12** is translated into the configuration at the new C_1 created by the suprafacial [1,5] hydrogen shift in the final step. Thus, *inversion* in the [1,3] shift leads to overall *retention of configuration* in **10**; clearly, *retention* during the [1,3] shift would cause *inversion of configuration* in **10** (and be manifested by extensive racemization). Homolytic cleavage and migration of the C_1 as a radical should likewise lead to racemization.

Scheme III. Partially Degenerate Phototransposition of Optically Active 1,2-Dimethylindene Assuming Inversion at C_1



The experiment required that the chirooptical data be corrected for the loss of optical activity in the product mixture caused by the achiral **14**. This was done both by chromatographically separating **10** and measuring its rotation and by assaying the percentage of **14** (by VPC or NMR) and correcting rotations obtained directly on the mixture. The two methods gave identical results. The analysis for **14** did, however, also provide an indication of the extent of the rearrangement, since studies with 1-methyl-2-(trideuteriomethyl)indene confirmed that the two possible [1,5] hydrogen shifts available to **13** occur with almost equal facility (eq 5). Thus, multiplying the experimentally observed conversion of (*S*)-(+)-(**10**) to **14** by 1.93 provides the overall conversion of **10** to **12**.[22]



(5)

0.93:1.0

In the event, 95% optically pure (*S*)-**10** was prepared and photolyzed. Several different experiments, taken to as much as a 28% conversion to **14** (and therefore an ~54% conversion of **10** to **12**), gave evidence for minimal (<1.5%) loss of optical activity. These data confirm that *the migration of C_1 occurs with clean inversion at that center*, as anticipated for the ground-state, four-electron, sigmatropic shift.[23]

(C) Excited-State Multiplicity and Further Discussion of the Reaction Mechanism. Two facts point to the indene rearrangement being derived from an excited singlet state: (1) photosensitization by acetophenone leads to (triplet) indene dimerization without concomitant rearrangement, and (2) a consideration of the photophysical

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(15) Padwa, A. In "Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 501.

(16) Further support derives from the observation of a product ratio from the photoysis of 1-phenyl-2-benzyl-3-methylindene indentical with that observed from 1-phenyl-2-methyl-3-benzylindene.[7d]

(17) For example: Field, D. J.; Jones, D. W. *J. Chem. Soc., Chem. Commun.* **1977**, 688.

(18) One permutation of Scheme II, for which there is no exact analogy, would be the direct transformation of **4** to **6**. Such a reaction could be thought of as a "conjugated" di-π-methane (Zimmerman) rearrangement.[19] In fact, our observation that acid intercepts a discrete intermediate between the excited state of **4** and **6** has led us to rule out this option.[8]

(19) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 131.

(20) Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 4851.

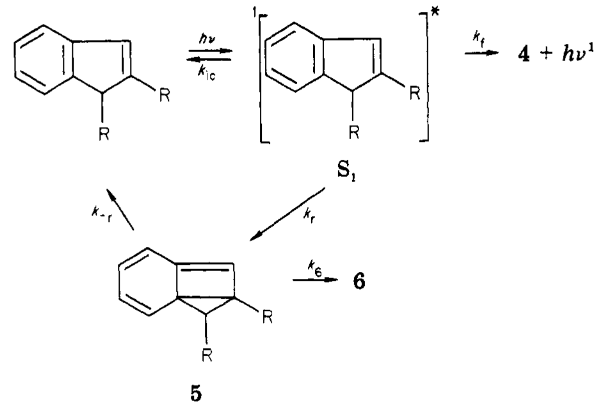
(21) The scheme is drawn by using one diastereomeric representation of **11** and **12**; though these structures would be sterically favored, the argument is unaffected by whether the cyclopropane ring is up or down.

(22) Compound **14** rearranges very inefficiently (cf. Table I), and the correlation of the optical rotatory data determined on purified **10** with that obtained on the product mixture confirms that there is minimal secondary photolysis of **14** in these experiments.

(23) Inversion would also be consistent with a concerted, six-electron transformation of **10** to **12** along an excited-state surface, as has been observed for the Zimmerman rearrangement.[24] See, however, footnote 18.

(24) Zimmerman, H. E.; Gannett, T. P.; Keck, G. E. *J. Am. Chem. Soc.* **1978**, *100*, 323. Zimmerman, H. E.; Robbins, J. D.; McKelvey, R. D.; Sammuel, C. J.; Sousa, L. R. *Ibid.* **1974**, *96*, 4630.

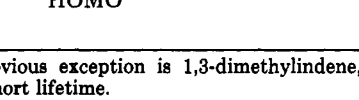
Scheme IV. Radiationless Decay Paths for Photoreactive Alkylindenes



data (Table II) and the reaction quantum efficiencies (Table I) indicates that reactive indenes have characteristically short (several nanoseconds) singlet lifetimes, while indene and the less reactive 3-alkyl derivatives have ${}^1\tau$'s of ~14–17 ns.[25] As regards the latter observation, it is clear from the data in Table II that the shortened ${}^1\tau$'s are not due to unusually large k_f's, nor is there reason to believe k_{isc} would be affected by alkyl substitution. One can conclude that a chemical pathway has been introduced into the reactive indenes' excited singlet-state photophysics.

However, it is also evident from the data in Table I that the overall quantum efficiencies for reaction are, in of themselves, insufficient to explain the magnitude of the reductions observed for the ${}^1\tau$'s. We therefore propose (cf. Scheme IV) that the "reactive" indene singlets are (1) deactivated by rapid electrocyclic closure (k_r), followed by a partition of **5** between rearrangement to **6** (k_6) and return to the initial indene (k_{-r}), and/or (2) by a much-enhanced internal conversion of S_1 back to indene (k_{ic}).

With the data in hand, we have no way to evaluate the k_6/k_{-r} ratio[26] and therefore no way to estimate the relative magnitudes of k_r and k_{ic}. However, there is ample theoretical justification for postulating that k_{ic} is greatly increased by the *partial* interaction of the vinyl and aryl groups along the excited-state surface leading to closure. This has been suggested[27] for the [2 + 2] butadiene/cyclobutene disrotatory transformation, where theoretical analyses (cf. Figure 1) of the reaction reveal that it progresses via an initial S_1/S_2 surface crossing. An "avoided crossing" of S_2 with the ground-state surface creates a "funnel"[28] which expedites S_2/S_0 decay and a partition between return to diene (i.e., k_{ic}) or closure to cyclobutene (i.e., k_r). A similar picture would seem reasonable for the indene reaction, and an extended Hückel calculation[29] demonstrates the indene HOMO and LUMO to have the same symmetry as butadiene in the reacting C_2, C_3, C_8, C_9 region. The correlation diagrams (cf. Figure 1) also predict the observed lack of triplet reactivity (T_1 transforms into the product T_1 state) and the existence of a thermal barrier for the [2 + 2] closure (S_1 initially rises before crossing to the S_2 surface). We have evidence for such a barrier from several low-temperature fluorescence measurements (cf. Table III) which show radiationless decay for reactive indenes (1,1-dimethyl and 1,2-dimethyl) to be about twice as sensitive to a decrease in temperature as an unreactive (3-methyl) indene.[30,31]



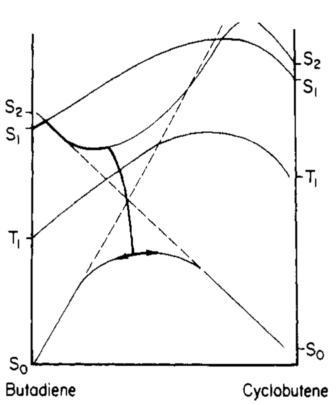


Figure 1. Simplified "natural state correlation diagram" for the butadiene–cyclobutene disrotatory transformation (from Bigot[27]).

The question of why the rearrangement is so sensitive to alkyl substitution remains to be addressed. An enhancement of closure (k_r) by substitution at C_1 or C_2 is readily rationalized by the classic observation of alkyl-enhanced cyclopropane formation.[32] The inhibition by an alkyl group at C_3 is less readily explained[33] and will be discussed further in the adjoining paper.[8]

Experimental Section

Complete experimental details for these studies may be found in the doctoral dissertations of F.J.P. and D.G.[2] Salient features are abstracted below.

Instrumentation. Most of the basic analytical and photochemical techniques and instrumentation have been previously described.[34] Polarimetric measurements were made on a Carl Zeiss polarimeter or on a Cary Model 60 recording spectropolarimeter, operating at 27 °C. Solutions were prepared in dry distilled benzene, and a 2-dm (Zeiss) or 10-mm (Cary) cell was used. For the Cary measurements, the slits were adjusted for a 1.5-nm band-pass throughout the range of interest, and ORD curves were recorded from 400 to 290 nm at rates of either 5 or 10 nm/min. The sensitivity of the instrument was set at either 0.1°, 0.2°, or 0.4° full scale deflection, depending upon the rotation of the sample. For avoidance of anomalous rotations, the sample cell, after being carefully positioned initially, was not removed from its holder.

Fluorescence lifetimes were obtained on a nanosecond fluorometer operating on the principle of pulse sampling and similar to one described by Lytle.[35] A complete description may be found

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[25] One obvious exception is 1,3-dimethylindene, which has an anomalously short lifetime.

[26] See ref 8 for a further discussion of this point.

[27] For an excellent discussion, see: Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *2*, 41 (cf. Figure 8). Support for this picture has recently come from a more detailed "natural-state correlation diagram". Cf.: Bigot, B. In "Quantum Theory of Chemical Reactions"; Daudel, R., et al. Eds.; D. Reidel: Dordrecht, The Netherlands, 1980; Vol. II. We are grateful to Dr. Bigot for a preprint of this chapter.

[28] Michl, J. *Top. Curr. Chem.* **1974**, *46*, 1. Michl, *J. Pure Appl. Chem.* **1975**, *41*, 507.

[29] We are grateful to Professor W. J. Jorgensen for providing this program.

[30] One might well expect the barrier to be significantly higher for the indene closure because of the high bicyclopentene ground-state energy; see the discussion of the Norrish Type I reaction in: Turro, N. J. "Modern Molecular Photochemistry"; Benjamin Cummings: Menlo Park, CA, 1978; p 227.

[31] ϕ_{pdt} for 1,2-dimethylindene likewise decreases as the temperature is lowered, disappearing at −196°. This is undoubtedly due to a superposition of barriers imposed at several points in the reaction scheme.

[32] The di-π-methane reaction is also greatly facilitated by substitution at the methane center.[19]

[33] The extended Hückel calculations give no evidence for any significant difference between C_2 and C_3 alkylindenes.

[34] Scully, F.; Nylund, T.; Palensky, F. and Morrison, H.; *J. Am. Chem. Soc.* **1978**, *100*, 7352.

[35] Lytle, F. E. *Photochem. Photobiol.* **1973**, *17*, 75.

in Appendix A of the thesis by D.G.[2] The fluorometer consists, in part, of an Optitron Model NF-100 nanosecond decay time fluorometer. The radiating medium is a small volume of high-pressure plasma (N_2 at ~200 psi), and the source is equipped with a variable pulse duration electrode assembly capable of producing pulses with nominal FWHM values of 1.5, 3, or 7 ns. The photomultiplier is an RCA Model 1P28A, wired for fast response and powered by an Optitron Model NF-100-PS power supply. The output is fed to a Tektronix 5S14N sampling unit housed in a Tektronix 510 oscilloscope mainframe, and the scope output is fed to a Houston Instruments Omnigraphic Model 2200-3-3 X-Y recorder. Interference filters were used for both the excitation and emission windows of the sample chamber. The data were analyzed by the convolute–compare method[35] using a Fortran program (TAU1)[36] to determine the best fitting convolute to the nearest 0.1 ns. A second program (TAU2) produces a plot showing the fluorometer lamp pulse, the experimental fluorescence decay, and the best fitting convolute. Listings for TAU1 and TAU2 are available from the authors.

Vapor-phase chromatography utilized Varian Model 90-P instruments for qualitative or preparative work and a Varian Model 1200 or 1400 FID chromatograph with a Hewlett-Packard 3380 recording integrator for quantitative studies. Columns were as follows: A, 150 ft × 0.010 in., stainless steel (ss), Golay column coated with UCON LB-550X; B, 5 ft × 0.125 in., ss, 10% Carbowax 20M on 100/120 AW-DMCS Chromosorb W; C, 20 ft × 0.125 in., ss, 20% XF-1150 on 60/80 AW-DMCS Chromosorb W; D, 10 ft × 0.125 in., ss, 5% SF-96 on 60/80 AW-DMCS Chromosorb W; E, 7 ft × 0.375 in., aluminum, 20% Carbowax 20M on 60/80 AW Chromosorb P; F, 18 ft × 0.125 in., ss, 20% Carbowax 20M on 60/80 AW-DMCS Chromosorb W; G, 12 ft × 0.125 in., ss, 10% $AgBF_4$/25% Carbowax 20M on 60/80 AW-DMCS Chromosorb W; H, 10 ft × 0.375 in., ss, 20% Carbowax 20M on 60/80 AW-DMCS Chromosorb W; I, 5 ft × 0.375 in., ss, 10% $AgBF_4$/25% Carbowax 20M on 60/80 AW-DMCS Chromosorb W; J, 10 ft × 0.25 in., aluminum, 10% Carbowax 20M on AW/DMCS Gas Pack; K, 20 ft × 0.25 in., ss, 10% SE-30 on 60/80 AW-DMCS Chromosorb W.

Quantitative photochemistry was done with matched sets of quartz or Vycor photolysis tubes, a rotating turntable, and a Hanovia low-pressure mercury resonance lamp (Model 688A-45) housed in Vycor and emitting at 254 nm. Quantum efficiencies were measured by using 1-phenyl-2-butene actinometry[37] with columns A (100 °C), F (150 °C), or G (95 °C) to analyze for E/Z isomerization. The E olefin (Aldrich) was initially purified by preparative VPC on column I (95 °C). Preparative photochemistry was done with a Hanovia 450-W medium-pressure lamp (Model 679A), using appropriate filter sleeves, or with a Rayonet Model RPR-100 reactor. Solvents were Burdick and Jackson "Distilled in Glass". The indenes were typically analyzed on column A and preparatively separated (when desired) on column E. Solutions were degassed with argon before photolysis.

Syntheses. 1-Methylindene. The method of Cedheim and Eberson[38] was used to prepare this compound in 70% yield. The NMR and IR data match those in the literature.[39,40]

2-Methylindene. 2-Methyl-1-indanone was prepared by the method of Burckhalter and Fuson;[41] bp mp 79–81 °C (0.1 mm) [lit.[41] mp 90 °C (3 mm)]. To a solution of this indanone (6.0 g, 41 mmol) in 40 mL 0.02 M methanolic NaOH solution was added, dropwise over a period of 20 min, a solution of $NaBH_4$ (1.6 g, 43 mmol) in 55 mL of 0.1 M methanolic NaOH. External cooling with a cold water bath served to keep the temperature below 30 °C. The mixture was stirred for 1 h after the addition, and then the methanol was removed under vacuum. Water (100 mL) was added, and the mixture extracted with 75 mL ether. The ether was dried over $MgSO_4$ and evaporated to give crude indanol. The indanol was dehydrated without further purification by dissolving 10-mmol quantities in 20 mL of glacial acetic acid containing 0.75 g of *p*-toluenesulfonic acid. After refluxing for 60 min, the mixture was cooled, poured into 150 mL of ice and water containing 20 g of NaOH, and extracted with hexane (3 × 50 mL). The bulk of the hexane was removed under vacuum, and the residue was passed through a 7 cm × 2.5 cm alumina plug, eluting with hexane. Removal of the hexane gave 2-methylindene in an overall yield of 3.85 g (29.6 mmol, 72%). The product was purified by VPC on column H (155 °C) and had IR and NMR spectral data which matched those in the literature.[42]

3-Methylindene. A solution of 1-methylindene (1.0 g, 7.7 mmol) in 4.0 mL of pyridine was refluxed for 1 h under nitrogen. The solution was cooled to room temperature and poured into 40 mL of 5% HCl. The solution was extracted with ether (2 × 5 mL), and the extracts were passed through a 1.0 × 5.0 cm alumina plug by using an additional 5 mL of ether as the eluent. Concentration of the ether gave the desired product in virtually quantitative yield. Purification on column H (155 °C) gave a sample having an NMR spectrum identical with that reported in the literature.[43]

1,3-Dimethylindene. A solution of 1-methylindene (10.0 g, 76.9 mmol) in 100 mL of dry diethyl ether was treated with 77.0 mmol of *n*-butyllithium (2.6 M in *n*-hexane) and the solution stirred at room temperature for 0.5 h. This solution was then added dropwise to a vigorously stirred solution of dimethyl sulfate (9.7 g, 77.0 mmol) in 50 mL of dry ether at 0 °C. After the addition (ca. 1 h), the solution was stirred at room temperature for 5 h and then poured into 200 mL of water. The ether layer was washed with 10% $NaHCO_3$ (2 × 100 mL) and water (2 × 50 mL), dried over $MgSO_4$, and concentrated to give 10.0 g of an oil consisting of 54% 1,3-dimethylindene, 32% 1,1-dimethylindene, and 14% 1,1,3-trimethylindene (column A, 110 °C). Purification on column H (165 °C) gave a product with NMR spectral data matching those in the literature.[43]

2,3-Dimethylindene. A solution of 1,2-dimethylindene (1.5 g, 10.4 mmol) in 5 mL of pyridine was refluxed under nitrogen for 2 h and then stirred overnight at room temperature. The mixture was poured into 100 mL of 10% HCl and extracted with 25 mL of pentane. The pentane was removed under vacuum and the residue passed through a 2 × 8 cm alumina plug, eluting with hexane. Removal of the hexane in vacuo afforded the product (1.3 g, 87%) as a clear, yellow oil. The NMR spectrum was identical with that in the literature;[44] further purification was achieved on column H (175 °C).

1-Ethyl-2-methylindene. A solution of 2-methylindene (1.3 g, 10 mmol) in 20 mL of dry diethyl ether was treated with 9.9 mmol of *n*-butyllithium (2.6 M in *n*-hexane) at room temperature and the resultant orange solution stirred for 0.5 h under nitrogen. This solution was added dropwise to a vigorously stirred solution of ethyl iodide (20.0 g, 128 mmol) in 35 mL of dry diethyl ether at room temperature under nitrogen. The solution was stirred at room temperature for 12 h and then worked up by the addition of 3 mL of water, separation and drying of the ether layer, and concentration in vacuo to give 1.3 g of a light yellow oil consisting of 71% product and 29% 2-methylindene (column A, 110 °C). Purification on column J (150 °C) gave a sample having NMR spectral data matching those in the literature.[45]

3-Ethyl-2-methylindene. This compound was prepared from 1-ethyl-2-methylindene by refluxing a pyridine solution as described for 2,3-dimethylindene. VPC analysis indicated complete conversion and purification on column H (180 °C) provided a sample having an NMR spectrum identical with that in the literature.[45]

2-Ethyl-1-methylindene. 2-Ethylindene was prepared from 2-indanone by treatment with ethylmangesium iodide and dehydration of the resultant indanol with *p*-toluenesulfonic acid. Purification on column K (140 °C) gave a sample having an NMR spectrum identical with that in the literature.[39]

2-Ethyl-3-methylindene. This compound was prepared from 2-ethyl-1-methylindene by refluxing a pyridine solution as de-

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[36] We are grateful to Dr. W. Schloman for his assistance in writing this program.

[37] Morrison, H.; Pajak, J. and Peiffer, R. *J. Am. Chem. Soc.* **1971**, *93*, 3978. Morrison, H. and Peiffer, R. *Ibid.* **1968**, *90*, 3428.

[38] Cedheim, L.; Eberson, L. *Synthesis* **1973**, 159.

[39] Yarboro, T. L.; Karr, C., Jr.; Estep, P. A. *J. Chem. Eng. Data* **1961**, *6*, 421.

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[41] Burkhalter, J. H., Fuson, R. *J. Am. Chem. Soc.* **1948**, *70*, 4184.

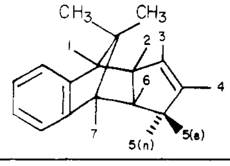
[42] Marechal, E.; Basselier, J.-J.; Sigwalt, P. *Bull. Soc. Chim. Fr.* **1964**, 1740.

[43] Bosch, A.; Brown, R. K. *Can. J. Chem.* **1964**, *42*, 1718.

[44] Parham, W. E.; Montgomery, W. C. *J. Org. Chem.* **1974**, *39*, 2048.

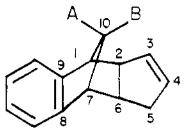
[45] Plenat, F.; Bergson, G. *Ark. Kemi.* **1966**, *25*, 109.

Table IV. ^1H NMR Data for **15**



chemical shift, δ	coupling constants, Hz	proton
6.90		arom
5.07	$J_{3,4} = 6.0$, $J_{4,5(e)} = 2.2$, $J_{4,5(n)} = 3.5$, $J_{2,4} = 1.3$	4
4.91	$J_{3,5(e)} = 3.8$, $J_{3,5(n)} = 2.3$, $J_{2,3} = 1.0$	3
3.60		2
3.15	$J_{2,6} = 12.4$	6
2.74	$J_{1,2} = 4.6$	1 (7)
2.63	$J_{6,7} = 4.6$	7 (1)
2.10	$J_{5(e),6} = 9.5$, $J_{5(e),5(n)} = 17.5$, $J_{2,5(e)} = 1.0$	5(e)
1.62	$J_{5(n),6} = 4.5$, $J_{2,5(n)} = 1.3$	5(n)
1.20		CH_3
0.69		CH_3

Table V. ^{13}C NMR Data for **15**



chemical shift, δ	multiplicity[a]	carbon
146.1	s	8, 9
143.0	s	
131.1	d	aryl, 3, 4
130.0	d	
123.7	d	
123.3	d	
123.1	d	
121.9	d	
59.0	s	10
56.2	d	1, 7
55.2	d	
52.0	m	2, 5, 6
38.6	m	
32.9	m	
22.3	q	B
20.7	q	A

[a] Determined in a separate off-resonance experiment.

scribed for 2,3-dimethylindene. VPC analysis indicated complete conversion, and purification on column H (180 °C) gave a sample suitable for analysis: IR (neat) 3.40, 6.10, 6.83, 7.20, 7.70, 8.32, 8.70, 8.82, 9.15, 9.50, 9.85, 10.50, 10.70, 13.25, 13.95 μm; NMR ($CDCl_3$) δ 7.32–6.92 (m, 4 H, arom), 3.19 (br s, 2 H, ring CH_2), 2.46 (br q, 2 H, J = 8.0 Hz, vinyl CH_2), 2.0 (s, 3 H, vinyl CH_3), 1.12 (t, 3 H, J = 8.0 Hz, CH_3); mass spectrum, calcd for $C_{12}H_{14}$ *m/e* 158.109, found *m/e* 158.110.

1-Ethyl-3-methylindene and 3-Ethyl-1-methylindene. A mixture of these indenes was prepared from 3-methyl-1-indanone[39] by treatment with ethylmagnesium iodide and dehydration of the resultant indanol with *p*-toluenesulfonic acid. The product was identified by its NMR spectrum as a 1:1 mixture.[45]

(+)-1,2-Dimethylindene. This compound has been previously reported.[11] 3-Phenylbutyric acid[38] was synthesized from crotonic acid, benzene, and aluminum chloride and resolved[39] by using 1-α-methylbenzylamine (Aldrich); five recrystallizations afforded a sample with $[\alpha]^{25}_D$ +56.8° (1.3 g/100 mL, benzene) [lit.[39] $[\alpha]^{25}_D$ +52.3° (benzene)]. This was reacted with sodium hydride and diethyl carbonate to give 3-methyl-2-carbethoxy-1-indanone,[11] which was converted to the thallium salt, methylated with methyl iodide, hydrolyzed, and decarboxylated to give 2,3-dimethyl-1-indanone.[11] The ketone was reduced with sodium borohydride and the resultant alcohol dehydrated with *p*-toluenesulfonic acid to give (+)-1,2-dimethylindene, $[\alpha]^{27}_D$ +109° (1.79 g/100 mL, benzene) [lit.[11] $[\alpha]^{25}_D$ +115° (2.0 g/100 mL, benzene)].

(+)-1-Methyl-2-(trideuteriomethyl)indene. This compound was made by using the previously outlined procedure for preparing (+)-1,2-dimethylindene, with the use of trideuteriomethyl iodide (Aldrich) in the alkylation step. Purification by alumina (Fisher A-540) with hexane as the eluent provided the product: IR (neat) 3.27, 3.31, 3.37, 3.48, 6.18, 6.84, 11.24, 12.47, 13.28, 13.64 μm; NMR ($CDCl_3$) δ 7.41–7.01 (m, 4 H, aromatic), 6.44 (s, 1 H, vinyl), 3.22 (q, 1 H, $CHCH_3$), 1.28 (d, 3 H, $CH\mathbf{CH_3}$); mass spectrum, calcd for $C_9H_9D_3$ *m/e* 147.113, found *m/e* 147.113; $[\alpha]^{27}_{589}$ +92° (0.1 g/100 mL, hexane).

Photolysis of 1,1-Dimethylindene and Trapping To Give 8,9-Benzo-10,10-dimethyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene (15). A solution of 500 mg of 1,1-dimethylindene in 400 mL of *n*-pentane (8 × 10^{-3} M) was photolyzed for 6 h at 0–10 °C in an ice bath. VPC analysis on column A indicated a 23% conversion to the isoindene. Freshly cracked cyclopentadiene (20 mL) was added to the reaction mixture while still at 0 °C, and then the solution was allowed to stand at 25 °C for 12–18 h under an argon atmosphere. VPC on column A showed complete conversion of the isoindene to a new product which could be isolated by preparative VPC on column E at 192 °C (100 mL of He/min): IR (neat) 3.45, 6.95, 7.04, 7.33, 7.42, 7.50, 8.10, 8.12, 8.50, 8.82, 9.10, 9.20, 9.96, 10.40, 10.72, 11.14, 11.30, 12.35, 12.95, 13.20, 13.50, 13.80, 14.25 μm; mass spectrum, calcd for $C_{16}H_{18}$ *m/e* 210.141, found *m/e* 210.139. The proton NMR data are given in Table IV and carbon-13 NMR data in Table V. The assignment of endo stereochemistry to **15** rests on (1) the observation of only one shielded methyl group, whereas an exo arrangement would have been expected to shield the second methyl due to its position over the double bond, and (2) the absence of the characteristically high-field signals expected for two or six endo hydrogens. Note that the relative positions of H_1 and H_7 vis á vis H_2 and H_6 are somewhat surprising, but the assignments follow from the coupling constant data.

Formation of 8,9-Benzo-10,10-dimethyltricyclo-[5.2.1.0.^{2,6}]dec-8-ene. This material was prepared by photolysis of 1,1-dimethylindene with cyclopentene or by hydrogenation of **15**. The photolysis procedure was similar to that used to isolate **15** but with a 48-h reaction time at 25 °C. The adduct was isolated by preparative VPC on column E at 192 °C (150 mL of He/min). Hydrogenation of **15** employed 70 mg of **15** in 5 mL of cyclohexane containing 100 mg of 10% Pd/C. After 11 h, VPC on column A indicated a quantitative conversion to a new product having spectral and chromatographic properties identical with those of the cyclopentene photoadduct: IR (neat) 3.45, 6.92, 7.02, 7.32, 7.41, 7.93, 8.00, 8.75, 9.12, 9.96, 10.85, 13.17, 13.70 μm; ^1H NMR ($CDCl_3$) δ 7.00 (s, 4 H, arom), 3.00 (m, 2 H, exo), 2.59 (m, 2 H, bridgehead), 1.60–1.10 (m, 3 H, *exo*-CH_2), 1.21 (s, 3 H, *exo*-CH_3), 1.10–0.75 (m, 3 H, *endo*-CH_2) 0.71 (s, 3 H, *endo*-CH_3); ^{13}C NMR ($CDCl_3$) δ 143.3 (s), 124.0 (d), 122.,5 (d), 60.5 (s), 56.3 (d), 43.4 (m), 27.1 (m), 26.3 (m), 22.1 (q), 20.9 (q); mass spectrum, calcd for $C_{16}H_{20}$ *m/e* 212.157, found *m/e* 212.156.

Acetophenone-Sensitized Dimerization of 2-Methylindene. 2-Methylindene (8 mg, 0.015 M) and acetophenone (125 mg, 0.24 M) were dissolved in 4 mL of hexane in a Pyrex tube, degassed with argon for 15 min, and irradiated with the 3000-Å lamps in a Rayonet reactor for 3 h and 50 min. VPC analysis on column C at 140 °C showed no evidence of rearrangement products while analysis on column B at 210 °C indicated the presence of dimers. A preparative experiment was run with 1 g of the indene, 10 g of acetophenone, and 150 mL of hexane by using the Hanovia medium-pressure lamp and two thicknesses of Pyrex. After several hours of photolysis, removal of solvent and acetophenone by distillation, chromatography on alumina, and one preparative VPC on column D at 250 °C, one product identified as a dimer could be isolated. No attempt was made to assign stereochemistry: IR (melt) 3.26, 3.32, 3.40, 3.46, 3.50, 6.78, 6.90, 7.00, 7.29, 12.76, 13.55, 13.87 μm; NMR ($CDCl_3$) δ 7.1–6.6 (m, 8 H aromatic), 3.21 (s, 2 H, tertiary benzylic), 2.99–2.27 (m, 4 H, secondary benzylic), 1.62 (s, 6 H, methyl); mass spectrum, calcd for $C_{20}H_{20}$ *m/e* 260.157, found *m/e* 260.156.

Photolysis of (+)-1,2-Dimethylindene. Experiments with the optically active indene were done by analyzing the photolysis

Table VI. ORD Data for Irradiated and Unirradiated (+)-1,2-Dimethylindene[a]

	unirradiated		irradiated		
λ, nm	α°	$[\alpha]_\lambda^{27}$[b]	α°	$[\alpha]_\lambda^{27}$	% drop[c]
395	0.0838	286.7	0.0874	287.0	−0.10
365	0.1093	373.9	0.1145	376.0	−0.56
355	0.1202	411.2	0.1250	410.5	0.17
350	0.1265	432.8	0.1321	433.8	−0.23
340	0.1403	480.0	0.1460	479.5	0.10
330	0.1574	538.5	0.1641	538.9	−0.07
320	0.1792	613.1	0.1861	611.2	0.31
310	0.2079	711.3	0.2146	704.8	0.91
305	0.2287	782.4	0.2386	783.6	−0.15
325	0.1661	568.3	0.1740	571.4	−0.55
345	0.1332	455.7	0.1395	458.1	−0.53
335	0.1487	508.7	0.1548	508.4	0.06
296	0.3850	1313	0.3953	1298	1.44

[a] Instrument sensitivity −0.4° full scale. [b] $[\alpha]_\lambda^T = \alpha/dc$ where d = 0.100 dm and c = concentration in grams per milliliter. [c] Average 0.06, standard deviation 0.58.

mixtures or by analyzing isolated 1,2-dimethylindene. An example of the latter is described below: a solution of 60 mg of the indene in 50 mL of hexane was added to a Vycor tube, argon degassed, and photolyzed with the Hanovia low-pressure lamp for 68 min. VPC analysis on column D at 100 °C indicated 9.97% conversion to 2,3-dimethylindene. The 1,2-dimethylindene was isolated by using column H; 30.45 mg of the recovered material was diluted to 10.00 mL with hexane and analyzed by ORD. The data are presented in Table VI.

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Registry No. **1**, 63265-70-3; **2**, 70416-69-2; **3**, 51293-55-1; **10**, 53204-57-2; **14**, 4773-82-4; **15**, 80540-41-6; 1-methylindene, 767-59-9; 2-methylindene, 2177-47-1; 2-methyl-1-indanone, 17496-14-9; 3-methylindene, 767-60-2; 1,3-dimethylindene, 2177-48-2; 1,1-dimethylindene, 18636-55-0; 1,1,3-trimethylindene, 2177-45-9; 1,2-dimethylindene, 70063-93-3; 2-indanone, 83-33-0; 2-ethyl-3-methyindene, 66703-20-6; 1-ethyl-3-methylindene, 52750-21-7; 3-ethyl-1-methylindene, 26084-58-2; 3-methyl-1-indanone, 6072-57-7; (+)-1-methyl-2-(trideuteriomethyl)indene, 80540-42-7; cyclopentadiene, 542-92-7; 8,9-benzo-10,10-dimethyltricyclo[5.2.1.$0^{2,6}$]dec-8-ene, 80540-43-8; cyclopentene, 142-29-0; 2-methylindene dimer, 80559-48-4; indene, 95-13-6; 2-ethylindene, 17059-50-6.

Acid-Catalyzed Photoisomerization of 2-Alkylindenes to 2-Alkylideneindanes[1,2]

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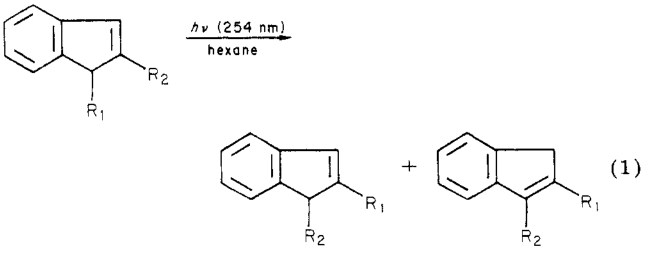
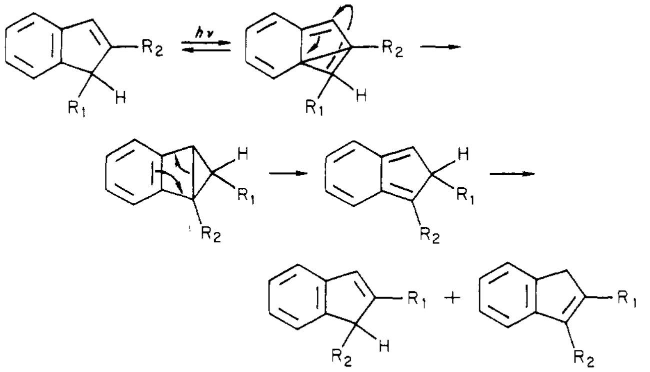
Photolysis of 2-alkylindenes in aprotic media containing hydrochloric acid leads to the formation of 2-alkylideneindanes with concomitant quenching of the previously reported phototransposition reaction. Quantum efficiencies range from 0.02 to 0.1 and, as with the transposition reaction, are highest for those indenes having short singlet lifetimes. Though there is evidence that the reaction is derived from the singlet excited state, acid has no effect on fluorescence and therefore intervenes by protonating an intermediate formed from S_1. This intermediate (proposed as the bicyclopentene "I") is common to both the transposition and the olefin migration (cf. Scheme III).

We have, in recent years, reported on a photochemical skeletal rearrangement of alkylindenes which has the net effect of interchanging carbons 1 and 2 (eq 1).[1,3,4] A mechanism has been proposed[1,3,4] which involves closure of the alkylindene to a bicyclopentene, a [1,3] sigmatropic shift, opening to an isoindene and 1,5 hydrogen shifts to form the new indenes (Scheme I). During the course of these studies, we came upon a second class of indene photorearrangements which involves exocyclic migration



(1)

Scheme I. Proposed Mechanism for the Alkylindene Phototransposition



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(1) Organic Photochemistry, 51. Part 50: Morrison, H., Giacherio, D.; Palensky, F. J. *J. Org. Chem.*, preceding paper in this issue.

(2) Abstracted from the Doctoral Dissertation of D.G., Purdue University, 1980.

(3) Palensky, F. J.; Morrison, H. *J. Am. Chem. Soc.* **1977**, *99*, 3507. Giacherio, D.; Morrison, H. *Ibid* **1978**, *100*, 7109.

(4) See also: Padwa, A.; Goldstein, S.; Loza, R.; Pulwer, H. *J. Org. Chem.* **1981**, *46*, 1858 and preceding papers in this series.

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