Sigmatropic Indenyl Rearrangements Induced by Electronic Excitation

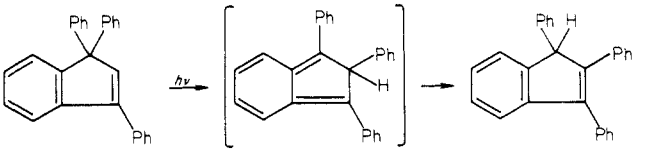
Albert Padwa,* Steven Goldstein, Roman Loza, and Mitchell Pulwer

Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received November 3, 1980

The photochemical rearrangement of several arylalkyl substituted indenes has been studied. The rearrangements were shown to be derived from the π,π^* singlet state since triplet sensitization led to no reaction or else resulted in a Paterno–Buchi reaction. Irradiation of 1-phenyl-2,3-dimethylindene in benzene gave rise to a 1:2 mixture of 1,2-dimethyl-3-phenyl and 1,3-dimethyl-2-phenylindene. This rearrangement may be depicted as proceeding via the following steps: (1) an electrocyclic ring closure, (2) a [1,3] sigmatropic shift, (3) ring opening to an isoindene, and (4) a [1,5] sigmatropic hydrogen shift. Support for an isoindene intermediate was obtained from the photolysis of 1-phenyl-2-benzyl-3-methyl- and 1-phenyl-2-methyl-3-benzylindene. The same ratio of rearranged indenes was obtained. The direction of hydrogen migration in the substituted isoindene system can be rationalized by both electronic and steric factors. The photoisomerization of 1-phenyl-1-methyl- and 1-phenyl-1,3-dimethylindene was found to proceed via a 1,2-phenyl shift. Our results indicate that the mechanism followed in the photoisomerization of aryl-substituted indenes is markedly dependent on the nature and location of the substituent groups present on the ring.

Considerable interest has been focused in recent years on phototransposition reactions which have the net effect of interchanging atoms within a five-membered ring.[1,2] Examples have been reported for variously substituted heterocycles[3-8] and cyclopentadiene derivatives.[9-11] Bicyclo[2.1.0]pent-2-enes and 3-vinylcyclopropene analogues are the most commonly invoked intermediates responsible for these rearrangements; in some instances, such molecules have been detected and characterized.[12-16] Recently, we described the photochemical rearrangement of indenes in which the sp^3 and adjacent sp^2 atoms were interchanged.[17] Similar skeletal rearrangements had also been reported by Morrison and co-workers.[18] There are a number of reports in the recent literature dealing with the photolytic rearrangement of indene derivatives.[19,20] Some time ago Griffin and co-workers reported the photomigration of a phenyl group in 1,1,3-triphenylindene (1) and proposed that formation of 1,2,3-triphenylindene (3) involved the intermediacy of 1,2,3-triphenylisoindene (2).[20]

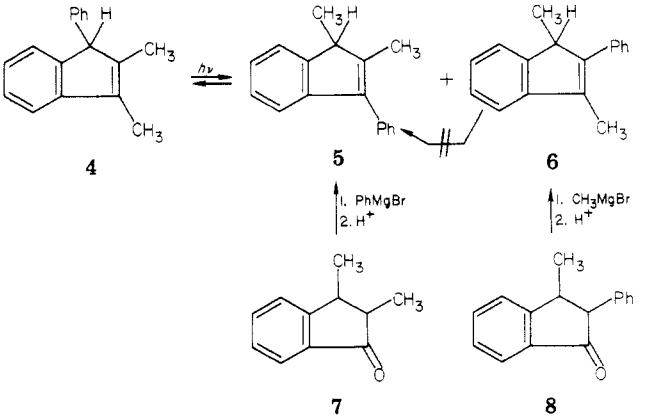


1 2 3

More recently, McCullough and co-workers showed that the suggested mechanism is correct and that photochemical aryl migration appears to be a general way of generating arylisoindenes.[19] This rearrangement is markedly different from the photoisomerization reaction uncovered by Morrison[18] and Padwa[17] which interchanges the adjacent carbon atoms of the indene skeleton. Because of the intriguing nature of the phototransposition reaction, we wished to explore its generality, its limitations, and structural effects governing the reaction course.[21] This paper summarizes our observations in this area with particular reference of the mechanism of the reaction.

Results and Discussion

Irradiation of 1-phenyl-2,3-dimethylindene (4) in benzene for 1 h under an argon atmosphere gave a 1:2 mixture of 1,2-dimethyl-3-phenyl (5) and 1,3-dimethyl-2-phenylindene (6). The structures of these indenes were confirmed by comparison with authentic samples prepared by treating 2,3-dimethyl- (7) and 2-phenyl-3-methylindanone (8) with the appropriate Grignard reagent followed by

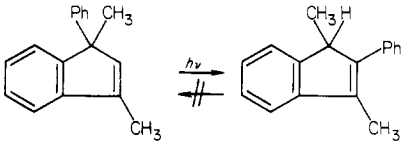


4 5 6 7 8

(1) Lablache-Combier, A. "Photochemistry of Heterocyclic Compounds"; Buchardt, O., Ed.; J. Wiley and Sons: New York, 1976; p 123.
(2) For a recent review see: Padwa, A. "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 501.
(3) Beak, P.; Messer, W. *Tetrahedron* **1969**, *25*, 3287.
(4) Kojima, M.; Maeda, M. *Tetrahedron Lett.* **1969**, 2379.
(5) Williams, W. M.; Dolbier, W. R. *J. Am. Chem. Soc.* **1972**, *94*, 3955.
(6) Barltrop, J. A.; Day, A. C.; Ward, R. W. *J. Chem. Soc., Chem. Commun.* **1978**, 131.
(7) Wynberg, H.; Kellogg, R. M.; vanDriel, H.; Beekhuis, G. E. *J. Am. Chem. Soc.* **1967**, *89*, 3501.
(8) Tiefenthaler, H.; Dorscheln, W.; Goth, H.; Schmid, H. *Helv. Chim. Acta* **1967**, *50*, 2244.
(9) Golden, D. M.; Brauman, J. I. *Trans. Faraday Soc.* **1969**, *65*, 464.
(10) Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 4851.
(11) Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331.
(12) Ullman, E. F.; Singh, B. *J. Am. Chem. Soc.* **1967**, *89*, 6911.
(13) Closs, G. L.; Boll, W. A.; Heyn, H.; Dev, V. *J. Am. Chem. Soc.* **1968**, *90*, 173.
(14) Reid, S. T. *Adv. Heterocycl. Chem.* **1970**, *11*, 1.
(15) vanTamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 6129.
(16) Barltrop, J. A.; Day, A. C.; Irving, E. *J. Chem. Soc., Chem. Commun.* **1979**, 881.
(17) Padwa, A.; Loza, R.; Getman, D. *Tetrahedron Lett.* **1977**, 2847; *J. Org. Chem.* **1978**, *43*, 1481.
(18) Palensky, F. J.; Morrison, H. A. *J. Am. Chem. Soc.* **1977**, *99*, 3507. Giacherio, D.; Morrison, H. A. *Ibid.* **1978**, *100*, 7109.
(19) McCullough, J. J. *Can. J. Chem.* **1968**, *46*, 43. McCullough, J. J.; McClory, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 1962. McCullough, J. J.; Yarwood, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 485. deFonseka, K. K.; Manning, C.; McCullough, J. J.; Yarwood, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 8257.
(20) Griffin, G. W.; Marcantonio, A. F.; Kristinsson, H.; Petterson, R. C.; Irving, C. S. *Tetrahedron Lett.* **1965**, 2951.
(21) Padwa, A.; Goldstein, S.; Loza, R.; Pulwer, M. *Tetrahedron Lett.* **1979**, 4895.

0022-3263/81/1946-1858$01.25/0

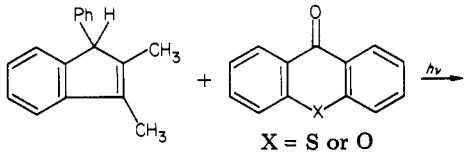
dehydration of the resulting alcohols. Irradiation a sample of indene **5** under similar conditions resulted in the isolation of **6** (95%). The formation of **6** from **5** was due to the conversion of **5** back to **4** which was further transformed to **6** under the reaction conditions. Photolysis of the isomeric 1,3-dimethyl-1-phenylindene (**9**) also gave **6**



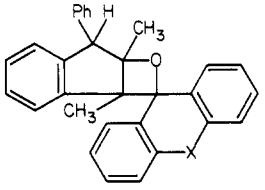
9 **6**

as the exclusive photoproduct. These reactions proceed exclusively in one direction since the irradiation of indene **6** resulted in recovered starting material, even under lengthy photolytic conditions.

The photochemistry of simple indene derivatives has been shown to be dependent on the multiplicity of the excited state involved.[19] Triplet-sensitized irradiation of indene itself afforded the *cis-anti-cis*-cyclobutane dimer in high yield.[22-24] However, on direct irradiation, in which the light is absorbed by indene, extensive polymerization occurs. Cyclobutanes can also be obtained by sensitized cross-addition reactions of indene with coumarin[22,24] or acrylonitrile.[25] Photolysis of indene and acrylonitrile with no sensitizer results in the formation of 2-(1-indenyl)-propionitrile as the major product.[25] In order to obtain further information on the multiplicity dependence of the indene rearrangement, a study of the sensitized behavior of indene **4** was undertaken. Irradiation of **4** in the



4 X = S or O



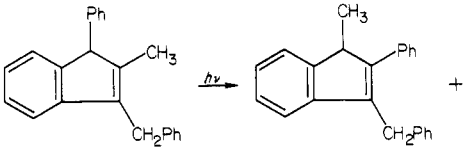
10, X = S
11, X = O

presence of thioxanthone led to the isolation of a single product which was identified as oxetane **10**. Careful inspection of the crude photolysate by NMR spectroscopy revealed the complete absence of the rearranged indenes.

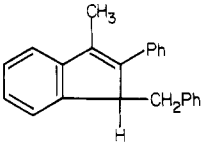
The triplet energy (E_T) in indene **4** is not known; however, it should be close to the value reported for styrene (E_T = 61.5 kcal/mol).[26] Since thioxanthone has a relatively low triplet energy (E_T = 65.5 kcal),[26] efficient energy transfer between the sensitizer and indene **4** may not be occurring. In order to avoid this potential problem, the irradiation of **4** was also carried out in the presence of xanthone (E_T = 74.2 kcal/mol)[26] as the sensitizer. Under these conditions oxetane **11** was isolated as the major photoproduct along with unreacted starting material. It should be noted that oxetane formation with the above system was found to be extremely inefficient relative to the rearrangement path. Barltrop and Carless had previously reported that oxetane formation is a minor competitive pathway in the benzophenone-sensitized photodimerization of dienes.[27] Since no indene dimers could be detected, it is still not clear whether energy transfer from the sensitizer to the indene was occurring.

The type II cleavage of valerophenone to give acetophenone and propene is known to be a triplet reaction which can be quenched by conjugated dienes.[28] We reasoned that if indene **4** were to quench the type II reaction of valerophenone, the efficiency of energy transfer to the indene could be derived from the rate of quenching. Irradiation of valerophenone in the presence of varying concentrations of indene **4** gave a linear Stern–Volmer plot with a slope of 40. Wagner and Kemppainen had reported that quenching of this ketone with 2,5-dimethyl-2,4-hexadiene also gave a Stern–Volmer plot with a slope of 40 ± 2.[28] The similarity of the values for the slope clearly indicates that the rate of quenching is diffusion controlled. Since indene **4** gave identical quenching results with those observed by Wagner and Kempainnen, energy transfer to the indene must be an efficient process. These results suggest that the phototransposition reaction of indene **4** is a singlet-derived process and that oxetane formation represents a minor competing pathway relative to energy transfer. Presumably severe steric interactions due to the presence of the methyl groups prevent the formation of indene dimers in the sensitized irradiation.

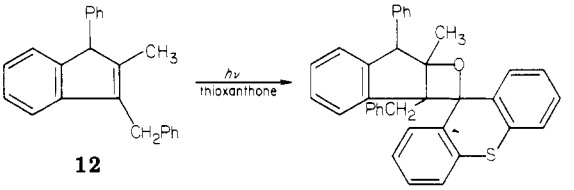
Attention was next turned to the photochemical behavior of 1-phenyl-2-methyl-3-benzylidene (**12**). Irradiation of **12** resulted in a mixture of two compounds in a 20:1 ratio. The structures of the products were identified as 1-methyl-2-phenyl-3-benzyl- (**13**, 95%) and 1-benzyl-2-phenyl-3-methylindene (**14**, 5%) by comparison with authentic samples. The observed rearrangement represents an exchange of the indene 1 and 2 carbon atoms and is analogous to the rearrangement encountered with indene **4** and to the process described by Morrison and Palensky for related substituted indenes.[18] Photolysis of indene **12**



12 **13**



14



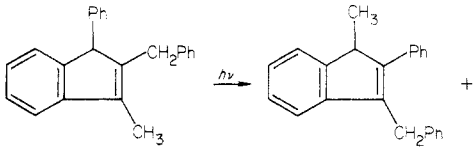
12

in the presence of thioxanthone gave one major product

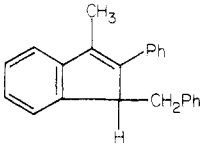
(22) Schenck, G. O.; Hartmann, W.; Mannsfeld, S. P.; Metzner, W.; Kranch, C. H. *Chem. Ber.* **1962**, *95*, 1642.
(23) Krauch, C. H.; Metzner, W.; Schenk, G. O. *Naturwissenschaften* **1963**, *50*, 710.
(24) Bowyer, J.; Porter, Q. N. *Aust. J. Chem.* **1966**, *19*, 1455.
(25) McCullough, J. J.; Huang, C. W. *Chem. Commun.* **1967**, 815.
(26) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.
(27) Barltrop, J. A.; Carless, H. A. J. *J. Am. Chem. Soc.* **1972**, *94*, 8761.
(28) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.
(29) Dolbier, W. R.; Matsui, K.; Dewey, H. J.; Horak, D. V.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 3376; *Ibid.* **1979**, *101*, 2136.

which was identified by its spectral properties as the oxetane derived from a Paterno–Buchi reaction. This observation is also compatible with the suggestion that the phototransposition reaction of the indenyl system only occurs from the electronically excited singlet state.

In order to help elucidate the correct mechanism for the rearrangement, the photochemistry of the isomeric 1-phenyl-2-benzyl-3-methylindene (**15**) was carried out in benzene. Irradiation of **15** through a Vycor filter sleeve gave rise to a mixture of indenes **13** and **14** in the same



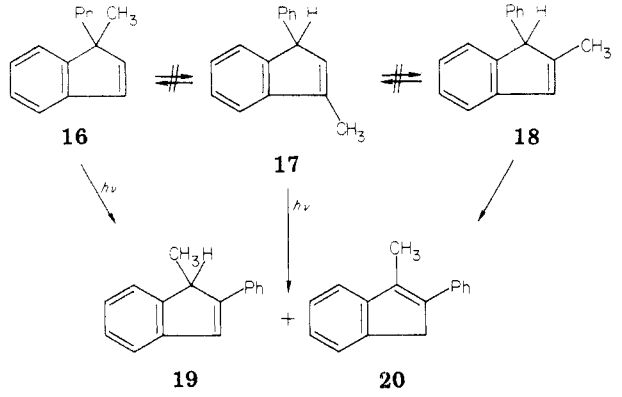
15 **13**



14

distribution as that obtained from the photolysis of **12**. It is particularly interesting to note that indene **13** is formed in much larger quantities than the isomeric indene **14** in both experiments. A possible explanation for the observed product distribution will be discussed shortly.

Additional examples of the phototransposition of the indene ring were provided by the photolysis of indenes **16**, **17**, and **18**. In all of these cases, the same two rearranged



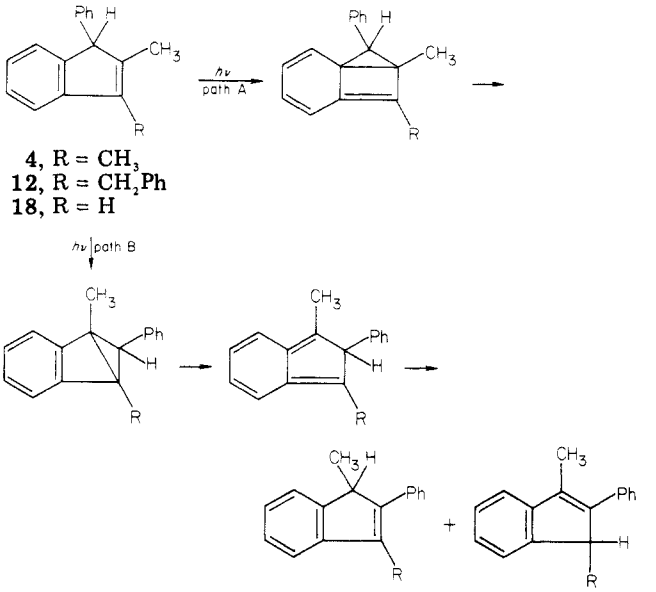
16 **17** **18**

19 **20**

compounds (i.e., **19** and **20**) were formed in the same ratio (**19**:**20** = 2:1). Appropriate control experiments established that no photoisomerization of either the starting materials or the products was operative under the reaction conditions. The structures of **19** and **20** were based on their spectroscopic and analytical properties and were further confirmed by comparison with authentic samples.

Two possible mechanisms have been suggested to rationalize the interconversions observed on irradiation of alkyl-substituted indenes.[18,21] These consist of a multistep process (Scheme I) involving initial [$_\pi$2 + $_\pi$2] intramolecular cycloaddition (path A) and a "conjugated di-π-methane" rearrangement (path B). Both of these pathways lead to an isoindene intermediate which undergoes a subsequent 1,5 sigmatropic hydrogen shift. In both of these paths, migration of the central atom represents the critical step. It should be noted that Baldwin and Andrews[10] have recently reported a photochemical carbon-skeleton rearrangement of a cyclopentadiene which proceeds by a photochemical 1,3-carbon migration of a transient bicyclo[2.1.0]pent-2-ene valence isomer. This provides excellent precedence for pathway A. This path is

Scheme I



4, R = CH_3
12, R = CH_2Ph
18, R = H

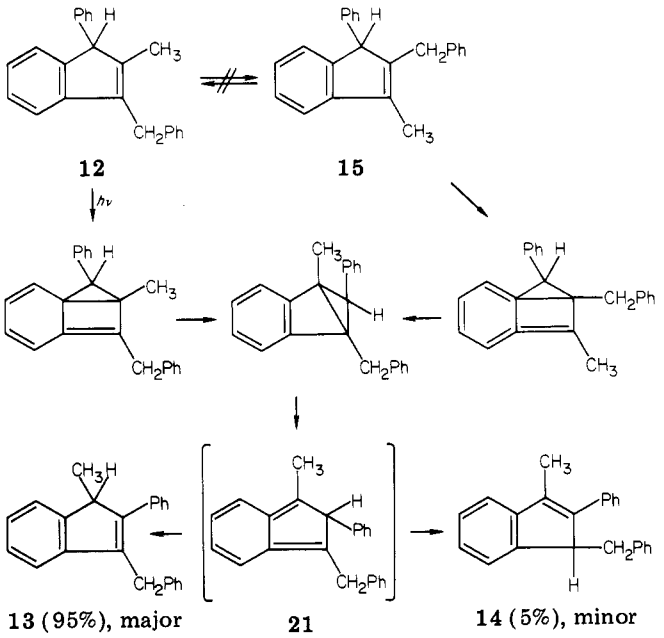
also analogous to the mechanism proposed to account for the photoisomerization of a number of five-membered heteroaromatic ring compounds.[2] More recently, work by Morrison and Giacherio has shown that the irradiation of 1-methyl-2-(trideuteriomethyl)indene proceeds with complete inversion at the migrating center.[18] This observation has been interpreted as being most consistent with the "conjugated di-π-methane" rearrangement. The photochemical rearrangement of indenes **4**, **12**, and **18** can be formulated by using either of the two mechanisms.

Considerable effort has been made in recent years on attempts to prepare isoindenes.[29,30] So far only 2,2-dimethylisoindene has been isolated.[29] The corresponding compounds without the blocking methyl groups exist entirely as 1*H*-indenes, although isoindenes have been invoked as intermediates in some of their reactions.[31,32] This is obviously due to the facile 1,5-hydrogen shift or acid/base-catalyzed prototropy from the ortho-quinoid structure to the more stable aromatic system. Dolbier and coworkers have recently been able to isolate a stable benzobicyclo[2.1.0]pentene derivative.[29] The thermal conversion of this species to the isoindene skeleton was found to have a remarkably low activation energy for a "forbidden" disrotatory electrocyclic opening of a cyclobutene.[33] Molecular models indicate that cyclic overlap of the atomic orbitals on the four centers involved is impossible to avoid during the reaction without unreasonable distortion of the σ framework, so that this reaction certainly is concerted even if the path of minimum energy involves a somewhat faster rotation of one of the termini. The low activation energy is undoubtedly related to the high ring strain of the benzobicyclopentene and the ease with which benzannelated cyclobutenes undergo ring opening.[34]

Further support for an isoindene intermediate in these rearrangements was obtained from the photolysis of indene **15**. As was noted previously, the photolysis of **15** produced the same mixture of products as that obtained from the

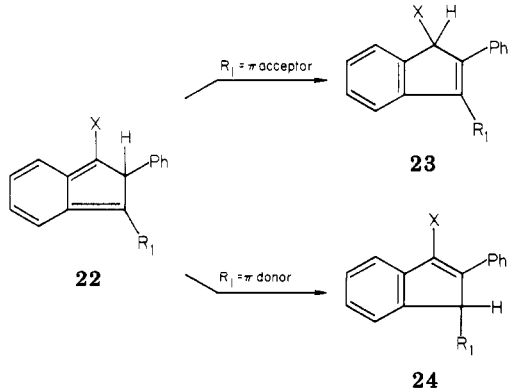
(30) Feast, W. J.; Preston, W. E. *J. Chem. Soc., Chem. Commun.* **1974**, 985.
(31) Cram, D. J.; Almy, J. *J. Am. Chem. Soc.* **1970**, *92*, 4316.
(32) Miller, L. L.; Boyer, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 650.
(33) Steiner, R. P.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6413; *Ibid.* **1979**, *101*, 512.
(34) Wilcox, C. F.; Carpenter, B. K.; Dolbier, W. R. *Tetrahedron* **1979**, *35*, 707.

Scheme II

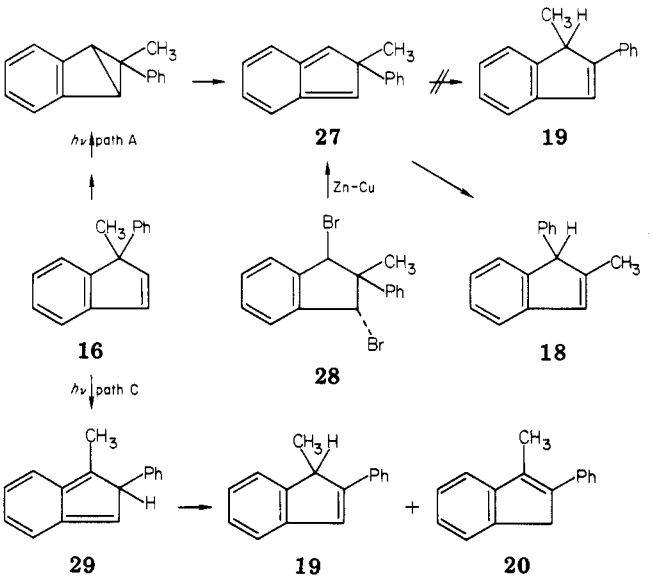


irradiation of **12**. This is perfectly compatible with the intermediacy of isoindene **21** (Scheme II).

Indenes **13** and **14** are formed from isoindene **21** by a concerted suprafacial hydrogen migration which is symmetry allowed when it occurs between two neighboring carbon atoms with coefficients of the same sign in the highest occupied molecular orbital. The general question of how substituents affect the course of the sigmatropic hydrogen migration of isoindenes was originally raised by Wilson and Pettit.[35] These workers correlated the direction of hydrogen migration in substituted isoindenes 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 the nature of the substituent group. Predictions by simple Huckel molecular orbital calculations were found to be in remarkable agreement with the experimental results. More recent calculations by Jean suggest that the position of the node and thus the direction of hydrogen migration will be related to the electronic properties of the substituent group.[36] The product of hydrogen migration in substituted isoindenes such as **22** was predicted to be indene **23** if R_1 is a π acceptor and **24** if R_1 is a π donor.[36] Thus, one possible explanation to

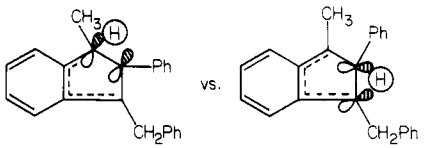


Scheme III



account for the preponderance of indene **13** from isoindene **21** is that the methyl group is a better π donor than the benzyl group. Calculations on 1-benzyl-3-methylallyl radical do in fact indicate that the π-donor character of the benzyl group is weaker than that of the methyl group.[36] A similar rationale would account for the fact that **19** is produced in larger quantities than **20** in the phototransposition reaction of indene **18**.

Another possible explanation to account for the product distribution is that the direction of hydrogen migration in the substituted isoindene system is controlled by steric factors. The product-determining step is the thermal 1,5 sigmatropic migration of a hydrogen atom on the middle carbon of an isoindene intermediate to either neighboring carbon. In the half-migrated form (i.e., **25** or **26**), the alkyl



substituent is forced into a cis relation with the phenyl group on the 2-position. Since benzyl is a more bulky group than methyl, it is tempting to suggest that transition state **25**, in which the phenyl and methyl groups are cisoid, is of lower energy than transition state **26**, in which the two larger groups are cisoid. Hence, the van der Waals repulsive forces between two large groups may be the decisive factor for the predominant formation of the 3-benzyl-substituted indene isomer. The available data do not decisively distinguish between these two possibilities.

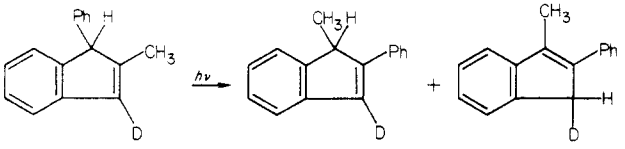
The photochemical conversion of 1-methyl-1-phenylindene (**16**) to indenes **19** and **20** represents an intriguing transformation. Two fundamentally, different mechanisms seem possible and are presented in Scheme III. Path A involves an electrocyclic ring closure followed by a 1,3 sigmatropic shift to give a benzobicyclo[2.1.0]pentene. This intermediate then opens to an isoindene derivative (**27**) which can undergo a 1,5 sigmatropic methyl shift. It should be noted that Dolbier and co-workers have reported that 2,2-dimethylisoindene undergoes a facile 1,5-methyl shift.[37] The gain in aromaticity resulting from the methyl

(35) Pettit, W. A.; Wilson, J. W. *J. Am. Chem. Soc.* **1977**, *99*, 6372.
(36) Jean, Y. *J. Org. Chem.* **1979**, *44*, 858. Jean, Y., Private communication.
(37) Dolbier, W. R.; Anapolle, K. E.; McCullagh, L.; Matsui, K.; Riemann, J. M.; Rolison, D. *J. Org. Chem.* **1979**, *44*, 2845.

shift significantly lowers the activation energy for this process (E_a = 26.1 kcal/mol).[37] The analogous 1,5-methyl shift in 5,5-dimethylcyclopentadiene is known to occur under relatively harsh thermal conditions and requires an activation energy of 41–46 kcal/mol.[38,39] The rearrangement of indene **16** via pathway A is closely related to that previously encountered with indenes **4**, **12**, and **18**.

An alternate path (C) which could also rationalize the rearrangement involves a 1,2-phenyl migration and is closely related to that described by Griffin and co-workers for the photolysis of 1,1-diaryl-substituted indenes.[20] In order to help elucidate the correct mechanism, we decided to prepare isoindene **27** and study its rearrangement. The key feature of path A is that the methyl group must migrate in preference to the phenyl group. Differences in migratory aptitudes of various substituent groups in 1,5 sigmatropic rearrangements have been examined by a number of groups in recent years.[40-42] The relative migratory aptitudes of a series of 2,2-dialkyl-substituted isoindenes has been found to reflect the relative stabilities of the migrating groups.[37] According to mechanism A, preferential methyl migration must occur. This was found not to be the case. We found that isoindene **27** could be generated conveniently by treating dibromide **28**, with zinc–copper couple.[43] Isoindene **27** was found to undergo exclusive 1,5-phenyl migration to give 1-phenyl-2-methylindene (**18**) in quantitative yield. The migratory aptitude observed with this system is consistent with earlier results encountered by Miller and Boyer.[32] These workers found that phenyl underwent 1,5-migration slower than hydrogen but faster than methyl in an indene system.[32] We conclude, therefore that the rearrangement of **16** is incompatible with path A. Instead, the photorearrangement is most consistent with a 1,2 sigmatropic phenyl shift to give isoindene **29** which then undergoes a subsequent aromatization reaction to produce indenes **19** and **20**. 1,3-Dimethyl-1-phenylindene (**9**) appears to follow the same mechanism.

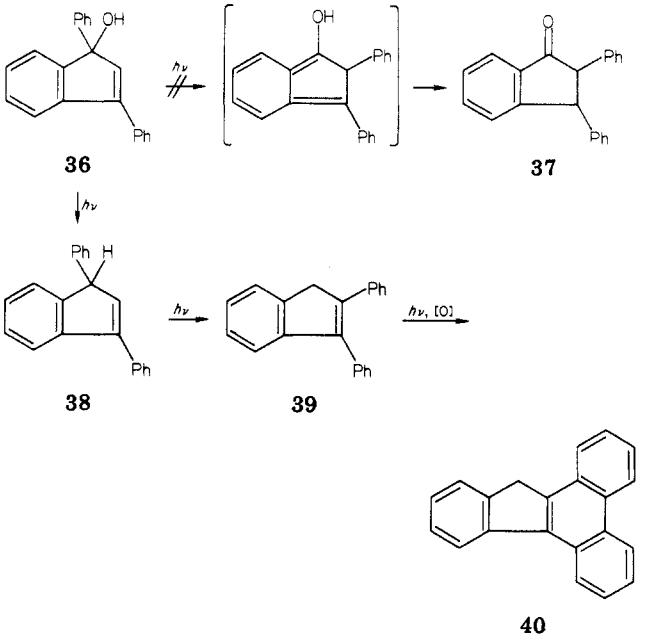
In contrast with the above results, the photorearrangement of 1-phenyl-2-methylindene (**18**) was found to proceed via the [$_\pi$2 + $_\pi$2] intramolecular cycloaddition route (path A). This was substantiated by irradiating the indene labeled with deuterium at the 3-position. The photolysis products were identified as 1-methyl-2-phenyl-3-deuterioindene (**32**) and 1-deuterio-2-phenyl-3-methylindene (**33**).



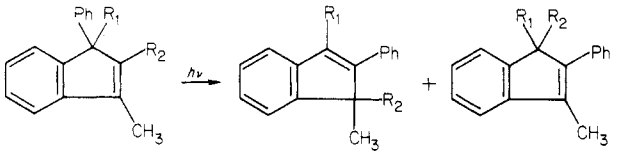
31 **32** **33**

With indene **17**, both the benzohousene path and the 1,2-phenyl migration route lead to the same set of products. However, a skeletal difference exists. The benzohousene path interchanges C-1 and C-2 of the indene ring while with phenyl migration no such skeletal change occurs.

Scheme IV



There is good evidence suggesting that the 1,2-phenyl migration route is the predominant path followed with indene **17**. Irradiation of **17** labeled with deuterium at C-2 (i.e., **34**) gave a mixture of **19** and **20** in good yield. Ex-



34, R_1 = H; R_2 = D
35, R_1 = D; R_2 = H

19 **20**

amination of the NMR of **19** showed a methyl singlet at δ 1.35 and a less intense (10%) doublet centered at δ 1.35. Similarly, irradiation of deuterium-labeled indene **35** also resulted in the formation of **19** and **20**. In this case, the methyl doublet for **19** amounted to 90% of the total formed by it and the singlet at δ 1.35. These observations clearly demonstrate that the photoisomerization of **17** goes mainly by the phenyl migration route (90%) and to a small but real extent (10%) by the benzohousene mechanism. One additional point worth noting is the question as to why some of the indene rearrangements proceed via the phenyl migration mechanism while others proceed via the benzobicyclopentane route. One possibility is that the benzobicyclopentane mechanism is a low-yield process which is observed only when the phenyl migration route is a nonproductive pathway, as it very well might be for indenes **4**, **12**, and **18**.

In an effort of uncover additional examples of the indene rearrangement, our attention was directed toward a study of the photochemistry of indenol **36** (Scheme IV). Our earlier observations suggested that **36** should rearrange to indanone **37** via a 1,2-phenyl shift. We found that the irradiation of **36** produced three products which could be separated by silica gel chromatography. The structures of these compounds were confirmed by comparison with authentic samples. No detectable quantities of indanone **37** were present in the crude photolysate. Consideration of the product distribution as a function of time showed an initial buildup of indene **38** followed by a decrease in amount. Evidence that **38** is an intermediate in the formation of the remaining products was obtained by the finding that the photolysis of a pure sample of **38** gave

(38) deHaan, J. W.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1594; *Ibid.* **1968**, *87*, 298.
(39) Herndon, W. C.; Manion, J. M. *J. Org. Chem.* **1968**, *33*, 4505.
(40) Field, D. J.; Jones, D. W.; Kneen, G. *J. Chem. Soc., Chem. Commun.* **1975**, 754; *Ibid.* **1976**, 873; *Ibid.* **1977**, 688; *J. Che. Soc., Perkin Trans.* $_1$, **1978**, 1050.
(41) Semmelhack, M. F.; Weller, H. N.; Foos, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 292.
(42) Schiess, P.; Funfschilling, P. *Tetrahedron Lett.* **1972**, 5195.
(43) Dolbier, W. R.; Matsui, K.; McCullagh, L.; Anapolle, K. E. *J. Org. Chem.* **1979**, *44*, 2842.

indenes **39** and **40** in about the same distribution as found in runs beginning with **36**. The structure of phenanthrene **40** was established by irradiating a sample of **39** in the presence of oxygen. Rigidly held stilbene moieties are known to yield phenanthrene derivatives on irradiation and provide excellent precedent for the latter transformation.[44-46]

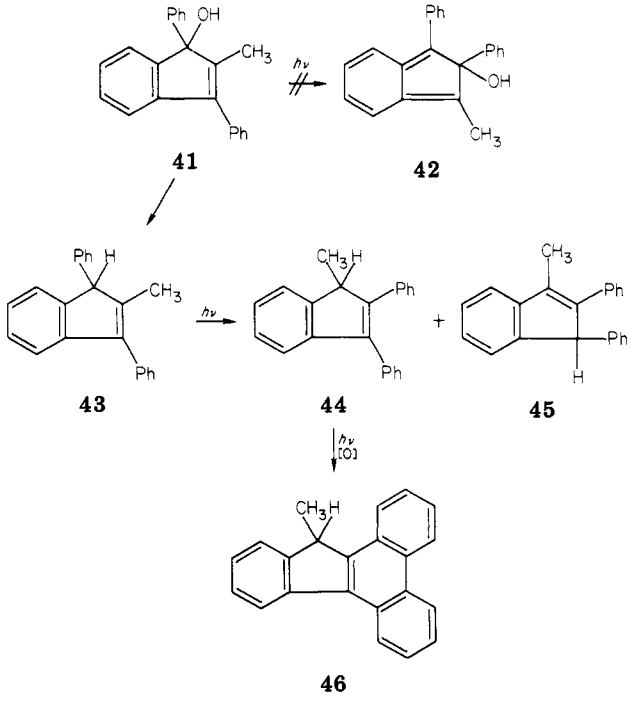
We have also carried out a study on the photobehavior of the structurally related indenol **41** (Scheme V). We originally anticipated that **41** would rearrange in a fashion analogous to that encountered with indenes **4** and **12**. However, close examination of the crude photolysate showed the complete absence of products derived from isoindene **42**. Instead, the major products were formed from indene **43**. When the irradiation of **41** was carried out for short periods of time, indene **43** was the major product produced. Further irradiation of **43** afforded indenes **44–46**. These compounds were assigned on the basis of their characteristic spectral properties and were further verified by comparison with independently synthesized samples.

The mechanism by which these indenols are converted to the corresponding indene skeleton is not known and further work must be done before this path can be established. Our results do, however, show that the mechanism followed in the photoisomerization of aryl-substituted indenes is markedly dependent on the nature and location of the substituent groups present on the ring. We are continuing to explore the scope and mechanistic details of the photoreduction reaction and will report additional findings at a later date.

Experimental Section[47]

Preparation of 1-Phenyl-2,3-dimethylindene (4). To a solution containing 1.0 g of 2-methyl-3-phenylindanone[48] in 150 mL of anhydrous ether was added 3 mL of a 3.0 M solution of methylmagnesium bromide in ether. The mixture was stirred for 2 h at room temperature and was then hydrolyzed with a saturated ammonium chloride solution. The ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind a light yellow oil which was taken up in 20 mL of glacial acetic acid. To this stirred solution was added 5 mL of concentrated sulfuric acid and 0.5 mL of water. The solution was stirred for 1 h at room temperature and was then poured into iced water. The mixture was extracted with ether and the ethereal layer was washed with water, a saturated sodium bicarbonate solution, and a saturated salt solution and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil which was chromatographed on a 1.5 × 100 cm silica gel column, using hexane as the eluent. The major component isolated from the column contained 0.54 g (55%) of a white crystalline solid identified as 1-phenyl-2,3-dimethylindene (**4**) on the basis of its physical and spectral properties: mp 67–68 °C; NMR ($CDCl_3$, 100 MHz) δ 1.85 (br s, 3 H), 2.10 (br s, 3 H), 4.28 (br s, 1 H), 6.95–7.47 (m, 9 H); IR (neat) 3.30, 3.47, 3.52, 6.14, 6.24, 6.72, 6.85, 6.94, 7.27, 9.82, 13.4, 13.9, 14.5 μm; UV (95% ethanol) 263 nm (ϵ 10 000). The physical properties of this compound were identical with those reported by Smith and Hanson.[49]

Scheme V



Direct Irradiation of 1-Phenyl-2,3-dimethylindene (4). A solution containing 120 mg of **4** in 200 mL of benzene was irradiated for 1 h with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Vycor filter sleeve under an argon atmosphere. The benzene was removed under reduced pressure, leaving behind a yellow oil which was percolated through silica gel, using hexane as the eluent. The major component isolated contained 92 mg (75%) of a colorless oil which was shown by NMR spectroscopy to be a 2:1 mixture of 1,3-dimethyl-2-phenylindene (**6**) and 1,2-dimethyl-3-phenylindene (**5**). The structures of these two compounds were established by comparison with independently synthesized samples.

A 440-mg sample of 2-phenyl-3-methylindanone (**8**)[50] was taken up in 50 mL of ether. To this solution was added 0.8 mL of a 3.0 M solution of methylmagnesium bromide in ether under a nitrogen atmosphere. The mixture was heated at reflux for 4 h and was then hydrolyzed with a saturated ammonium chloride solution. The ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil which was taken up in 20 mL of glacial acetic acid. To this stirred solution was added 0.5 mL of water and 5 mL of concentrated sulfuric acid. The mixture was stirred for 30 min and then poured onto ice water. The aqueous solution was extracted with ether and the ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil which solidified on standing. Recrystallization from ethanol gave 250 mg (57%) of 1,3-dimethyl-2-phenylindene (**6**) as a white crystalline solid: mp 72–73 °C; IR (KBr) 3.54, 6.24, 7.05, 13.23, 13.50, 14.45 μm; UV (95% ethanol) 292, 228 nm (ϵ 258 000, 15 200); NMR ($CDCl_3$, 100 MHz) δ 1.15 (d, 3 H, J = 7.0 Hz), 2.21 (d, 3 H, J = 3.0 Hz), 3.65–4.00 (m, 1 H), 7.08–7.52 (m, 9 H); mass spectrum, m/e 220 (M^+ and base), 205.

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H. 7.32. Found: C, 92.40; H, 7.57.

A sample of 1,2-dimethyl-3-phenylindene (**5**) was prepared in the following fashion. To a solution containing 2.4 g of 2,3-dimethylindanone[51] (**7**) in 100 mL of anhydrous ether was added 7.8 mL of a 2.9 M solution of phenylmagnesium bromide in ether.

(44) Lappin, G. R.; Zanucci, J. S. *J. Org. Chem.* **1971**, *36*, 1808.
(45) Schoenberg, A.; Sidky, M. M. *Chem. Ber.* **1974**, *107*, 1207.
(46) Mudry, C. A.; Frasca, A. R. *Tetrahedron* **1974**, *30*, 2983.
(47) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer, using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz, using a JEOLCO-MH-100 spectrometer, and at 90 MHz, using a Varian EM-390 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All irradiations were carried out by using a 450-W Hanovia medium-pressure mercury arc.
(48) Zimmerman, H. E. *J. Am. Chem. Soc.* **1956**, *78*, 1168.
(49) Smith, L. I.; Hanson, L. I. *J. Am. Chem. Soc.* **1935**, *57*, 1326.
(50) Koelsch, C. F.; Johnson, P. R. *J. Am. Chem. Soc.* **1943**, *65*, 567.
(51) Barltrop, J. A.; Acheson, R. M.; Philott, P. G.; MacPhee, K. E.; Hunt, J. S. *J. Chem. Soc.* **1956**, 2928.

The solution was refluxed for 8 h and was then hydrolyzed with a saturated ammonium chloride solution. The mixture was extracted with ether and the organic layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind a light yellow oil which was taken up in 20 mL of glacial acetic acid. To this stirred solution was added 3 mL of concentrated sulfuric acid and 0.5 mL of water. The mixture was stirred for 45 min and was then poured into ice–water. The mixture was extracted with ether and the organic layer was washed with water, a saturated sodium bicarbonate solution, and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind a light yellow oil which was chromatographed on a 1.5 × 100 cm silica gel column, using hexane as the eluent. The major fraction isolated contained 1.8 g (55%) of a light yellow oil which was identified as 1,2-dimethyl-3-phenylindene (**5**) on the basis of its characteristic spectral properties: NMR ($CDCl_3$, 60 MHz) δ 1.38 (d, J = 8 Hz, 3 H), 2.05 (s, 3 H), 3.38 (q, J = 8 Hz, 1 H), 7.22–7.62 (m, 9 H); IR (neat) 3.28, 3.32, 3.38, 3.42, 3.50, 6.24, 6.71, 6.85, 8.62, 9.35, 9.80, 13.0, 13.5, 14.3 μm. These peaks were identical with those reported by Jones, Baron, and Hendrick.[52]

Direct Irradiation of 1,2-Dimethyl-3-phenylindene (5). A solution containing 200 mg of 1,2-dimethyl-3-phenylindene (**5**) in 200 mL of benzene was irradiated for 2 h under an argon atmosphere with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure left behind a light yellow oil which was shown by NMR spectroscopy to be a 4:1 mixture of 1,3-dimethyl-2-phenylindene (**6**) and 1-phenyl-2,3-dimethylindene (**4**). The structures of these two compounds were verified by comparison with authentic samples.

Sensitized Irradiation of 1-Phenyl-2,3-dimethylindene (4) with Thioxanthen-9-one. A solution containing 50 mg of **4** and 40 mg of thioxanthen-9-one in 250 mL of benzene was irradiated for 2.5 h under an argon atmosphere, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a uranium filter sleeve. Removal of the solvent under reduced pressure left behind a yellow oil which was chromatographed on a preparative thick-layer plate, using a 10% acetone–hexane mixture as the eluent. The major component isolated contained 58 mg (50%) of a white crystalline material which was identified as oxetane **10** on the basis of its physical and spectral properties: mp 208–209 °C (ethanol); NMR ($CDCl_3$, 100 MHz) δ 1.14 (s, 3 H), 1.23 (s, 3 H), 4.78 (s, 1 H), 6.70–7.53 (m, 16 H), 7.97 (dd, J = 7, J = 2 Hz, 1 H); IR (KBr) 3.42, 6.24, 6.97, 7.29, 7.93, 8.50, 9.32, 9.87, 11.20, 13.15, 13.45, 13.94, 14.45 μm; UV (cyclohexane) 264 nm (ϵ 11300); mass spectrum, m/e 220 (base), 212, 205, 184.

Anal. Calcd for $C_{30}H_{24}OS$: C, 83.30; H, 5.59. Found: C, 83.09; H, 5.63.

Sensitized Irradiation of 1-Phenyl-2,3-dimethylindene (4) with Xanthone. A solution containing 250 mg of **4** and 225 mg of xanthone was irradiated for 8 h under an argon atmosphere, using a 550-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve. Removal of the solvent left behind a yellow oil which was chromatographed on a preparative thick-layer plate, using a 10% acetone–hexane mixture as the eluent. The first component isolated contained 106 mg (42%) of a colorless oil which was identified as unreacted starting material. The second component isolated contained 169 mg (36%) of a white crystalline material identified as oxetane **11** on the basis of its physical and spectral properties: mp 189–190 °C (ethanol–chloroform); NMR ($CDCl_3$, 100 MHz) δ 0.96 (s, 3 H), 1.33 (s, 3 H), 4.87 (s, 1 H), 6.32–7.51 (m, 16 H), 7.90–8.04 (m, 1 H); IR (KBr) 3.44, 6.24, 6.85, 6.97, 7.27, 7.67, 8.08, 9.88, 10.82, 13.29, 13.70, 14.39 μm; UV (cyclohexane) 283, 269 nm (ϵ 4520, 3300); mass spectrum, m/e 373, 221, 220 (base), 219, 206, 205, 204, 203, 196, 181, 100, 99.

Anal. Calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.34; H, 5.88.

Direct Irradiation of 1,3-Dimethyl-1-phenylindene (9). To a solution containing 1.5 g of 3-methyl-3-phenyl-1-indanone[53] in 150 mL of ether was added 4.5 mL of a 3.0 M solution of methylmagnesium bromide in ether. The mixture was stirred for 3 h at 25 °C and was then hydrolyzed with a saturated ammonium chloride solution. The ether layer was washed with water, dried, and concentrated under reduced pressure. The resulting yellow oil was taken up in 25 mL of glacial acetic acid. To this solution was added 5 mL of sulfuric acid and 0.5 mL of water. After being stirred at 25 °C for 1 h, the solution was poured into ice–water. The mixture was extracted with ether and the ethereal layer was washed with water and a 10% sodium carbonate solution and was then dried over magnesium sulfate. Removal of the solvent under reduced pressure left a crude oil which was distilled at 110 °C (0.01 mm) to give 0.78 g (52%) of 1,3-dimethyl-1-phenylindene (**9**) as a white solid: mp 48–49 °C (lit.[54] mp 50–51 °C); UV (95% ethanol) 207, 220, 260 nm (ϵ 22100, 19000, 4100); NMR ($CDCl_3$, 60 MHz) δ 1.62 (s, 3 H), 2.05 (d, 3 H, J = 1.5 Hz), 6.08 (q, 1 H, J = 1.5 Hz), 7.8 (m, 9 H).

A solution containing 200 mg of indene **9** in 200 mL of benzene was irradiated for 1 h with a 450-W Hanovia medium-pressure arc with a Vycor filter sleeve under an argon atmosphere. Removal of the solvent under reduced pressure left behind a yellow oil which slowly crystallized on standing to give 1,3-dimethyl-2-phenylindene (**6**) as a crystalline solid, mp 72–73 °C. The structure of the photoproduct was verified by comparison with an authentic sample.

Preparation of 1-Phenyl-2-methyl-3-benzylindene (12). 2-Methyl-3-phenylindanone was prepared according to the procedure of Zimmerman.[48] A 2.4-g sample of this compound was dissolved in 100 mL of anhydrous ether and 16 mL of a 1.0 M solution of benzylmagnesium chloride in ether was added dropwise. The mixture was stirred for an additional 2 h and then hydrolyzed with a saturated ammonium chloride solution. The ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind a yellow oil which was taken up in 45 mL of glacial acetic acid. To this solution were added at 0 °C 5 mL of concentrated sulfuric acid and 2 mL of water. The mixture was stirred for 30 min and was then poured into ice–water. The mixture was extracted with ether and the organic layer was washed several times with water, a saturated sodium bicarbonate solution, and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil which solidified on standing. Recrystallization from ethanol afforded 1.2 g (37%) of 1-phenyl-2-methyl-3-benzylindene (**12**): mp 103–104 °C; NMR ($CDCl_3$, 100 MHz) δ 1.88 (s, 3 H), 3.88 (s, 2 H), 4.30 (s, 1 H), 6.8–7.3 (m, 14 H); IR (KBr) 6.25, 6.72, 8.43, 9.31, 9.72, 10.60, 13.26, 13.80, 14.54 μm; UV (95% ethanol) 265 nm (ϵ 9400); mass spectrum, m/e 296 (M^+), 205 (base), 91.

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.26; H, 6.74.

Direct Irradiation of 1-Phenyl-2-methyl-3-benzylindene (12). A solution containing 120 mg of **12** in 250 mL of dry benzene was irradiated under an argon atmosphere for 2.5 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left behind a yellow oil which solidified when treated with ethanol. Recrystallization from ethanol afforded 90 mg (75%) of a white crystalline solid which was identified as 1-methyl-2-phenyl-3-benzylindene (**13**): mp 74–75 °C; NMR ($CDCl_3$, 100 MHz) δ 1.22 (d, 3 H, J = 8.0 Hz), 3.88 (q, 1 H, J = 8.0 Hz), 3.98 (s, 2 H); 6.9–7.4 (m, 14 H); IR (neat) 3.30, 6.24, 6.71, 6.83, 6.89, 12.28, 14.32 μm; UV (95% ethanol) 296, 229 nm (ϵ 16800, 15200); mass spectrum, m/e (M^+), 205 (base), 190, 177, 164, 91.

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.33; H, 6.79.

The structure of indene **13** was further verified by comparison with an authentic sample. 2-Phenyl-3-methylindanone was prepared according to the procedure of Koelsch.[50] A 1.8-g sample of this compound was taken up in 50 mL of anhydrous ether. To the solution was added 12 mL of a 1.0 M solution of benzylmagnesium chloride in ether. The mixture was refluxed for 1.5 h and was then hydrolyzed with a saturated ammonium chloride solution. The ethereal layer was washed with water and a satu-

(52) Baron, W. J.; Hendrick, M. E.; Jones, M. *J. Am. Chem. Soc.* **1973**, *95*, 6286.

(53) Koelsch, C. F.; Hochmann, H.; Leclaire, C. D *J. Am. Chem. Soc.* **1943**, *65*, 59.

(54) Gelin, R.; Chantegrel, B.; Gelin, S. *Bull. Soc. Chim. Fr.* **1969**, *11*, 4136.

rated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which solidified when treated with ethanol. Recrystallization from ethanol afforded 1.2 g (50%) of a white crystalline solid, mp 74–75 °C, which was identical in every detail with a sample of 1-methyl-2-phenyl-3-benzylindene (13) obtained from the irradiation of 12. The second component eluted from the column contained 6 mg of a clear oil whose structure was assigned as 1-benzyl-2-phenyl-3-methylindene (14) by comparison with an authentic sample.

Sensitized Irradiation of 1-Phenyl-2-methyl-3-benzylindene (12). A solution containing 130 mg of 12 and 80 mg of thioxanthen-9-one in 250 mL of benzene was irradiated for 4 h under an argon atmosphere, using a 450-W Hanovia medium-pressure arc lamp equipped with a uranium filter sleeve. Removal of the solvent left behind a yellow solid which was chromatographed on a preparative thick-layer plate, using a 10% acetone–hexane mixture as the eluent. The major fraction isolated contained 90 mg (47%) of a colorless oil which solidified on treatment with ethanol. The solid was recrystallized from an acetone–ethanol mixture to give colorless cubic crystals which were identified as the expected oxetane on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.40 (s, 3 H), 2.70 (d, J = 15 Hz, 1 H), 3.64 (d, J = 15 Hz, 1 H), 4.65 (s, 1 H), 6.96–7.80 (m, 21 H), 8.30 (dd, J = 8, J = 2 Hz, 1 H); IR (KBr) 3.36, 6.89, 9.80, 10.81, 11.02, 13.19, 13.48, 14.25 μm; UV (cyclohexane) 265 nm (ϵ 11 400); mass spectrum, m/e 296, 294, 213, 212, 206, 205 (base), 184.

Anal. Calcd for $C_{36}H_{28}OS$: C, 85.00; H, 5.55. Found: C, 84.90; H, 5.68.

Preparation of 1-Phenyl-2-benzyl-3-methylindene (15). To a solution containing 800 mg of 3-phenylindanone[55] in 10 mL of tetrahydrofuran under a nitrogen atmosphere at −78 °C was added an equivalent quantity of lithium diisopropylamide. The solution was allowed to warm to room temperature over a 4-h period. The yellow solution was cooled to 0 °C and then 0.48 mL of benzyl bromide in 2 mL of tetrahydrofuran was added. After the mixture was stirred for 8 h at 25 °C, 10 mL of a saturated ammonium chloride solution was added. The mixture was extracted with ether and the ethereal layer was washed with water and a saturated sodium chloride solution and was then dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed by medium-pressure chromatography, using a 15% acetone–hexane mixture as the eluent. The major fraction contained 508 mg (44%) of a clear oil whose structure was assigned as 2-benzyl-3-phenylindanone; NMR ($CDCl_3$, 60 MHz) δ 2.82–3.40 (m, 3 H), 4.10 (d, 1 H, J = 3.5 Hz), 6.60–7.80 (m, 14 H).

The above indanone was used in the next step without further purification. To a solution containing 508 mg of 2-benzyl-3-phenylindanone in 10 mL of ether was added an excess of methylmagnesium bromide at 0 °C. The mixture was stirred at 25 °C for 8 h and then 10 mL of a saturated ammonium chloride solution was added. The mixture was extracted with ether and the ethereal layer was washed with water and a saturated sodium bicarbonate solution and was then dried over magnesium sulfate. The ether was removed under reduced pressure, leaving behind a white solid which was recrystallized from ethanol to give 400 mg (79%) of 1-phenyl-2-benzyl-3-methylindene (15): mp 110–111 °C; IR (KBr) 3040, 1600, 1490, 1465, 1450, 1430, 1382, 1182, 1075, 1022, 1010, 755, 710, 690, 675 cm^{-1}; UV (ethanol) 266 nm (ϵ 12 400); NMR ($CDCl_3$, 100 mHz) δ 2.22 (d, 3 H, J = 1.5 Hz), 3.18 (d, 1 H, J = 15 Hz), 3.89 (d, 1 H, J = 15 Hz), 4.23 (q, 1 H, J = 1.5 Hz), 6.83–7.40 (m, 14 H); mass spectrum, m/e 296 (M^+), 205.

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.00; H, 6.85.

Direct Irradiation of 1-Phenyl-2-benzyl-3-methylindene (15). A solution containing 50 mg of 15 in 250 mL of benzene was irradiated under an argon atmosphere for 1.5 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Vycor filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a medium-pressure silica gel column, using hexane as the eluent, to give 36 mg (72%) of 1-methyl-2-phenyl-3-benzylindene (13). The structure of this material was established by comparison with an independently synthesized sample. The second component eluted from the column contained 2 mg of a clear oil whose structure was assigned as 1-benzyl-2-phenyl-3-methylindene (14) by comparison with an authentic sample.

Preparation of 1-Methyl-1-phenylindene (16). A 3.0-g sample of 3-methyl-3-phenyl-1-indanone[53] was dissolved in 30 mL of anhydrous ether and a solution of 0.7 g of lithium aluminum hydride in 30 mL of ether was slowly added to the ketone solution. After being heated at reflux for 3 h the mixture was quenched with a 10% sulfuric acid solution. After ether extraction, drying, and concentration, a white solid, mp 126–127 °C, was obtained whose structure was assigned as 3-methyl-3-phenyl-1-indanol; NMR ($CDCl_3$, 60 MHz) δ 1.67 (s, 3 H), 2.45 (m, 2 H), 5.24 (t, 1 H), 7.75 (m, 9 H). A 1.5-g sample of this alcohol and 0.1 g of p-toluenesulfonic acid in 20 mL of acetic acid was heated at reflux for 1 h. The mixture was cooled, poured into 50 mL of water, and extracted with ether. The ether layer was washed with a 10% sodium bicarbonate solution, dried, and concentrated to give 1-methyl-1-phenylindene (16) as a clear oil;[32] NMR ($CDCl_3$, 60 MHz) δ 1.65 (s, 3 H), 6.55 (d, 2 H, J = 6.0 Hz), 7.15 (m, 9 H).

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.21; H, 6.76.

Preparation of 1-Phenyl-2-methylindene (18). To a solution containing 3.33 g of 2-methyl-3-phenylindanone in 200 mL of anhydrous ether under an atmosphere of nitrogen was added 0.22 g of lithium aluminum hydride. The resulting mixture was allowed to stir for 30 min and was then refluxed for an additional 2 h. After the solution cooled, 0.5 mL of water was added followed by 0.25 mL of a 30% sodium hydroxide solution followed again by water. The ether solution was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure, leaving behind 3.09 g (92%) of 3-phenyl-2-methylindanol as a yellow oil. A 200-mg sample of 3-phenyl-2-methylindanol was added to a solution containing 20 mL of glacial acetic acid, 1 mL of water, and 1 mL of concentrated sulfuric acid. The solution was allowed to stir for 2 h at room temperature and then 100 mL of ether was added. The ethereal layer was separated, washed with water a saturated sodium bicarbonate solution, and a saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, leaving behind a black oil which was chromatographed on a preparative thick-layer plate, using a 5% acetone–hexane mixture as the eluent. The major fraction isolated contained 165 mg (90%) of 1-phenyl-2-methylindene (18) as a white crystalline solid: mp 50.0–50.5 °C; NMR ($CDCl_3$, 100 MHz) δ 1.86 (br s, 3 H), 4.20 (br s, 1 H), 6.48 (br s, 1 H), 6.80–7.28 (m, 9 H); IR (KBr) 3050, 3020, 2900, 1610, 1590, 1485, 1460, 1445, 1430, 1380, 880, 850, 745, 725, 695 cm^{-1}; mass spectrum, m/e 206 (M^+, base), 191, 128.

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.08; H, 6.85.

Preparation of 1-Phenyl-2-methyl-3-deuterioindene (31). A solution containing 500 mg of 2-methyl-3-phenylindanone in 50 mL of anhydrous ether was added slowly to a suspension of 94 mg of lithium deuteride in 100 mL of anhydrous ether. The mixture was allowed to stir for 30 min and was then refluxed for 2.5 h. After the mixture cooled to room temperature, 0.5 mL of water was added followed by 0.25 mL of a 30% sodium hydroxide solution followed again by 2 mL of water. The organic layer was dried over magnesium sulfate and the ether was removed under reduced pressure, leaving behind 456 mg (90%) of a yellow oil whose structure was assigned as 1-deuterio-2-methyl-3-phenylindaol. A 456-mg sample of the above 1-deuterio-2-methyl-3-phenylindanol was taken up in 25 mL of glacial acetic acid which contained 1 mL of water and 1 mL of concentrated sulfuric acid. The solution was allowed to stir for 30 min at room temperature and was then extracted with 100 mL of ether. The ethereal layer was washed with water, a saturated sodium bicarbonate solution, and a saturated sodium chloride solution and then dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a preparative thick-layer plate, using a 95% acetone–hexane mixture as the eluent. The major fraction isolated from the plate contained 357 mg (85%) of 1-phenyl-2-methyl-3-

(55) Corson, B.; Dorsky, J.; Nickels, J.; Kutz, W.; Thayer, H. *J. Org. Chem.* **1954**, *19*, 17.

deuterioindene (31) as a white crystalline solid: mp 48.5–49.5 °C; NMR ($CDCl_3$, 100 MHz) δ 1.86 (s, 3 H), 4.2 (s, 1 H), 6.84–7.28 (m, 9 H); mass spectrum, *m/e* 207 (M^+, base), 206, 205, 192, 191, 190, 129.

Preparation of 1-Phenyl-2-deuterio-3-methylindene (34). To a solution containing 10 mg of sodium in 10 mL of deuteriomethanol was added 400 mg of 3-phenylindanone. The solution was allowed to stir under a nitrogen atmosphere for 8 h and was then quenched by the addition of deuterium oxide. The mixture was extracted with 100 mL of ether and the ethereal layer was washed with a saturated sodium chloride solution and was then dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, leaving behind an orange solid. This material was dissolved in 50 mL of anhydrous ether and was cooled to 0 °C under a nitrogen atmosphere. To this cooled solution was added 1 mL of a 3.0 M methylmagnesium bromide solution in ether. The mixture was allowed to stir at 0 °C for 2 h and was then quenched with deuterium oxide. The ethereal layer was washed with a saturated sodium chloride solution and then dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, leaving behind a yellow oil which was taken up in 20 mL of glacial acetic acid which contained 1 mL of water and 1 mL of concentrated sulfuric acid. After being stirred for 1 h, the mixture was extracted with ether and the ethereal layer was washed with water, a saturated sodium bicarbonate solution, and then a saturated sodium chloride solution followed by drying over anhydrous magnesium sulfate. The ether was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a preparative thick-layer plate, using a 5% acetone–hexane mixture as the eluent. The major fraction isolated contained 270 mg (68%) of 1-phenyl-2-deuterio-3-methylindene (34) as a white solid: mp 59.5–60.5 °C (lit.[55] mp 63–64 °C); NMR ($CDCl_3$, 60 MHz) δ 2.16 (d, 3 H, *J* = 2.0 Hz), 4.43 (q, 1 H, *J* = 2.0 Hz), 6.88–7.28 (m, 9 H); mass spectrum, *m/e* 207 (M^+, base), 206, 205, 192, 191, 190, 129.

Preparation of 1-Deuterio-1-phenyl-3-methylindene (35). To a solution containing 500 mg of 1-phenyl-3-methylindene in 100 mL of hexane at −78 °C under a nitrogen atmosphere was added 0.2 mL of tetramethylethylenediamine followed by 2.1 mL of a 1.4 M *n*-butyllithium solution in hexane. After being stirred at −78 °C for 3 h, the solution was quenched at −78 °C by the addition of methanol-*d*. The organic layer was washed with a saturated sodium chloride solution and was then dried over anhydrous magnesium sulfate. The hexane was removed under reduced pressure, leaving behind 460 mg of a yellow oil which was shown by NMR analysis to be a 1:1 mixture of 1-deuterio-1-phenyl-3-methylindene (35) and 1-detuerio-1-methyl-3-phenylindene. This mixture was chromatographed on a 1 × 65 cm 10% w/w silver nitrate–silica gel column, using a medium-pressure chromatographic setup with hexane as the eluent. The last portion of the major peak eluted from the column was shown to consist of a 1:9 mixture of 1-deuterio-1-methyl-3-phenylindene and 1-deuterio-1-phenyl-3-methylindene (35). Fractional recrystallization of this material afforded 60 mg of pure 1-deuterio-1-phenyl-3-methylindene (35) as a white solid: mp 60.5–61.0 °C; NMR ($CDCl_3$, 100 MHz) δ 2.33 (d, 3 H, *J* = 7 Hz), 6.33 (q, 1 H, *J* = 1.7 Hz), 6.90–7.43 (m, 9 H); mass spectrum, *m/e* 207 (M^+, base), 206, 205, 192, 191, 190.

Irradiation of 1-Methyl-1-phenylindene (16). A solution containing 200 mg of 16 in 200 mL of anhydrous benzene was irradiated for 2 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Vycxor filter sleeve. Removal of the solvent under reduced pressure left a pale yellow oil which is shown by NMR spectroscopy to contain a 1:2 mixture of 2-phenyl-3-methylindene (20) and 1-methyl-2-phenylindene (19). The structures of the indenes were unambiguously established by comparison with independently synthesized samples.

To a suspension containing 100 mg of lithium aluminum hydride in 200 mL of anhydrous ether was added 830 mg of 2-phenyl-3-methylindanone in 50 mL of anhydrous ether under a nitrogen atmosphere. The mixture was stirred for 30 min at 25 °C and was then heated for an additional 2.5 h. After the mixture cooled to room temperature, 0.5 mL of water was added followed by 0.5 mL of a 15% sodium hydroxide solution, followed again by 2.0 mL of water. The organic solution was dried over anhydrous magnesium sulfate and the ether was removed under reduced pressure, leaving behind 738.0 mg (88%) of 2-phenyl-3-methylindanol as a white crystalline solid: mp 72.5–73.5 °C; NMR ($CDCl_3$, 100 MHz) δ 1.28 (d, 3 H, *J* = 7 Hz), 2.04–2.16 (m, 1 H), 2.76 (dd, 1 H, *J* = 7, 11 Hz), 3.04–3.28 (m, 1 H), 5.12–5.31 (m, 1 H), 7.07–7.38 (m, 9 H). Addition of deuterium oxide to the NMR sample tube resulted in the disappearance of the signal at δ 2.04–2.16 and collapsed the multiplet at δ 5.12–5.31 to a doublet at δ 5.18 (1 H, *J* = 11.0 Hz). A sample containing 500 mg of 2-phenyl-3-methylindanol was taken up in 25 mL of glacial acetic acid which also contained 1 mL of water and 1 mL of concentrated sulfuric acid. The mixture was allowed to stir for 2 h at 25 °C and was then extracted with 100 mL of ether. The ethereal layer was washed with water, a saturated sodium bicarbonate solution, and a saturated sodium chloride solution and was then dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a medium-pressure chromatographic column (1 × 65 cm), using hexane as the eluent. The major fraction isolated contained 362 mg (80%) of 1-methyl-2-phenylindene (19) as a white crystalline solid: mp 58.0–59.0 °C; NMR ($CDCl_3$, 100 MHz) δ 1.32 (d, 3 H, *J* = 8 Hz), 3.88 (q, 1 H, *J* = 8 Hz), 7.00 (s, 1 H), 7.08–7.56 (m, 9 H); IR (neat) 3050, 3020, 2955, 2925, 2830, 1600, 1490, 1455, 875, 760, 740, 690 cm^{-1}; mass spectrum, *m/e* 206 (M^+, base), 205, 192, 191, 190.

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.08; H, 6.82.

To a solution containing 1.4 g of 2-phenyl-1-indanone[56] in 25 mL of anhydrous ether was added 5.8 mL of a 2.9 M solution of methylmagnesium bromide in ether. The solution was stirred at 25 °C for 6 h and was then hydrolyzed with a saturated ammonium chloride solution. The ether layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a yellow oil. This material was purified on a silica gel column, using hexane as the eluent, to give 980 mg of 2-phenyl-3-methylindene (20) as yellow crystals: mp 79–80 °C (lit.[57] mp 80 °C); NMR[58] ($CDCl_3$, 60 MHz) δ 2.3 (t, 3 H, *J* = 2.0 Hz), 3.7 (q, 2 H, *J* = 2.0 Hz), 7.5 (m, 4 H).

Irradiation of 1-Phenyl-2-methylindene (18) in Benzene. A solution containing 150 mg of 1-phenyl-2-methylindene (18) in 250 mL of anhydrous benzene was irradiated for 2 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Vycor filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a preparative thick-layer plate, eluting with a 5% acetone–hexane mixture. The major component isolated from the plate contained 139.2 mg (88%) of a colorless oil which was shown by NMR spectroscopy to be a 1:2 mixture of 2-phenyl-3-methylindene (20) and 1-methyl-2-phenylindene (19). The structures of the indenes were unambiguously established by comparison with independently synthesized samples.

A solution containing 50 mg of 1-phenyl-2-methyl-3-deuterioindene (31) in 250 mL of anhydrous benzene was irradiated for 15 min, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Vycor filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a preparative thick-layer plate, using a 5% acetone–hexane mixture as the eluent. The major component isolated from the plate contained 35.5 mg (71%) of a colorless oil which was shown to consist of a three-component mixture of 1-deuterio-2-phenyl-3-methylindene (33, 26%), 1-methyl-2-phenyl-3-deuterioindene (32, 40%), and 1-phenyl-2-methyl-3-deuterioindene (31, 34%) by NMR analysis: 1-deuterio-2-phenyl-3-methylindene (33), δ 2.28 (br s, 3 H), 3.69 (m, 1 H); 1-methyl-2-phenyl-3-deuterioindene (32), δ 1.32 (d, 3 H, *J* = 8 Hz), 3.88 (q, 1 H, *J* = 8 Hz); 1-phenyl-2-methyl-3-deuterioindene (31), δ 1.84 (s, 3 H), 4.22 (s, 1 H).

Irradiation of 1-Phenyl-3-methylindene (17) in Benzene. A solution containing 100 mg of 1-phenyl-3-methylindene (17) in 250 mL of anhydrous benzene was irradiated for 2 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with

(56) Koelsch, C. F.; Johnson, P. R. *J. Org. Chem.* **1941**, *6*, 534.
(57) Christol, H.; Martin, C.; Mousseron, M. *Bull. Soc. Chim. Fr.* **1960**, 1696.
(58) Heindel, N. D.; Lemke, S. M.; Mosher, W. A. *J. Org. Chem.* **1966**, *31*, 2680.

a Vycor filter sleeve. At the end of this time the solvent was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a preparative thick-layer plate, using a 5% acetone–hexane mixture as the eluent. The major fraction isolated from the plate contained 72 mg (72%) of a colorless oil which was shown by NMR spectroscopy to be a 1:2 mixture of 2-phenyl-3-methyl-indene [**20**; NMR ($CDCl_3$, 100 MHz) δ 2.29 (br s, 3 He, 3.75 (br s, 2 H), 7.20–7.60 (m, 9 H)] and 1-methyl-2-phenylindene [**19**; NMR ($CDCl_3$, 100 MHz) δ 1.32 (d, 3 H, J = 8 Hz), 3.88 (q, 1 H, J = 8 Hz), 7.00 (s, 1 H), 7.08–7.56 (m, 9 H)]. The structures of these compounds were verified by comparison with independently synthesized samples.

A sample containing 50 mg of 1-phenyl-3-methylindene (**17**) and 10 mg of thioxanthen-9-one in 250 mL of anhydrous benzene was irradiated for 2 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a uranium filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a preparative thick-layer plate, using a 5% acetone–hexane mixture as the eluent. The major component isolated from the plate contained 33.4 mg (67% of a colorless oil which was shown by NMR spectroscopy to consist of 1-phenyl-3-methylindene (**17**, 54%), 1-methyl-2-phenylindene (**19**, 28%), and 2-phenyl-3-methylindene (**20**, 18%). The structures of the indenes were verified by comparison with authentic samples.

A solution containing 50 mg of 1-phenyl-2-deuterio-3-methylindene (**34**) in 250 mL of anhydrous benzene was irradiated for 1 h, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Vycor filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a preparative thick-layer plate, using a 5% acetone–hexane mixture as the eluent. The major component isolated from the plate contained 30 mg (60%) of a colorless oil which was shown by NMR spectroscopy to consist of 1-deuterio-2-phenyl-3-methylindene (**33**, 24%), 1-methyl-2-phenyl-3-deuterioindene (**32**, 9%), 1-deuterio-1-methyl-2-phenylindene (49%), and 1-phenyl-2-deuterio-3-methylindene (18%). The yield of products was ascertained from integration of the methyl resonances in the NMR spectrum: 1-deuterio-2-phenyl-3-methylindene, δ 2.30 (d, 3 H, J = 1.5 Hz); 1-methyl-2-phenyl-3-deuterioindene, δ 1.33 (d, 3 H, J = 8 Hz); 1-deuterio-1-methyl-2-phenylindene, δ 1.33 (br s, 3 H); 1-phenyl-2-deuterio-3-methylindene, δ 2.16 (d, 3 H, J = 2.0 Hz).

Irradiation of 1-Deuterio-1-phenyl-3-methylindene (35) in Benzene. A solution containing 50 mg of 1-deuterio-1-phenyl-3-methylindene (**35**) in 250 mL of anhydrous benzene was irradiated for 15 min, using a 450-W Hanovia medium-pressure arc lamp equipped with a Vycor filter sleeve. The solvent was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a preparative thick-layer plate, using a 5% acetone–hexane mixture as the eluent. The major component isolated from the plate contained 38.5 mg (77%) of a colorless oil which was shown by NMR analysis to contain a mixture of 1-deuterio-1-methyl-2-phenylindene (4%), 1-methyl-2-phenyl-3-deuterioindene (42%), 1-deuterio-1-phenyl-3-methylindene (28%), and 1-deuterio-2-phenyl-3-methylindene (26%). The ratios were determined by integration of the characteristic methyl signals in the NMR spectrum.

Rearrangement of 2-Methyl-2-phenylisoindene (27). A mixture containing 2.0 g of 2-phenyl-1,3-indandione,[59] 0.62 g of sodium metal, 10 mL of methanol, and 1.7 mL of iodomethane was heated in a sealed tube at 140 °C for 6 h. The solid that formed was filtered and washed with 200 mL of water and 300 mL of ether. The ether layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The resulting solid contained 1.4 g of 2-methyl-2-phenyl-1,3-indandione: mp 154–155 °C (lit.[60] mp 154–155 °C); NMR ($CDCl_3$, 90 MHz) δ 1.69 (s, 3 H), 7.22–7.38 (m, 5 H), 7.80–8.15 (m, 4 H).

To a stirred suspension containing 129 mg of lithium aluminum hydride in 200 mL of ether was added 1.0 g of the above indandione in 50 mL of ether. The solution was allowed to stir for 30 min and was then heated at reflux for 4 h. To the cooled solution was added 2 mL of water, 2 mL of a 10% sodium hydroxide solution, and 10 mL of water. The ether layer was dried over magnesium sulfate and concentrated under reduced pressure to give 1.01 g of 2-methyl-2-phenyl-1,3-indandiol as a thick colorless oil; IR (neat) 3400 cm^{-1}.

A solution containing 1.75 g of the above indandiol in 25 mL of chloroform was added to a solution containing 2 mL of phosphorus tribromide in 100 mL of chloroform. The mixture was heated for 2 h and was then cooled to room temperature. The solution was diluted with water and dried over magnesium sulfate. Removal of the organic solvent left a yellow oil which slowly solidified to give 800 mg of *trans*-2-methyl-2-phenyl-1,3-dibromoindene (**28**) as a white solid: mp 215–216 °C; NMR ($CDCl_3$, 90 MHz) δ 1.53 (s, 3 H), 5.50 (s, 1 H), 6.00 (s, 1 H), 7.2–7.6 (m, 9 H); IR (KBr) 2990, 1600, 1580, 1490, 1460, 1440, 1380, 1370, 1290, 1230, 1220, 1180, 1160, 1080, 1015, 920, 895, 860, 765, 750, 680 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.85. Found: C, 52.45; H, 3.86.

To a mixture containing 1.0 g of zinc–copper couple[61] in 10 mL of *N,N*-dimethylformamide (DMF) was slowly added 214 mg of the above dibromide in 10 mL of DMF. The deep green solution that formed was allowed to stir for 6 h at 25 °C and was then diluted with 100 mL of ether. The mixture was filtered through a small plug of Celite and was then washed with a 10% hydrochloric acid solution followed by water. The solution was dried over magnesium sulfate and the solvent was removed under reduced pressure to give a pale oil whose NMR spectrum was identical with that of an authentic sample of 1-phenyl-2-methylindene (**18**); NMR ($CDCl_3$, 90 MHz) δ 1.90 (d, 3 H, J = 1.5 Hz), 4.30 (br s, 1 H), 6.50 (q, 1 H, J = 1.5 Hz), 6.90–7.30 (m, 9 H).

Direction Irradiation of 1,3-Diphenylindenol (36). To a solution containing 200 mg of 3-phenylindenone[62] in 50 mL of ether at 0 °C was slowly added 0.7 mL of a 1.6 M solution of phenylmagnesium bromide in ether. The mixture was allowed to stir for 6 h and then was quenched by the addition of 10 mL of a saturated ammonium chloride solution. The ether layer was washed with water and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, leaving behind a yellow oil which was chromatographed on a medium-pressure silica gel column, using a 10% acetone–hexane mixture as the eluent. The major fraction contained 200 mg (73% yield) of 1,3-diphenylindenol (**36**) as a clear oil: IR (neat) 3440, 1590, 1500, 750, 700 cm^{-1}; UV (95% ethanol) 280 nm (ϵ 1500), 235 (9000); NMR ($CDCl_3$, 90 MHz) δ 2.53 (s, 1 H), 6.30 (s, 1 H), 7.03–7.56 (m, 14 H); mass spectrum, m/e 284 (M^+), 207, 206, 205, 178, 100, 77.

Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.58; H, 5.61.

A solution containing 193 mg of idenol **36** in 250 mL of benzene was irradiated for 30 min, using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. The solvent was removed under reduced pressure and the resulting yellow residue was chromatographed on a medium-pressure silica gel column, using hexane as the eluent. The first fraction contained 236 mg of 1,3-diphenylindene (**38**) which was identified by comparison with an authentic sample;[32] NMR ($CDCl_3$, 90 MHz) δ 4.53 (d, 1 H, J = 2.5 Hz), 6.46 (d, 1 H, J = 2.5 Hz), 6.90–7.60 (m, 14 H). The second fraction isolated from the column contained 2,3-diphenylindene (**39**). The structure of this compound was verified by comparison with authentic sample;[19] NMR ($CDCl_3$, 90 MHz) δ 3.8 (s, 2 H), 7.0–7.40 (m, 14 H).

The third component isolated from the column was a crystalline solid, mp 158–159 °C, whose structure was assigned as phenanthrene **40** on the basis of the following data: IR (KBr) 1460, 1435, 1240, 1180, 1040, 940, 785, 775, 720, 640 cm^{-1}; UV (95% ethanol) 339 nm (ϵ 14 600), 318 (16 100), 310 (11 200), 309 (11 200), 300 (9650), 280 (16 600), 263 (31 400), 242 (35 900); NMR (CCl_4, 90 MHz) δ 4.15 (s, 2 H), 7.2–9.2 (m, 12 H); mass spectrum, m/e 266 (M^+), 223, 221, 205.

Anal. Calcd for $C_{21}H_{14}$: C, 94.70; H, 5.30. Found: C, 94.62; H, 5.34. This same material was formed from the irradiation of

(59) Zalukajevs, L. *Latv. PSR Zinat.* **1954**, *3*, 101.
(60) E. Geistlich Belg. Patent 628,255, 1963; *Chem. Abstr.* **1963**, *60*, 14516*f*.
(61) LeGoff, E. *J. Org. Chem.* **1964**, *29*, 2048.
(62) Rockett, B. W.; Hauser, C. R. *J. Org. Chem.* **1963**, *29*, 1394.

either 1,3- (38) or 2,3-diphenylindene (39) in the presence of oxygen in good yield.

Direct Irradiation of 1,3-Diphenyl-2-methylindenol (41). To a solution containing 407 mg of 3-phenyl-2-methylindenone[48] in 100 mL of ether at 0 °C was added 1.2 mL of 1.6 M phenylmagnesium bromide in ether. The mixture was allowed to stir for 6 h and then was quenched by the addition of a saturated ammonium chloride solution. The ether layer was washed with water and dried over anhydrous magnesium sulfate. Removal of the ether left behind 550 mg of a white foam whose spectral properties were consistent with 1,3-diphenyl-2-methylindenol (41); IR (neat) 3450, 3070, 3030, 1600, 1495, 1450, 1340, 1190, 1105, 1055, 1030, 950, 915, 785, 765 cm^{-1}; UV (95% ethanol) 280 nm (ϵ 4700), 227 (30600); NMR ($CDCl_3$, 90 MHz) δ 1.70 (s, 3 H), 2.28 (br s, 1 H), 7.0–7.53 (m, 14 H); mass spectrum, *m/e* 298 (M^+), 283, 221, 220, 189, 165, 115, 105.

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.54; H, 6.11.

A solution containing 300 mg of indenol 41 in 250 mL of benzene was irradiated for 30 min, using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Vycor filter sleeve. The solvent was removed under reduced pressure and the residual oil was subjected to medium-pressure chromatography, using a silica gel column and eluting with hexane. The first fraction contained 103 mg of 1,3-diphenyl-2-methylindene (43); NMR ($CDCl_3$, 90 MHz) δ 1.86 (s, 3 H), 4.39 (br s, 1 H), 6.88–7.47 (m, 14 H). The structure of this material was verified by comparison with an authentic sample.[63] The second fraction isolated from the column contained 60 mg of a white solid, mp 105–106 °C, whose structure was assigned as 1-methyl-2,3-diphenylindene (44) by comparison with an authentic sample;[63] NMR ($CDCl_3$, 90 MHz) δ 1.08 (d, 3 H, J = 7.0 Hz), 4.02 (q, 1 H, J = 7.0 Hz), 7.05–7.38 (m, 14 H). The third fraction isolated from the column (30 mg) was a white crystalline solid, mp 90–91 °C, whose structure was assigned as 1,2-diphenyl-3-methylindene (45); NMR ($CDCl_3$, 90 MHz) δ 2.32 (d, 3 H, J = 2.0 Hz), 4.91 (q, 1 H, J = 2.0 Hz), 6.90–7.40 (m, 14 H). The structure of this material was established by comparison with an authentic sample preared according to the procedure of Koelsch and Johnson.[50]

The last material isolated from the column contained 94 mg of a white solid, mp 138–139 °C, whose structure was assigned as phenanthrene 46 on the basis of its spectral properties: IR (KBr) 1535, 1500, 1480, 1440, 1340, 1280, 1120, 940, 780, 730 cm^{-1}; UV (95% ethanol) 336 nm (ϵ 7800), 320 (7800), 313 (5300), 308 (5600), 278 (8500), 270 (12800), 263 (14000), 250 (14000), 243 (18800); NMR ($CDCl_3$, 90 MHz) δ 1.60 (d, 3 H, J = 6.5 Hz), 4.23 (q, 1 H, J = 6.5 Hz), 7.13–8.90 (m, 12 H).

Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.18; H, 5.56.

This same material was also formed from the irradiation of either 1,3-diphenyl-2-methyl- (43) or 1-methyl-2,3-diphenylindene (44) in the presence of oxygen in good yield.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation.

Registry No. 4, 74272-43-8; 5, 42842-58-0; 6, 58310-20-6; 7, 36230-99-6; 8, 62907-55-5; 9, 26465-84-9; 10, 76773-25-6; 11, 76773-26-7; 12, 65086-15-9; 13, 65086-14-8; 14, 76773-27-8; 15, 76773-28-9; 16, 31366-37-7; 17, 22360-63-0; 18, 37634-53-0; 19, 3661-63-0; 20, 10425-96-4; 27, 76773-44-9; 28, 76773-29-0; 31, 76773-30-3; 32, 76773-31-4; 33, 76773-32-5; 34, 76773-33-6; 35, 76773-34-7; 36, 76773-35-8; 38, 4467-88-3; 39, 5324-00-5; 40, 201-65-0; 41, 76773-36-9; 43, 51310-26-0; 44, 51310-25-9; 45, 62747-73-7; 46, 76773-37-0; 2-methyl-3-phenylindanone, 52957-74-1; thioxanthen-9-one, 492-22-8; xanthone, 90-47-1; 3-methyl-3-phenylindanone, 26466-19-3; 7,7a-dihydro-7a-methyl-7-phenyl-2a-(phenylmethyl)spiro[indeno[2,1-*b*]oxete-2(2a*H*),9′-[9*H*]thioxanthene], 76773-38-1; 3-phenylindanone, 16618-72-7; 2-benzyl-3-phenylindanone, 76773-39-2; 3-methyl-3-phenyl-1-indanol, 76773-40-5; 3-phenyl-2-methylindanol, 65426-37-1; 1-deuterio-2-methyl-3-phenylindanol, 76773-41-6; 1-deuterio-1-methyl-3-phenylindene, 76773-42-7; 2-phenyl-3-methylindanol, 65451-65-2; 2-phenyl-1-indanone, 16619-12-8; 1-deuterio-1-methyl-2-phenylindene, 76773-43-8; 2-phenyl-1,3-indandione, 83-12-5; 2-methyl-2-phenyl-1,3-indandione, 2136-69-8; 2-methyl-2-phenyl-1,3-indandiol, 36613-96-4; 3-phenylindenone, 41916-15-8; 3-phenyl-2-methylindenone, 13304-52-4; methyl bromide, 74-83-9; phenyl bromide, 108-86-1; benzyl chloride, 100-44-7; benzyl bromide, 100-39-0.

(63) Padwa, A.; Chou, C. S.; Rieker, W. F. *J. Org. Chem.* **1980**, *45*, 4555.

tert-Butyl Group as Thiol Protection in Peptide Synthesis[1]

Juliusz Jacek Pastuszak and Andrzej Chimiak*

Department of Organic Chemistry, Technical University of Gdańsk, 80-952 Gdańsk, Poland

Received July 30, 1980

S-tert-Butylcysteine was obtained by a new method. A number of its N-protected derivatives and esters were synthesized. Syntheses of several peptides containing *tert*-butyl and acetamidomethyl or benzyl thioethers of cysteine were carried out. The *tert*-butyl group was removed from the thiol group of peptides by treatment with (2-nitrophenyl)sulfenyl chloride (NpsCl). The *S*-(2-nitrophenyl)sulfenyl derivatives so obtained were converted either into cysteine by reduction or into cystine derivatives by disproportionation. Owing to the mild deprotection conditions and the great stability of the *S-tert*-butyl group, the other protecting groups, particularly those of the thiols, could be easily removed from a variety of combinations.

Though about 70 protecting groups for the thiol group have hitherto been described,[2] the problem of cysteine protection has still remained unsolved. It is essential, particularly under conditions of peptide synthesis, to find a suitable protecting group which is very stable but easy to remove in the last step, which is only feasible by using specific reagents. The *S*-benzyl group, formerly a common protection in complex peptide syntheses, is practically no longer used[3] and has been replaced by the *S*-acetamidomethyl group.[4]

As far back as 1962, one of us was the first to suggest using *tert*-butyl thioether as a protecting group for cysteine.[5] A method was then reported for a direct synthesis

(1) Taken from the Ph.D. Thesis of J.J.P.; presented at the 15th European Peptide Symposium, Gdańsk, Poland, Sept 1978.

(2) See, for example, "Methoden der Organischen Chemie (Houben-Weyl)", Georg Thieme Verlag, Stuttgart, 1974, Vol. 15/1.

(3) L. Zervas, "Proceedings of 8th European Peptide Symposium, Noordwijk, 1966", North-Holland Publishing Co., Amsterdam, 1967, p 112.

(4) D. F. Veber, J. D. Milkowski, S. L. Varga, R. G. Denkewalter, and R. Hirschmann, *J. Am. Chem. Soc.*, **94**, 5456 (1972).

0022-3263/81/1946-1868$01.25/0