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Photochemical Transformations. XIII. Photorearrangements of 3-Phenylcycloheptene and Some Phenylnorcaranes[1,2]

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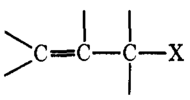
Abstract: While irradiation of 3-phenylcycloheptene (**12**) in cyclohexane or acetonitrile did not lead to isomeric products, that in benzene led to a mixture of 2-phenylmethylenecyclohexane (**15**) and *cis*- and *trans*-2-phenylnorcarane (**16** and **17**) rather than to the anticipated di-π-methane product, *endo*- (or *exo*-)-7-phenylnorcarane. *endo*-7-Phenylnorcarane (**13**) isomerized to the exo isomer (**14**) when irradiated in ketonic solutions (or by base-catalyzed isomerization) and to benzylidenecyclohexane (**18**) and 1-benzylcyclohexene (**19**) upon irradiation in benzene or acetonitrile. 1-Phenylnorcarane (**23**) gave 3-phenylcycloheptene (**12**) and 1-phenylcycloheptene upon irradiation in benzene. Irradiation of *o*-(3-cycloheptenyl)phenol (**32**) gave cyclization products from addition of the hydroxyl group to the double bond. Plausible reaction paths for the photoreactions of **12** are discussed; it is concluded that the epimeric 2-phenylcarbenes (**28**) are the most plausible intermediates.

Photochemical 1,2-migrations of allylic substituents, accompanied by a ring-closure process, provide general synthetic methods for cyclopropanes. A good deal of attention in this laboratory has been focused on the photosensitized rearrangement-cyclization of allylic halides (**1**) to halocyclopropanes (**2**), which is a quite general reaction,[3] with only a few failures. These reactions, which involve sensitization with triplet sensitizers, have stereochemical consequences, which are observable in appropriate cases. Thus 3-chlorocycloheptene (**3**) gives[3d,f] exclusively *endo*-7-chloronorcarane (**4**), and the 1,3-dichloropropenes[3b] and crotyl chlorides[3e] give principally the products of anti disrotatory ring closure (cis olefin to cis-disubstituted cyclopropane and trans to trans). These results suggested the possibility that the rearrangement-cyclization was concerted, or at least that one step in the process involved carbon–halogen bond formation concerted with cyclization.



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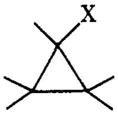

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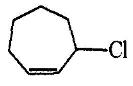

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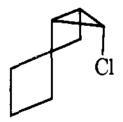

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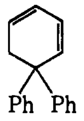
At the time our work on the stereochemistry of **1** to **2** rearrangements was going on, initial studies of the stereochemistry of the di-π-methane rearrangement[4] were appearing, and a number have appeared in the intervening period. Thus it was reported[5] that the triplet of 5,5-diphenyl-1,3-cyclohexadiene (**5**) gave principally the endo rearrangement product **6**, with little[5c] or no[5a,b] exo epimer **7**, even though diradical intermediates are believed[4] to intervene. On the other hand, the triplet rearrangement of 3,3-diphenylcyclohexene (**8**) was reported[6] to give equal amounts of endo (**9**) and exo (**10**) products, although interpretations of this experiment are clouded by the reported photoreactivity of **9** and **10**. More recently,[7] it has been reported that direct irradiation of **11**, which by its nature is precluded from ready anti disrotatory ring closure, instead undergoes ready syn disrotatory reaction. This was a singlet process—the triplet failed to produce detectable amounts of product.



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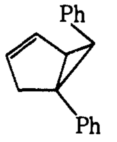

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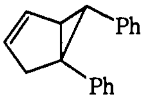

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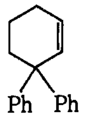

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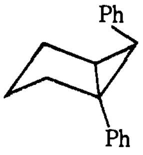

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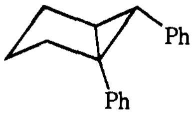

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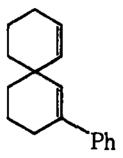

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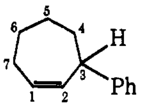

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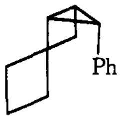

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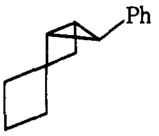

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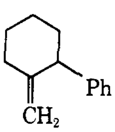
With the idea that we might find a closer analogy to our own work on allylic halides than with those di-π-methane rearrangements described by Swenton, by Zimmerman, and by Dauben, all of which were disubstituted at the allylic position, we decided to look at the photoreaction of 3-phenylcycloalkenes. We chose to study 3-phenylcycloheptene (**12**) as the obvious analog of 3-chlorocycloheptene.[3d] However, irradiation did not lead to di-π-methane rearrangement. The present paper describes and discusses the reactions which did occur and our related studies.

The products anticipated[4] from a di-π-methane rearrangement of 3-phenylcycloheptene (**12**) are *endo*- (**13**) and *exo*-7-phenylnorcarane (**14**), from anti disrotatory and syn disrotatory migration-closure, respectively. These compounds were prepared for comparison purposes by the method of Elphimoff-Felkin.[8]

When a solution of **12** in heptane or in acetonitrile was irradiated, no isomeric material was formed, although **12** was consumed slowly. On the other hand, when a benzene solution was irradiated (Vycor filter–Hanovia 450-W lamp), **12** underwent a slow reaction leading in large part to dimeric or polymeric material, but also to about 20% of a mixture of three isomeric materials in 2:1:1 ratio. As these isomers were not produced in acetonitrile or in heptane, the isomerizations are probably benzene-sensitized triplet reactions. Such a conclusion is tentative, however, pending further study, as the efficiencies of the rearrangements (moles of product per einstein of light absorbed by the solution) may be less than the fraction of light absorbed by **12** rather than by benzene.

The three volatile products were separated by gas chromatography. Although they were isomers of **12**, none of them was either of the two di-π-methane-related isomers **13** and **14**. The major product was shown to be 2-phenylmethylenecyclohexane (**15**) by ^{1}H NMR analysis and by synthesis (Wittig reaction with 2-phenylcyclohexanone).



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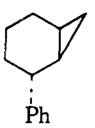

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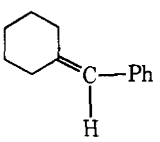

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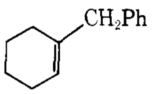

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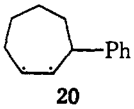
The two minor components of the photomixture were identified as the cis (**16**) and trans (**17**) isomers of 2-phenylnorcarane, although we have not proven which is which. They were synthesized (89:11 mixture) by a Simmons–Smith reaction[9] on 3-phenylcyclohexene. As the Simmons–Smith reaction is hindered by steric factors,[9d] the major product of this reaction may be tentatively assigned the structure **17**.

The three photoproducts (**15**, **16**, and **17**) were irradiated in benzene under conditions where 95% of **12** would have disappeared (2–3 days). They appeared to be almost photoinert.

Although neither **13** nor **14** was detected in the photoisomerization reaction, it seemed possible that they might be photolabile intermediates in the reactions of **12**. When the endo isomer **13** was irradiated in acetone (or with other aliphatic ketones) through Pyrex, rapid isomerization to the exo isomer **14** occurred. (The exo isomer may also be produced by equilibration with potassium *tert*-butoxide in Me$_2$SO.) Extended irradiation of **14** in acetone caused no further reaction. However, solutions of **13** and **14** in benzene, or in acetonitrile, gave further reaction to two principal products in approximately equal amounts (25% each). One of these was shown to be benzylidenecyclohexane (**18**) (Wittig synthesis from cyclohexanone) and the other had a ^{1}H NMR spectrum consistent with that anticipated for 1-benzylcyclohexene (**19**). As these products did not react further to give **15**, **16** or **17**, it is clear that **13** and **14** were not formed in the photoreaction of **12**.

The failure of **12** to undergo a di-π-methane rearrangement under either direct or sensitized conditions deserves comment. If the Zimmerman mechanism[4] holds, the reaction with **12** depends upon the necessity of the first-formed diradical (possibly[4] **20**) to rearrange to **21**, a 1,3 diradical without either allylic or benzylic stabilization. Generally the yields and efficiencies are greater when benzylic-allylic 1,3 diradicals are formed than they are when benzylic-secondary ones are produced.[6] Few less stabilized 1,2-phenyl migrations have been reported.[4,10]



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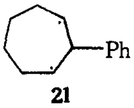

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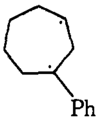

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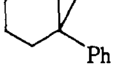

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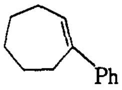

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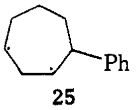
Although failure to observe the di-π-methane rearrangement precluded a study of its stereochemistry, we did uncover these new unanticipated rearrangements and were curious about their reaction paths.

1,2-Hydrogen shifts in allylic systems, accompanied by ring closure, to give cyclopropanes, are known[11] and one has recently been observed in a di-π-methane system.[12] If the hydrogen on C-3 (geminal to phenyl) in **12** migrated, the triplet of **12,** that is, the 1,2 diradical **20,** would rearrange to the 1,3 diradical **22,** which would then produce 1-phenylnorcarane (**23**). To test this possibility, we irradiated a solution of **23** in benzene. A mixture of **12** and 1-phenylcycloheptene (**24**) resulted. As reported,[13] **24** gives polymeric material rapidly on continued irradiation. The formation of **12** and **24** (besides solvent addition products) from direct irradiation of **23** in protic solvents has also been previously reported.[14] Thus **23** cannot be a precursor of **15, 16,** and **17.**

There are also hydrogens on C-7 in **12** which are capable of undergoing 1,2 migration. This would lead to the diradical **25,** which on closure would give the 2-phenylnorcaranes **16** and **17.** This mechanism can account for two of the three actual products. However, it seems likely that if this mechanism operates, the hydrogen on C-3 also would migrate to produce **23,** since the latter migration leads to the more stable intermediate. Furthermore, this mechanism cannot account for the formation of 2-phenylmethylenecyclohexane, as both **16** and **17** have been shown to be stable to the conditions of the photochemical rearrangement.



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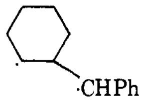

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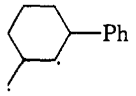

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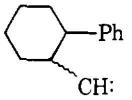

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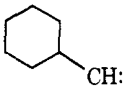
We also considered the possibility that the allylic carbon-carbon bonds would move. 1,2-Alkyl migration of C-4 from C-3 to C-2, with accompanying cyclopropane formation, would yield the isomers of 7-phenylnorcarane **13** and **14** via the diradical **26.** As this diradical is undoubtedly[15] the intermediate in the isomerization of **13** to **14** and of **14** to **18** and **19,** this cannot be a path in the **12** reactions.

Migration of C-6 from C-7 to C-1 would give the cis and trans radicals **27** which on closure would give **16** and **17.** Again, however, the mechanism which accounts for products is expected to be a higher energy pathway than the 1,2-alkyl migration not observed, i.e., that to **26.**

Thus, two of the 1,3 diradicals produced by a 1,2 shift from **20** (i.e., **25** and **27**) can account for the formation of **16** and **17.** However, their formation seemed less likely than those of the more stable diradicals for which no evidence can be found, and neither of these radicals can lead to the major product **15,** without further group migration.

It is clear that the rearrangement of **12** to **15** requires a 1,2-alkyl migration. 1,2-Migration of one of the alkyl groups attached to the double bond accounts for all of the products. Thus migration of C-3 from C-2 to C-1 (or of C-7 from C-1 to C-2) in excited **12** would lead to the cis and trans isomers of the carbene **28.** Alkyl- and dialkylcarbenes are known to undergo very rapid 1,2-hydrogen migrations to give olefins,[16] and thus either isomer might be expected to give **15.** As insertion into γ-carbon-hydrogen bonds is also generally observed,[16] cyclopropanes would also be expected. Thus, *cis*-**28** should give **16** and *trans*-**28** should give **17** and **23.** As **23** is more photoreactive than **12,** and leads to **12** and **24,** which is also very photolabile, its absence may be rationalized. A referee has suggested that it might be detectable at low conversions. This has not been attempted.

2-Phenylcyclohexylcarbene (**28**) has apparently not been reported, so a comparison of products cannot be made. The parent cyclohexylcarbene (**29**) has been generated from cyclohexylmethyl chloride and sodium in cyclohexane and is reported[17] to rearrange to a 12:1 mixture of methylenecyclohexane (**30**) and norcarane (**31**). A similar mixture results when **29** is prepared by thermolysis of the sodium salt of the *p*-toluenesulfonylhydrazone of cyclohexanecarboxaldehyde in refluxing diglyme.[18] Thus the reactions we have proposed have very close analogy in the literature.



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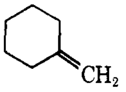

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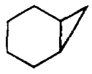
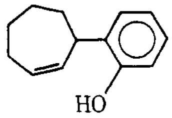


31

Although complex carbenes are generally too reactive via unimolecular rearrangements to allow for intermolecular trapping, we attempted the reaction of **12** in benzene-methanol, hoping to divert a portion of the **28** to the methyl ether. In fact, only **15, 16,** and **17** were produced.[19] We decided to study *o*-3-cycloheptenylphenol (**32**), which, if a similar path were followed, would give the carbene **33** isomers. Intramolecular trapping of the carbene site of **33** by the phenolic OH bond would give the ether **34.** In fact, irradiation of **32** in benzene led to loss of reactant with formation of two volatile products in a 7:3 ratio. These were isomeric with **32,** but each had only one proton α to the oxygen (**34** has two such protons). The products appear to be those of normal[13] addition of the phenol moiety to the double bond (**35** and/or **36**), but conclusive structure proof work remains to be done.



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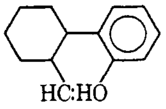

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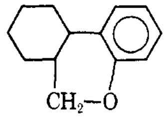

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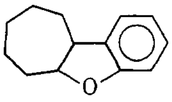

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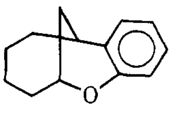

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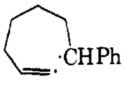

37

We have thus far discussed the overall reaction (i.e., that of the excited state of **12** to **15, 16** and **17**) as involving energy transfer from triplet benzene ($E_T \sim 84$ kcal/mol) to **12** to give **20** which then rearranges to isomers of **28,** although, as mentioned above, the multiplicity is not certain. Bond dissociation energy data suggest[20] that the rearrangement of **12** to **28** is endothermic by about 68 kcal/mol, which is less than the triplet energy transferred from benzene, so that the reaction is feasible even if some energy is lost thermally. The rearrangement might involve cleavage of the vinyl-carbon bond to give the diradical **37,** followed by reclosure either to **20** or to **28,** but we estimate[22] a bond dissociation energy of 81 kcal/mol from **12** for the formation of **37.** Although the calculated bond dissociation energy is less than the triplet energy of benzene, it is probably greater than that of **12.** The intermediacy of **37** therefore seems less likely than the concerted rearrangement of **20** to **28.**

It has been reported[23] that mercury-sensitized irradiation of 1-butene leads to methylcyclopropane, and others[24] have suggested that methylethylcarbene, the 1,2-hydrogen shift product from the 1-butene triplet, intervenes. One may note that the 1,2-ethyl shift product 1-butylidene, could also give methylcyclopropane. These workers[24] have also suggested that the excitation of solid phase ethylene by short-wavelength light (147 nm), which leads to methylcyclopropane, involves an analogous rearrangement from excited ethylene to ethylidene (methylcarbene). Ethylidene then is presumed to add to ethylene to give methylcyclopropane.

More recently[25] Yates showed that oxacarbenes intervened in photochemical ring expansion of ketones in alcohol solvents leading to cyclic acetals, and similar work was reported by others.[26] Such reactions have been studied in detail by Turro.[27] The oxacarbenes which are produced from certain excited cyclic ketones by a 1,2-alkyl shift have been captured with olefins and by alcohols. Those studied have structures not readily amenable to intramolecular reaction. The stereospecificity observed by Quinkert[26c] makes it clear that the rearrangement from excited ketone to oxacarbene is concerted and does not involve cleavage and recombination. Certain of these reactions are singlet and certain triplet.

Still more recently, Fields and Kropp[28] have reported that tetrasubstituted ethylenes yield mixtures of rearranged olefins and cyclopropanes upon direct irradiation through quartz. These products are believed to be derived from carbenes resulting from 1,2-alkyl shifts of the excited olefin, and indeed, carbenes produced by thermolysis of *p*-toluenesulfonylhydrazones give similar mixtures of products. The authors propose that the rearrangement to carbenes occurs from the Rydberg π, R(3s) excited state, and they do not observe rearrangements of this sort from less substituted olefins or by photosensitization of tetrasubstituted ethylenes with xylene. We would agree with Kropp's assessment[28b] of the present state of understanding of these rearrangements, namely that it is not at all clear what relationship, if any, our work has to theirs, and we would extend this question to the other work we have cited as well. We hope that further work will clarify the factors that cause such dissimilar phenomena in olefin photochemistry.[29]

Experimental Section

Spectroquality solvents were used (benzene and methanol from Fisher and acetonitrile from Matheson Coleman and Bell or Eastman) for the photochemical experiments. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Proton magnetic resonance (^{1}H NMR) spectra were recorded on a Varian A-60A spectrometer in carbon tetrachloride with tetramethylsilane internal reference. Mass spectra were obtained with a Varian MAT CH-7 spectrometer.

Irradiation of 3-Phenylcycloheptene (12).[30] 3-Phenylcycloheptene (109 mg, 0.64 mmol) was dexoygenated in 15 ml of acetonitrile and irradiated through a Vycor filter with a 450-W Hanovia lamp for 47 hr. Gas chromatography indicated that **12** was the only volatile material present. Analysis by ^{1}H NMR indicates that only 10% of the aromatic protons could be accounted for by the presence of **12**.

12 (0.97 g, 5.6 mmol) was irradiated in 125 ml of benzene, with attendant nitrogen bubbling, with a 450-W Hanovia lamp through a Corex filter for 44 hr. At this time the immersion well was coated with a yellow solid. Removal of benzene by distillation was followed by distillation in a Kügelrohrofen at 0.05 Torr and up to 120° (most of the material distilled at an oven temperature of 85°), which gave 240 mg of product. Gas chromatography on 20% Carbowax 20M at 150° showed the presence of three signals at 16, 22, and 26 min in relative amounts 42:37:21, respectively. Under these conditions the three compounds were collected. The 16-min compound was collected in 5% (45 mg) yield. The ^{1}H NMR spectrum and gas chromatography retention time were identical with those of 2-phenylmethylenecyclohexane (**15**, see below).

Collection of the 22-min fraction gave 44 mg of a product with an ^{1}H NMR spectrum that corresponded to a 50:50 mixture of **12** and the major synthetic isomer of 2-phenylnorcarane (2.5% yield). Coinjection of these two compounds gave only one signal on Carbowax 20M columns, as well as on all other columns tested.

The compound with the longest retention time was collected in 3% yield (27 mg). The ^{1}H NMR spectrum and GLC retention time of this compound were identical with those of the minor isomer of 2-phenylnorcarane.

Preparation of 2-Phenylmethylenecyclohexane (15). Butyllithium (60 ml, 48 mmol, 0.80 *M*) in hexane solution (Alfa Inorganics, Inc.) was added to 19.5 g (71 mmol) of methyltriphenylphosphonium bromide in 100 ml of ether. Foaming occurred during addition of all but the last 5 ml. After 15 min, 11.0 g (63 mmol) of 2-phenylcyclohexanone[31] was added to this deep red solution. The reaction mixture was stirred for 16 hr. The reaction mixture was washed twice with water and dried over anhydrous Na_2SO_4. After filtration of the reaction mixture and removal of the ether on a rotary evaporator, the product was chromatographed on alumina. A first fraction contained 7.5 g (62%) of 90% pure 2-phenylmethylenecyclohexane (**15**). A second fraction contained mostly **15**. The product was purified by additional chromatography: ^{1}H NMR (CCl_4) δ 7.18 (5 H), 4.70 (1 H), 4.14 (1 H), 3.2 (1 H), 1.2–2.5 (8 H).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.58; H, 9.32.

Preparation of 2-Phenylnorcarane Isomers 16 and 17. The 2-phenylnorcaranes were synthesized by a Simmons-Smith reaction.[9] Only the LeGoff zinc activation procedure[9b] and the use of 30-mesh granular zinc was found to give reproducible results for the addition of methylene to 3-phenylcyclohexene.[32] About 50% conversion was accomplished each time the reaction was run. After two repetitions,[9] gas chromatographic analysis showed 10% biphenyl, 10% 3-phenylcyclohexene, and 80% of an 8:1 mixture of the two isomers of 2-phenylnorcarane (**17** and **16**). The product was distilled to give a 50% yield. No fractionation of the two isomers and biphenyl and reactant occurred.

The major isomer (presumably **17**) had the shorter retention time on Carbowax 20M columns. Collection resulted in a product which gave the following ^{1}H NMR: δ 7.26 (5 H), 2.78 (1 H), 0.4–2.0 (9 H), 0.12 (q, 1 H, J = 4.5 Hz). The mass spectrum showed a base peak of *m/e* 104 and a parent ion of 65% of *m/e* 172.

The minor isomer (presumably **16**) was also collected by gas chromatography. An ^{1}H NMR was obtained: δ 7.26 (5 H), 3.1 (1 H), 0.5–2.4 (9 H), 0.30 (q, 1 H, J = 5 Hz). The mass spectrum was similar to that of the major isomer.

Attempted equilibration of the two isomers of 2-phenylnorcarane was not successful since decomposition occurred faster than isomerization in potassium *tert*-butoxide–dimethyl sulfoxide.

Irradiation of 2-Phenylmethylenecyclohexane (15). About 50 mg of **15** was irradiated in 20 ml of benzene through a Vycor filter with a 450-W Hanovia lamp for 2 days. Gas chromatography and ^{1}H NMR showed that only reactant was present after removal of the benzene on a rotary evaporator.

Irradiation of 2-Phenylnorcarane. The major isomer (98 mg) of 2-phenylnorcarane was irradiated in 16 ml of benzene through a Vycor filter for 3 days with a 450-W Hanovia lamp. The sample had previously been deoxygenated by bubbling nitrogen. No reaction had occurred as indicated by ^{1}H NMR.

The minor isomer (16 mg) of 2-phenylnorcarane was irradiated in 10 ml of benzene for 2 days, after deoxygenation. The ^{1}H NMR spectra of reactant and product were identical.

Irradiation of *endo*-7-Phenylnorcarane (13) and *exo*-7-Phenylnorcarane (14). **13**[7] (80 mg, 0.46 mmol) was dissolved in 15 ml of acetone, deoxygenated, and irradiated through Pyrex for 41 hr. The ^{1}H NMR of the crude material was identical with that of *exo*-7-phenylnorcarane (**14**). Gas chromatography showed the presence of no other products. Subsequent experiments indicated that only about 2 hr was required for the conversion to >99.8% exo isomer (**14**).

The irradiation of 0.172 g of **14**[7] in 35 ml of acetone for 11 hr resulted in recovery of pure reactant.

Sensitization of **13** with acetophenone, benzophenone, and xanthone resulted in no isomerization. Aliphatic ketones (cyclohexanone, 2-butanone, and 3-pentanone) did lead to isomerization. A solution of 110 mg (0.63 mmol) of **13** in 2 ml of benzene and 13 ml of acetonitrile was deoxygenated and irradiated through a Vycor filter for 12 hr. Three products were indicated by gas chromatography with retention volumes of 0.64, 0.89, and 1.1 relative to reactant. Products were in the approximate ratio of 2:9:12, respectively. The two major products were collected by gas chromatography.

The major product (28 mg) was collected (25% yield). The ^{1}H NMR was identical with that of benzylidenecyclohexane synthesized by an alternate route.[33]

The other product (26 mg) was collected (24% yield): ^{1}H NMR (CCl_4) δ 7.0 (5.3 H), 5.4 (1 H), 0.9–3.4 (9.7 H). These data are consistent with the suggested structure **19**.

endo-7-Phenylnorcarane (**13**, 107 mg, 0.62 mmol) was deoxygenated in 12 ml of acetonitrile and irradiated for 7 hr with a 450-W Hanovia lamp through a Vycor filter. The three signals observed in the benzene-sensitized experiments were produced in a 3:5:9 ratio.

Irradiation of 1-Phenylnorcarane (23). **23**[8a,34] (806 mg) in 200 ml of benzene was irradiated with an Ultraviolet Products low-pressure lamp (254 nm). After 3 hr, gas chromatography showed three major signals corresponding to reactant (65%), **12** (13%), and **24** (22%). The vinyl hydrogens of each olefin were observed in the NMR spectrum of the crude material.

Irradiation of 1-Phenylcycloheptene (24). A solution of **24** (0.019 *M* in benzene) was completely reacted upon 42-hr irradiation through Vycor. Only trace amounts of volatile compounds were produced.

Irradiation of 3-Phenylcycloheptene (12) in Benzene–Methanol. **12** (875 mg, 5.0 mmol) was irradiated in 120 ml of benzene and 660 ml of reagent, absolute methanol. Deoxygenation was accomplished by bubbling nitrogen through the solution for 30 min before the 450-W Hanovia lamp was turned on. Nitrogen bubbling was continued during the irradiation. After irradiation, the reaction mixture was chromatographed through alumina. The first petroleum ether eluent contained a 5:3:2 mixture of **15**:**12** plus the major isomer of 2-phenylnorcarane–the minor isomer of 2-phenylnorcarane mixture. No other compound was observed in the gas chromatography spectrum except for a small amount of a compound with a retention time between those of **15** and **12**. The NMR spectrum showed no absorption at a frequency expected for protons α to oxygen.

***o*-(3-Cycloheptenyl)anisole.** A Grignard coupling reaction[30] was used to synthesize *o*-(3-cycloheptenyl)anisole. To 9.6 g (0.40 mol) of dry magnesium in a flask equipped with a dropping funnel, reflux condenser, and nitrogen inlet, a few crystals of iodine and some *o*-bromoanisole in dry THF were added to initiate reaction. More *o*-bromoanisole (a total of 76.5 g, 0.41 mol) in THF was added over 2 hr. Not all of the magnesium dissolved even upon reflux. Cuprous bromide (2.7 g, 0.01 mol) was added and after 5 min, 35.0 g (0.20 mol) of 3-bromocycloheptene[35] was added. The reaction mixture was cooled to 0° and 200 ml of saturated ammonium chloride was added slowly. The product was extracted into ether. The extract was washed once with saturated $NaHSO_3$, twice with water, twice with saturated $NaHCO_3$, and twice with saturated NaCl. The organic layer was dried over anhydrous $MgSO_4$, and the ether and THF were removed on a rotary evaporator. The ^{1}H NMR spectrum indicated that the product consisted of 50% anisole and 50% *o*-(3-cycloheptenyl)anisole. The anisole was removed by distillation at 15 Torr, and the *o*-(3-cycloheptenyl)anisole was distilled at 115° (0.1 Torr). The first fractions weighed 8.0 g which gas chromatography indicated contained about 8% of impurities. The second fraction was 28 g (87% total yield) of material containing no impurities by gas chromatography analysis (Carbowax 20M). The ^{1}H NMR spectrum was consistent with the expected structure: δ 6.65–7.35 (4 H, aromatic), 5.76 (2 H, olefinic) 3.98 (1 H, benzyl), 3.72 (3 H, methoxyl), 2.0–2.4 (2 H, allylic), 1.3–2.4 (6 H, other aliphatic).

***o*-(3-Cycloheptenyl)phenol (32).** The demethylation of *o*-(3-cycloheptenyl)anisole to the corresponding phenol was carried out by the use of anhydrous lithium iodide in collidine. Formation of the anhydrous salt from the monohydrate was conducted by drying in vacuo over a free flame for 3 hr. This procedure was preferable to heating with a flame under nitrogen as considerable decomposition was avoided. After the lithium iodide had been dried, the system was flushed with nitrogen and 75 ml of collidine (distilled from CaH_2) and 12.8 g (63.3 mmol) of *o*-(3-cycloheptenyl)anisole were added. The solution was heated at reflux under nitrogen for 20 hr at a bath temperature of 205–210°. The mixture was cooled and 400 ml of ether was added. This was washed twice with 200 ml of 10% HCl, once with 100 ml of saturated $NaHCO_3$, and once with water. The reaction mixture was dried over anhydrous $MgSO_4$ and the ether was removed with a rotary evaporator. The reaction mixture was chromatographed through 250 g of alumina. The product eluted with ether. The 6.6 g (65%) of **32** was distilled at 85–88° (0.1 Torr) to yield 4.0 g (40%). The ^{1}H NMR spectrum was consistent with that expected: δ 6.55–7.25 (4 H, aromatic), 5.80 (2 H, olefinic), 5.06 (1 H, phenoxy), 3.5–4.0 (1 H, benzyl), 2.0–2.5 (2 H, allyl), 1.3–2.0 (6 H, other aliphatic).

Irradiation of *o*-(3-Cycloheptenyl)phenol (32). **32** (2.04 g, 1.09 mmol) in 800 ml of benzene was irradiated with continuous nitrogen bubbling for 4 days. Irradiation was with a 450-W Hanovia lamp through a Vycor filter. Total destruction of reactant had occurred (NMR spectrum). Gas chromatography showed only one peak. The reaction was chromatographed through 100 g of alumina and the product was collected by gas chromatography (Carbowax 20M); 239 mg (12%) was recovered. The ^{1}H NMR indicated that a mixture of **35** (cis or trans) and **36** had been isolated: δ 6.4–7.2 (4 H, aromatic), 4.4–5.0 (1 H, α to oxygen), 3.2–3.7 (3 H, benzylic), 2.8–3.2 (7 H, benzylic), 1.0–2.5 (8 H, other aliphatic). The mass spectrum was consistent with the formula $C_{13}H_{16}O$. The peak of *m/e* 189 was 14.3% of the parent peak at *m/e* 188 (calculated for $C_{13}H_{16}O$, 14.3%).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.86; H, 8.54.

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(19) Irradiation of **12** in methanol containing sulfuric acid leads to *ionic* addition reaction products, as one would anticipate from Kropp's work.[13] The differences in the product composition from the photoaddition and ground-state additions will be described elsewhere.

(20) Thermochemical data are taken from Benson.[21] The page numbers in parentheses refer to this book. The model chosen for the olefin to carbene rearrangement is allylbenzene to β-phenylethylmethylene. The heat of formation of allylbenzene may be calculated from individual bond data to be 33 kcal/mol [5 C_B–(H) + 1 C_B–(C) + 1 C–(C_d)(C_B)$(H)_2$ + 1 C_d–(H)(C) + 1 C_d–(H_2), p 178]. The heat of formation of γ-phenylpropyl radical can be calculated from the heat of formation of propylbenzene (2 kcal/mol, p 178), the carbon–hydrogen bond dissociation energy (97 kcal/mol), and the heat of formation of the hydrogen atom (52 kcal/mol, p 195). The value is 47 kcal/mol (2 + 97 − 52). The difference in heats of formation of the γ-phenylpropyl radical and β-phenylethylmethylene is estimated at 54 kcal/mol, which is the difference in the heat of formation of methyl radical (34 kcal/mol, p 204) and that of methylene (88 kcal/mol, p 204). This gives a heat of formation of β-phenylethylmethylene of 101 kcal/mol (47 + 54) and the heat of reaction for the conversion of allylbenzene to β-phenylethylmethylene of 68 kcal/mol (101 − 33).

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(22) The model chosen for the calculation of the vinyl–benzyl bond energy is allylbenzene (ΔH_f = 33 kcal/mol), since the heats of formation of the vinyl radical (69 kcal/mol, p 204) and the benzyl radical (45 kcal/mol, p 204) are known.[21] The bond dissociation energy (heat of reaction) for eq 1 is therefore 69 + 45 − 33 or 81 kcal/mol.

$$CH_2{=}CHCH_2Ph \rightarrow CH_2{=}CH\cdot + \cdot CH_2Ph \qquad (1)$$

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Stereoelectronic Control in the Photorearrangement of α-Chloro Ketones. Mechanistic Studies in Photochemistry. XIII[1,2]

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Abstract: The photorearrangement of *anti*- and *syn*-2-chlorobenzobicyclo[2.2.2]octadien-3-one (**1** and **2**) in methanol gave naphthalene, methyl 1-naphthylacetate (**6**) and 7-carbomethoxy-2,3-benzonorcaradiene (**5**). The photolysis of *anti*-2-chlorobicyclo[2.2.2]octen-3-one (**3**) gave the 7-carbomethoxynorcarene (**7**) in 55% yield. The corresponding *syn*-chloro ketone (**4**) did not rearrange to the norcarene product illustrating the stereospecificity of the rearrangement. The reactions were not quenched with piperylene nor sensitized with acetophenone or acetone establishing them as singlet rearrangements. Quantum yields for disappearance of ketone were measured: $\Phi_1 = 0.35$; $\Phi_2 = 0.33$; $\Phi_3 = 0.22$; $\Phi_4 = 0.44$. Finally, flash photolysis in the presence of iodide did not yield I_2^- transients, indicating an absence of free chlorine atoms in this reaction.

Our studies on the photochemistry of β,γ-unsaturated ketones[1,4-6] have been extended to investigate the effects of substituents on the course of the reaction. Direct comparisons of the relative photoreactivity of two competing reaction types has been the subject of numerous investigations in photochemistry (e.g., type I vs. type II reactivity in ketones,[7] etc.). The studies on the 1,3-acyl migration and oxadi-π-methane rearrangement[1,8] have produced a very detailed understanding of β,γ-unsaturated ketone photochemistry. Likewise, α-halo ketone photochemistry has also been extensively studied and appears to be well understood.[9]

Our objective has been the study of interacting substituents in photochemical reactions, and the competition of α-chloro ketone and β,γ-unsaturated ketone photochemistry provides such a possibility. Also, a recent report of the photorearrangement of *exo*-2-chloronorbornenone (**9**)[10] suggested that all three substituents are involved. Our study deals with the β,γ-unsaturated α-chloro ketones **1–4** which are related to the corresponding unsubstituted β,γ-unsaturated ketones reported earlier.[4-6]

Results

The synthesis of chloro ketones **1–4** was accomplished by the addition of nitrosyl chloride to the corresponding olefin and acid hydrolysis of the resulting dimeric addition product as shown in Scheme I. In the benzobicyclic series, a single chloro ketone isomer was formed in 53% yield from the olefin. This could be equilibrated to a 1:2 epimeric mixture by a 10-min treatment of the chloro ketone with dimethylamine.

The assignment of the major isomer as *anti*-2-chlorobenzobicyclo[2.2.2]octadien-3-one (**1**) was made from the NMR chemical shifts of the C-2 protons for **1** [δ 4.14 (d)] and **2** [δ 3.87 (d)]. The greater shielding of the C-2 proton for **2** is in accord with the assignment of the proton above the shielding cone of the aromatic ring in other systems.[11]

The 2-chlorobicyclo[2.2.2]octen-3-ones (**3** and **4**) were synthesized by the same sequence. The hydrolysis of the nitroso chloride dimers gave a mixture of *syn*- and *anti*-2-chlorobicyclo[2.2.2]octen-3-ones which could be separated by silica gel chromatography.

The assignment of the *syn*-2-chlorobicyclo[2.2.2]octen-3-one (**4**) to the solid product (mp 29–31°) was based on the comparison of its NMR spectrum with that of the epimeric product. Chloro ketone **4** displayed the C-2 proton doublet at δ 3.87 (J = 2.6 Hz) whereas the C-2 proton of chloro ketone **3**, having almost the identical chemical shift, appeared as a doublet of doublets at δ 3.92 (J = 1.4 and 3.5 Hz) due to the additional long range coupling of the C-8 anti proton. The W arrangement of the C-2 and C-8 protons gives rise to the 3.5 Hz coupling as shown by double irradiation experiments. When the bridgehead proton was irradiated at δ 3.08 ppm, the doublet of doublets collapsed to a doublet with a coupling constant of 3.5 Hz ($J_{\text{H-2,anti-H-8}}$).