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REACTIONS OF 2-PHENYLCYCLOHEXANONE DERIVATIVES. A RE-EXAMINATION

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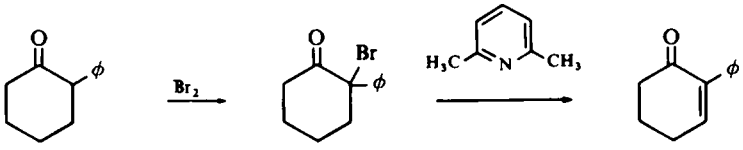
Abstract—The product commonly obtained from bromination of 2-phenylcyclohexanone is *cis*-2-bromo-6-phenylcyclohexanone, formerly considered to be 2-bromo-2-phenylcyclohexanone. The initial bromination product, however, is *trans*-2-bromo-6-phenylcyclohexanone. The two stereoisomers are readily interconverted in acid, and the *cis*-isomer is normally obtained due to its lower solubility in several solvents. Dehydrobromination of the *cis* or *trans* bromoketones gives a mixture of 2-phenylcyclohex-2-en-1-one and 6-phenylcyclohex-2-en-1-one, which do not interconvert under the reaction conditions. Alkylation and cyanoethylation of 2-phenylcyclohex-2-en-1-one proceed normally at C-2.

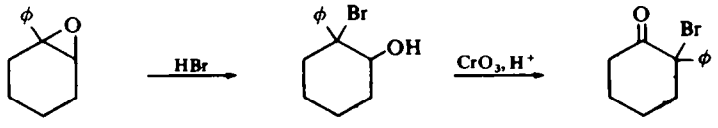
WE HAVE RE-EXAMINED some reported reactions of 2-phenylcyclohexanone and its derivatives. In several instances, our results differ significantly from those previously reported.

Bromination of 2-phenylcyclohexanone. Bachmann and Wick reported that bromination of 2-phenylcyclohexanone (**1**) gave the expected 2-bromo-2-phenylcyclohexanone, **2**.[1] The structure assigned the bromination product was supported[1] by



1 **2** **3**

its dehydrobromination to 2-phenylcyclohexenone (**3**), which has since been synthesized by several apparently unambiguous routes.[2] Berti *et al.*[3] later observed that chlorination of 2-phenylcyclohexanone with sulfuryl chloride, earlier reported to give 2-chloro-2-phenylcyclohexanone,[4] actually gave mixtures of 2- and 6-chloro-2-phenylcyclohexanones. This raised some doubts about the structure of the bromination product. However, an independent synthesis by addition of HBr to 1-phenylcyclohexene oxide, followed by chromic acid oxidation of the bromohydrin (eq. 1) gave the same product obtained by direct bromination of **1**.[3] This appeared to provide convincing confirmation of the original structural assignment.



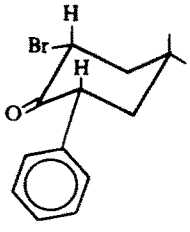
(1)

Repetition of the procedure of Bachmann and Wick (bromination of **1** in CCl_4, followed by recrystallization of the product from MeOH)[1] gave a bromoketone, m.p. 101–102°, presumably identical with the product (m.p. 103–104,[1] 98–101[3]) previously assigned structure **2**. The NMR spectrum of the product, however, indicates that it should be assigned the structure *cis*-2-bromo-6-phenylcyclohexanone (**4**), rather than **2**. In $CDCl_3$ solution the spectrum shows, in addition to multiplets for the aromatic ring (5H) and the methylene groups on the cyclohexane ring, (6H) apparent quartets of broad peaks (1H each) at δ 4·68 and δ 3·66. The signal at δ 4·68 can be assigned to the hydrogen at C-2, since its chemical shift is essentially identical with those previously reported for axial methine hydrogens in 2-bromocyclohexanones.[5,6] The chemical shift of the absorption at δ 3·66 is close to that of the methine proton in 2-phenylcyclohexanone (δ 3·52). The small downfield shift can reasonably be attributed to the inductive effect of the bromide at C-2. In benzene solution each of these absorptions, which are shifted to δ 4·05 and δ 3·05, appears as a reasonably clear doublet of doublets.

The axial positions of the protons at C-2 and C-4 can be assigned on the basis of their coupling constants with the adjacent methylene protons. The coupling constants (in benzene) for the proton at C-2 are J_{ax} = 13·0 Hz, J_{eq} = 6·0 Hz. These values are appropriate for interactions with an axial proton, while coupling of the adjacent methylene protons with an equatorial proton should give small, essentially equal coupling constants.[7] The "overall" coupling constant ($J_{ax} + J_{eq}$) of 18 Hz is essentially identical with those reported for axial methine protons in a large group of 2-bromocyclohexanones, while the overall coupling constants for the equatorial protons are only 5–6 Hz,[5,6] Similarly, the coupling constants for the proton at C-6 are J_{ax} = 12·5, J_{eq} = 6·0 Hz). The overall coupling constant is essentially identical with that of 2-phenylcyclohexanone (18 Hz), in which the C-2 hydrogen is almost certainly in the axial position.[8]

The IR spectrum of the product of bromination of **1** shows a carbonyl stretching absorption (in $CHCl_3$) at 1728 cm^{-1}, compared with 1710 cm^{-1} for 2-phenylcyclohexanone. The shift of 18 cm^{-1} to higher frequency clearly demonstrates that the bromine atom is in the equatorial position,[9] in agreement with the NMR assignments.

When heated in AcOH containing a few drops of HBr, bromoketone **4** partially rearranged to an isometic bromoketone, m.p. 72–74°, which was assigned the structure *trans*-2-bromo-6-phenylcyclohexanone (**5**). Its IR spectrum (in $CHCl_3$) showed a carbonyl peak at 1712 cm^{-1}, demonstrating that the bromine was in the axial position. Its NMR spectrum showed a two hydrogen multiplet around δ 4.45, which is assigned



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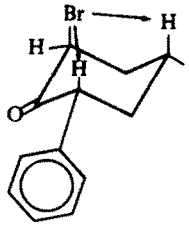


5 (Arrows show 1,3 interactions)

to the combined resonances for the hydrogens α-to the phenyl group and the bromine atom. The shape of this multiplet is consistent with the assumption that it consists of a rather sharp (small overall coupling constant) multiplet superimposed on a multiplet with a much larger overall coupling constant. This is consistent with the assignment of the bromine to the axial position and of the phenyl group to the equatorial position. The small (*ca.* 0·2 ppm) upfield shift of the resonance for the hydrogen at C-2 on going from **4** to **5** agrees with previous observations that axial C-2 hydrogens in bromoketones resonate at lower fields than equatorial hydrogens.[5,6] The large downfield shift of the resonance for the hydrogen at C-6 (*ca.* 0·8 ppm) is ascribed to the combined polar and steric effects of the axial bromine atom on the axial hydrogen at C-2. Garbisch has reported a similar shift caused by axial bromine in other 2-bromocyclohexanones.[5] It is of interest that the center of gravity of the absorptions for the methylene protons on the ring is shifted significantly downfield in the spectrum of **5** compared to that of **4**. This may be accounted for, in part, by the effect of the axial bromine on the axial hydrogen at C-4. This phenomenon does not seem to have been noted previously, and may be of general utility in structural assignments in the cyclohexane series.

Bromoketone **5** showed only limited thermal stability, decomposing slowly with evolution of HBr even at room temperature in crystalline form, or on heating in most solvents. By comparison, **4** was stable indefinitely at room temperature. The thermal instability of **5** made it impossible to determine precisely the equilibrium constant for the reaction **4** → **5**. However, even after short reaction times in AcOH containing HBr, bromoketone **4** gave mixtures of **4** and **5** in which the percentage of **5** ranged from 50–70 percent of total. As expected,[5,10] therefore, the isomer with the bromine atom in the axial position is more stable.*

In view of the fact that **5** is more stable than **4**, it seemed surprising that bromination of **1** should initially yield the equatorially brominated isomer, rather than the product of "normal" axial bromination. However, examination of the spectra of the bromination product immediately after removal of the CCl_4 solvent, before contact with MeOH, showed it to consist predominantly, and in some runs entirely, of the axially brominated isomer **5**. After **5** was heated in MeOH for a short time, crystals of almost pure **4** began to deposit from the cooled solution. Even trituration of oily, non-crystalline **5** with MeOH at room temperature resulted in predominant formation of **4** in the resulting crystals. Thus, bromination of **1** occurs normally[12] to give the axial bromination product, **5**. Equilibration of the two stereoisomers occurs rapidly in MeOH, however, and the much lower solubility of **4** results in the equilibrium being shifted in its direction during crystallization.

The unexpected bromination of **1** to give **5** rather than **2** is presumably due to the appreciable steric strain which would exist in **2**. Molecular models show that the preferred conformation for the phenyl group in 2-phenylcyclohexanones is perpendicular to the "average plane" of the cyclohexane ring. In this conformation, there

* Bachmann and Fornefeld[11] reported that in one run bromination of **1** gave a product melting at 68·5–69°, which changed on standing and recrystallization to the 103–104° "form". Berti *et al.*[3] reported a 74–77° m.p. "modification" of the bromination product, which similarly gave the higher melting material on recrystallization. They reported that the IR spectra of both forms in $CHCl_3$ were identical. It is not clear whether Berti's group, at least, had obtained **5**, since the IR spectra of **4** and **5** are quite distinctive (experimental). The differences in their spectra are only partially obscured in $CHCl_3$ solution.

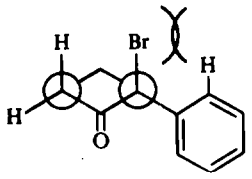


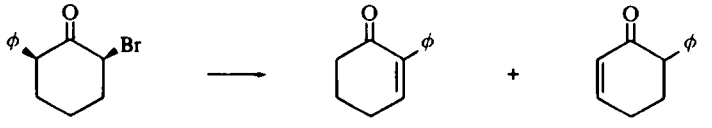
FIG 1. Newman projection of 2-bromo-2-phenylcyclohexanone

would be significant repulsions between the bromine atom and the *ortho*-hydrogens of the aromatic ring (Fig 1). Indeed, it seems probable that **2** would rearrange rapidly to **4** or **5** if it did form in the reaction. Formation of **4** by the method of Berti *et al.*[3] can be most readily explained as resulting from isomerization of **2** during chromic acid oxidation of 2-bromo-2-phenylcyclohexan-1-ol.

To account for formation of 2-chloro-6-phenylcyclohexanone from reaction of **1** with sulfuryl chloride, Berti suggested that chlorination proceeds by direct attack of sulfuryl chloride on **1**, rather than *via* a prior enolization step.[3] The demonstration that bromination of **1** similarly occurs at C-6 removes the necessity for postulating such unusual mechanisms, since there seems every reason to believe that bromination of **1** proceeds by the well established path of attack of bromine on its enol. The steric arguments which account for the direction of bromination of **1** also apply, in lesser degree, to the chlorination of **1**.

Dehydrobromination of 2-bromo-6-phenylcyclohexanones. Bachmann and Wick reported that dehydrobromination of the supposed 2-bromo-2-phenylhexanone, now known to be **4**, gave cyclohexenone **3**.[1] As was mentioned above, the structure of **3** has been abundantly confirmed by independent syntheses.[2] Formation of **3** from **4** must therefore proceed *via* a rearrangement process. Berti *et al.* observed that **3** was obtained by dehydrochlorination of 2-chloro-6-phenylcyclohexanone. They suggested that elimination of HCl occurred normally to give 6-phenylcyclohex-2-en-1-one (**6**), which rearranged to give **3**.[3]

We found that dehydrobromination of **4** in refluxing 2,6-dimethylpyridine did indeed give **3** as major product. However, **3** was accompanied by lesser amounts of



4 (or **5**) **3** **6**

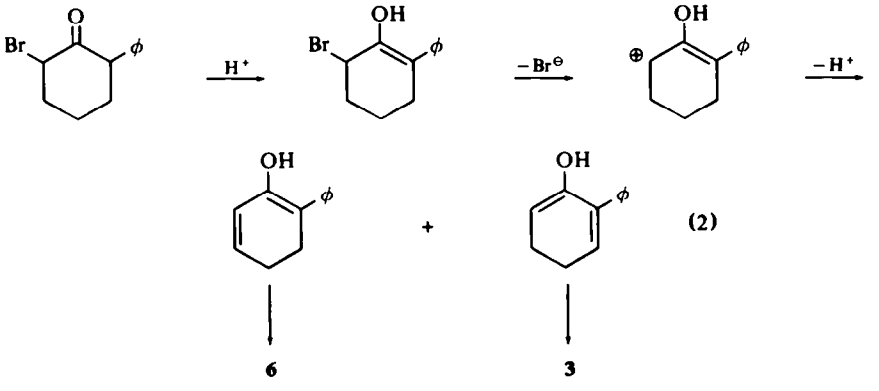
the previously unreported isomer, **6**. The structures of ketones **3** and **6** were readily determined by their NMR spectra (experimental). The ratio of the two isomers was 2·6 : 1·0. Dehydrobromination of **5** gave essentially the same product ratio. It seems probable that the two bromoketones are rapidly isomerized under the reaction conditions.

Since **6** was now available, we could test the suggestion[3] that **6** is an intermediate in formation of **3** from dehydrohalogenation of 2-halo-6-phenylcyclohexanones. Upon refluxing **6** with 2,6-dimethylpyridine and 2,6-dimethylpyridine hydrobromide,

under conditions closely resembling those employed in the dehydrobromination of **4**, no isomerization to **3** was observed. Ketone **6** cannot, therefore, be an intermediate in dehydrobromination of **4** to form **3**.

Dehydrobromination of **4** in HBr solution, or in refluxing dioxane (presumably also an acid-catalyzed reaction) gave **3** as the predominant product. Thus, bases appear to play no major role in the dehydrobromination-rearrangement of **4**.

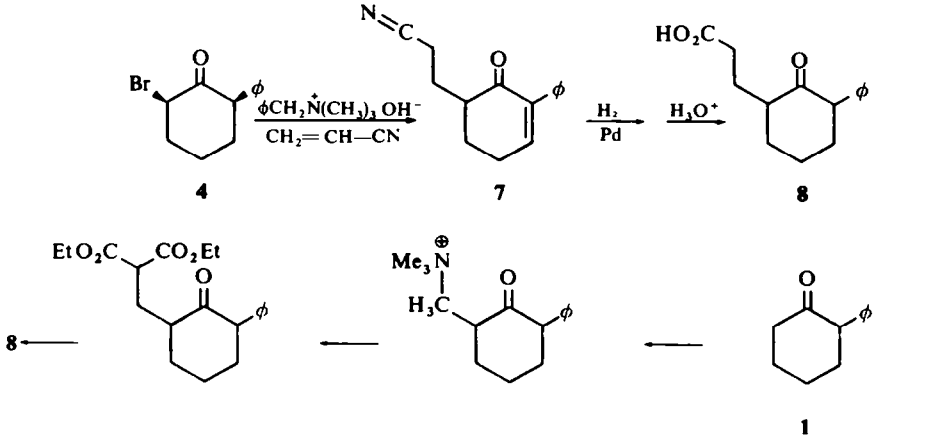
The available evidence suggests that the elimination of HBr from **4** can best be accounted for by initial enolization of the ketone, followed by formation of an allylic carbonium ion and loss of a proton (eq. 2). House has previously suggested that



(2)

rearrangements during similar dehydrohalogenations proceed through initial enolization, but his suggestion that enolization is followed by a concerted E_2' elimination[13] seems to provide a greater role for the base than seems justified by our observations. In reactions giving less stable carbonium ions, however, the role of base might well be larger.

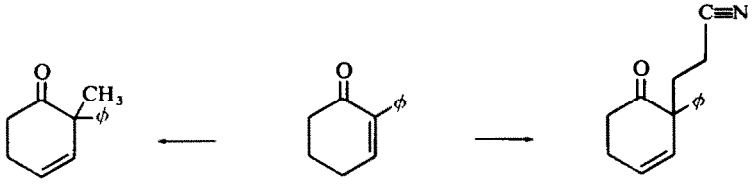
Base catalyzed reactions of phenylcyclohexenones. Bachmann and Wick[1] reported that reaction of **2** (actually **4**) with acrylonitrile in the presence of Triton B gave a cyanoethylation product, formulated as **7**, which on reduction and hydrolysis gave



(3)

an acid, **8**, whose structure was demonstrated by independent synthesis shown in equation 3. This report suggests that base catalyzed alkylation of **3**, like acid-catalyzed bromination of **1**, occurs at C-6 rather than C-2. Alternatively, dehydrobromination of **4** in strong base might give rise largely to **6**, in which case structure **7** assigned to the cyanoethylation product would require modification.

Our attempts to determine the nature of the product obtained by Bachmann and Wick[1] were frustrated by our inability to repeat their work. We could obtain no pure products from the reaction of **4** with acrylonitrile and Triton B. The IR spectrum of the crude product suggested that a good deal of **4** remained unchanged. In the absence of acrylonitrile, **4** was indeed recovered largely unchanged from reaction with Triton B at room temperature for three hr. After 14 hr, almost all **4** had disappeared, but the products were largely base soluble, presumably resulting from Favorski rearrangements. We could not identify any components in the small amount of neutral material obtained from the reaction.



10 **3** **9**

Reaction of **3** with acrylonitrile in the presence of Triton B gave, in addition to recovered **3**, a product which, on the basis of its IR and NMR spectra, (experimental) was assigned structure **9**. Similarly, alkylation of **3** with MeI catalyzed by t-BuOK in t-BuOH gave the expected alkylation product **10**. Thus, base catalyzed alkylation of **3** proceeds normally to give the products of alkylation at C-3.

It was of interest to determine the products of alkylation of cyclohexenone **6**, since there seems little information on which to base a decision as to whether alkylation will occur on the side of the molecule bearing a double bond or a phenyl group. Unfortunately, **6** appeared to be destroyed readily in basic solutions, and we were unable to isolate any alkylation products from these reactions.

EXPERIMENTAL

NMR spectra were recorded on a Varian A-60 spectrometer in $CDCl_3$, unless otherwise indicated. IR spectra were recorded on a Perkin–Elmer 237B spectrometer. All m.ps are uncorrected. Microanalyses were by the University of Massachusetts Microanalytical Laboratory, Amherst, Mass. VPC data were obtained on a Varian model 202C instrument using one of the following columns: Column A, 6 ft. × $\frac{1}{4}$ in., packed with 3% SE-30 on chromosorb W; column B, 5 ft. × $\frac{3}{8}$ in. packed with 20% SE-30 on chromosorb W.

trans-2-*Bromo-6-phenylcyclohexanone.* (a) *Bromination of 2-phenylcyclohexanone.* A solution of bromine (3·2 g, 0·02 mol) in 15 ml CCl_4 was added slowly to a solution of 2-phenylcyclohexanone (3·5 g, 0·02 mol) in 30 ml CCl_4, maintaining temperature at 0–5°. After addition of the first few drops of the bromine solu-

tion, further addition was halted until the solution became colorless (about 10 min). Addition of the remainder of the bromine took about 15 min. The solution was immediately washed three times with ice-water and dried ($MgSO_4$). Evaporation of solvent left 5·0 g of pale yellow fluid, which crystallized on standing cold. Rapid recrystallization in small portions from cyclohexane (prolonged heating results in decomposition of the compound) gave 1·2 g (24%) of *trans*-2-bromo-6-phenylcyclohexanone, white crystals, m.p. 72–74°. It can also be recrystallized from AcOH—H_2O. (Calc for $C_{12}H_{13}OBr$; Br 31·6. Found: Br, 31·3%). Its IR spectrum ($CHCl_3$ solution) showed a carbonyl peak at 1712 cm^{-1}. IR (nujol) characteristic peaks occurred at 1710 (s), 960 (m), 775 (m), 730 (s), 682 (s), and 637 (m) cm^{-1}. The NMR spectrum of the product is reported in text.

(b) *Isomerization of* cis-2-*bromo-6-phenylcyclohexanone. cis*-2-Bromo-6-phenyl-cyclohexanone (0·40 g) was suspended in 3 ml AcOH containing 3 drops HBr. The mixture was heated gently on steam bath until solid dissolved, and was then cooled and water added drop by drop with constant shaking. After *ca.* 0·3 ml of water had been added, a white solid was separated and found to consist of a mixture of *cis* and *trans* bromoketones. Addition of water was continued until *ca.* 1 ml had been added, and the precipitate again isolated. It was recrystallized from AcOH—H_2O to give white needles (0·15 g, 38%), m.p. 67–70°. Its NMR spectrum indicated it to consist of *trans*-2-bromo-6-phenylcyclohexanone containing *ca.* 8% *cis* isomer.

cis-2-*Bromo-6-phenylcyclohexanone. trans*-2-Bromo-6-phenylcyclohexanone (0·50 g) was suspended in 2 ml MeOH and the mixture heated (steam bath) until the solid dissolved. The solution was allowed to stand at room temperature until crystals appeared, and then cooled. Filtration gave 0·25 g (50%) of *cis*-2-bromo-6-phenylcyclohexanone, white needles, m.p. 98–100°. Recrystallization from MeOH raised the m.p. to 101–102° (reported, 103–104°). Its IR spectrum ($CHCl_3$) showed a carbonyl absorption at 1728 cm^{-1}. IR (nujol) showed characteristic peaks at 1715 (s). 937 (m), 875 (m), 812 (m), 790 (m), 735 (m-s), 702 (s), 685 (s), and 660 (m-s) cm^{-1}. Its NMR spectrum is reported in the text.

2-*Phenylcyclohex-2-en-1-one and 6-phenylcyclohex-2-en-1-one.* Following the procedure of Bachmann and Wick, *cis*-2-bromo-6-phenylcyclohexanone (8·83 g, 0·035 mol) in 132 ml of 2,6-lutidine was refluxed for one hr. After most of the solvent had been removed, ether was added and the resulting solution washed with dilute HCl and sat $NaHCO_3$ aq. The solution was dried (Na_2SO_4) and the solvent evaporated to give 6·0 g of colorless solid. VPC on column A at 200° showed the presence of two components with retention times of 3·2 and 3·5 min, in the area ratio 2·64 : 1·0. Part of the solid (4·91 g) was chromatographed on 120 g of silica gel, eluting with a 3 : 1 mixture of petroleum ether (b.p. 30–60°) and CH_2Cl_2. The first product was 2-*phenylcyclohex-2-en-1-one* (2·4 g, 49% based on amount chromatographed), m.p. 94–95° (reported, m.p. 95·0–95·5°). Its IR spectrum ($CHCl_3$) showedpeaks at 1680 (s), 1610 (w), 1500 (m), 1460 (w), 1450 (m), 1431 (m), 1365 (s), 1160 (s), 1129 (s), 980 (m) 910 (m), 8·40 (m), amd 700 cm^{-1}. Its NMR spectrum showed a singlet (5H, Ph) at δ 7·30, a triplet (1H, J = 4 Hz) at δ 7·05 (vinyl proton β-to carbonyl) and a multiplet (6H) in the region δ 2·8–1·8.

Further elution gave a mixture of ketones **3** and **6** (0·8 g), followed by 6-*phenylcyclohex-2-en-1-one* (0·9 g, 18%) as white prisms, m.p. 68–69°. (Calc for $C_{12}H_{12}O$: C, 83·7; H, 6·97. Found: C, 83·8; H, 7·29%). IR ($CHCl_3$) 1680 (s), 1628 (w), 1610 (w), 1500 (m), 1460 (m), 1430 (m), 1390 (m), 1160 (m), 1130 (s), 850 (m), and 700 (m) cm^{-1}. Its NMR spectrum showed a multiplet (*ca.* 5H, Ph), an apparent triplet of a doublet at δ 6·9 (J_d *ca.* 10 Hz, J_t = 4 Hz) with the lower half of the doublet partially obscured by the Ph absorptions (vinyl proton β-to carbonyl), a triplet of doublets (1H, J_d = 10 Hz, J_t = 1·5 Hz) at δ 6·1 (vinyl proton α-to carbonyl), a triplet at δ 3·58 (1H, J = 7·5 Hz, proton α-to Ph group), and a multiplet from δ 2·6 to 1·9 (4H).

Attempted isomerization of 6-*phenylcyclohex-2-en-1-one.* A solution of 2,6-dimethylpyridine (20 ml) 6-phenylcyclohex-2-en-1-one (0·2 g) and 2,6-litidine hydrobromide (1·0 g) was refluxed for one hr. After most of the litidine had been removed under reduced pressure, ether was added and the solution washed with dilute HCl and $NaHCO_3$ aq. Evaporation of solvent left 0·9 g of yellow oil. VPC analysis (column A at 190°) showed that no isomerization of the double bond into conjugation with the phenyl ring had taken place.

Thermal and acid-catalyzed dehydrobromination of cis-2-*bromo-6-phenylcyclohexanone.* (a) *cis*-2-Bromo 6-phenylcyclohexanone (0·30 g) in 20 ml of dibutyl ether was refluxed for one hr. The solvent was removed giving 0·2 g of waxy solid as product, shown by IR and VPC retention time to be 2-phenylcyclohex-2-en-1-one.

(b) A solution of *cis*-2-bromo-6-phenylcyclohexanone (0·5 g) and 48% HBr acid (6 ml) in 14 ml of AcOH was refluxed for 24 hr. It was diluted with water, neutralized (Na_2CO_3 aq) and extracted with ether. The ether layer was dried and the solvent evaporated to give 0·2 g of oily product. VPC analysis at 190° on

column A showed that ketones **3** and **6** were formed, area ratio 1·27 : 1·0.

2-Methyl-2-phenylcyclohex-3-en-1-one. 2-Phenylcyclohex-2-en-1-one (0·60 g, 3·48 mmol) was added to a solution of t-BuOK (0·39 g, 3·48 mmol) in 40 ml of t-BuOH. The mixture was stirred at room temp for 20 min, and MeI (0·50 g, 3·48 mmol) added slowly at room temp. The mixture was still basic after 24 hr. Another 0·50 g MeI was added. After stirring for an additional 24 hr, the solution became almost neutral. Water containing one drop of conc. HCl was added and the solvent removed. The residue was extracted with CH_2Cl_2 and the extract washed with water, dried (Na_2SO_4), and the solvent evaporated to give 0·50 g yellow oil. VPC analysis on column A showed the presence of three components in the area ratio 4 : 1 : 1·3 (compounds listed in order of increasing retention time). The product was chromatographed at 25 g of silica gel, eluting with a 1 : 1 mixture of petroleum ether (b.p. 30–60°) and CH_2Cl_2. The fractions obtained were further purified by prep VPC on column B at 230°. The compound with the longest retention time was identified as recovered 2-phenylcyclohex-2-en-1-one by its IR spectrum and VPC retention time. The product with intermediate retention time could not be obtained in pure form. The major product (lowest retention time) was identified as 2-methyl-2-phenylcyclohex-3-en-1-one by its IR and NMR spectra. Its IR spectrum (neat) had peaks at 3010 (m), 2980 (m), 2940 (m), 1860 (w), 1715 (s), 1600 (m), 1495 (m), 1480 (m), 1450 (m), 1370 (w), 1350 (w), 1170 (m), 1090 (w), 1030 (w), 890 (w), and 700 (m) cm^{-1}. Its NMR spectrum showed multiplets around δ 7·35 (5H, Ph), 5·95 (2H, vinyl protons), and 2·5 (4H, methylene groups), and a singlet at 1·5 (3H, Me at C-2)

Reaction of 2-phenylcyclohex-2-en-1-one with acrylonitrile. Triton B (1·0 ml) was added to a solution of 2-phenylcyclohex-2-en-1-one (0·30 g, 1·72 mmol) in 10 ml dimethoxyethane. The mixture was cooled in ice and acrylonitrile (0·15 g, 2·3 mmol) added. The mixture was kept in ice for thirty min, and at room temp for three hr. It was acidified with dilute HCl, extracted with CH_2Cl_2 and the organic layer washed with water and dried ($MgSO_4$). Evaporation of solvent left 0·35 g of yellow oil, which had IR peaks at 1680 and 1715 cm^{-1} (neat). The product was chromatographed on 15 g of Florisil. Elution with a mixture of petroleum ether (b.p. 30–60°) and CH_2Cl_2 (10 : 1) gave 0·10 g of recovered 2-phenylcyclohex-2-en-1-one. Further elution with CH_2Cl_2 gave 2-cyanoethyl-2-phenylcyclohex-2-en-1-one (0·060 g, 20% based on recovered 2-phenylcyclohex-2-en-1-one) as a pale yellow oil. (Calc for $C_{15}H_{15}NO$: C, 80·0; H, 6·66. Found: C, 79·7; H, 6·79%). IR (neat) showed peaks at 1720 cm^{-1} (unconjugated carbonyl) and 2240 cm^{-1} (C≡N). Its NMR spectrum showed multiplets around δ 7·30 (5H, Ph), and 5·88 (2H, vinyl protons) and from δ 2·9 to 1·9 (8H, methylene groups on ring and cyanoethyl chain).

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