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KINETICALLY DISTINCT TRIPLETS IN THE PHOTOREARRANGEMENT OF 2-PHENYLCYCLOHEXANONE TO *cis*- AND *trans*-6-PHENYL-5-HEXENALS

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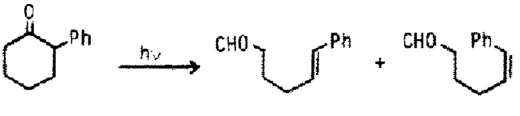
Abstract—A reinvestigation of the photochemistry of 2-phenylcyclohexanone reveals that the two aldehyde products, *cis*- and *trans*-6-phenyl-5-hexanal, come from triplets of different lifetimes. That the two distinct triplets are not simply the two conformers with phenyl axial and equatorial is demonstrated by the similar behavior of *cis*-4-t-butyl-2-phenylcyclohexanone. The *trans* isomer of this ketone is photostable. It is concluded that *trans*-enal arises by an almost concerted out-of-plane cleavage which forms a 1,6-biradical in the perfect geometry for disproportionation to *trans*-enal. The precursor to *cis*-enal may be a minor rotamer of 1 which is forced by nonbonded interactions into a cleavage mode which twists the biradical into a geometry suitable for at least partial formation of *cis*-enal. In both cases biradicals must be very short-lived and not rotationally equilibrated.

Some years ago, in a comparison of substituent effects on the photorearrangements of cycloalkanones, we reported that 2-phenylcyclohexanone 1 yields two isomeric products, the major one of which is not readily quenched by triplet quenchers.[2] We did not characterize the two products but assumed that the quenchable one was the enal 2 expected to be formed by analogy to other cycloalkanones. Baum later reported that this minor product in fact is the *cis*-enal while the major product is the *trans*-enal.[3]



1 trans-2 cis-2

At the same time several investigators began considering the relationship between conformational mobility and excited state reactivity.[4,5] Lewis reported beautifully compelling evidence that benzoylcyclohexanes form different products from kinetically distinct triplets.[5] This behavior represents the situation wherein different conformations of the reactant yield different products at rates faster than conformational interconversion;[5,6] we have provided additional examples.[7,8] At the same time several different research groups reported results which suggest that substituents alter product ratios in cycloalkanone photorearrangements by affecting the conformational mobility of the intermediate biradicals.[9,10]

The different sensitivities toward quenching of the two enals formed from 1 suggested that conformational factors may be affecting product ratios in 1. Therefore we undertook a more thorough study of the photochemistry of 1.

RESULTS

Product identification. A benzene solution 1 M in 1 was irradiated at 313-nm until 1 had almost completely disappeared. Column chromatography yielded the major product as a yellow oil; its spectroscopic properties clearly indicated that it was *trans*-2 as reported by Baum.[3] In particular the vinyl region of its nmr spectrum was very similar to that of *trans*-1-phenylpropene. During gas chromatographic (GC) analysis, trans-2 elutes several minutes after the minor but only other high boiling product, identified by Baum as *cis*-2. GC-MS analysis confirmed this assignment.

Comparable irradiation of 0.2 M *cis*-4-t-butyl-2-phenylcyclohexanone, *cis*-3, yielded a mixture of *cis* and *trans*-4-t-butyl-6-phenyl-4-hexenal, 4. These products were isolated by column chromatography and identified by comparison of their spectroscopic properties to those of 2. The two isomers show slightly different aldehyde proton chemical shifts as Baum reported for 2[3] and the characteristically different vinyl patterns of *cis* and *trans*-1-phenylpropene. As with 2, *trans*-4 was the major product and eluted after *cis*-4 during GC analysis.

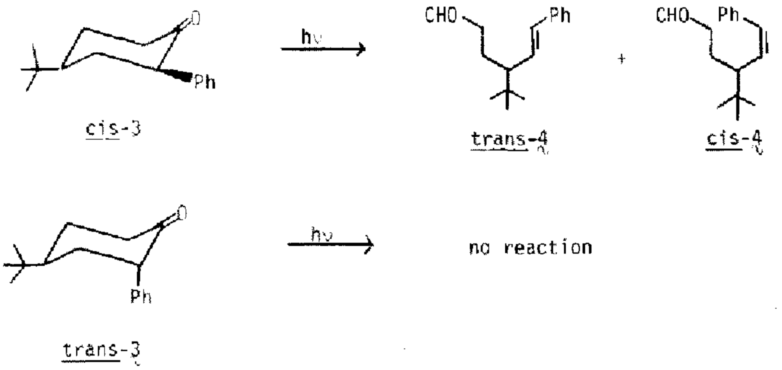
The two isomers of 3 were prepared as described by Bordwell and Yee[11] and were separated by column chromatography on silica gel. Their UV and NMR spectra distinguished them, *trans*-3 having a strongly enhanced n, π^* transition (λ_{max} 288 nm, ε 80) while the n, π^* transition of *cis*-3 was buried underneath the tail of the phenyl absorption. The chemical shift of the axial benzylic proton in *cis*-3 is 1.0 ppm upfield from the corresponding equatorial proton in *trans*-3.

Quantum yield measurements. Degassed benzene solutions 0.1 M in ketone and 0.005 M in internal standard were irradiated at 313-nm in parallel with 0.1 M valerophenone actinometers.[12] Product yields and ketone disappearance were measured by GC analysis after 14% conversion. Measured values are recorded in Table 1.

Table 1. Photokinetics of 1 and *cis*-3[a]

Ketone	Φ_{-K}	Φ_{trans}	Φ_{cis}	$k_q\tau_{trans}$	$k_q\tau_{cis}$
1	0.6	0.45	0.015	0.41±.04	1.7± .2
cis-3	0.6	0.30	0.030	2.8 ±.7	18 ±3

[a] 313-nm, 0.1 M degassed benzene solutions. Analyses at 14% conversion.



Over a range of conversions from 3-15%, the percentage of *cis*-2 rose only slightly from 2.5% to 3.5%. In contrast, Baum reported a 93/7 *trans*-2/*cis*-2 ratio at an unspecified "low" conversion.[3] For both 1 and *cis*-3, several early eluting product peaks occur even at low conversion and suggest either decarbonylation reactions of ketene byproduct or type II elimination of 2. The material balances probably are not as low as measured, because of imprecision in the measurement of ketone disappearance at relatively low conversion.

After ten times the irradiation which produced 14% conversion in 1 and *cis*-3, *trans*-3 showed no GC measurable products and no epimerization to *cis*-3. The maximum reaction quantum yield can be set as <0.001.

Energy transfer studies. Degassed benzene solutions 0.1 M in 1 or *cis*-3 were irradiated with varying amounts of added diene quencher. The resulting Stern–Volmer plots are shown in Fig. 1 and the slopes are recorded in Table 1. As the early study noted,[2] the minor *cis*-enal product is quenched 4–6 times more readily than the major *trans*-enal product.

The photoreaction of 1 was also quenched with biacetyl (0.02–0.10 M). *Trans*-2 formation was quenched with a $k_q\tau$ value of 22 ± 1 M^{-1}. *Cis*-2 formation was doubled by 0.02 M biacetyl then quenched at higher concentration. Presumably triplet biacetyl sensitizes *trans* → *cis*-2 isomerization.

Irradiation at 313-nm of 0.05–0.4 M 1 in 1-methylnaphthalene solvent produced 2 in quantum yields from 0.018 to 0.077, with *cis*-2 and *trans*-2 being formed in approximately equal yields. Extrapolation[13] yields a total Φ of 0.14 at infinite ketone concentration, 32% of the value measured upon direct irradiation.

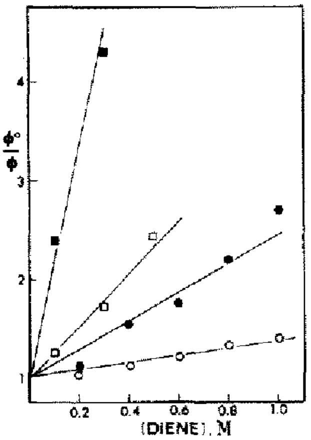


Fig. 1 Stern–Volmer quenching plots, formation of enals: O, *trans*-2; ●, *cis*-2; □, *trans*-4; ■, *cis*-4; 1,3-pendadiene used with 1; 2,5-dimethyl-2,4-hexadiene with 3.

The *cis*-*trans* isomerization of various concentrations of 1,3-pentadiene was sensitized with 0.2 M 1 and compared to that sensitized by acetone. Quantum yields (measured relative to 0.6 M acetone–0.5 M pentadiene) were extrapolated to infinite diene concentration to yield an intersystem crossing yield[14] value of 0.88 ± 0.05. The intercept/slope value of 0.6 provides an independent measure of $k_q\tau$.

Spectroscopy. The fluorescence of 1 was found to be just about identical in intensity and band shape to that of 2-methylcyclohexanone, both 0.01 M in cyclohexane. Methylcyclohexane solutions of 1 at 77°K did not show any phosphorescence characteristic of aliphatic ketones but did show weak emission characteristic of phenyl ketones (0,0 band at 386 nm). Since some cyclopentyl phenyl ketone was isolated from the preparation of 3, it is suspected that Favorskii rearrangement of reactant chloroketone is a minor side reaction in the preparation of the 2-phenyl ketones.

As mentioned above, *trans*-3 shows an enhanced n, π^* uv transition whereas *cis*-3 does not. The n, π^* transition of 1 itself (λ_{max} 300 nm, ε 46) is enhanced and somewhat red-shifted compared to that of 2-methylcyclohexanone (λ_{max} 290 nm, ε 26).

Isomerization of 1-*phenylpropene.* Dilute solutions of pure *cis* or *trans*-1-phenylpropene in benzene containing a trace of I_2 were irradiated until no further change in the *cis*/*trans* ratio was observed by GC analysis. The final mixtures contained 3% *cis*-isomer, which represents the thermodynamic equilibrium percentage.

DISCUSSION

Our current results reconfirm that the *trans*/*cis* enal ratio formed during the photorearrangement of 2-phenylcyclohexanone is large, approximately equal to the thermodynamic ratio. They also reconfirm the earlier observation that the two products arise from different excited states. The major *trans* isomer, formed in >40% quantum yield, arises primarily from a short-lived triplet, while the minor, *cis* isomer arises from a longer-lived triplet. The basis for these conclusions will be discussed first.

Excited state multiplicity. The normal fluorescence efficiency of 1 and the biacetyl quenching combine to suggest that the predominant reaction of singlet excited 1 is intersystem crossing to the triplet. The high extrapolated intersystem crossing yield confirms this conclusion. Since k_q for singlet ketone quenching by biacetyl is 1×10^{10} M^{-1} s^{-1},[15] $1/\tau$ for singlet 1 is $5\times$

$10^8\ s^{-1}$, much the same as for other similarly substituted ketones.[16].

Nonetheless, we suspect that some *trans*-**2** does come from the lowest excited singlet of **1**. The chief evidence is the 14% extrapolated quantum efficiency in methylnaphthalene solvent. This value represents complete singlet energy transfer from naphthalene to ketone with partial static quenching of triplet ketone.[13] Under such conditions, triplet benzophenone is quenched at a rate of $5\times10^{10}\ s^{-1}$.[17] If all reaction came from triplet ketone, equation 1 would describe the situation, with $\Phi^0/\Phi = 0.44/0.14 = 3.1$. Consequently $1/\tau_T$ would equal $2.5\times10^{10}\ s^{-1}$.

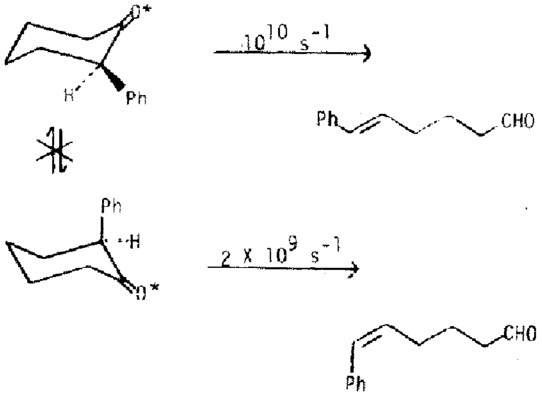
$$\Phi^0/\Phi = 1 + k_{et}\tau_T. \qquad (1)$$

However, the actual Stern–Volmer quenching slope of $0.4\ M^{-1}$ was measured under conditions such that quenching is mostly diffusional, with $k_q = 4\times10^9\ M^{-1}\ s^{-1}$.[18] This experiment sets $1/\tau_T \geqslant 1.0\times10^{10}\ s^{-1}$. It is known that conjugated dienes quench excited singlet ketones with rate constants $< 10^8\ M^{-1}\ s^{-1}$.[19] Given the steric effect expected from the α-phenyl,[16] $k_q\tau_S$ would be expected to be less than $0.1\ M^{-1}$. Therefore most of the measured $k_q\tau$ value must represent triplet quenching. The two-fold difference between τ_T values estimated from static and dynamic quenching suggests that as much as half of the unquenched reaction in methylnaphthalene arises from a singlet. We can set a maximum quantum yield of 0.07 for singlet rearrangement of **1** to *trans*-**2**. Therefore the major amount of *trans*-**2** (> 85%) must arise from a short-lived triplet, with a rate of α-cleavage $\sim 1.0\times10^{10}\ s^{-1}$. This rate corresponds well to that predicted by the behavior of dibenzyl ketone[20] and corrects the too-slow value originally estimated from quenching of *cis*-**2** formation.[2] α-Cleavage reactions of singlet alkanones are about 1/100 as fast as those of triplets.[9] Therefore, singlet **1** would be expected to cleave with a rate constant on the order of $10^8\ s^{-1}$. Such a rate would be compatible with the high intersystem crossing yield and a low singlet reaction quantum yield.

The *cis*-**2** apparently comes entirely from a triplet, since its formation is fairly easily quenched, completely so by large concentrations of diene.

Identity of different triplets. The fact that *cis*-**2** is formed exclusively from a triplet some six times longer-lived than that which forms *trans*-**2** suggests that there may exist two different triplets of **1** which do not interconvert (or do so only partially) and which form different products. Benzoylcyclohexane provided the first example of this phenomenon,[5] the explanation being that cyclohexane ring flipping is slower than the distinct chemical reactions of the different chair conformers.

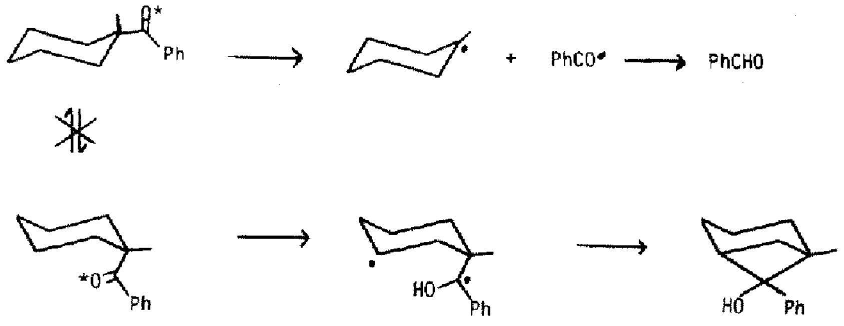
The first possibility for **1** that must be explored is whether the two conformers with phenyl axial or equatorial lead to the two different products. Certainly the two measured triplet lifetimes are too short to allow any ring-flipping. The latter reaction has a rate constant of only $10^5\ s^{-1}$ for dimethylcyclohexane[21] and would be somewhat faster for cyclohexanone but not $10^9\ s^{-1}$.



The equatorial/axial preference of a phenyl group on cyclohexane is several hundred to one.[22] The increased sp^2 bond angle at C-1 in cyclohexanone moves C-2 and C-6 farther apart such that 1,3-diaxial interactions of α-substituents are not as severe as in cyclohexane. The 40:1 *trans*:*cis* product ratio which we find might then correspond to the ground state equatorial:axial ratio. In fact, the enhanced n, π* transition of **1** indicates that a significant fraction of its ground state molecules exist with phenyl axial, since equatorial phenyls do not give rise to any enhancement.[23]

Interaction of any axial phenyl with the CO might also explain the slower cleavage of this conformer. Such interactions are somewhat stabilizing in the excited state; this stabilization would be lost during α-cleavage.

Several problems exist with this conformational argument. One is that the actual excited state reaction forming both *cis*- and *trans*-**2** is presumably the same, α-cleavage to generate the 1-acyl-6-benzyl biradical. Our original study[2] established this mechanism for rearrangements of triplet cycloalkanones and later studies have confirmed the intermediacy of such biradicals. In particular, the formation of the same *cis*/*trans* enal ratio from both *cis*- and *trans*-2, 3-dimethylcyclohexanone[24] is often cited as direct evidence for the intermediacy of a common biradical. We took special care in the preceding section to show minimal involvement of excited singlets, which often react with considerable stereo-specificity even when biradical intermediates are involved.[25] In the absence of differential quenching, the high *trans*/*cis* enal



product ratio would most plausibly be ascribed by a Curtin–Hammett argument[26] to differing transition state energies leading from a common biradical to the two products. Such effects have been observed before in biradical cleavages.[27] Since α-cleavage of the two ketone conformations would lead to different initial biradical geometries, product formation would have to be faster than rotational equilibration of the biradical for different starting conformations to give different products. Such rapid biradical reactions are especially unusual given the triplet origin of these biradicals.

The two diastereomers of **3** were studied with the obvious intention of checking the relative reactivities of ketones with α-phenyl substituents fixed axial or equatorial. To our surprise, the former, *trans*-**3**, proved to be unreactive while the latter, *cis*-**3**, displayed the same behavior as **1**. As observed for cyclohexanone itself,[9] a 4-t-Bu group slows down triplet α-cleavage, by a factor of ~5 for **3** relative to **1**.

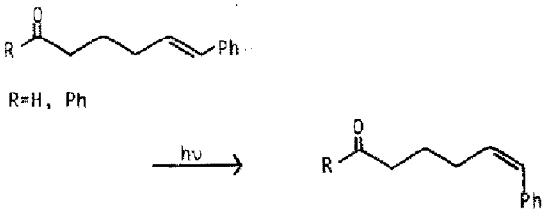
The behavior of **3** apparently rules out the otherwise attractive possibility that kinetically distinct chair conformers of **1** yield different products. However, several interesting conclusions do emerge.

Unreactivity of trans-**3**. Apparently excited state interaction between an axial α-phenyl and the carbonyl is strong enough to quench α-cleavage. This interaction is of a charge transfer nature[23] and such interactions are now known to generally promote rapid quenching. In acyclic ketones, α-phenyls do not quench reactivity[28] whereas β-phenyls do.[29] The difference probably reflect different conformational limitations on orbital overlap. As suggested above, an axial α-phenyl probably does lower the rate constant for α-cleavage for two reasons: (1) The ~3 kcal/mole excited state stabilization lowers the exothermicity of cleavage; (2) The twist angle of the phenyl which promotes maximum stabilization of the n, π^* state[23] does not provide maximum benzylic resonance in the developing radical site on the α-carbon.

Identity of different triplets. If one of the kinetically distinct triplets, that which leads to *cis*-enal, is not a conformer with phenyl axial, it must be either some other minor conformer or a different molecule altogether.

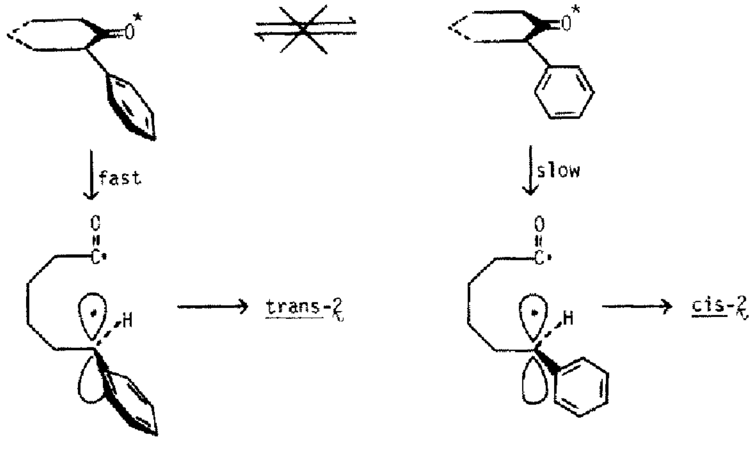
Given the rapidity of α-cleavage, it might be possible for rotamers involving the α-carbon–phenyl bond to stay distinct and cleave at different rates because of different conjugation in the developing benzyl radical site. This possibility will be returned to below.

The comparable t-Bu effect on the lifetimes of the triplets which lead to both *cis*- and *trans*-enals does suggest that different rates of α-cleavage determine the lifetimes. Baum reported that *trans*-**2** is converted to *cis*-**2** at high conversions. We see only a slight variation in the yield of *cis*-**2** at low conversions and certainly do not extrapolate to zero *cis*-**2** at zero conversion. However, we do see efficient sensitization of *trans* → *cis* conversion by both biacetyl and naphthalene, as expected from the known behavior of 1-phenylpropene toward triplet sensitizers.[14] The high conversion increase in *cis*-**2** undoubtedly reflects light absorption by *trans*-**2** and internal energy transfer from triplet aldehyde to 1-phenylalkene chromophore. Cowan and Baum have measured the rate constant for this process in the analogous phenyl ketone as $1\times10^{10}\,s^{-1}$.[30] *Trans*-**2** should undergo such internal energy transfer just as fast, whereas the triplet precursor to *cis*-**2** at low conversion decays with a rate constant only 20% as fast. It is conceivable that a t-Bu group might slow down this internal energy transfer, but no precedent is known for such an effect.



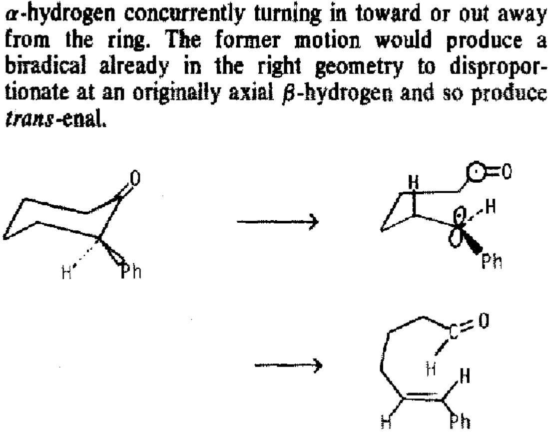
At 14% conversion, with a 35/9 ratio of 313-nm extinction coefficients for **1** relative to aliphatic aldehydes and a 0.51 quantum yield for sensitized *trans-cis* isomerization of 1-phenyl-propene,[14,29] one would expect about 1% *cis*-**2** resulting from photoisomerization of *trans*-**2**. With **3**, the much higher quantum yield of *cis*-**4** cannot be due to isomerization of *trans*-**4**. The low conversion runs with **1** establish that at least half the *cis*-**2** formed at 14% conversion comes directly from **1**. Therefore we feel that, even though competitive isomerization of *trans*-enal may produce some of the total *cis*-enal and thus confuse the quantitative aspects of this problem, some *cis*-enal does arise from longer-lived triplets of **1** and **3** than those which lead to *trans*-enal.

Origin of trans-*enal.* It is clear that triplet **1** does not produce triplet **2**, otherwise a ratio closer to 50:50 of *cis*- and *trans*-isomers would have been formed.[14] Instead we need a model for the rearrangement which proceeds almost concertedly, since a long-lived biradical

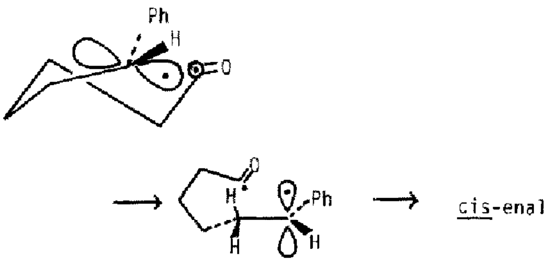


would give the 3% *cis*-enal expected thermodynamically. There are two pertinent facts not normally considered in analyses of cycloalkanone photorearrangements. First, whereas most triplet ketone reactions produce triplet radical pairs which undergo very little cage reaction, α-cleavage reactions involve substantial cage recombination.[28,31] It may thus be possible for the triplet biradical from **1** to proceed to products so rapidly that initial biradical geometries control product geometries. There is already one report of partially stereospecific α-cleavage by a cyclic ketone.[32] Second, α-cleavage probably proceeds by out-of-plane motion.[33] This motion may introduce the spin-orbit coupling required for rapid triplet→singlet conversion[34] and also would cause increased non-bonded interactions across the ring such as the large rate effect of 4-alkyl substituents[9] requires.

The following scheme is presented as a possible explanation for our observations, although not all aspects are readily explicable. The α-carbon can move below or above the ring plane during cleavage, with the axial α-hydrogen concurrently turning in toward or out away from the ring. The former motion would produce a biradical already in the right geometry to disproportionate at an originally axial β-hydrogen and so produce *trans*-enal.



The other motion would produce a biradical which would need to undergo more rotations in order for a β-hydrogen to come within bonding distance of the carbonyl. If an axial hydrogen were reached first, as is usually the case,[35] and before significant rotation occurred around the C_2–C_3 bond, *cis*-enal would be formed. It is not essential that this path be stereospecific since a small amount of *trans*-enal formed by this minor and slower pathway would not be discerned by our methodology.



Given the possibility of the first of the above motions being able to produce only *trans*-enal, it would be necessary for the rotational aspect of the phenyl ring to affect the rates of the two competing α-cleavage motions and for a *tert*-butyl group to affect the ratio of rotamers. The former possibility was discussed in the previous section. The latter is difficult to judge. In either event non-bonded interactions between *ortho* and ring hydrogens must force the minor rotamer into the cleavage pathway which twists the phenyl ring in.

The above explanation is admittedly speculative. It is presented as a basis for formulating further work, since the results themselves are not explicable by simple models.

EXPERIMENTAL

Chemicals. 2-Phenylcyclohexanone (Aldrich) was recrystallized from EtOH m.p. 55–56°. It was also prepared as described by Newman and Farbman.[36] 2-Chlorocyclohexanone was reacted with PhMgBr; the product was collected by vacuum distillation (0.2 Torr) and recrystallization from EtOH, m.p. 55–56° (lit.[36] 53–55°). Identical results were obtained with both purchased and synthesized **1**.

Cis and *trans*-**3** were prepared by the same Grignard precedure. 4-t-Butylcyclohexanol (Aldrich, 31.2 g, 0.2 mole) in 120 ml acetone was placed in a flask held in a room-temp water bath. Jones reagent[37] (50 ml) was added dropwise and the soln was stirred overnight. $NaHSO_4$ was added, after which the solution was extracted with petroleum ether. The organic phase was washed with $NaHCO_3$aq and sat NaClaq, then dried over $MgSO_4$. After the solvent had been removed, the crude 4-t-butylcyclohexanone was recrystallized from pentane, yield 22.6 g (73%).

The ketone was chlorinated as described by Allinger and colleagues.[38] Molecular Cl_2 was bubbled rapidly into a stirred 90% AcOH soln of ketone held in an ice bath. After solvent had been removed, vacuum distillation provided a mixture of the two α-chloro epimers, b.p. 98–104° (0.7 Torr). The chloroketones were reacted with PhMgBr as described by Bordwell and Yee.[11] Short path vacuum distillation at 0.05 Torr provided a fraction, b.p. 90°, which solidified upon cooling and a later fraction, 100–120°, which remained a yellow oil. This oil was chromatographed on silica gel with $CHCl_3$ as eluent and yielded first *trans*-**3** as white crystals, m.p. 78–79°. IR (CCl_4) 2955, 2860, 1735, 695 cm^{-1}; UV (cyclohexane) λ_{max} 288 nm ($\varepsilon = 80$); ^{1}H-HMR (CCl_4) δ 1.0 (s, 9H) 1.2–2.3 (m, 7H) 4.4 (d of d, 1H, J = 10, 5 Hz) 7.2 (br *s*. 5 H): MS *m/e* 230 (parent).

Later fractions yielded *cis*-**3**, also as white crystals, m.p. 82–83° (lit.[11] 81–83°). IR (CCl_4) 2950, 2860, 1715, 690 cm^{-1}; UV (cyclohexane) λ_{max} 247 nm ($\varepsilon = 265$); ^{1}H-NMR (CCl_4) δ 1.0 (s, 9H) 1.2–2.5 (m, 7H) 3.4 (d of d, 1H, J = 8, 4 Hz) 7.03 (br s, 5 H); MS *m/e* 230 (parent).

Also isolated from the earliest eluting fractions was a small amount of a clear liquid with MS *m/e* 230, 105; IR 1685 cm^{-1}; ^{1}H-NMR δ 7.9 (m, 3H) 7.5 (m, 2 H). All of these spectroscopic characteristics suggest a phenyl alkyl ketone structure.

Valerophenone was prepared by adding benzonitrile to phenyl magnesium bromide.[12] Internal standards were available from previous studies.[12] Pentadiene and 2,4-dimethyl-2,4-hexadiene (both Chemical Samples Co.) were used as received. Aldrich biacetyl was distilled before use. Aldrich 1-methylnaphthalene was used as received. Solvent benzene was acid washed and distilled.[12]

Product identification. Several 3 ml aliquots of a degassed benzene soln 1 M in **1** were irradiated at 313 nm for 56 hr at which time no **1** remained. The samples were combined and evaporated. The residue was taken up in 1 ml of benzene and chromatographed through 20 g of alumina with benzene eluent. The fourth and fifth 4 ml fractions yielded *trans*-**2**, 83% pure by GC. (The rest was identified by GC as *cis*-**2**.) IR (CCl_4) 3020, 2930, 2810, 2710, 1728, 965, 670 cm^{-1}; ^{1}H-NMR (CCl_4) δ 1.80 (m, 2H) 2.30 (m, 4H) 5.80–6.53 (m, 2H, identical to vinyl region in *trans*-1-phenylpropane) 7.24 (br s, 5H) 9.72 (tr, 1H, J = 1.5 Hz).

A GC-MS analysis of irradiated **1** showed nearly identical fragmentation patterns for both isomeric products, *m/e* 174 (M^+), 130 (M-CH_3CHO), 117 (M-CH_2CH_2CHO).

The aldehyde products from irradiation of several aliquots of 0.2 M *cis*-**3** in benzene were similarly isolated as a mixture by chromatography on silica gel with $CHCl_3$ as eluent. IR (CCl_4) 3020, 2960, 2810, 2710, 1728, 1490, 1360, 1255, 965, 685 cm^{-1}; ^{1}H-NMR (CCl_4) δ 1.15 (s, 9H) 1.4–2.6 (m, 5H) 5.3–6.75 (m, 2H, similar to a mixture of *cis*- and *trans*-1-phenyl propene) 7.33 (br s, 5H) 9.59 (tr, 1/2 H, J = 1.3 Hz) 9.72 (tr, 3/2 H, J = 1.3 Hz). The two aldehyde peaks indicated a 3:1 *trans*-**4**/*cis*-**4** ratio. For *cis* and *trans*-**2**, δ 9.67 and 9.72 are reported for the aldehydic protons.[3]

Procedures for quantitative studies were similar to those in earlier studies.[12] Samples were placed in 13 mm Pyrex tubes, degassed, sealed, and irradiated on a "merry-go-round" apparatus[39] with an alkaline chromate filter solution to isolate the 313-nm region of a mercury arc.[12] GC analysis was performed on Varian 600 or 1200 chromatographs with an Infortronics Model CRS-208 digital integrator. The reactions of **1** were analyzed on a 9 ft × 1/8 in column containing 4% QF-1 and 1.2% Carbowax 20 M on 60/80 mesh Chromosorb G at 175° with 0.005 M heneicosane as internal standard. The reactions of **3** were analyzed on a 6 ft × 1/8 in column containing 5% SE-30 on 60/80 Chromosorb W at 195°, with 0.005 M pentadecane as internal standard.

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