proportion. (b) J. Pataki, C. Duguid, P. W. Rabideau, H. Huisman, and R. G. Harvey, *J. Med. Chem.*, **14**, 940 (1971).
(3) R. G. Harvey and L. Arzadon, *Tetrahedron*, **25**, 4887 (1969). Reductive methylation of anthracene, however, furnished *cis*- and *trans*-9,10-dimethyl-DHA (4:1).
(4) D. F. Lindow, C. N. Cortez, and R. G. Harvey, *J. Amer. Chem. Soc.*, **94**, 5406 (1972).
(5) The *cis*-9,10-diisopropyl-DHA structure was initially assigned to this product in analogy with *cis*-9,10-diethyl-DHA demonstrated to arise from similar reaction. It is now clear that the *trans*-9,10-diisopropyl-DHA structure is correct on the basis of comparative nmr spectral analysis of both isomers by Zieger, *et al.*,[6] and Redford[7] and confirmed in our laboratory.
(6) (a) H. E. Zieger, D. J. Schaeffer, and R. M. Padronnagio, *Tetrahedron Lett.*, 5027 (1969); (b) D. J. Schaeffer and H. E. Zieger, *J. Org. Chem.*, **34**, 3958 (1969); (c) D. J. Schaeffer, R. Litman, and H. E. Zieger, *Chem. Commun.*, 483 (1971).
(7) D. A. Redford, Ph.D. Thesis, The University of Saskatchewan, 1967; *Diss. Abstr. B*, **28**, 4074 (1968).
(8) R. G. Harvey and C. C. Davis, *J. Org. Chem.*, **34**, 3607 (1969).
(9) H. E. Zieger and L. T. Gelbaum, *J. Org. Chem.*, **37**, 1012 (1972).
(10) R. M. Magid and S. E. Wilson, *Tetrahedron Lett.*, 4925 (1969).
(11) Thus, addition of ethyllithium to anthracene in THF at 0° or below followed by alkylation with ethyl iodide or ethyl bromide afforded >95% conversion to *cis*-9,10-diethyl-DHA.[8] These and related reactions have been repeated numerous times in our laboratory by different individuals with essentially similar results. The lower yields and stereoselectivity reported by some investigators[6] apparently reflects differences in experimental conditions.
(12) 9-*tert*-Butyl-9,10-dihydroanthracene was obtained by addition of *tert*-butyllithium to anthracene and chromatographic separation from the two *tert*-butyldihydroanthracene isomers also formed.[8,13]
(13) A. W. Brinkmann, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **92**, 5912 (1970).
(14) R. G. Harvey and H. Cho, *J. Amer. Chem. Soc.*, **96**, 2434 (1974).
(15) The chlorides are insufficiently reactive, and the iodides often provide side products.
(16) G. M. Badger, M. L. Jones, and R. S. Pearce, *J. Chem. Soc.*, 1700 (1950); A. H. Beckett and R. G. Lingard, *ibid.*, 2409 (1959); L. M. Jackman and J. W. Lown, *ibid.*, 3776 (1962).
(17) H. Zieger and D. Schaeffer, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 155.
(18) See ref 13, and references therein.
(19) Nmr analysis of the 9-isopropyl-10-methyl-DHA isomers by these techniques has been reported.[9]
(20) W. Carruthers and G. E. Hall, *J. Chem. Soc. B*, 861 (1966).
(21) The dissociation of ion pairs of 9-lithio-DHA was found to be sensitive to the presence of an alkyl group in the 9 position; *cf.* D. Nicholls and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **301**, 223 (1967).
(22) R. Lapouyade, M. Mary, H. Bouas-Laurent, and P. Labandibar, *J. Organometal. Chem.*, **34**, C 25 (1972).
(23) E. J. Panek and T. J. Rodgers, *J. Amer. Chem. Soc.*, **96**, 6921 (1974).
(24) Efficient epimerization of *trans*- to *cis*-9,10-diisopropyl-DHA with the *n*-butyllithium–TMEDA reagent was previously noted.[14]
(25) Although only contact and solvent-separated ion pairs are represented in Scheme I, completely dissociated ions may also be present, particularly in solvents such as HMPA.
(26) Association with a cation may be expected to influence charge localization within the anion distorting electron-density distribution into the region of the cation with consequent effects on ring geometry. The lithium–TMEDA complexes of aromatic dianions have been shown to exist with the metal cation located above or below the face of a puckered aromatic ring system; *cf.* J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, **94**, 7346 (1972), and references therein. It is conceivable, however, that in certain cases, ion-pair association may occur preferentially with the equatorial anion.
(27) Existence of 9-methyl-DHA as an equilibrium mixture of cis and trans conformers was previously demonstrated by nmr experiments.[13]
(28) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).
(29) Mechanism studies[4] indicate two major pathways to be competitive: (1) dialkylation of the dianion, and (2) monoprotonation by ammonia followed by alkylation, proton abstraction, and a second alkylation. Alkylation at the radical anion stage appears less important.
(30) The facile isomerization of 9,10-diisopropylanthracene to the thermodynamically more stable 9-isopropylidene-9,10-dihydroanthracene reported in the accompanying paper[31] may conceivably occur prior to reduction.
(31) H. Cho, R. G. Harvey, and P. W. Rabideau, *J. Amer. Chem. Soc.*, **97**, 1140 (1975).
(32) R. G. Jones and H. Gilman in "Organic Reactions," Vol. VI, R. Adams, Ed., Wiley, New York, N.Y., 1951, Chapter 7.
(33) P. W. Rabideau and J. W. Paschal, *J. Amer. Chem. Soc.*, **94**, 5801 (1972).
(34) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, Elmsford, N.Y., 1965, p 392.
(35) Maximum coupling from the aromatic protons to the benzylic protons is observed for a dihedral angle of 90°; *cf.* ref 13, and references therein.

Retention of Configuration at the Migrating Atom in the Photochemical 1,3-Allylic Shift of a Benzyl Group[1]

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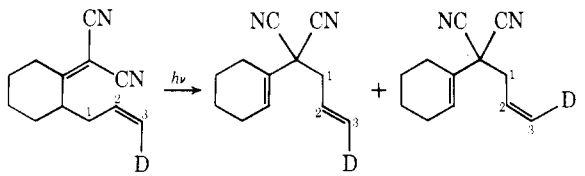
Abstract: 3-Phenylcyclohexylidenemalononitrile was synthesized and rearranged photochemically to the nonconjugated isomer, 2,2-dicyano-1-methylene-3-phenylcyclohexane. The investigation concentrated mainly on stereochemical aspects in order to confirm the mechanism detected previously for such allylic and diallylic rearrangements. With the help of a methyl marker at C-5 of the cyclohexyl moiety, both stereoisomers of 5-methyl-3-phenylcyclohexylidenemalononitrile were isolated. Both the cis and the trans isomers were photolyzed separately under identical conditions. The photoproducts, isolated by column chromatography, were confirmed by spectroscopic evidence as cis and trans isomers of 2,2-dicyano-1-methylene-5-methyl-3-phenylcyclohexane, respectively. The degradation of the trans photoproduct and the *trans*-3-methyl-5-phenylcyclohexanone gave *trans*-3-methyl-5-phenylpimelic acid. Condensation of 3-phenylcyclohexanone with methyl cyanoacetate gave a mixture of cis and trans products. One pure geometrical isomer was isolated and photolyzed. The photoproduct was identified as a mixture of two stereoisomers of 2-carbomethoxy-2-cyano-1-methylene-3-phenylcyclohexane. The recovered starting material from incomplete rearrangement also lost its geometrical purity. Synthesis and condensation of 2-methyl-3-phenylcyclohexanone with malononitrile afforded only the cis isomer. The photoproducts of the pure cis isomer was confirmed by nmr as one isomer with the methyl at the exocyclic double bond being trans to the nitrile groups. 3-Phenylcyclohexylidenemalononitrile was found to be quite stable to sensitized photolysis; thermal treatment of the photoproduct failed to reverse the photochemical rearrangement.

Cookson and coworkers have discovered that during the photochemical rearrangement of the diallyl derivatives of the 1,5-hexadiene system only one allyl group undergoes 1,3 shift.[2a] This simple fact draws attention to the possibility of a concerted 1,3 shift in the excited state rather than dissociation into a pair of radicals followed by recombination. The complete lack of inversion of the migrating allyl group has also been demonstrated by the photolytic reaction **1** → **2**, **1** being a stereospecifically deuterated diallyl derivative.[2b] The cis–trans equilibration in the product seems to be an integral part of the rearrangement. This photochemical rearrangement is thermally reversible, however, with the in-

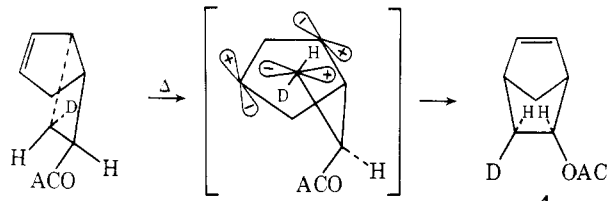


1 2

version of the allyl group occurring as in all Cope rearrangements.

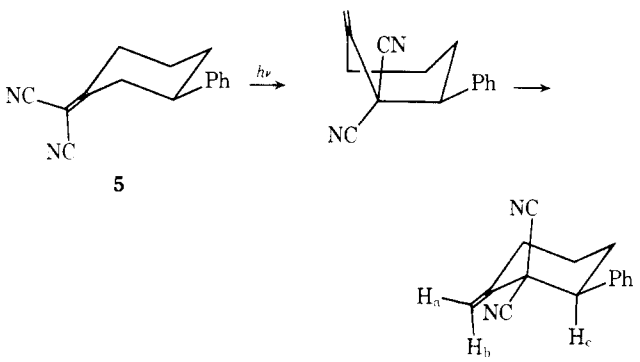
The stereochemical aspects of the 1,3-allyl shift can be clarified by following Woodward and Hoffmann's predictions[3] based on the symmetry of the orbitals of the allyl radical, shown in Figure 1. As illustrated in Figure 2, since the orbital of highest energy in the excited state ψ_3 is symmetric about the mirror plane normal to the allyl group, a saturated carbon can undergo a 1,3 shift while retaining bonding by simply presenting the same face to the allyl group throughout the movement. The same process in the ground state, however, would have to proceed through a transition state with the symmetric alkyl carbon orbital overlapping the antisymmetric allyl orbital ψ_2. Bonding can be maintained only by a clockwise rotation of the alkyl carbon atom through 90° in going to the transition state, continuing through another 90° to reach the product. In short, a concerted 1,3-allyl shift should result in inversion of configuration of the migrating alkyl group in the thermal rearrangement but retention in the photochemical rearrangement.

The following example by Berson and Nelson[4] of thermal rearrangement, **3** → **4** where deuterium trans to the acetoxy group becomes cis in the product, emphasizes the value of orbital symmetry in understanding concerted reactions.



3 4

In the course of our investigation, we have photolyzed 3-phenylcyclohexylidenemalonitrile where the benzene ring has replaced the nonconjugated double bond in a system similar to **1**.[5] Such a framework (**5**) with slight modification has proved quite useful in elucidating the stereochemical fate of all the centers involved. In fact, our findings through the stereochemical test of Woodward and Hoffmann's prediction based on molecular-orbital symmetry combined with the information supplied by previous investigators have made it possible to depict a clear mechanistic picture of the photochemical allylic and diallylic rearrangement.



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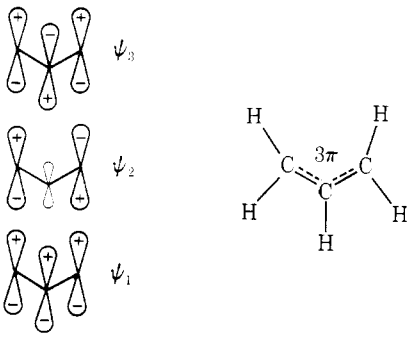


Figure 1.

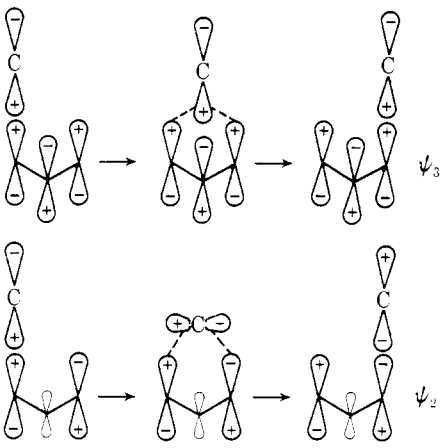
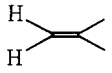


Figure 2.

Results and Discussion

3-Phenylcyclohexylidenemalononitrile (**5**) was synthesized from 3-phenylcyclohexanone in very good yield according to the method of Cope and Hoyle.[6] Catalytic hydrogenation of 5-phenyl-2-cyclohexenone on 10% palladium/charcoal gave 3-phenylcyclohexanone in excellent yield.

Photolysis of the dicyano derivative **5** in ethanol through silica gave a thick oil which was subjected to column chromatography on silica gel. The photoproduct was isolated by elution with 5% ether in petroleum ether (40–60°) as a crystalline solid material, mp 79–80°. The yield was 12%. The photoproduct was characterized by spectral evidence and elemental analyses as 2,2-dicyano-1-methylene-3-phenylcyclohexane (**6**). The infrared spectrum of **6** had a strong absorption at 925 cm^{-1} due to the out-of-plane bending of the exocyclic system



along with a moderately strong double bond stretching at 1640 cm^{-1}. The strong absorption due to the conjugated nitrile groups of **5** at 1600 and 2200 cm^{-1} became weaker and shifted to 2300 cm^{-1}, characteristic of nonconjugated nitrile absorption. The nmr data ($CDCl_3$) given in Table I also supported structure **6**. Analysis of the peaks centered at 2.9 ppm shows that the benzylic proton H_c by coupling with the adjacent axial proton at C_4 gives a doublet (J = 12 Hz). Further coupling with the equatorial proton at C_4 splits each line of the doublet resulting in two doublets (J = 4 Hz). The order of magnitude of the coupling constants is in

Table I

Proton	Multiplicity	Chemical shift (δ), ppm	Coupling constant, Hz
Aromatic	Multiplet	7.3	
H_a	Singlet	5.18	
H_b	Singlet	5.50	
H_c	Doublets of a doublet	2.90	J_{aa} = 12 J_{ea} = 4

agreement with the axial orientation of H_c in **6**. Two olefinic protons in **6** can be easily distinguished in the nmr spectrum. The one cis to the nitrile group is strongly deshielded, and this accounts for the greater downfield chemical shift at 5.5 ppm for the proton H_b.

Elution with 10% ether in petroleum ether (40–60°) afforded another fraction of crystalline solid which was identified as the starting material **5**. The rest of the material was polymeric gum.

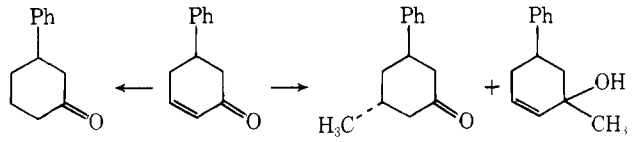
Having achieved the anticipated result based on a 1,3-allyl shift, we directed our attention to the stereochemical aspects of such a rearrangement. Previous investigators ruled out the possibility of cleavage into a pair of radicals followed by recombination within an efficient narrow solvent cage as a mechanism. The only alternative path seems, therefore, to be a concerted, electrocyclic, 1,3 shift. As stated already, according to Woodward and Hoffmann's orbital symmetry rules for such electrocyclic reactions involving 1,3 shift, we should be able to see the retention of stereochemistry for the photochemical and the inversion of stereochemistry for the thermal rearrangement. With this end in view, we concentrated first on testing the stereochemistry at the benzylic end of the system **5**.

With the help of a methyl marker at C-5 of the cyclohexyl moiety of **5**, the stereoisomers of the dinitrile derivatives of 3-methyl-5-phenylcyclohexanone were isolated. Each isomer was photolyzed separately under identical conditions.

Besides the ease of synthesis and structural simplicity for spectral analyses, the merit of such a choice lies in the fact that the methyl marker at C-5 is absolutely inert toward any photochemical or thermal rearrangement involving a 1,3-allyl shift. The readily available 3-methylcyclohexanone was condensed with malononitrile, and photolysis of the dinitrile derivative under conditions similar to those above gave a polymer. Any structural change at the benzylic end during the rearrangement should, therefore, be easily detectable by simply comparing the orientation of the phenyl at C-3 with respect to the methyl at C-5 in the starting isomers as well as products derived therefrom.

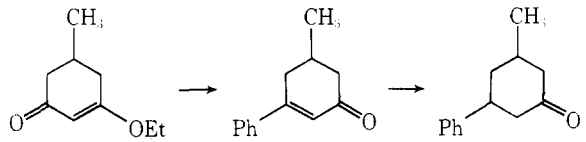
Since the cis isomer is the thermodynamically more stable one, the trans isomer is not obtained in good yields by methods leading to thermodynamically controlled products. For the synthesis of *trans*-3,5-dimethylcyclohexanone, Allinger and Riew[7] considered the Michael addition of methylmagnesium iodide to readily available 5-methyl-2-cyclohexenone. Addition of methylmagnesium iodide (1.1 mol) to 5-methyl-2-cyclohexenone (1 mol) in ethyl ether in the presence of cuprous chloride (1 mol %) gave 3,5-dimethylcyclohexanone in 55–65% yield. Vapor-phase chromatography and comparison with authentic sample showed that the ketone contained 94–96% of the trans isomer and 4–6% of the cis isomer.

Following a similar procedure where methylmagnesium iodide was added to 5-phenyl-2-cyclohexenone, we had more encouraging results. Sixty-seven per cent of the overall yield came from 1,4 addition, and the product by vpc was shown to consist of only one isomer to which we assigned a trans stereochemistry following the arguments of Allinger and Riew.



8 **7** **9** **10**

Perhaps the bulky phenyl group was responsible for the better outcome. To synthesize the cis isomer of **9**, reaction 1



(1)

11 **12** **13**

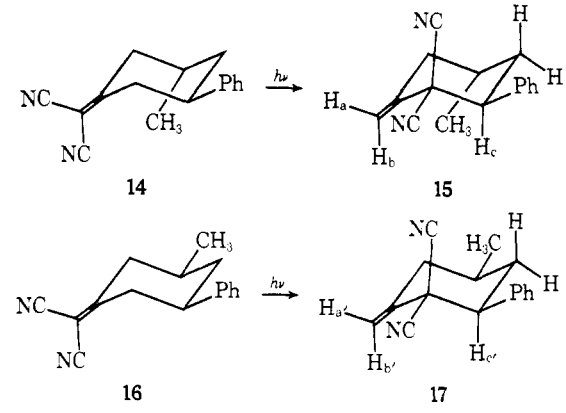
was carried out successfully. The enol ether **11** was prepared in 75% yield by azeotropic reflux of 5-methyl-1,3-cyclohexanedione in benzene and absolute alcohol in presence of *p*-toluenesulfonic acid. Treatment of the enol ether **11** with phenyllithium afforded **12** in 90% yield. Vpc analysis of the catalytically reduced product of **12** was found to be a mixture of cis and trans isomers in the ratio 1:1. Attempts to separate by thin-layer and column chromatography were unsuccessful. The retention period of both the isomers in vapor-phase chromatography was too close to make use of preparative chromatography for complete separation. The semicarbazone derivative of **13** melted over a wide range. Separation of the two isomers by fractional crystallization of this derivative proved impossible.

Condensation of the pure trans ketone with malononitrile gave crystalline solid, mp 90–91°, and was characterized by both spectral evidence and elemental analyses.

The catalytically reduced product **13** was also condensed with malononitrile under similar experimental conditions. Work-up in the usual way gave a viscous yellow oil (1.5 g). The crude oil was crystallized from ether and petroleum ether (40–60°), mp 65–72°. Fractional crystallization from methanol afforded colorless needle-shaped crystals (500 mg) with mp 74–75°; mmp (with the trans dinitrile derivative) 55–69°. Tlc on alumina indicated this fraction to be a single isomer but different from the trans derivative. The fraction with mp 74–75° must, therefore, be the cis isomer.

Both the isomers were photolyzed separately under identical experimental conditions. The photoproducts were isolated by column chromatography and characterized by spectral evidence. **14** rearranged to **15** in 9% yield and **16** to **17** in 12% yield (Scheme I). The nmr data (in $CDCl_3$) of **15**

Scheme I



14 **15**

16 **17**

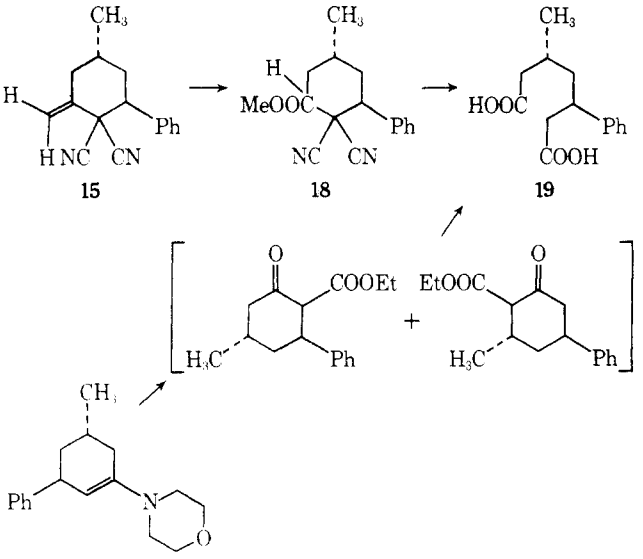
Table II

Proton	Multiplicity	Chemical shift (δ), ppm	Coupling constant, Hz	Photo-product
Aromatic	Multiplet	7.32		
H_a	Singlet	5.21		**15**
H_b	Singlet	5.63		
H_c	Doublets of a doublet	3.23	$J_{aa} = 12$ $J_{ea} = 3$	
C-5 methyl	Doublet	0.96	$J = 6$	
Aromatic	Multiplet	7.4		
$H_{a'}$	Singlet	5.24		
$H_{b'}$	Singlet	5.56		
$H_{c'}$	Doublets of a doublet	3.03	$J_{aa} = 10$ $J_{ea} = 6$	**17**
C-5 methyl	Doublet	1.06	$J = 6$	

and **17** are given in Table II. Clearly long-lived diradical intermediates are ruled out by the stereospecific rearrangement of **14** to **15** and **16** to **17**, although there is obvious possibility of such rearrangement *via* diradicals. The presence of one and only one isomer in each photoproduct was confirmed by tlc and nmr spectra of the crude photoproducts. The mixture melting point of **15** and **17** is 50–60°, and their individual melting points are 71–72 and 95°, respectively.

The complete retention of stereochemistry at the benzylic end during the photochemical rearrangement was also proved unequivocally through the chemical degradation of Scheme II. The trans photoproduct **15** was subjected to

Scheme II



ozonolysis. During the reductive hydrolysis with zinc and water, the ozonized product was converted in high yield to a methyl ester (**18**) in the presence of formic acid produced as a by-product and of methanol as a solvent. The crystalline ester **18** was converted by acid hydrolysis into **19** as a high-melting amorphous solid, mp 180°. This yield was nearly quantitative. The structure was confirmed by spectral evidence and elemental analyses. The molecular ion at 232 in the mass spectrum corresponds to the anhydride of the dibasic acid **19.**

Large-scale preparation of the photoproduct **15** was difficult because of poor yield in the photolysis and tedious isolation of the photo isomer by chromatography on a tightly packed column. Therefore, efforts were directed to the conversion of the easily available pure trans ketone **9** into the dibasic acid **19.**

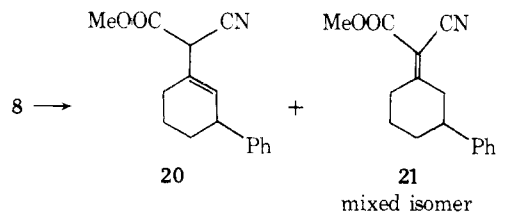
The morpholine enamine was prepared easily following the method of Stork, *et al.*[8] The infrared spectrum of the crude product had strong absorption at 1640 cm^{-1} due to the double bond stretching of the enamine. The absorption at 1700 cm^{-1} due to the carbonyl of the starting ketone completely disappeared. The crude enamine was treated with ethyl chloroformate in freshly distilled sodium-dried ethanol. The use of ethanol as solvent maintained the homogeneity of the reaction mixture throughout.

Basic hydrolysis of the crude acylated product[9] gave a solid compound in 40% yield. The melting point was 180°; the mixture melting point with **19** had no depression. The infrared spectrum in Nujol mull was superimposable on that of **19.** The mass spectrum had a molecular ion at 232, and the fragmentation pattern was identical with that of **19.**

Ozonolysis of **17** followed by acid hydrolysis of the crude product afforded another solid material, mp 115°; mixture melting point with **19** was 105–111°. The molecular ion corresponded to the anhydride with *m/e* 232.

The successful results in testing the stereochemical fate of photochemical rearrangement of the benzylic end encouraged us to explore the stereochemical situation at both ends of the allylic group.

One end of the allylic group in the system of our study has been doubly substituted with cyano groups throughout the investigation. It is impossible to notice any change suffered during the rearrangement at the extreme allylic end when both the substitutents are equivalent. It was planned, therefore, to condense 3-phenylcyclohexanone with an unsymmetrical XCH_2Y-type reagent, isolate the resulting geometrical isomers and photolyze each isomer of known geometry separately under identical experimental condition. Condensation of **8** with methyl cyanoacetate gave a mixture of **20** and **21,** characterized by infrared analysis. **20**

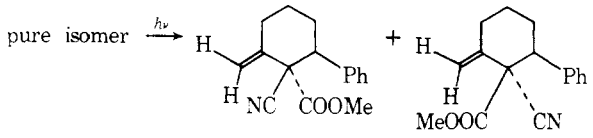


was separated from **21** by fractional distillation as a colorless mobile liquid, bp 140° (0.7 mm), which constituted 20% of the total product. The major product was a high-boiling [bp 170° (0.7 mm)] viscous liquid with infrared absorptions at 700, 760, 1220, 1600 (s), 1720, and 2250 (s) cm^{-1}. This fraction was shown by nmr to consist of a mixture of the geometrical isomers in the ratio of 2:1. The nmr spectrum had two distinct methoxy signals at τ 6.32 and 6.28. Crystallization of the viscous liquid product (1.2 g) from ethyl acetate gave a low melting solid, mp 75–83°, which upon fractional crystallization from methanol yielded a pure fraction (400 mg), mp 84–85°. Nmr analysis clearly indicates this fraction to consist of a single component with a sharp methoxy signal at τ 6.21. Attempts to isolate the other isomer from the mother liquor were not successful. Correct assignment of geometry is difficult when only one isomer is available.

The photoproduct from the pure isomer was isolated as an oil in 12% yield by column chromatography on silica gel with 5% ether in petroleum ether (40–60°). The oil could not be crystallized. Nmr analysis indicated the photoproduct to be a mixture of two stereoisomers of 2-carbomethoxy-2-cyano-1-methylene-3-phenylcyclohexane. Some of the most characteristic signals in the nmr spectrum of **22**

Table III

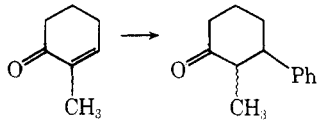
Proton	Multiplicity	Chemical shift (δ), ppm
Methoxy	Singlet	3.38
	Singlet	3.42
Olefinic	Singlet	4.65
	Singlet	4.98
	Singlet	5.05
	Singlet	5.43



22

were as shown in Table III. The infrared spectrum of **22** has absorptions at 700, 760, 920 (s), 1200–1235, 1600, 1640, 1735, and 2300 (w) cm^{-1} in agreement with the structure. The recovered starting material from incomplete rearrangement also lost its geometrical purity. The nmr spectrum showed two singlets at τ 6.32 and 6.28 indicating two different methoxy groups resulting from cis–trans equilibration. Such an observation suggests that the cis–trans equilibration is faster than the 1,3-allylic shift leading to the photoproducts. As a result, no conclusion regarding the stereochemical fate of the rearrangement **21** → **22** could be drawn at the substituted end of the allyl group.

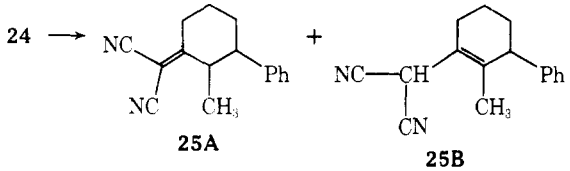
In order to test the stereochemistry of the C-1 atom of the allyl group, efforts were directed toward the synthesis of 2-methyl-3-phenylcyclohexanone. Conjugate addition of phenylmagnesium bromide to 2-methyl-2-cyclohexenone afforded the desired ketone in 33% yield. The ketone **24** was



23 **24**

shown by vpc to consist of only one isomer, most probably the thermodynamically more stable trans isomer. The 2,4-dinitrophenylhydrazone of **24** melted at 220–221°, and its elemental analyses were in agreement with structure **24.**

Condensation of **24** with malononitrile gave a viscous liquid which solidified upon standing at room temperature, mp 60–80°. The infrared spectrum of the crude solid had absorptions at 1600 (s), 1630 (w), 2200 (s), and 2300 (w) cm^{-1}. Nmr analysis of the product indicated **25** to be a mixture of **A** and **B.** Perhaps steric interference of the equa-



25A **25B**

torial methyl with nitrile groups makes the trans isomer of **25A** unstable and, in the presence of ammonium acetate used as a catalyst in the condensation reaction, it may rearrange to **25B.** One pure isomer of mp 90–91° was isolated from the mixture by fractional crystallization. The nmr data given in Table IV clearly point out the cis stereochemistry of the methyl group at C-2 with respect to the phenyl at C-3 in **25A.**

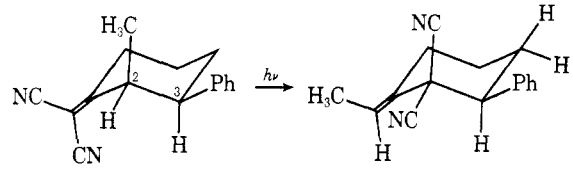
The analysis of peaks centered at 3.35 ppm shows that

Table IV

Proton	Multiplicity	Chemical shift (δ), ppm	Coupling constant, Hz
Aromatic	Multiplet	7.16	
C-2 H	Double quartets	3.22–3.48	$J = 4$
C-3 H	Multiplet	2.82–3.02	
Methyl	Doublet	1.15	$J = 6$

C-2 H by coupling with the methyl protons gives a quartet (J = 6 Hz). Further coupling with C-3 H should split each line of the quartet into two, resulting in eight lines (J_{HH} = 4, J_{HCH_3} = 6 Hz). The order of magnitude of the coupling constant J = 4 Hz is in agreement with the cis stereochemistry of the two protons C-2 H and C-3 H. In other words, the methyl at C-2 must be axial and cis to the phenyl at C-3 in **25A.**

The pure cis isomer was photolyzed as before, and the photoproduct was isolated as usual by column chromatography in silica gel. The yield of crystalline solid, mp 101–102°, was 25%. The infrared spectrum in Nujol had absorptions at 705, 775, 890, 1600 (w), and 2300 cm^{-1}. The nmr spectrum of the photoproduct was in excellent agreement with the structure **26.** Besides proving the existence of only

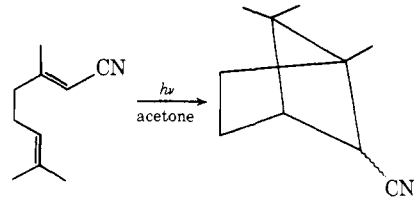


25A **26**

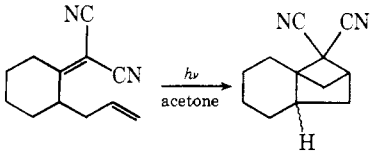
one isomer, the chemical shift of the olefinic proton is in agreement with the cis olefinic proton of the photoproduct of 3-phenylcyclohexylidenemalononitrile. It was mentioned in connection with the nmr analysis of the photoproduct **6** that the olefinic proton cis to the nitrile groups is deshielded relative to the trans proton. The nmr spectrum of **26** supports trans orientation of the methyl group at the exocyclic double bond with respect to the nitrile groups. Although such an observation clearly indicates the absence of stereochemical change at the C-1 atom, no rigorous conclusion can be drawn regarding retention of stereochemistry at C-1 of the allyl group in the photochemical 1,3-allyl shift of a benzyl group based on the result of one isomer only.

The cis photo isomer **17** was subjected to pyrolysis at different temperatures. The photoproduct was quite stable up to 450°. Pyrolysis at higher temperatures converted it into a black tar. It was not possible, therefore, to test the inversion of stereochemistry predicted by Woodward and Hoffmann's rule for such a 1,3-allylic shift.

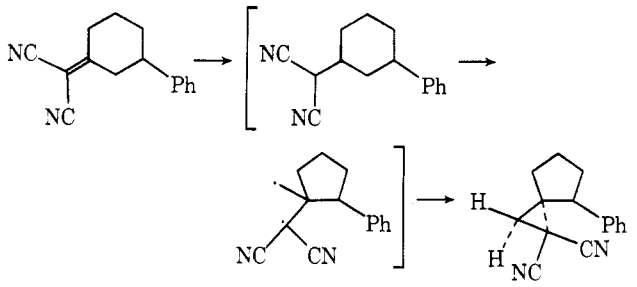
It has been observed[5] that triplet photosensitizers, such as acetone, divert the reaction of geranonitrile from allylic rearrangement to cyclobutane formation giving the two epimers of 1,6,6-trimethylbicyclo[2.1.1]hexane-5-carbonitrile. Irradiation of **1** in acetone gave the tricyclic cyclobu-



tane isomer in high yield.[2] The different electronic nature



of the excited state appears to be responsible for the different photoproduct from the same starting isomer. Similar rearrangement in our system (**5**) would necessitate disruption of the benzene ring, and a cyclobutane derivative cannot be expected. But on the basis of literature reports for β,γ-unsaturated ketones,[10-12] we were curious as to whether the following sequence involving a 1,2 shift would occur when 3-phenylcyclohexylidenemalononitrile was irradiated



in acetone. The observation of such an experiment was interesting. **5** was found to be quite stable in acetone but rearranged to **6** in ethanol under identical conditions. It is quite tempting for us to suppose, therefore, that for the rearrangement of **5** to **6**, the triplet excited state is not the reactive species. $\pi \rightarrow \pi^*$ transition involving the excited singlet state appears to be responsible for the photochemical 1,3-allylic shift.

Experimental Section

Microanalyses were determined by Dr. H. Bieler (Vienna). Melting points (mp) were not corrected. Infrared spectra (ir) were recorded on a Unicam S.P. 200 spectrophotometer. Solids were run as Nujol mulls and liquids as thin films. Strong and weak intensities are denoted by (s) and (w), respectively. Ultraviolet (uv) spectra were recorded on a Unicam S.P. 800 spectrophotometer in 95% ethanol. The nuclear magnetic resonance (nmr) spectra were recorded on a Varian Associates A-60 and 100-MHz instruments using tetramethylsilane as an internal standard. Resonance positions are expressed as τ values. Column chromatography was performed on silica gel (Silica Gel, Ltd.) without special preparations. Thin-layer chromatography (tlc) plates were prepared using Kieselgel C (Woelm) or alumina (BDH) by the method of Randeroth.[13] Analytical vapor-phase chromatography (vpc) was performed on a Perkin-Elmer F11 model. Mass spectra were recorded on a MS12 spectrometer. Ultraviolet irradiations were performed by an air-cooled Rayonet photochemical reactor (8 × 8 W, 254 nm) in a silica tube of 125-ml capacity unless otherwise stated.

3-Phenylcyclohexanone (8). A solution of 5-phenyl-2-cyclohexenone (5 g, 30 mmol) in absolute ethanol (100 ml) was hydrogenated at atmospheric pressure using 10% Pd/C (100 mg). Filtration of the catalyst and removal of solvent gave a product which was heated to reflux with 5% aqueous hydrochloric acid (10 ml) in acetone (20 ml) for 2 hr in steam bath. Acetone was removed with a rotary evaporator. The aqueous layer was extracted with ether. The ether layer was washed with 5% sodium bicarbonate solution and water and dried over magnesium sulfate, and the ether was evaporated. The crude product was distilled under reduced pressure: yield 4.2 g (85%); bp 110-111° (0.5 mn); ir (film) 697, 752, 1600, and 1704 cm^{-1}; mp of the dinitrophenylhydrazone derivative 188-189°.

Anal. Calcd for the derivative $C_{18}H_{18}O_4N_4$: C, 61.01; H, 5.12; N, 15.81. Found: C, 60.90; H, 4.97; N, 15.65.

3-Phenylcyclohexylidenemalononitrile (5). **8** (1.7 g, 10 mmol) was condensed with malononitrile (15 mmol) according to the method of Cope and Hoyle.[6] The product distilled over as a thick, viscous liquid at 170° (0.5 mm) and solidified on standing at room temperature. It was recrystallized from ether and petroleum ether (40-60°): yield 1.8 g (82%); mp 69-70°; ir (Nujol) 700, 750, 1600 (s), 2240 (s) cm^{-1}; uv λ_{max} ethanol 239 nm (ϵ 9800).

Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.85; H, 6.15; N, 12.75.

Photolysis of the Dinitrile Derivative (5). One gram of **5** was taken in freshly distilled anhydrous ethanol (70 ml). The solution was degassed by repeated evacuation, and the sealed tube was irradiated. The photolysis was followed by recording the ir of aliquots drawn at regular intervals of 6 hr and stopped after 24 hr. The crude product was chromatographed on a column of silica gel. The photoproduct was isolated by eluting in 5% ether in petroleum ether (40-60°) and identified as **6**: yield 100 mg (10%); mp 79-80°.

Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.95; H, 6.21; N, 12.70.

***trans*-3-Methyl-5-phenylcyclohexanone (9).** Phenylmagnesium bromide prepared from magnesium (2.65 g, 0.11 mol) was added dropwise to 5-phenyl-2-cyclohexenone (17.2 g, 0.1 mol) in ether in the presence of cuprous chloride (1 mol %) with stirring in a nitrogen atmosphere at *ca.* −10°. After reaching room temperature, the reaction mixture was refluxed for 1 hr. It was cooled and treated with a saturated solution of aqueous ammonium chloride neutralized with ammonium hydroxide. The ether layer was separated, and the aqueous layer was extracted with ether. The combined ethereal layers were washed repeatedly with water and dried over magnesium sulfate, and the ether was removed with a rotary evaporator. The desired product was purified through the formation of a semicarbazone derivative, mp 179-180°, yield 12 g.

Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.72; H, 8.10; N, 17.23.

Hydrolysis of the semicarbazone with 10% aqueous hydrochloric acid regenerated the pure ketone **13**: bp 120° (1 mm); yield 9 g (50%); ir (thin film) 700, 760, 1240, 1600, 1700 cm^{-1}; nmr ($CDCl_3$) 9.07 (3, doublet, J = 6 Hz), 6.75 (benzylic proton, multiplet), 2.84 (aromatic protons, singlet).

Dinitrile derivative of (9) was prepared by refluxing for 48 hr a mixture of the ketone **9** (1.869, 10 mmol) with malononitrile (15 mmol) in benzene azeotropically. Work-up in the usual way gave **14** in 80% yield: mp 90-91°; ir (Nujol) 705, 765, 1240, 1600 (s), 2210 (s) cm^{-1}; uv λ_{max} (ethanol) 239 nm (ϵ 9800); nmr ($CDCl_3$) 8.93 (3, doublet, J = 6 Hz), 8.2-6.9 (8), 2.8 (5, singlet).

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.52; H, 6.84; N, 11.79.

5-Methyl-3-phenyl-2-cyclohexenone (12). A solution of the enol ether of **11** (15.3 g, 0.1 mol) in anhydrous ether (20 ml) was added dropwise to phenyllithium prepared from lithium metal (1.8 g, 0.15 mol) in ether (50 ml). The reaction flask was immersed in an ice-water bath during the addition. The reaction mixture was filtered to get rid of free lithium metal, if any, and the filtrate was poured slowly with stirring into a beaker of ice containing concentrated sulfuric acid (20 ml). The ether layer was separated, and the aqueous layer was extracted with ether. The combined ether layers were washed with 5% aqueous sodium bicarbonate solution and water and dried over anhydrous magnesium sulfate, and the ether was evaporated in a rotary evaporator. The desired product distilled at 150° (2.5 mm) as a viscous liquid that solidified upon standing at room temperature: yield 17.5 g (90%); mp 34-35°; uv λ_{max} (ethanol) 284 nm (ϵ 12,800); ir (Nujol) 695, 750, 1580, 1600, and 1645 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.91; H, 7.61.

Catalytic hydrogenation of **12** in ethanol using 10% Pd/C in the presence of 3 *N* hydrochloric acid (2 ml) gave the desired product which was purified by forming a semicarbazone derivative, mp 152-170°. Hydrolysis of the semicarbazone with 10% aqueous hydrochloric acid regenerated the ketone.

Anal. Calcd for the semicarbazone $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.39; H, 7.65; N, 17.20.

***cis*-5-Methyl-3-phenylcyclohexylidenemalononitrile (16)** was prepared similarly to **14**; the refluxing period was 24 hr. The product was crystallized from ether and petroleum ether (40-60°), mp 65-72°. Fractional crystallization from methanol gave a pure product **21**, mp 74-75°, mmp with **19** 55-65°; ir (Nujol) 697, 760, 859, 1600, and 2200 cm^{-1}; uv λ_{max} (ethanol) 237 nm (ϵ 11,000);

nmr ($CDCl_3$) 8.89 (3, doublet, J = 6 Hz), 8.2–6.9 (8), 2.82 (5).

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.50; H, 6.90; N, 11.65.

Photolysis of the stereoisomers 14 and 16 and isolation of the photoproduct from each were carried out as described previously in the case of **5**.

Photoproduct from **14**; yield 9%; mp 71–72°; ir (Nujol) 700, 729, 765, 930, 1600 (w), 1645, and 2230 (w) cm^{-1}.

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.50; H, 7.00; N, 11.68.

Photoproduct from **16**: yield 12%; mp 95°; ir (Nujol) 695, 760, 870, 920, 1600 (w), 1640, and 2230 cm^{-1}.

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.45; H, 7.09; N, 11.67.

Ozonolysis of the Trans Photoproduct 15. The trans photoproduct (200 mg, 1 mmol) was taken in a mixture of anhydrous methanol (30 ml) and Analar chloroform (5 ml). Ozone was bubbled through gently until the solution turned blue. After reductive hydrolysis with zinc dust (100 mg) and water (125 ml), the reaction mixture was filtered. The residue was washed with methanol. The filtrate and the washings were combined, and most of the methanol was removed in a rotary evaporator. The aqueous layer was extracted with ether. The ether layer was washed with 2% sodium carbonate solution and water. After drying over anhydrous magnesium sulfate, the ether was evaporated. The residue was a crystalline solid: yield 160 mg (70%); mp 88°; ir (Nujol) 720, 800, 1170–1210, 1600, 1725, and 2300 cm^{-1}; nmr ($CDCl_3$) 9.07 (3, doublet, J = 7 Hz), 1.8–1.75 (5), 6.74 (1, multiplet), 6.34 (3, singlet), 6.05 (doublet, J = 6.5 Hz), 2.60 (5, singlet).

Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.95; H, 6.67; N, 10.45.

Acid Hydrolysis of the Ozonized Product 18. The ester **18** (150 mg, 0.55 mmol) was taken in a mixture of acetic acid (7 ml), concentrated hydrochloric acid (7 ml), and water (7 ml). The solution was heated on a steam bath for 48 hr; then it was poured into a beaker of crushed ice. The precipitated solid was filtered, washed thoroughly with water, and dried in a vacuum desiccator: yield 120 mg (86%); mp 180°; ir (Nujol) 700, 770, 1700, and 1720, 3400 cm^{-1}; mass spectrum 232 (M^+), 204, 173, 144, 131, 107, 91, and 77.

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.20; H, 7.25. Found: C, 66.95; H, 7.40.

Acylation of the Trans Ketone 9 with Ethyl Chloroformate. The morpholine enamine of **9** was prepared following the procedure of Stork, *et al.*[8] The crude enamine (1 mmol) was placed in a three-necked flask in freshly distilled sodium-dried ethanol (100 ml). To this, while stirred and cooled by ice-cold water, was added ethyl chloroformate (1.5 mmol) in anhydrous ethanol (10 ml). The reaction mixture was refluxed for 24 hr. The solvent was removed under reduced pressure. The residue was treated with 10% aqueous hydrochloric acid (20 ml) for 30 min at room temperature and extracted with ether. The ether layer was washed with water, dried over magnesium sulfate, and evaporated. The crude oil showed a characteristic band of β-keto ester in ir and gave positive ferric chloride test.

Basic hydrolysis[13] of the crude acylated product gave **19**: yield 20%; mp 180°; mass spectrum 232 (M^+).

Pyrolysis of the Cis Photoproduct 17. The photoproduct (100 mg) was placed in a small glass tube which was flushed with nitrogen and sealed. The glass tube was put in a steel jacket and placed in a preheated oven at 200° for 2 hr. After work-up, the dinitrile was recovered unchanged. The photoproduct was found to be quite stable up to 450°. Pyrolysis at higher temperatures converted it into a black tar.

Photolysis of 3-Phenylcyclohexylidenemalononitrile in Acetone. Compound **5** (1 g) was dissolved in Analar acetone (70 ml) and irradiated following the same conditions described previously for the photolysis of the ethanolic solution of **5**. The aliquots drawn at regular intervals were analyzed by ir and nmr as unchanged starting material. Repetition of this experiment using longer periods of irradiation also failed to produce any change.

Condensation of Methyl Cyanoacetate with 3-Phenylcyclohexanone. A mixture of 3-phenylcyclohexanone (5.4 g, 30 mmol), methyl cyanoacetate (3.6 g, 40 mmol), benzene (150 ml), and ammonium acetate (100 mg) was heated to reflux under a Dean-Stark trap for 12 hr. Ammonium acetate was added intermittently in 20-mg portions. The reaction mixture was diluted with ether, and the combined organic layer was washed thoroughly with water and dried over magnesium sulfate. Evaporation in a rotary evaporator gave a yellow liquid which was fractionally distilled under reduced pressure. The desired product distilled at 183° (0.7 mm), yield 3.8 g. Treatment with ethyl acetate afforded crystalline material (1.8 g), mp 65–75°. Fractional crystallization from methanol gave a pure fraction (400 mg), mp 84–85°, which was identified by nmr analysis as one isomer only: uv λ_{max} (ethanol) 239 nm (ϵ 11,320).

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.25; H, 6.71; N, 5.49. Found: C, 75.10; H, 6.55; N, 5.60.

Preparation of the Enol Chloride of 2-Methyl-1,3-cyclohexanedione.[14] Dione (13.49 g, 0.1 mol) was added to phosphorus trichloride (30 g, 0.22 mol) in anhydrous chloroform (30 ml). The suspension, while heated on a steam bath for 2 hr, gradually went into solution. Most of the chloroform was distilled off. Ice-cold water was added to the residue which was extracted with ether. The ether layer was washed with aqueous potassium hydroxide (5%) twice and water once and carefully dried over calcium chloride. After removal of the ether, the product was distilled under reduced pressure: yield 10.7 g (78%); bp 80° (3.5 mm).

Sodium Borohydride Reduction of the Enol Chloride. Sodium borohydride (760 mg, 20 mmol) was added portionwide to a solution of the enol chloride (6 g, 40 mmol) in 2-propanol (30 ml) containing water (3 ml). The mixture was left at room temperature overnight. The reaction mixture was diluted with water and extracted with ether. The ether layer was dried over magnesium sulfate and evaporated. The residue was a colorless solid, recrystallized from chloroform: yield 5.29 g (87%); mp 68–69°; ir (Nujol) 1660 (s) and 3300 cm^{-1}.

Anal. Calcd for $C_7H_{11}OCl$: C, 57.33; H, 7.50; Cl, 24.23. Found: C, 57.20; H, 7.37; Cl, 23.40.

2-Methyl-2-cyclohexenone (23). The alcohol (5 g, 40 mmol) was added in small portions to 75% sulfuric acid (20 ml) at 0° and then stirred at room temperature overnight. The pink-colored solution was poured into a beaker of crushed ice and extracted with ether. The ether layer was washed with 5% sodium bicarbonate solution and water. After drying over magnesium sulfate, the ether was evaporated off. The crude product distilled at 80° (14 mm). The distilled product was chromatographed on a column of silica gel. Elution with 7% ether in petroleum ether (40–60°) gave the desired ketone in 50% yield: ir (thin film) 1630 and 1660 (s) cm^{-1}; uv λ_{max} (ethanol) 238 nm (ϵ 14,000).

Anal. Calcd for the 2,4-dinitrophenylhydrazone derivative of **5**, $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30. Found: C, 53.69; H, 4.73; N, 19.50.

2-Methyl-3-phenylcyclohexanone (24) was synthesized by conjugate addition of phenylmagnesium bromide to **23**. The procedure followed was described in the synthesis of *trans*-5-methyl-3-phenylcyclohexanone. The crude product was chromatographed on silica gel. Elution with 10% ether in petroleum ether (40–60°) gave the desired ketone in 33% yield: ir (thin film) 700, 760, 1600, and 1704 cm^{-1}; melting point of the 2,4-dinitrophenylhydrazone derivative 220–221°.

Anal. Calcd for the derivative $C_{19}H_{20}N_4O_4$: C, 61.95; H, 5.47; N, 15.21. Found: C, 61.88; H, 5.34; N, 14.93.

The Malononitrile Derivative of 24. Condensation of the free ketone **24** with malononitrile in benzene in the presence of ammonium acetate as described before gave a thick viscous liquid that solidified upon standing at room temperature: yield 80%; mp 60–80°. Fractional crystallization from methanol afforded a pure product (500 mg), mp 90–91°.

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.50; H, 6.74; N, 11.69.

Photolysis of the pure dinitrile derivative **25** (1 g) in ethanol for 24 hr gave a yellow oil which was chromatographed on silica gel. The photoproduct was isolated as usual in 5% ether in petroleum ether (40–60°) as a crystalline solid and identified as **26**: yield 200 mg (25%); mp 101–102°.

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.41; H, 6.70; N, 11.70.

Acknowledgment. The author is indebted to Professor R. C. Cookson, FRS, for his helpful suggestions, discussions, and encouragement throughout this piece of investigation.

Financial support from the University of Southampton is gratefully acknowledged. The interest and encouragement of Dr. W. R. Slaunwhite, Jr., professor of biochemistry, SUNY/B, in preparing the manuscript are deeply appreciated.

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Photodetachment of Electrons from Large Molecular Systems. Pyrrolate Ion. Electron Affinity of C_4H_4N

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Abstract: The relative cross section for the gas-phase photodetachment of electrons has been determined for pyrrolate ions in the wavelength region 300–510 nm (4.13–2.43 eV). An ion cyclotron resonance spectrometer was used to generate, trap, and detect the negative ions, and a 1000-W xenon arc lamp with a grating monochromator was employed as the light source. The following quantities were determined: $EA(C_4H_4N\cdot) \simeq 2.39 \pm 0.13$ eV; $D(C_4H_4N\text{-}H) = 99 \pm 6$ kcal/mol. The electronic structure of pyrrolyl radical is discussed.

Photodetachment experiments, $A^- + h\nu \rightarrow A\cdot + e^-$, can provide information regarding electron affinities[3a] and electronic structures.[3b] Our recent examination of some rather complex anions suggests that much remains to be learned in this area.[3a] In order to explore further the cross-section behavior for detachment from delocalized systems and to study the influence of heteroatoms, we undertook a study of the pyrrolate anion $C_4H_4N^-$. This ion is an obvious analog to the previously examined $C_5H_5^-$; both are cyclic molecular ions with highly delocalized, aromatic π systems. The electronic structure of pyrrolate is additionally complicated by the presence of a localized, "nonbonding," σ pair of electrons.

In favorable cases, the onset of photodetachment (the vertical detachment energy) can be related to the adiabatic electron affinity. An estimate of the electron affinity can be made independently from bracketing reactions involving proton transfer in the gas phase:

$$AH + B^- \rightleftharpoons BH + A^- \qquad (1)$$

Neglecting the change in $\Delta S°$, the determination of the preferred direction of reaction 1 identifies the sign of $\Delta H°$. Given D for A–H and B–H, and EA for B·, we can then define limits for the electron affinity of A.

Experimental Section

Pyrrole (98%, Aldrich Chemical Co.) was distilled and stored at 4°. Nitrogen trifluoride, phosphine (Matheson), and hydrogen sulfide (Matheson) were used without further purification.

All experiments were performed on a Varian V-5900 icr spectrometer[4] with a modified square cell design.[3] Typical cell conditions employed high trapping voltages (2.5–1.6 V), moderate source drift voltages (0.7–0.2 V), and low analyzer drift voltages (less than 0.05 V). A 1000-W xenon arc lamp in conjection with a grating monochromator was employed as the light source. Gratings blazed at 300 nm (24.6-nm fwhm) and 1500 nm (23.8-nm fwhm) were used to investigate the short- and long-wavelength photodetachment behavior, respectively. Both gratings were used in the first order with long-wavelength pass filters to block light of higher orders. A conservative estimate of the total uncertainty in the wavelength calibration and zero grating position is 3 nm. An Eppley thermopile was used to measure the relative photon flux immediately after each run. Detailed explanations of the data collection and analyses have been previously reported.[3]

No additional ions were detected when irradiating with the xenon lamp and a 400-nm longpass filter. Conventional double resonance and pressure variation experiments were used to determine the preferred direction of various proton-transfer reactions.[4]

Pyrrolate ions were formed *via* two pathways. The first involved proton transfer to F^-, generated from NF_3 at 0.6–1.3 eV (electron energy minus trapping voltage). The total pressure[5] was $5\text{–}10 \times 10^{-8}$ Torr during the experiments with the monochromator, although qualitatively the same results were obtained with long-wavelength pass filters at pressures up to 6×10^{-7} Torr. At total pressures exceeding 9×10^{-7} Torr, the photodetachment signal even with filters had significantly deteriorated.[6]

Results and Discussion

Figure 1 presents the results for photodetachment of $C_4H_4N^-$ (generated from F^- with pyrrole) in the range 300–510 nm. Four runs were averaged together, with an average maximum fractional signal decrease of 0.038. Standard deviations are approximately ±10% throughout the wavelength region studied. A linear least-squares fit to all the data yields an intercept of 519 ± 3 nm [2.389 ± 0.014 eV (55.1 ± 0.3 kcal/mol)].

Several reactions were studied with the purpose of estimating the electron affinity of the pyrrolyl radical indepen-