# Mechanistic and Exploratory Organic Photochemistry. IX.[1] Phenyl Migration in the Irradiation of 4,4-Diphenylcyclohexenone[2,3]

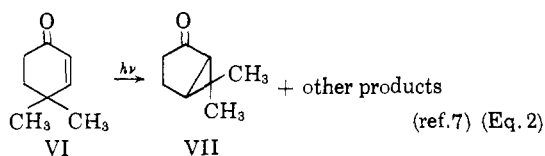BY HOWARD E. ZIMMERMAN AND JOSEPH W. WILSON

The role of the second double bond in the photolysis of 4,4-disubstituted cyclohexadienones has been assessed by a study of the irradiation of 4,4-diphenylcyclohexenone and comparison of the reaction course with that of the previously studied 4,4-diphenylcyclohexadienone. 4,4-Diphenylcyclohexenone on irradiation in ethanol or benzene was found to afford as major products the stereoisomeric 5,6-diphenylbicyclo[3.1.0]hexan-2-ones, and the stereoisomers were found to be photochemically interconvertible. Thus the absence of the second double bond enforces a phenyl migration not observed for the related dienone where participation of the second double bond results in effective C-4 migration. Since phenyl migration in the dienone is an unobserved *a priori* possibility, it is concluded to be a less preferred pathway. Similarly, although C-4 ring contraction observed for literature cyclohexenones not having aryl groups at C-4 is an *a priori* possibility for 4,4-diphenylcyclohexenone, this is not found, indicating that ring contraction of 4-alkyl-substituted cyclohexenones is the least efficient of the three type processes encountered. The possibility of reaction of electronically unexcited but vibrationally excited species is also discussed. For reactions requiring appreciable activation energy and where available energies are those obtained photochemically by ketones, it is concluded that in solution collisional deactivation effectively precludes hot molecule pathways.

In previous publications[1,4,5] we have described the photochemical rearrangement of 4,4-diphenylcyclohexadienone (I) to afford 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (II) and have detailed a reaction scheme following our general mechanistic treatment of organic photochemical reactions.[6] The reaction scheme begins with 3,5-bridging of the triplet[1] excited state III
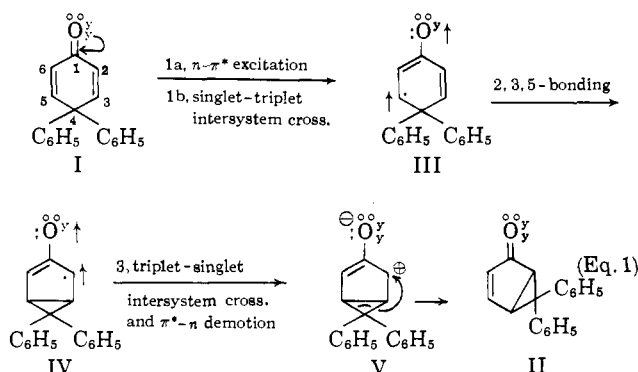
of dienone I. However, subsequently it has been shown that 4,4-disubstituted cyclohex-2-enones may rearrange in a formally parallel manner. Thus Chapman[7] found the rearrangement of 4,4-dimethylcyclohexenone (VI) to afford (*inter alia*) 6,6-dimethylbicyclo-[3.1.0]hexan-2-one (VII) and Gardner[8] earlier showed

cholest-4-en-3-one to undergo the same rearrangement. Recently Chapman[9] as well as Hammond and Turro[10] have commented that therefore the first bonding step of our formulation cannot be an absolutely necessary feature of these reactions. The present paper presents evidence on this point,[11] evidence deriving from a study of the photochemistry of 4,4-diphenylcyclohexenone (VIII). This particular enone was especially suited for our investigation because of its close structural relationship to the previously studied dienone I.

Photolysis of 4,4-diphenylcyclohexenone (VIII) in 95% ethanol or benzene with a Pyrex filter gave a mixture of products which were separated using scanning liquid–liquid partition chromatography.[5] The major products were two crystalline ketones, m.p. 74° (IXa) and m.p. 118° (IXb).[16] In a typical run the irradiation of 2.00 g. of 4,4-diphenylcyclohexenone (VIII) afforded 1.62 g. of the former (IXa) and 120 mg. of the latter (IXb). Furthermore, it was discovered that the two photoketones IXa and IXb were photochemically interconvertible.

Structure Elucidation.—The two photoketones IXa and IXb were shown to be the stereoisomeric 5,6-diphenylbicyclo[3.1.0]hexan-2-ones. The structure assignments rest partially on elemental analysis, spectral data, and chemical behavior observed for IXa and IXb and their degradation products. Final proof was obtained by degradation of IXa and IXb separately to known compounds.

(1) For Paper VIII of this series *cf.* H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964).

(2) Support of this research by the National Institutes of Health Grant GM 07487 is hereby gratefully acknowledged.

(3) Preliminary report presented at the 9th Reaction Mechanisms Conference, Brookhaven, N. Y., 1962.

(4) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961).

(5) H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962).

(6) This was first outlined by H. E. Zimmerman at the 17th National Organic Symposium of the American Chemical Society, Bloomington, Ind., June, 1961; *cf.* Abstracts, p. 31. Also note ref. 5.

(7) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963).

(8) W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *J. Am. Chem. Soc.*, **84**, 2268 (1962).

(9) O. L. Chapman, "Advances in Photochemistry," Interscience Publishers, Inc., New York, N. Y., 1963, Chapter IX.

(10) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

(11) It should be remarked that the mesoionic intermediates and their conjugate acids, as originally proposed by us (ref. 1, 4–6) as being involved in much of dienone photochemistry, do not seem to be in dispute. Thus we note that these are successfully employed in subsequent interpretive discussions by Chapman (ref. 7, 9, 12), Kropp (ref. 13, 14), and Jeger (ref. 15). Similarly, the mesoionic mechanism for the formation of photosantonic acid as detailed in our footnote 53 in ref. 5 is presented with supporting evidence by Chapman (ref. 12) (*cf.* also ref. 14). The separate matter of the mode of formation of these mesoionic-zwitterionic species, in contrast, still seems to be controversial.

(12) O. L. Chapman and L. F. Englert, *J. Am. Chem. Soc.*, **85**, 3028 (1963).

(13) P. J. Kropp and W. F. Erman, *ibid.*, **85**, 2456 (1963).

(14) P. J. Kropp, *ibid.*, **85**, 3779 (1963).

(15) C. Ganter, E. C. Utzinger, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2403 (1962).

(16) The structures of the by-products are presently under investigation.

TABLE I

ULTRAVIOLET SPECTRA OF 2,4-DNP DERIVATIVES

Derivative	$(\lambda_{max},\ m\mu\ (\log \epsilon))^a$	Ref.
IXa	368 (EtOH) (4.40)	..
IXb	370 (EtOH) (4.42)^b	...
Bicyclo[3.1.0]hexan-2-one	369 (CHCl₃) (4.38)	17a
Dihydroumbellulone	369 (EtOH) (4.37)	17a
Cyclohexanone	363 (EtOH) (4.37)	17b
Cyclopentanone	363 (EtOH) (4.33)	17c
Cyclohex-2-en-1-one	378 (CHCl₃) (4.44)	17d
Cyclohex-3-en-1-one	362 (CHCl₃) (4.36)	17d
4-Isopropylcyclohex-3-en-1-one	364 (CHCl₃) (4.37)	17a
Bicyclo[3.1.0]hexan-3-one	360 (EtOH) (4.36)	17e

^{a} A *ca.* 3-mμ wave length increase is observed in CHCl₃ relative to EtOH for some of these compounds, less in others. ^{b} Also a 226 mμ (4.15) band.
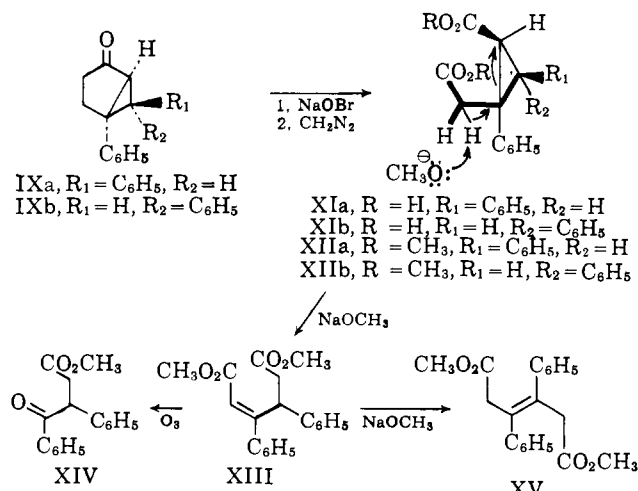
Regarding IXa and IXb themselves, these compounds were found to be isomeric with the cyclohexenone starting material VIII. The absence of an unsaturated moiety was evidenced by the n.m.r. which showed ten (aromatic) protons below 3.5 τ and six protons above 7 τ but no olefinic hydrogen absorption. The ultraviolet possessed only end absorption and the infrared had carbonyl peaks at 5.83 (for IXa) and 5.80 μ (for IXb). Neither isomer reacted with permanganate and both reacted only slowly with bromine in carbon tetrachloride. The ultraviolet spectra of the 2,4-dinitrophenylhydrazones were enlightening (*cf.* Table I), suggesting a dihydroumbellulone structure. At the

IXa　　　IXb　　　X
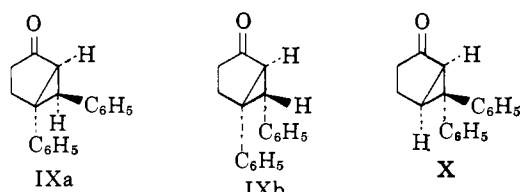
outset structures IX and X were entertained as strong possibilities.

The definite presence of the cyclopropane ring and the location of the two phenyl groups were established by the degradative scheme outlined in Chart I. The

CHART I

1. NaOBr
2. CH₂N₂

IXa, R₁ = C₆H₅, R₂ = H
IXb, R₁ = H, R₂ = C₆H₅

XIa, R = H, R₁ = C₆H₅, R₂ = H
XIb, R = H, R₁ = H, R₂ = C₆H₅
XIIa, R = CH₃, R₁ = C₆H₅, R₂ = H
XIIb, R = CH₃, R₁ = H, R₂ = C₆H₅

NaOCH₃

XIV　　　XIII　　　XV

degradation began with a hypobromite oxidation of the photoketones IXa and IXb to the dicarboxylic acids

(17) (a) N. A. Nelson and G. A. Mortimer, *J. Org. Chem.*, **22**, 1146 (1957); (b) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945); (c) J. D. Roberts and C. Green, *J. Am. Chem. Soc.*, **68**, 214 (1946); (d) A. J. Birch, *J. Chem. Soc.*, 593 (1946); (e) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

XIa and XIb, respectively.[18] Diazomethane was used to convert the acids to their respective methyl esters XIIa and XIIb. Confirmation of the structural assignments at this stage was derived from the n.m.r. (*cf.* Table II) of the acids and their esters.[19]

TABLE II

N.M.R. DATA FOR CYCLOPROPANE DIACIDS AND DIESTERS XIa,b AND XIIa,b

Acid XIa — τ	J, c.p.s.	Rel. area	Assignment	Ester XIIa — τ	J, c.p.s.	Rel. area
2.3–2.9		10	Aromatic H	2.4–2.9		10
			Ester CH₃	6.35		3
				6.58		3
6.89				6.77	17	
		2	CH₂	7.05		
6.93^b				7.12		1.8
				(7.40)^a	17	
7.06			CH	(7.11)^a		
7.22				7.28		
	11	2			11	2.2
7.30			CH	7.39		
7.46				7.56		

Acid XIb — τ	J, c.p.s.	Rel. area	Assignment	Ester XIIb — τ	J, c.p.s.	Rel. area
2.7–3.2		10	Aromatic H	2.9–3.5		10
			Ester CH₃	6.26		3
				6.51		3
6.80		2	CH₂	6.95		18
6.95				7.05		
7.05			CH	7.17		
	6	2			7	2
7.10				7.27		
7.20			CH	7.39		

^{a} Assumed present under major peak. ^{b} Two widely spaced but weak members of a quartet expected could not be distinguished from background noise.

The carbon skeleton was unambiguously established in the next step in which each of the methyl esters XIIa and XIIb was subjected to a methoxide-catalyzed reverse Michael reaction.[20]

Liquid–liquid partition chromatography afforded the known[21] dimethyl *trans*-3,4-diphenyl-3-hexenedioate (XV) and the previously unknown dimethyl 3,4-diphenyl-2-hexenedioate (XIII). The n.m.r. spectrum of XIII showed absorption by 10 aryl hydrogens, a single vinyl hydrogen peak at 4.17 τ, methoxyl hydrogen peaks at 6.45 and 6.59 τ, and an ABX pattern con-

(18) This reaction has precedent in the oxidative cleavage of aralkyl ketones reported by R. Levine and J. J. Stevens, *ibid.*, **72**, 1642 (1950); M. W. Farrar and R. Levine, *ibid.*, **71**, 1496 (1949).

(19) Thus typical AB quartets were observed for the cyclopropane methine hydrogens, methoxyl hydrogen absorption was seen for the esters, and aromatic hydrogens integrating properly were found. In the case of acid XIa and ester XIIa the methylene hydrogens are nonequivalent, being adjacent to an asymmetric center, and appear as an AB quartet. The methylene hydrogen absorption for XIb and XIIb appears in each case as a singlet apparently due to fortuitously equivalent average environment.

(20) This has analogy in the reaction of methyl 1-isopropyl-2-carbomethoxycyclopropylacetate; O. Wallach, *Ann.*, **388**, 49 (1912); *cf.* R. Breslow in "Molecular Rearrangements," P. De Mayo, Ed., Interscience Publishers, Inc., New York, N. Y. 1963, p. 282. For still other examples, *cf.* H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2346 (1962); Widmark, *Arkiv Kemi*, 11, 195 (1957); L. Crombie, J. Crossley, and D. A. Mitchard, *J. Chem. Soc.*, 4957 (1963).

(21) (a) G. M. Badger, *J. Chem. Soc.*, 999 (1948); (b) H. E. Fiertz-David, L. Blangey, and M. Uhlig, *Helv. Chim. Acta*, **32**, 1414 (1949).

CHART II
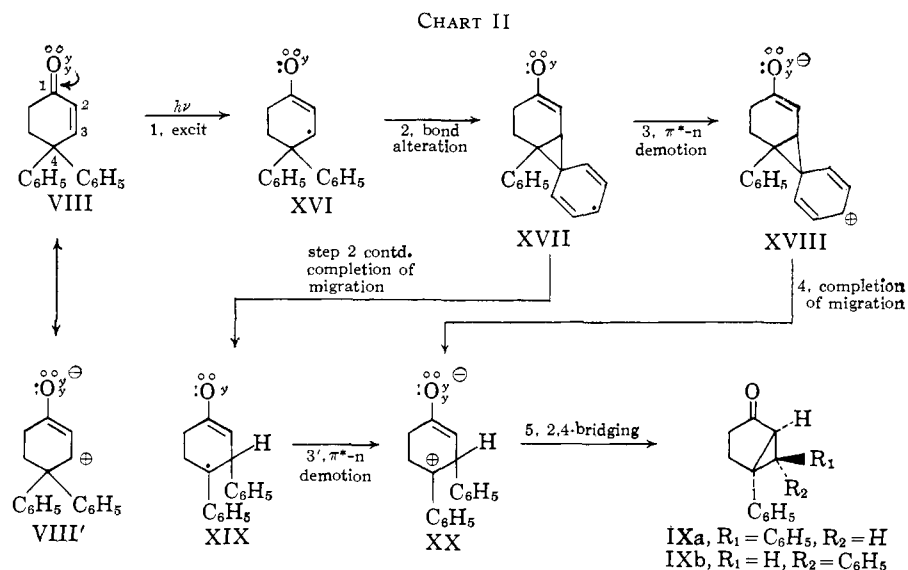
sisting of a methine triplet centering at 5.82 τ and a methylene quartet centering at 7.25 τ.[22] Final proof was found in the ozonolysis of unsaturated diester XIII to the known[23] methyl 4-keto-3,4-diphenylbutanoate (XIV).

Formation of the same ultimate degradation products from the two photoketones IXa and IXb thus requires these to be stereoisomers differing in the phenyl configuration at C-6. The assignment of the configurations indicated was based on the larger cyclopropane CH–CH coupling constants found (cf. Table II) for acid XIa (10 c.p.s.) and ester XIIa (10 c.p.s.) relative to the stereoisomeric acid XIb (6 c.p.s.) and ester XIIb (7 c.p.s.).   This agrees well with the average assignments of 5.7 c.p.s. for trans-cyclopropane CH–CH coupling and 8.4 c.p.s. for cis-cyclopropane CH–CH coupling reported by Graham and Rogers.[24]

Interpretative Discussion

The first striking feature of these results to be noted is the absence of the C-4 migration processes of eq. 1 and 2 observed for the closely related 4,4-diphenylcyclohexadienone. Thus it can be clearly stated that in the 4,4-diphenyl system the second double bond is a requisite for the C-4 rearrangement of eq. 1.   Furthermore, phenyl migration as observed in the presently studied monoenone reaction may be seen to be an a priori but experimentally unobserved possibility in the photochemistry of 4,4-diphenylcyclohexadienone. From this we may conclude that C-4 migration by the mechanism of eq. 1, involving a second double bond, is a more efficient process than phenyl migration, for only in the absence of the second double bond does phenyl migration occur. We may continue our logic further by noting that when both the second double bond and the phenyl groups are eliminated from the molecule irradiated, the C-4 migration process reappears (cf. the example of 4,4-dimethylcyclohexenone studied by Chapman[7]). As a consequence of this reasoning, the following photochemical rearrangement processes may be listed in order of de-

creasing efficiency: (a) C-4 migration of dienones to form [3.1.0]bicyclic product (most efficient);   (b) phenyl migration, enforced in the present case by lack of a second double bond; (c) C-4 migration of monoenones to form [3.1.0]bicyclic product (least efficient), enforced by lack of both the second double bond and a C-4 phenyl group.

Hence, although 4,4-disubstituted cyclohexenones may rearrange in a formally parallel manner to 6,6-disubstituted bicyclic ketones, the consequence is that the mechanism of eq. 1 involving the second double bond is not available and the photochemical pathways remaining are much less efficient.[25]

Thus far we have not categorized the less efficient phenyl migration process leading to bicyclic ketone stereoisomers IXa and IXb. We suggest the mechanism delineated in Chart II.[26]

This mechanism envisages delocalization of the antibonding electron of the n–π* excited state XVI with gradual participation of the C-4 phenyl group, leading to further delocalization of this electron throughout the migrating phenyl group. As we have clearly noted earlier,[5] some of the processes we have proposed in our treatment of n–π* reactions may be concerted; in the present case it is uncertain at which precise stage π*–n electron demotion actually occurs. In one extreme, migration (step 2) is envisaged as complete prior to demotion (3'). In a second mechanistic gradation electron demotion occurs in step 3 following formation of a half-migrated phenyl species XVII. Also possible and encompassed by our mechanistic treatment as previously delineated is demotion during the beginning of the phenyl-bridging process to form XVII.   It may be seen that this mechanism approaches but does not reach the proposal advanced more recently by Chapman as the "polar state concept," wherein structures such as VIII' are written as leading to product.   In our view, if demotion occurs prior to any molecular change, then electronic ground state VIII is

(22) The ABX pattern derives from the nonequivalence of the average environment of the methylene hydrogens (AB) adjacent to the methine. The presence of the triplet suggests equality of J_{AX} and J_{BX}. Further minor allylic splitting was observed.

(23) (a) J. Thiele and F. Strauss, Ann., 319, 164 (1901); (b) E. Knoevenagel, Chem. Ber., 21, 1350 (1888).

(24) J. D. Graham and M. T. Rogers, J. Am. Chem. Soc., 84, 2249 (1962).

(25) This conclusion seems to be substantiated qualitatively by the longer photolysis times required for the rearrangement of 4,4-disubstituted cyclohexenones compared with 4,4-disubstituted cyclohexadienones. More quantitative data in the form of quantum yield studies will be reported at a later date.

(26) The "circle, dot, y" notation (representing sp-hybrid unshared electrons, π-electrons, and p_y nonbonding electrons, respectively) is described and referenced in ref. 1, 4, and 5.

TABLE III

SELECTED EXAMPLES OF VIBRATIONALLY EXCITED MOLECULE REACTIONS

Hot molecule and source	Reaction	Reaction rate, sec.$^{-1}$	Ref.
trans-Cyclopropane-d_2 (CH$_2$: + *trans*-CHD=CHD)	Stereoisomerization of propylene	1.6×10^{11}	
		1.1×10^{10}	30
Methylcyclopropane (CH$_2$: + cyclopropane)	Formation of isomeric butenes	4.2×10^8 to	
		4.3×10^9	31
Methylcyclopropane (CH$_2$: + propylene)	Formation of isomeric butenes	5.8×10^8	31
Methylcyclobutane (CH$_2$: + cyclobutane)	Ethylene + propylene	4.0×10^8 to	
		3.4×10^9	32
Dimethylcyclopropane (CH$_2$: + isobutylene)	Formation of isomeric pentenes	3.1×10^7	31

regenerated.[27] One might concern oneself about the possibility that electron demotion in XVI *prior* to molecular change could lead to an electronically unexcited but vibrationally excited molecule which then could rearrange by the equivalent of a pyrolytic process. Thus, if the singlet electronically excited state of 4,4-diphenylcyclohexenone (*i.e.*, XVI with paired p_y and π^* electron spins) were to undergo adiabatic radiationless internal conversion,[29] the entire 75.4 kcal./mole singlet excitation energy would appear in the demoted species VIII as vibrational energy. Similarly, radiationless electron demotion of the corresponding triplet (XVI with odd electrons unpaired) would give rise to VIII vibrationally excited to the extent of 68.5 kcal./mole. However, the evidence is strongly against such a mechanism. We have commented earlier[5] that liquid-phase photochemical reactions do not in general parallel the pyrolytic transformations of the same reactants. Additionally, while thermal reactions of vibrationally "hot" molecules, sometimes engendered photochemically, are known in the gas phase at high dilution, the evidence is that for organic molecules of appreciable complexity the addition of inert gases readily suppresses such reactions by collisional deactivation of the hot molecules. Table III collects some examples of reactions of vibrationally hot molecules observed in the gas phase and their unimolecular reaction rates. These data are useful in considering the relative probabilities of reaction *vs.* collisional quenching of such hot species (*e.g.*, by an inert gas). The general order of magnitude for the pseudounimolecular rate of collision is in the range of 10^{10} sec.$^{-1}$ at about 100 mm. total pressure to 2.8×10^{11} sec.$^{-1}$ at several atmospheres (*cf.* ref. 30). Thus we see in agreement with the literature[30-33] that even in the gas phase the rate of deactivation by colli-

sion can compete successfully with molecular transformation of the vibrationally excited species.[34]

It is now necessary to see whether this gas-phase information is of help in determining the likelihood of liquid phase reactions of vibrationally hot molecules produced by electron demotion of an electronically excited species. We first note that application of the 1.0×10^{10} l. mole^{-1} sec.$^{-1}$ value[35] for the bimolecular rate of diffusion in benzene at 20° to the rate of collision of a solute with benzene gives a pseudounimolecular rate constant of 1.1×10^{11} sec.$^{-1}$ for collision of solute molecules with benzene. Thus solvent collision would effectively compete with reaction of hot molecules of the type listed in Table III. To understand an extrapolation to larger molecules such as 4,4-diphenylcyclohexenone (VIII) we do well to consider the Slater–Kassel–Rice–Ramsperger treatments[36] of the rate of reaction of vibrationally excited species which are then given by

$$k = A \left[\frac{E - E_0}{E} \right]^{n-1} \qquad (3)$$

where A is the frequency factor of the ordinary thermal reaction, E is the actual energy of the vibrationally excited molecules reacting, E_0 is the (minimum) activation energy required in the ordinary thermal reaction, and n is the number of vibrational modes capable of interacting energetically with the portion of the molecule reacting.[37,38]

Inspection of eq. 3 shows that the quotient $(E - E_0)/E$ is less than unity and that therefore the pseudounimolecular rate constant k will decrease rapidly with n and hence with increasing molecular complexity. This is the trend noted in Table III. In the case of 4,4-diphenylcyclohexenone (VIII) the O–O energy of the first excited singlet is 75.4 kcal./mole and that of the triplet is 68.5 kcal./mole.[39] Using the higher figure as the energy E of a hot molecule formed by adiabatic conversion of electronic to vibrational energy, also making the conservative estimate that a thermal rearrangement of a stable molecule as VIII will not have a lower activation energy than 20 kcal./mole, additionally assuming that n is 49 or about half the $3n - 6$

(27) Although in Chart II Compound VIII' is pictured as a resonance structure contributing with VIII to the electronic ground state, it probably also is a heavy contributor to the $\pi-\pi^*$ singlet electronic excited state. Evidence that the $n-\pi^*$ and not the $\pi-\pi^*$ excited state triplet is involved in the rearrangement of 4,4-diphenylcyclohexadienone has been presented (ref. 1). Further evidence on this point and on the greater electron density at the β-carbon of $n-\pi^*$ triplet excited states compared with the ground state will be described in forthcoming publications. For singlet excited states this electron distribution is well established (ref. 28) and has been discussed by us previously.[1,5]

(28) (a) E. M. Kosower and D. C. Remy, *Tetrahedron*, **5**, 281 (1959); E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958); (b) V. Georgian, *Chem. Ind.* (London), 930 (1954); 1480 (1957). In these references the 6-hetero-$\Delta^{1,9}$-octalones were shown to have decreasing singlet excitation energies as the 6-hetero group, near the β-carbon of the unsaturated ketone moiety, becomes more electronegative.

(29) This would occur by crossing of the potential energy surfaces of the electronically excited and ground states and could occur only at a point where the energy was at least that of the lowest vibrational level of the excited state.

(30) B. S. Rabinovitch, E. Tschuikow-Roux, and E. W. Schlag, *J. Am. Chem. Soc.*, **81**, 1081 (1959).

(31) J. N. Butler and G. B. Kistiakowsky, *ibid.*, **82**, 759 (1960).

(32) H. M. Frey, *Trans. Faraday Soc.*, **56**, 1201 (1960).

(33) H. M. Frey, *Proc. Roy. Soc.* (London), **A250**, 409 (1959); (b) **A251**, 575 (1959); (c) *J. Am. Chem. Soc.*, **82**, 5947 (1960).

(34) The approximation is made in such studies (*e.g.*, ref. 32) that each collision with an inert gas molecule leads to deactivation of the hot molecule.

(35) P. Debye, *Trans. Electrochem. Soc.*, **82**, 165 (1942).

(36) *Cf.* N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press (1959), p. 125.

(37) A variation of this theory including the zero-point energy has been proposed by R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1951), and is used in a number of the cited references. The Marcus-Rice version leads to a value of n closer to the total theoretical $3n - 6$ vibrational modes of freedom.

(38) In practice n is in the range of half of the $3n - 6$ degrees of freedom; *cf.* K. J. Laidler, "Reaction Kinetics," Vol. I, The Macmillan Co., New York, N. Y., 1963, p. 126.

(39) Unpublished work of H. E. Zimmerman with J. S. Swenton and G. A. Zimmerman.

vibrational modes of VIII, and finally employing a typical frequency factor of $A = 10^{13}$ sec.$^{-1}$, we find k in eq. 3 is given by A $(0.733)^{49} = 2.5 \times 10^{-7}A$, or only about 10^6 sec.$^{-1}$. Clearly collisional quenching of benzene with a rate of 10^{11} sec.$^{-1}$ is an efficient process which would deactivate such a hot species prior to thermal rearrangement.[40]

Having presented the mechanism of Chart II with the molecular and electronic details proposed for the formation of the bicyclic ketones IXa and IXb from 4,4-diphenylcyclohexenone, it remains to consider whether our general approach[5,6] is compatible with the C-4 migration reaction observed by Gardner[8] and Chapman.[7,41] We note that alkyl migration must be involved in these rearrangements. It is suggested that the n–π^* excited state (XXII) of the 4,4-dialkyl-cyclohexenone (XXI) undergoes homolytic fission of bond 4–5 leaving C-5 odd electron bearing. Bonding of C-5 then to C-3 and π^*–n electron demotion is seen
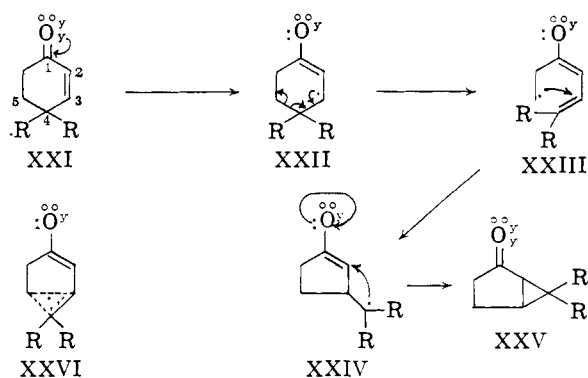
to afford product XXV. Although we have depicted C-5 as being totally released,[42] it is by no means clear that C-5 would necessarily be predicted to be released from the remaining π-system prior to bonding to C-3.[43] Thus a species such as XXVI may intervene. Additionally, there remain the question of the exact point at which a π-system electron is demoted[44] and the prob-

(40) Of the assumptions, the weakest are the rate of collisional quenching by solvent benzene and secondly the choice of 49 interacting vibrational modes. Regarding the former, the rate employed derives from theory assuming penetration of a second reactant molecule through a "hole" in the solvent shell surrounding the first reactant molecule. Where the solvent shell itself interacts with the enclosed solute the rate should be much higher. Counterbalancing this is the assumption commonly made in hot molecule calculations that only one collision is needed for deactivation of the hot molecule. Turning to the second assumption, we note that even with far fewer vibrational modes being energy acceptors, the rate of hot molecule reaction is still lower than the rate of solvent collision. Even for $n = 20$, close to the value used for the much simpler methylcyclopropane (ref. 31), $k = 2.7 \times 10^{10}$ sec.$^{-1}$.

(41) The unpublished observation by M. Semmelhack, R. Lewis, and H. E. Zimmerman of the rearrangement of $\Delta^{1,9}$-10-methyl-2-octalone to 10-keto-2-methyltricyclo[5.3.0^{1,7}0^{2,5}]decane is a similar example.

(42) Cf. H. E. Zimmerman, in "Advances in Photochemistry," W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter VI; in this discussion the extreme version of complete radical release was considered.

(43) We note that there is a driving force favoring interaction of the odd electron bearing C-5 and the π-system just as there is energy gained by π-bonding of a methyl radical with ethylene. In the latter case the electronics can be crudely approximated by considering the cyclopropenyl radical which does have a lower π-energy than the sum of the π-energies of the two isolated fragments.

(44) Electron demotion in XXVI would leave a zwitterionic analog. We note that on one hand free-radical elimination does have literature analogy (e.g., J. A. Berson, C. L. Olson, and J. S. Walia, J. Am. Chem. Soc., **84**, 3337 (1962), involving a formal migration) and on the other that intervention of a zwitterionic species would lower the energy of the species at a mechanistically critical stage. In any event, the necessity for initiation of an alkyl rearrangement process by an odd-electron-containing system is reflected in the low efficiency of the C-4 migration reaction.

lem of singlet vs. triplet categorization; these matters will be discussed in forthcoming publications.

Finally, meriting attention is the photochemical equilibration of IXa and IXb. This, too, is explicable on the basis of our general treatment.[5,6] Here the excited states of (e.g.) IXa (i.e., XXVII) might be expected to undergo homolytic fission of either or both bonds 2–4 and 2–3. Reclosure may then afford the stereoisomer.[45]
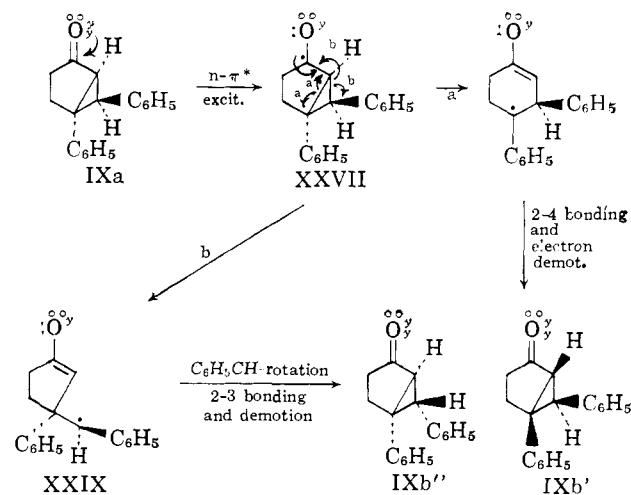
Future publications will deal with further tests of the ideas presently advanced.

Experimental[46]

4,4-Diphenylcyclohex-2-en-1-one was prepared by the method of Zimmerman and Schuster.[5]

Photolysis of 4,4-Diphenylcyclohex-2-en-1-one.—In a typical run a solution of 2.00 g. (8.07 mmoles) of 4,4-diphenylcyclohex-2-en-1-one in 500 ml. of 95% ethanol was irradiated under nitrogen[47] through a Pyrex filter using a 450-watt Hanovia medium pressure immersion lamp. Concentration in vacuo at 40° left a yellow oil. This was subjected to liquid–liquid partition chromatography (cf. ref. 5 for additional details) using a cyclohexane-dimethylformamide–ethyl acetate–water (100:40:25:3, v./v.) system at 29° and a 150 × 3.5 cm. column. Of 700 g. of diatomaceous earth (Celatom FW-80, Eagle Picher Co.) bearing 280 g. of lower phase, 760 g. was used for dry packing. The eluate was scanned at 260 mμ and collected in 20-ml. fractions. The fractions were washed with water and concentrated in vacuo. Fractions 35–45 afforded 1.47 g. of 5,6-trans-diphenylbicyclo[3.1.0]-hexan-2-one (IXa); 43–45 contained 148 mg. of IXa, 4,4-diphenylcyclohexenone (VIII), and IXb; 46 gave 10 mg. of IXa, VIII, and IXb; 47–59 yielded 119 mg. of IXb contaminated with VIII; 60–74, 60 mg. containing IXb; fractions 75–123 totaled 196 mg. with the central fractions consisting of a third ketonic product under study.

Characterization of IXa.—5,6-trans-Diphenylbicyclo[3.1.0]-hexan-2-one was recrystallized to a m.p. of 73–74° from the above chromatography using 95% ethanol. Prominent infrared peaks were found at 3.32, 5.83 (s), 6.25, 6.70, 6.92, 7.11, 7.60, 7.70, 8.52, 9.30, 9.72, 10.55, 10.86, and 11.30 μ. End absorption was observed in the ultraviolet (EtOH): (ϵ 17,160 at 215; 14,820 at 220; and 7490 at 230 mμ).

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.10; H, 6.45. Found: C, 86.92; H, 6.64.

(45) Starting with racemic IXa as in the present work, one would expect racemic product whether path a or path b is followed. It is of interest to note that photolysis of resolved IX would afford one or the other (IXb' or IXb'') of the enantiomers of IXb or a racemic mixture depending on whether path a, path b, or both mechanisms were utilized. The reaction has analogy with the photolysis of bicyclic ketone II in which there is clear evidence of three ring bond fissions.

(46) All melting points were taken on a hot stage calibrated with compounds of known melting point.

(47) Purified with vanadous sulfate by the method of L. Meites and T. Meites, Anal. Chem., **20**, 984 (1948).

Two 2,4-dinitrophenylhydrazones, separated by fractional crystallization, were obtained from IXa: m.p. 114–116° (orange needles from chloroform–hexane), λ_{max}^{EtOH} 368 mμ (ϵ 23,400) and end absorption; m.p. 196–198° (yellow needles from chloroform–hexane), λ_{max}^{EtOH} 368 mμ (ϵ 24,800) and end absorption.

Degradation of 5,6-trans-Diphenylbicyclo[3.1.0]hexan-2-one (IXa).—Because the yields of acidic material varied widely, the nonacidic material recovered from the oxidation was often recycled. A typical series of three such runs (XIII–XV) follows. Bromine (10.3 ml., 32.1 g., 301 mmoles) was added to a cold solution of 37 g. (649 mmoles) of potassium hydroxide in 135 ml. of water. The resulting yellow potassium hypobromite solution was mixed with a solution of 1.91 g. of photoketone IXa (7.7 mmoles) in 1000 ml. of dioxane in a flask equipped with nitrogen inlet, Trubore stirrer, and condenser topped with KOH drying tube. The mixture was stirred at room temperature for 9.5 hr. and then maintained at reflux for 9.5 hr. more. The solvent was concentrated to 200 ml. in vacuo at 50° and 50 g. of sodium bisulfite and 200 ml. of 2 N sodium hydroxide was added. This mixture was chloroform extracted. The extracts yielded 2.53 g. of a red-orange oil whose only absorption in the carbonyl region of the infrared was at 5.76 μ. The cooled aqueous layer was acidified with 50% sulfuric acid and extracted with 2 l. of ether. The ether was dried and removed to leave a yellow solid weighing 343 mg.

The nonacidic material was recycled with 10.5 ml. of bromine, 44 g. of potassium hydroxide, 150 ml. of water, and 700 ml. of dioxane. After being stirred for 7 hr. at room temperature, 200 ml. more water was added and the mixture was maintained at reflux temperature for 12 hr. From the reaction mixture were isolated 1.49 g. of nonacidic and 1.26 g. of acidic material.

The nonacidic fraction was once more treated with potassium hypobromite (7 ml. of bromine plus 22 g. of potassium hydroxide in 80 ml. of water) in a solution of 250 ml. of dioxane and 70 ml. of water for 12 hr. at room temperature and 12 hr. at reflux temperature. A solid acidic fraction weighing 806 mg. was isolated. The total weight of acidic material isolated was 2.41 g. This was converted directly to methyl ester (vide infra).

Acidic material from a previous oxidation was purified by six recrystallizations from acetone–water to a constant m.p. of 216–228°. The infrared absorption in KBr showed maxima at 2.9–3.7 (broad), 5.85 (s), 6.07, 6.23, 6.7, 6.95, 7.03, 7.15, 7.43, 7.75, 8.15, 8.25, 8.48, 9.28, 9.37, 9.74, 10.4 (broad), 10.85, 11.25, 12.65, 13.0, 13.4, 13.6, and 14.3 (s) μ. The ultraviolet spectrum showed strong end absorption (ϵ at 220 mμ is 15,700). The n.m.r. spectrum of acid XIa in acetone-d_6 is recorded in Table II. The neutralization equivalent was 147 g. per equiv. or 294 g. per mole ($C_{18}H_{16}O_4$: 296 g. per mole).

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 73.12; H, 5.49.

Ester XIIa.—In a typical run, diacid XIa (up to 10 mmoles) was dissolved in 100 ml. of ether, cooled in ice, and treated with excess diazomethane.

The three batches of acid XIa, described in the previous section and weighing a total of 2.411 g., were combined and esterified in this fashion to yield a yellow oil weighing 2.018 g. This material was chromatographed on a silica gel column (2.8 × 78 cm. of Davison, Grade 950, 60–200 mesh). The ester was eluted in 15% ether–85% hexane after 500-ml. portions of hexane, 1, 2, and 5% ether–hexane, and 1500 ml. of 10% ether–hexane had been passed through the column. A total weight of 1.068 g. of crystalline ester XIa was collected, m.p. 70–82°.

A sample of ester XIa was crystallized twice from ether–hexane to m.p. 84.5–85.5°. The infrared shows absorption maxima at 3.25–3.5, 5.76, 6.25, 6.70, 6.95, 7.10, 7.32, 7.81, 8.40, 8.60, 9.29, 9.80, 10.60, 12.22, and 14.32 μ. The n.m.r. spectrum is recorded in Table II.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.07; H, 6.17. Found: C, 74.02, 74.12; H, 5.97, 6.08.

Ring Opening of Ester XIIa.[48]—Ester XIIa (1.40 g., 4.33 mmoles) was dissolved in 25 ml. of dry methanol in which 109 mg. (4.74 g.-atoms) of sodium had been dissolved and the yellow solution was stirred under nitrogen at reflux for 6 hr., then at room temperature for 2 days. The chloroform reaction mixture was diluted with cold water and chloroform extracted affording, on concentration, an oil weighing 1.21 g. The aqueous layer was acidified with 50% sulfuric acid and chloroform extracted to give an oily solid weighing 122 mg. after concentration.

The neutral mixture was separated into its components by

liquid–liquid partition chromatography on a 100 × 3.5 cm. water-jacketed column packed with 518 g. of a mixture of 500 g. of Celatom and 200 g. of "lower phase." The eluate was scanned at 260 mμ and collected in 20-ml. fractions. Fractions 28–35 yielded 547 mg. of dimethyl trans-3,4-diphenylhex-3-enedioate. Fractions 37–44 gave 180 mg. of dimethyl 3,4-diphenylhex-2-enedioate.

Fractions 28–35 were recrystallized to m.p. 114.5–115.5°. The infrared spectrum was identical with that of an authentic sample of dimethyl trans-diphenyl-3-hexenedioate (see below); m.m.p. 114–115.5°.

Fractions 37–44 contained a yellow oil. This was subjected to a long tube fractional molecular distillation. The sample was placed in the sealed end of a 520 × 12 mm. Pyrex tube previously treated with dichlorodimethylsilane in benzene to prevent surface wetting. The tube was placed in a horizontal gradient temperature oven, the hot end at 200° and the cold end at 65°, and evacuated to 0.001 mm. Most of the material moved ca. $^1/_3$ the length of the tube and condensed as a clear oil. The n.m.r. spectrum of this material was identical, except for minor impurity peaks, with the spectrum of another sample of this product from an earlier base-catalyzed ring-opening reaction, which had been isolated by chromatography on silica gel. Prominent peaks in the infrared of the purer of these two samples were located at 3.30, 3.37, 3.50 (w), 5.80 (s), 6.10, 6.25, 6.70, 6.88 (sh), 6.95 (s), 8.56 (s), 9.30 (w), and 14.32 (s) μ.

Synthesis of Dimethyl trans-3,4-Diphenyl-3-hexenedioate (XV).—Diethyl meso-3,4-dihydroxy-3,4-diphenyladipate, m.p. 174–178° (reported 168°), was prepared by the method of Beschke,[49] from benzil and ethyl bromoacetate. Hydrolysis gave the meso-diacid, m.p. 191–193 (lit.[49] 205°). The meso-diacid was converted to the unsaturated diacid XV by the method of Badger.[21a] trans-Unsaturated diacid, m.p. 310–312° (lit.[21] 297–299°), separated from the cis-diacid by fractional crystallization from 95% ethanol, was converted to the trans-dimethyl ester with excess diazomethane. The chromatographed ester recrystallized from methanol to constant m.p. 114–115° (lit.[21b] 112–113°).

Ozonolysis of Dimethyl 3,4-Diphenyl-2-hexenedioate from Ring Opening of Ester XIIa.—A 180-mg. sample of silica gel-chromatographed dimethyl 3,4-diphenyl-2-hexenedioate was dissolved in 8.5 ml. of ethyl acetate and 2 ml. of glacial acetic acid. Ozone (0.62 mmole) was bubbled through the cold solution. Then 10 ml. of water and 2 ml. of a 40% solution of peracetic acid in acetic acid was added followed by stirring at room temperature for 10 hr. Ether was added and the reaction mixture was extracted with water and then 3% sodium hydroxide. The ethereal phase was dried over sodium sulfate and concentrated, leaving 41 mg. of an oil (27% yield). Although the infrared indicated that the oil was largely methyl 3-benzoyl-3-phenylpropionate, this would not crystallize. A 31-mg. portion of the crude ester was saponified in 5 ml. of 95% ethanol, 87 mg. of potassium hydroxide, and 2 ml. of water. Dilution with water, extraction with chloroform, acidification of the aqueous layer, followed by chloroform extraction afforded from the last extracts 22 mg. of an oil which crystallized. Two recrystallizations from ether–hexane afforded white crystals, m.p. 161–163°, which did not depress the melting point of authentic 3-benzoyl-3-phenylpropionic acid and whose infrared spectrum was identical with that of authentic material.

Synthesis of 3-Benzoyl-3-phenylpropionic Acid.[23]—A stirred mixture of 5 g. (0.026 mole) of deoxybenzoin and sodium methoxide from 0.75 g. (0.033 g.-atom) of sodium in 10 ml. of dry methanol under nitrogen was cooled to −10°. Methyl bromoacetate (3.90 g., 0.026 mole) was dropped in slowly to keep the reaction mixture below 20°. Stirring was continued overnight at room temperature. The mixture was cooled before water dilution and ether extraction. The dried extracts were concentrated leaving a clear oil. Thin layer chromatography and infrared spectra indicated a mixture of expected product and reactants. The reaction product was saponified with 10 g. of potassium hydroxide in 50 ml. of water at reflux for 2 hr. The reaction mixture was chloroform extracted to remove deoxybenzoin. The aqueous layer was acidified and cooled. The white solid that precipitated was collected and dried to give 2.77 g. (23.4% based on deoxybenzoin), m.p. 147–153°. Two recrystallizations from 95% ethanol gave 1.76 g. of 3-benzoyl-3-phenylpropionic acid, m.p. 164–166° (lit.[23a] 162°).

A portion of this acid was converted to methyl 3-benzoyl-3-phenylpropionate, m.p. 49–51° (lit.[23a] 49°).

(48) Experimental method of D. Arigoni, O. Jeger, et al., ref. 20.

(49) E. Beschke, Ann., **384**, 143 (1911).

Characterization of 5,6-*cis*-Diphenylbicyclo[3.1.0]hexane-2-one (IXb).—Photoketone IXb recrystallized to constant m.p. 116.5–117.5°, from 95% ethanol. Prominent peaks in the infrared are located at 3.31, 3.39, 5.80 (s), 6.24, 6.70, 6.91, 7.10, 7.74, 8.10, 8.55, 9.31, 9.75, 11.21, 11.90, and 14.38 μ. The ultraviolet (EtOH) spectra shows strong end absorption (ε at 215 mμ, 17,010; at 220 mμ, 15,100; at 230 mμ, 10,810).

Anal. Calcd. for C₁₈H₁₆O: C, 87.10; H, 6.45. Found: C, 86.89; H, 6.40.

A 2,4-dinitrophenylhydrazone was obtained; m.p. 119–119.5° (orange needles from chloroform–hexane); λ_{max}^{EtOH} 370 mμ (ε 26,470), 226 mμ (ε 14,230), and end absorption.

Degradation of 5,6-*cis*-Diphenylbicyclo[3.1.0]hexan-2-one (IXb).—The procedure used for the oxidation of photoketone IXa was employed. In a typical run 233 mg. of photoketone IXb (0.943 mmole) was dissolved in 100 ml. of dioxane and treated with a cold mixture of 4.6 g. (81 mmoles) of potassium hydroxide and 1.3 ml. (4.0 g., 26 mmoles) of bromine in 30 ml. of water, first for 3 hr. at room temperature and then for 8.5 hr. at reflux. The usual work-up gave 59 mg. of nonacidic material and 190 mg. of acidic material. Acid IXb crystallized to a constant melting point of 200–210° from methanol–water. Prominent peaks in the infrared spectrum (KBr pellet) are located at 2.95, 3.30, 3.42, 3.72, 5.90 (s), 6.22, 6.71, 6.87, 6.98 (s), 7.73, 7.85, 8.21 (s), 9.32, 9.81 (s), 13.03 (s), and 14.3 (s) μ. The n.m.r. spectrum in acetone-*d*₆ with TMS as an internal standard is recorded in Table II.

Ester XIIb was prepared using diazomethane as described above for the stereoisomer. A series of oxidations in which 2.24 g. (9.05 mmoles) of photoketone from liquid–liquid partition chromatography was used and in which nonacidic material was recycled through the oxidation procedure yielded 2.195 g. of acidic material. This was converted with diazomethane to an oil weighing 1.808 g. This material was placed on a 3 × 94 cm. silica gel column slurry-packed in 5% ether in hexane. The ester was eluted in eight 250-ml. fractions of 20% ether–hexane, after elution with 500 ml. of hexane, 500 ml. of 1% ether–hexane, 500 ml. of 2% ether–hexane, 1000 ml. of 5% ether–hexane, 2500 ml. of 10% ether–hexane, 2000 ml. of 15% ether–hexane, and 250 ml. of 20% ether–hexane. The eight fractions weighed 771 mg. representing a 26% yield of XIIb base on photoketone IXb. A portion of this material was recrystallized four times from methanol to a constant melting point of 112–113°. Prominent peaks in the infrared spectrum are located at 3.30, 3.37, 5.80 (s), 6.24, 6.70, 6.95, 7.40, 7.68, 8.56 (s), 9.30, 9.77, and 14.38 μ.

Anal. Calcd. for C₂₀H₂₀O₄: C, 74.07; H, 6.17. Found: C, 73.85, 74.03; H, 6.23, 6.12.

Ring Opening of XIIb.[48]—A solution of 585 mg. of XIIb (1.815 mmoles) and sodium methoxide from 46 mg. of sodium (2.00

g.-atoms) in 10 ml. of dry methanol was stirred under nitrogen at reflux temperature for 4 hr., then for 9.5 hr. at room temperature. From the work-up were obtained 133 mg. of acidic material and 447 mg. of nonacidic material. The acidic portion was treated in ether with an excess of diazomethane to yield an oil weighing 188 mg. This material was combined with the nonacidic product and chromatographed on a 25 mm. × 1 m. column packed with 234 g. of a mixture of Celatom (400 g.) and stationary phase (161 g.). The eluate was scanned at 260 mμ and collected in 20-ml. fractions. The optical density trace showed four major peaks plus two minor ones.

Fractions 22–25 were dissolved in methanol and seeded with a small crystal of dimethyl 3,4-diphenyl-3-hexenedioate. The oily crystals that were deposited were recrystallized from methanol to yield 28 mg., m.p. 110–115°. Several recrystallizations gave white prisms, m.p. 114–116°, whose infrared spectrum was identical with that of authentic dimethyl 3,4-diphenyl-3-hexenedioate and with no mixture m.p. depression. In the original filtrate more crystals were deposited; weight 60 mg., m.p. 112–113°. One recrystallization gave white prisms, m.p. 112.5–113°, whose infrared spectrum was identical with that of an authentic sample of ester XIIb.

The infrared spectrum of fractions 26–29 was almost identical with that of the dimethyl 3,4-diphenyl-2-hexenedioate obtained earlier. This oil was subjected to long tube molecular distillation. The n.m.r. of the distillate was identical with that of the earlier samples of this compound with the exception of the earlier-noted minor impurity peaks.

Photolysis of 5,6-*trans*-Diphenylbicyclo[3.1.0]hexan-2-one (IXa). —Using the same procedure and apparatus as described above, 2.07 g. of photoketone IXa in 500 ml. of 95% ethanol was photolyzed through a Pyrex filter under nitrogen for 48 hr. The crude reaction product was dissolved in 3 ml. of upper phase and chromatographed on a liquid–liquid column 130 × 3.5 cm. dry-packed with 865 g. of a mixture of 700 g. of Celatom and 280 g. of lower phase. The eluate was scanned at 254 mμ and collected in 40-ml. fractions. The optical density trace showed seven imperfectly defined peaks. There was isolated 512 mg. of photoketone IXa and 578 mg. of photoketone IXb from fractions 38–45 and 46–51, respectively.

Photolysis of 5,6-*cis*-Diphenylbicyclo[3.1.0]hexan-2-one (IXb). —In a manner similar to the above, 247 mg. of photoketone IXb in 65 ml. of 95% ethanol was photolyzed for 49 hr. The product was separated into its components by chromatography on a column 100 × 2.5 cm. packed with 200 g. of a mixture of 300 g. of Celatom and 120 g. of lower phase. The eluate was scanned at 260 mμ and collected in 20-ml. fractions. The optical density trace showed seven peaks. Fractions 21–24 gave 27 mg. of photoketone IXa and 25–28 gave 32 mg. of photoketone XIb.

[Contribution from the Department of Chemistry, The University of Chicago, Chicago 37, Ill.]

Carbenoid Formation of Arylcyclopropanes from Olefins, Benzal Bromides, and Organolithium Compounds and from Photolysis of Aryldiazomethanes[1,2]

By G. L. Closs[3] and R. A. Moss[4]

A number of arylcyclopropanes have been prepared by the reaction of benzal bromide with alkyllithium in the presence of olefins. The same cyclopropanes have also been isolated from the photolysis of the corresponding aryldiazomethanes in olefins. Aryl substituents investigated include *p*-methyl, *p*-methoxy, *p*-chloro, and *m*-chloro. Olefins used as substrates were 1-butene, isobutene, *cis*- and *trans*-2-butene, and 2-methyl-2-butene. The configurations of the adducts have been determined by n.m.r. Relative rates of olefin additions have been measured. The data have been interpreted in terms of addition to the olefin of (a) a free carbene in the case of the photolysis of the diazoalkanes and (b) the α-bromolithium compounds as the only intermediate in the reaction involving the organolithium compound.

The most common reactions associated with divalent carbon intermediates are insertion into saturated carbon–hetero bonds and addition to unsaturated centers.[5]

The latter reaction, in particular the addition to olefins yielding cyclopropanes, has been demonstrated to be of great preparative value. Although cyclopropane formation is conveniently formulated as the addition of a free carbene to a double bond, it is by no means neces-

(5) For reviews on the chemistry of divalent carbon see: W. Kirmse, *Angew. Chem.*, **73**, 161 (1961); P. Miginiac, *Bull. soc. chim. France*, 2000 (1962); J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.