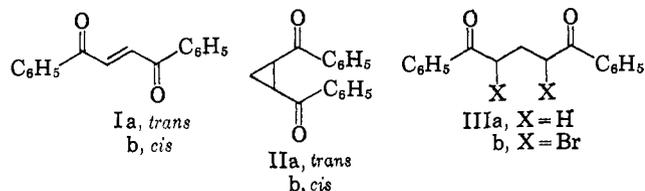


COMMUNICATIONS TO THE EDITOR

PHOTOREDUCTION AND ISOMERIZATION OF THE 1,2-DIBENZOYL-CYCLOPROPANES

Sir:

In view of the well known kindred behavior of many cyclopropyl and olefinic systems¹ and as a logical extension of our photochemical studies on the 1,2-dibenzoyl-ethylenes (I)² it was of interest to determine if the photochemical properties of 1,2-dibenzoylcyclopropane (II) would parallel those of I.



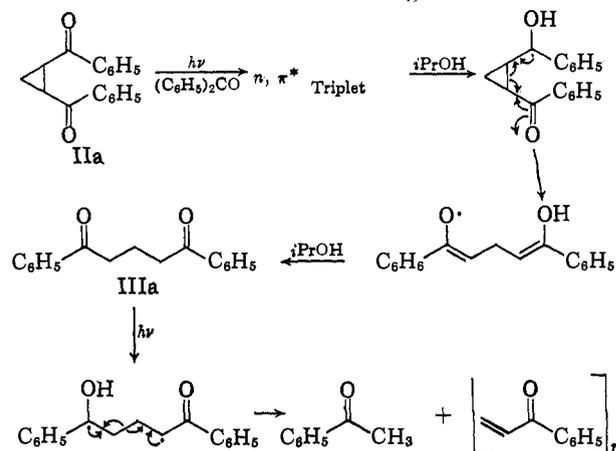
trans-1,2-Dibenzoylcyclopropane (IIa) (m.p. 103–104°) was prepared, in essentially quantitative yield, by treating 1,3-dibenzoylpropane (IIIa) with iodine in methanolic sodium hydroxide. This isomer was initially prepared by Conant and Lutz from 1,3-dibromo-1,3-dibenzoylpropane (IIIb).³ The gross structure was confirmed and *trans*-stereochemistry established by n.m.r. analysis. In addition to a complex set of peaks in the aromatic region ($\tau = 1.8$ to 2.7) the spectrum shows two triplets⁴ of equal intensity centered at $\tau = 6.68$ and $\tau = 8.32$. The integrated peak areas are in the ratio of 5:1:1. The infrared spectrum determined in carbon tetrachloride shows a carbonyl band at 1656 cm^{-1} . The ultraviolet spectrum of IIa observed in cyclohexane possesses at least three maxima: 245 $\text{m}\mu$ ($\epsilon_{\text{max}} = 3130$), 278 $\text{m}\mu$ ($\epsilon_{\text{max}} = 2130$) and 317 $\text{m}\mu$ ($\epsilon_{\text{max}} = 194$).

Irradiation of degassed solutions⁵ of *trans*-1,2-dibenzoylcyclopropane (IIa) in Pyrex vessels with a General Electric sunlamp (275W) affords *cis*-1,2-dibenzoylcyclopropane (IIb) (m.p. 123–124°; *Anal.* Calcd. for $\text{C}_{17}\text{H}_{14}\text{C}_2$: C, 81.58; H, 5.64. Found: C, 81.34; H, 5.45). The n.m.r. spectrum is consistent with the assignment of *cis*-stereochemistry. The latter shows a quartet centered at $\tau = 6.85$, two sextets centered at $\tau = 7.9$ and $\tau = 8.5$, as well as signals due to the aromatic protons. The integrated intensities were within experimental error of the expected values of 2:1:1:10, respectively. The infrared spectrum of IIb is similar to that of IIa; however, the carbonyl frequency of the latter (1689 cm^{-1}) is shifted to higher frequency. A similar shift is observed for the 1,2-dibenzoyl-ethylenes. The ultraviolet spectrum is similar to that of IIa and possesses maxima at 243 $\text{m}\mu$ ($\epsilon_{\text{max}} = 2670$), 277 $\text{m}\mu$ ($\epsilon_{\text{max}} = 1800$) and 320 $\text{m}\mu$ ($\epsilon_{\text{max}} = 140$).

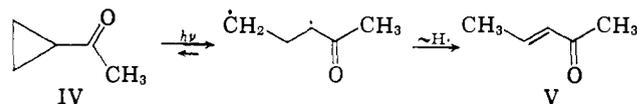
The photoisomerization of *trans*-1,2-dibenzoylcyclopropane was shown to be reversible.⁶ Irradiation of a pure sample of the *cis* isomer IIb affords IIa. The

cis-trans ratio of the photostationary state remains to be determined. Isomerization of IIb to the thermodynamically more stable *trans* form also may be effected with ethanolic sodium hydroxide.

The course of the over-all reaction in hydrogen donor solvents can be altered drastically by introducing a photosensitizer. For example, the primary product formed on irradiation of IIa in a mixture of 2-propanol and benzene in the presence of benzophenone is 1,3-dibenzoylpropane (IIIa). This reaction is complicated by the fact that the reduction product is photochemically unstable, and on irradiation fragments into acetophenone and a second product which is isolated as a polymer.⁷ The reduction of IIa to IIIa is completely analogous to the reduction of I to dibenzoyl-ethane² and probably proceeds by way of the n, π^* triplet state of IIa (with radical character on oxygen) generated indirectly by photosensitization. The over-all reaction scheme is assumed to be the following.



The *cis,trans*-photoconversion requiring reversible bond scission is more difficult to rationalize. In the case of the 1,2-dibenzoylcyclopropanes maximum stabilization of the incipient radicals would be achieved if the bond-breaking process involves the ring bond beta to both carbonyl chromophores. Such a process is not without analogy. Pitts and Norman,⁸ for example, have observed that the vapor phase photolysis of acetylcyclopropane (IV) affords almost exclusively 2-penten-4-one (V). Initial homolysis of the cyclopropyl bond beta to the carbonyl group followed by 1,2-hydrogen migration was advanced to explain the formation of the α, β -unsaturated ketone V. Furthermore, only the recyclization reaction appears to compete effectively with hydrogen transfer.



Isomerization through reversible photodissociation of the benzoyl groups in IIa or IIb seems improbable, particularly in view of the conspicuous absence of major by-products derived from secondary reactions of either the benzoyl or cyclopropyl radicals. The light absorbed by IIa or IIb possesses sufficient energy to effect

(7) The polymer is conceivably low molecular weight polyvinylphenyl ketone. The infrared spectrum possesses features in common with that of an authentic higher molecular weight sample of this material prepared independently by H. G. Cassidy and R. E. Moser. A detailed study of the photochemistry of IIIa which includes the fragmentation reaction is in progress.

(8) J. Pitts, Jr., and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954).

(1) R. A. Raphael in "Chemistry of Carbon Compounds," E. H. Rodd, Ed., Vol. IIa, Elsevier Publishing Co., New York, N. Y., 1953, p. 25.

(2) G. W. Griffin and E. J. O'Connell, *J. Am. Chem. Soc.*, **84**, 4148 (1962).

(3) J. B. Conant and R. E. Lutz, *ibid.*, **49**, 1083 (1927).

(4) J. D. Roberts, "An Introduction to Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin Inc., New York, N. Y., 1961, pp. 77, 98.

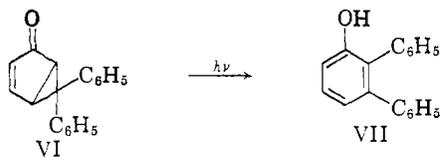
(5) Benzene, ether, 2-propanol and methanol have been employed as solvents. A bright yellow color appears instantaneously, however, when alcohols are utilized.

(6) A related *cis-trans* isomerization of the 1,2-dimethylcyclopropane formed by the addition of the carbene generated from diazofluorene to 2-butene has been observed by W. von E. Doering and M. Jones, Jr., of this Laboratory.

the proposed bond cleavage. The energy corresponding to 320 m μ radiation (90 kcal./mole) is substantially greater than the maximum energy required for bond dissociation in cyclopropane itself (53.4 kcal./mole)⁹ and this in turn is probably higher than that required for bond rupture in IIa or IIb.¹⁰

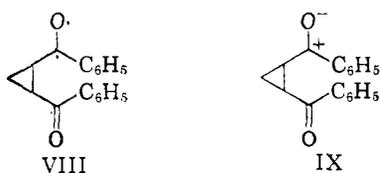
Particular interest is attached to the problem of the mode of energy transfer from the activated carbonyl chromophore to the beta bond. It remains to be established whether the cleavage process leading to isomerization involves an electronically excited species (perhaps in a high vibrational level)¹¹ or is a thermal reaction of the molecule in the ground state requiring prior conversion of electronic energy to vibrational energy.¹² A study of the pressure dependence of the gas phase isomerization of 1,2-diacetylcyclopropane, which is in progress, should provide information on this matter. Internal conversion of electronic energy to thermal energy has recently been invoked to explain the conversion of 1,3,5-cycloheptatriene to toluene in the gas phase.¹³ In the case at hand, it seems unusual that collisional deactivation of the electronically excited species would not compete efficiently with internal conversion since the reaction is effected in the condensed phase.

The isomerization reaction described herein is undoubtedly related to the irreversible photochemical conversion of the ketone VI to 2,3-diphenylphenol (VII). A vibrationally excited ground state (thermal) mechanism for this reaction was excluded on the basis



that n, π^* photochemical reactions do not in general parallel thermal reactions.¹⁴

Classical, radical and ionic structures such as VIII and IX which allow delocalization of the electrons in the beta bond may be invoked to explain the isomerization.¹⁵ Although such representations appear to be functional it is questionable whether they accurately represent the excited state.¹⁶



Acknowledgment.—We gratefully acknowledge support of this work by the Army Research Office (Durham).

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RECEIVED JANUARY 22, 1963

(9) S. W. Benson and A. Amano, *J. Chem. Phys.*, **36**, 3464 (1962).

(10) The low energy (320 m μ) bands in the spectra of IIa and IIb are undoubtedly the significant absorption bands since Pyrex vessels and hence light above 300 m μ was employed.

(11) G. Zimmerman, L. Chow and U. Paik, *J. Am. Chem. Soc.*, **80**, 3528 (1958).

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(13) R. Srinivasan *ibid.*, **84**, 3432 (1962).

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(15) O. L. Chapman, A. I. Dutton and P. Fitton, *Abstr. Am. Chem. Soc. National Meeting, Atlantic City, N. J., September, 1962*, p. 88-Q; O. L. Chapman and S. L. Smith, *J. Org. Chem.*, **27**, 2291 (1962).

(16) M. Kasha in "Comparative Effects of Radiation," ed. by M. Burton, J. S. Kirby-Smith and J. L. Magee, John Wiley and Sons, Inc., New York, N. Y., 1960, p. 85.

THE STRUCTURE OF PHENYLMAGNESIUM BROMIDE DIETHERATE AND THE NATURE OF GRIGNARD REAGENTS

Sir:

Since their discovery over sixty years ago,¹ the nature of the Grignard reagents has been the subject of continuous investigation and speculation.^{2,3} We report here the structure of phenylmagnesium bromide dietherate and certain other observations which have a strong bearing on this problem and seem to require a major modification of some current interpretations.

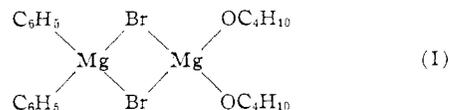
Phenylmagnesium bromide was prepared by the action of phenyl bromide and magnesium in diethyl ether. Upon concentration of the reagent by removing ether under reduced pressure, crystals of empirical formula $C_6H_5MgBr \cdot 2(C_4H_{10}O)$ can be obtained upon cooling and rewarming, confirming observations of Schlenk.⁴ The composition of the crystals does not depend upon concentration so long as the ratio of ether to phenylmagnesium bromide is greater than two. At the stoichiometric composition the entire solution may be crystallized at 15–20°. Further removal of ether is possible only at higher temperatures and/or lower pressures. At lower ether content an amorphous polymer forms, and the entire reagent polymerizes if all the ether is removed. The polymer redissolves in ether.

Crystals of $C_6H_5MgBr \cdot 2(C_4H_{10}O)$ are orthorhombic, $a = 12.25$, $b = 12.81$, $c = 11.02$ Å, space group $P2_12_12_1$, $Z = 4$. The crystals give a positive color test for active organometallic compounds, such as the Grignard reagent.⁵ A three-dimensional Patterson map yielded bromine and oxygen positions. The structure determination has proceeded far enough that the phenyl group has been well resolved, rough ethyl positions of the ethers have been found, and $R = 17.8\%$ for three-dimensional data. The structure consists of phenylmagnesium bromide dietherate monomers (Fig. 1) with the phenyl group, a bromine atom and two ether molecules bonded tetrahedrally to a single magnesium atom.

A preliminary study of diphenylmagnesium crystallized from diethyl ether shows that it is also a dietherate consisting of monomers, undoubtedly with tetrahedral coordination of phenyls and ethers to magnesium. It is well known that $MgBr_2$ forms etherates soluble in ether. We have obtained crystals of an etherate, but have not yet examined them by X-rays.

Though the structural work reported here has validity only for the solid state, the following conclusions concerning this Grignard in ether solution seem warranted:

(1) The often suggested species, such as $(C_6H_5)_2Mg \cdot MgBr_2 \cdot n(C_4H_{10}O)$, are unlikely because they would most probably have an ether/Mg ratio of less than two. For example, a probable structure, based on known structures of organometallic compounds and metal halides such as Al_2Br_6 , etc., would be



Higher complexes should contain even lower ether/magnesium ratios. The observed fact that removing ether until the ether/magnesium ratio is less than two

(1) V. Grignard, *Compt. rend.*, **130**, 1322 (1900).

(2) See G. E. Coates, "Organometallic Compounds," 2nd Ed., John Wiley and Sons, New York, N. Y., 1960, and older reviews listed therein.

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(4) W. Schlenk, Thesis, Univ. of Charlottenburg, 1929.

(5) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).