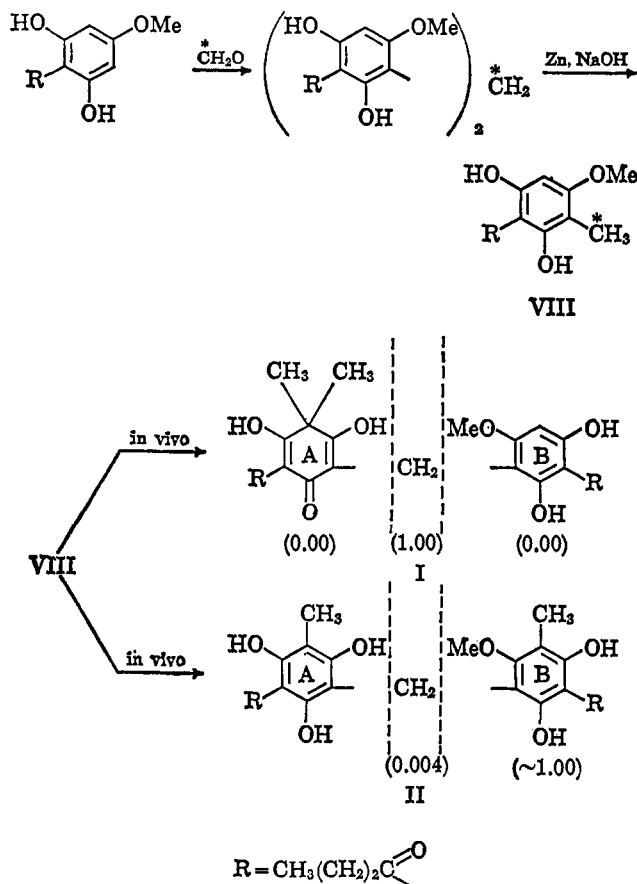


The methylene bridge also is derived from methionine with the same efficiency, suggesting that it has evolved from the methyl group of a monomeric species perhaps via an *o*- or *p*-quinone methide⁶ such as V or VI (or their hydration products).

For this reason, methyl-labeled aspidinol (VIII)⁷ was prepared as shown and fed (12.7 curies/mole, 16.8×10^6 d.p.m. total) with radioactivity recovered (incorporation: 1.17% in raw filicin) in both I (26.5 μ curies/mole) and II (112 μ curies/mole). Degradation of I, as above, showed that all of its activity resides in



the methylene bridge, strongly indicating that VIII is the precursor of both the B ring and methylene bridge, via the aforementioned oxidation process. By contrast, only traces of activity were found in the methylene carbon of II,⁸ most of the activity residing in the B ring section. Here, VIII is directly the precursor of the B ring while the methylene bridge and A ring are presumably derived from a naturally occurring C-methyl isomer of VIII.

Lederer⁹ has recently drawn attention to the function of methylene quinones such as V and VI in oxidative phosphorylation. Desaspidin is in fact a potent un-

coupling agent,¹⁰ and we suggest that the function of these compounds in the plant may be to act as oxidative phosphorylation regulators whose efficiency in this process is modified by the degree of methyl substitution.

(10) L. Runeberg, Thesis, University of Helsinki, 1963, Societas Scientiarum Fennica, Commentationes Biologicae, XXVI, 7.

(11) Fulbright Research Scholar, 1964-1965, on leave from Medica Ltd., Helsinki, Finland.

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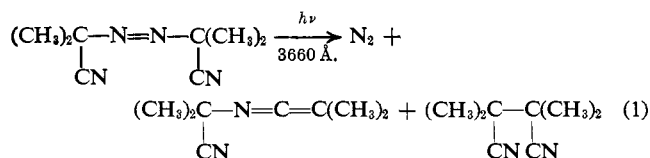
Photochemistry of Adsorbed Organic Molecules. II. "Cage" Effects in the Photolysis of Azobisisobutyronitrile and Tetramethyl-1,3-cyclobutanedione on Silica Gel¹

Sir:

We¹ and others² have previously reported that physical adsorption strongly perturbs electronic absorption spectra of relatively polar organic molecules. Obviously, then, the electronic configurations of the bound, or adsorbed, species are not the same as the species "free" in solution. One could, and should, therefore, expect different photochemical behavior in the two different environments on this ground alone, but also it is highly reasonable that the secondary reactions will also be considerably different.

We wish now to report two photochemical reactions that are profoundly affected by physical adsorption in solvent-silica gel matrices

Azobisisobutyronitrile (AIBN) in benzene solvent has been reported to undergo photodecomposition with light of 3660 Å. to yield approximately 60% of the ketenimine, dimethyl-N-(2-cyano-2-propyl)ketenimine (eq. 1),³ the remainder being tetramethylsuccinonitrile.



The quantum yield for destruction of AIBN (in benzene) was measured by Smith and found to be 0.46. The ketenimine has a very characteristic absorption band at about 2900 Å., and our own observations of the photolysis of AIBN in benzene show the pronounced appearance of this band with time and a corresponding disappearance of the $n-\pi^*$ (at 3300-3500 Å.) band of the azo compound. We have found that when the medium is changed to benzene-silica gel, AIBN decomposes at a virtually identical rate, but *no ketenimine is formed*, the sole product being the tetramethylsuccinonitrile. Irradiations were carried out in 0.1-cm.-path-length cells at 3660 Å.; the ultraviolet spectrum was scanned at various time intervals. The $n-$

(1) Number I of this series is: P. A. Leermakers and H. T. Thomas, *J. Am. Chem. Soc.*, **87**, 1620 (1965).

(2) For an excellent review see A. Terenin, *Advan. Catalysis*, **15**, 227 (1964).

(3) P. Smith and A. M. Rosenberg, *J. Am. Chem. Soc.*, **81**, 2037 (1959).

(6) A. B. Turner, *Quart. Rev. (London)*, **18**, 347 (1964).

(7) Monomers such as VIII have been isolated (e.g., R. C. Blakemore, K. Bowden, J. L. Broadbent, and A. C. Drysdale, *J. Pharm. Pharmacol.*, **16**, 464 (1964)), but recent studies (A. Penttila and J. Sundman, unpublished results) show that VIII, at least, never occurs in nature and must be considered an artifact arising from excess heat or alkali during isolation.

(8) To the extent that activity resides in the bridge carbon, methylation of VIII must have occurred. Although further confirmation is required on this point, this suggests that aromatic C-methylation occurs after the polyketone stage; cf. ref. 2.

(9) E. Lederer, *J. Biol. Chem.*, **93**, 449 (1964).

π^* band of AIBN disappeared in both benzene and in the adsorption matrix, but in the latter there was no corresponding appearance of the 2900 Å. band of the ketenimine. Such a band would be expected to be somewhat blue shifted in the matrix, but it was obviously not present at all. For gross product analysis 5 g. of AIBN in a matrix containing 180 ml. of benzene and 188 g. of silica gel was irradiated at primarily 3660 Å. in a Hanovia immersion reactor until 88% of the theoretical yield of nitrogen was evolved (in 150 min.). The crude net yield of tetramethylsuccinonitrile isolated was 90%. Identification was based on comparison of infrared and n.m.r. spectra with those of an authentic sample.

Apparently in benzene solution the cyanopropyl radicals can rotate within the solvent cage to give the unsymmetrical coupling product, whereas on the silica gel surface the radicals are not allowed this freedom and carbon-carbon coupling is the exclusive reaction.

Tetramethyl-1,3-cyclobutanedione was also irradiated in a solvent-silica gel matrix; in this case the solvent was cyclohexane, and irradiation was carried out at 3130 Å. where both adsorbed and nonadsorbed dione have approximately equal extinction coefficients. The photochemistry of this class of compounds in solution has been summarized recently.⁴ The quantum yield for decomposition (to carbon monoxide and tetramethylethylene *via* a cyclopropanone intermediate) in benzene at 3660 Å. is a remarkably high 0.38. We have found in the adsorption matrix the *quantum yield for decomposition is reduced threefold*. This is a real effect and not due to light scattering, since the matrices are transparent down to 2200 Å., and for AIBN the quantum yield for destruction is insensitive to the medium (*i.e.* it is as high in the matrix as in the pure solvent). Probably the most reasonable explanation of these facts is that in the AIBN decomposition (as is the case for azo compounds in general^{5,6}) nitrogen is lost in a concerted step, and the N₂ molecule itself being quite nonpolar readily leaves the adsorbant surface. However, in photolysis of the cyclobutanedione the leaving carbon monoxide molecule is probably lost in two steps; thus acyl-alkyl bond *re-formation*, due to the "super cage" effect of the surface, predominates over unredeemable photodecarbonylation.

Acknowledgments. This work has been supported by the Petroleum Research Fund of the American Chemical Society and by the National Science Foundation.

(4) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *J. Am. Chem. Soc.*, **87**, 2613 (1965).

(5) H. C. Ramsperger, *ibid.*, **49**, 912, 1495 (1927); **50**, 714 (1928); **51**, 2134 (1929).

(6) See, however, S. Selzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965).

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Two Diisotactic Processes in the Anionic Polymerization of Isopropyl Acrylate with Phenylmagnesium Bromide

Sir:

We have reported¹ that anionic polymerization of methyl acrylate- α,β -*d*₂ in toluene at -78° with LiAlH₄

(1) T. Yoshino, J. Komiyama, and M. Shinomiya, *J. Am. Chem. Soc.*, **86**, 4482 (1964).

catalyst is stereoregular with respect to both the CD₂COOR and the CHD groups. Schuerch, *et al.*,² have reported, however, that when isopropyl acrylate- α,β -*d*₂ is polymerized in toluene at -78° by using phenylmagnesium bromide as catalyst the configuration of the polymer obtained is random with respect to the CHD groups and stereoregular with respect to the CD₂COOR groups. Their conclusion was derived from their observation that the two *meso*-methylene proton signals were nearly equal in intensity.

The equal signal intensity, however, does not necessarily mean random placement of the CHD groups, but it is also expected for a polymer with syndiotactic CHD groups and for a 1:1 mixture of *threo*- and *erythro*-diisotactic polymers or sequences. Settlement of this problem is important for the study of anionic polymerization. We shall report in this communication that the diisotactic mixture is responsible for the equal intensity described above.

In Figure 1a is shown the backbone proton spectrum of polyisopropyl acrylate- β -*d*₁ with isotactic CHCOOR groups and random CHD groups.³ This polymer was prepared from isopropyl acrylate- β -*d*₁ with the ratio, γ , of *trans*- β -*d*₁:*cis*- β -*d*₁ isomer equal to unity by an anionic process in toluene at -78° initiated with *n*-butylmagnesium bromide. The signals at τ 7.41, 7.87, and 8.30 are assigned to the α -, β_g -, and β_t -protons in isotactic sequences, respectively, on the analogy of the assignment of the proton signals of polymethyl acrylate- α,β -*d*₂.^{1,4} Here β_g and β_t mean the β -positions *gauche* and *trans* to the carboxyl groups, respectively, for the hypothetical *trans* zigzag skeletal conformation.

We shall suppose two diisotactic acrylate- β -*d*₁ polymers obtainable from monomer with $\gamma = 0$ through *trans* and *cis* openings of the double bond, respectively. The signal patterns expected for the α -protons decoupled from β_t of these diisotactic polymers and the 1:1 mixture of them (with corrections due to $\gamma = 1/6$, indicated by broken lines) are shown in Figures 1c-e. For the α -protons decoupled from β_t of a polymer with syndiotactic CHD groups and isotactic CHCOOR groups, a doublet shown in Figure 1f is expected, because each α -proton is coupled with a single β_g -proton. The peak separations and intensity distributions in these signal patterns were estimated from the observed chemical shift and coupling constant (7.5 c.p.s.) between the α - and β_g -protons.

The decoupled α -proton signal of a polymer with isotactic CHCOOR groups and random CHD groups will be expressed by superposing, in 1:1 intensity ratio, the decoupled α -proton signal of the polymer with syndiotactic CHD groups on that of the diisotactic polymer mixture.

According to the above consideration, an isotactic acrylate- β -*d*₁ polymer showing *meso*-methylene signals of equal intensity can be found whether the polymer is isotactic, syndiotactic, or random with respect to the CHD groups by measuring the α -proton signal of the polymer decoupled from the β_t -protons.

(2) C. Schuerch, W. Fowells, A. Yamada, F. A. Bovey, F. B. Hood, and E. W. Anderson, *ibid.*, **86**, 4481 (1964).

(3) The equal intensity of the *meso*-methylene proton signals of this polymer indicates that the ratio of *cis*:*trans* opening of the double bond is equal for the both isomers.

(4) T. Yoshino, M. Shinomiya, and J. Komiyama, *J. Am. Chem. Soc.*, **87**, 387 (1965).