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 N_2 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.

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(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).

Peter A. Leermakers, Lawrence D. Weis, Harold T. Thomas
Hall Laboratory of Chemistry, Wesleyan University
Middletown, Connecticut 06457

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

Sir:

We have reported[1] that anionic polymerization of methyl acrylate-α,β-d_2 in toluene at $-78°$ with $LiAlH_4$

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

catalyst is stereoregular with respect to both the CDCOOR and the CHD groups. Schuerch, *et al.*,[2] have reported, however, that when isopropyl acrylate-α,cis-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 CDCOOR 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 $\gamma = \frac{1}{6}$, 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.
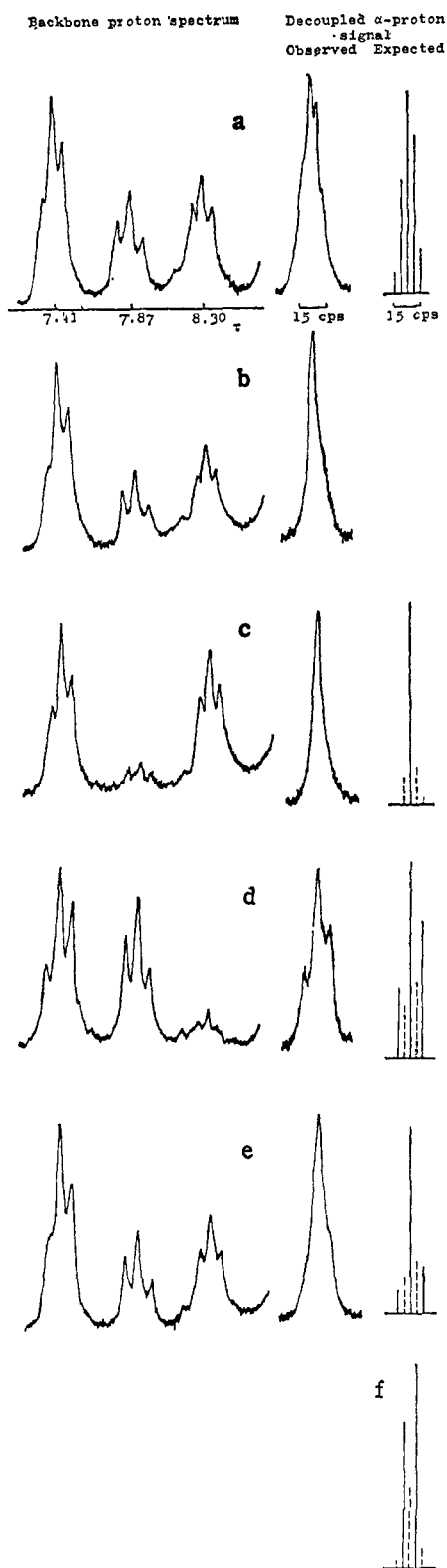(4) T. Yoshino, M. Shinomiya, and J. Komiyama, *J. Am. Chem. Soc.*, 87, 387 (1965).
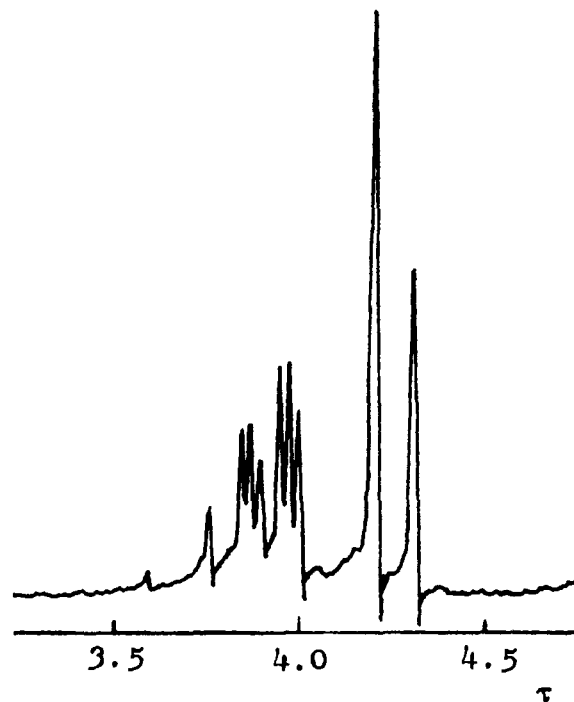
Figure 2. Vinyl proton spectrum of isopropyl acrylate-β-d_1 with γ = $^1/_6$. The doublets at lower and higher fields are assigned to the *cis* and *trans* β-protons, respectively, and the others to the α-proton, according to the assignment for nondeuterated isopropyl acrylate by W. Breugel, *et al.*, *Z. Elektrochem.*, **64**, 1121 (1960).

Figure 1. Proton signals of polyisopropyl acrylate-β-d_1 (a) with random CHD groups, (b) prepared in toluene at $-78°$ using Ph-MgBr catalyst, (c) with κ = $^1/_6$, (d) with κ = 4, (e) prepared by mixing c and d, and (f) with syndiotactic CHD groups. The spectral measurements were carried out by a Varian HR-100 spectrometer for 10% solutions in chlorobenzene at room temperature. The full lines in the expected signal patterns apply to completely regular or irregular polymers and the broken lines represent corrections due to γ = $^1/_6$.

Polyisopropyl acrylate-β-d_1 with the ratio κ of the β_g- to the β_t-proton signal nearly equal to unity (see

Figure 1b) was prepared from monomer with γ = $^1/_6$ in toluene at $-78°$ by using phenylmagnesium bromide catalyst[5] prepared by the usual method in ethyl ether. Polymers with κ = $^1/_6$ and κ = 4 were also prepared from the monomer with γ = $^1/_6$ in toluene at $-78°$. The catalysts used were, respectively, *n*-butylmagnesium bromide prepared in ether (for κ = $^1/_6$ polymer) and the supernatant solution (phenyl:Br = 3) of the product obtained by evaporation of ether from a mixture of toluene and phenyl Grignard in ether. The backbone proton spectra of these polymers and the 1:1 mixture of them are shown in Figure 1c–e. The decoupled α-proton signals of these three polymers and the polymer with random CHD groups mentioned before are shown in Figure 1c–e,a. Coincidence of the observed and the expected decoupled signals of these polymers justifies the signal pattern for the decoupled α-protons of the polymer with syndiotactic CHD groups.

The decoupled α-proton signal of the polymer prepared with phenylmagnesium bromide is the same as that of the diisotactic mixture and is different from the observed decoupled signal of the polymer with random CHD groups and from the signal pattern expected for the decoupled α-protons of the polymer with syndiotactic CHD groups. We can, therefore, conclude that diisotactic processes accompanied by *cis* and *trans* openings of the double bond, respectively, occur in the anionic polymerization with phenylmagnesium bromide to give polyisopropyl acrylate-β-d_1 with $\kappa \approx 1$.

(5) Independent of whether the catalyst contains ether or not, polyisopropyl acrylate-α,β-d_2 with $\kappa \approx 1$ was obtained from monomer with γ = 5. The value of κ changes with polymerization temperature. Details of various Grignard reagents as polymerization catalysts will be described in other place.

This conclusion may be transferred to the polymerization of α,β-d_2 and d_0 monomers.

Isopropyl acrylate-β-d_1 with $\gamma = \frac{1}{6}$ was prepared by the following procedure. After the hydroxyl group of propargyl alcohol was protected by an addition reaction with 2,3-dihydropyran,[6] a THF solution of the adduct was added to an excess amount of ethyl Grignard in THF to form the Grignard reagent of the adduct, and heavy water was added to the Grignard solution. After addition of 20% sulfuric acid to the product the deuterated adduct was extracted and purified by vacuum distillation. The deuteration was repeated twice. Deuterated propargyl alcohol liberated by acid hydrolysis of the adduct was extracted, vacuum distilled, then converted to acid by Wolf's method,[7] and esterified. The acetylenic proton content in the deuterated ester was found to be less than 0.5% by n.m.r. inspection. The deuterated ester was hydrogenated at $-20°$ using the Lindlar catalyst.[8] The value of γ of isopropyl acrylate-β-d_1 thus obtained was estimated from the intensities of the β-proton signals of the acrylate shown in Figure 2.

Isopropyl acrylate-β-d_1 with $\gamma = 1$ was prepared from monomers with $\gamma = \frac{1}{6}$ and $\gamma = \frac{3}{2}$. The monomer with $\gamma = \frac{3}{2}$ was obtained by addition of DCl to acetylene, conversion to Grignard reagent, carboxylation, and esterification.

(6) H. B. Henbest, E. R. H. Jones, and I. M. S. Walls, *J. Chem. Soc.*, 3646 (1950).
(7) V. Wolf, *Chem. Ber.*, **86**, 735 (1953).
(8) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

Tsuneo Yoshino, Kiyoshi Kuno
Basic Research Laboratories, Toyo Rayon Company
Kamakura, Kanagawa, Japan

Ozone: A New Cleavage Reagent for Organosilanes

Sir:

Previous studies of the combustion of alkylsilanes in the vapor phase[1,2] have yielded flame velocities for these compounds approximately two to four times greater than those for their corresponding all-carbon analogs. It was also noted that whereas such burning rates for silanes vary significantly with molecular structure, those for a wide variety of hydrocarbons all have approximately the same value independent of structure.[3]

(1) R. L. Schalla, G. R. McDonald, and M. Gerstein in "Fifth Symposium (International) on Combustion," Reinhold Publishing Corp., New York, N. Y., 1955, pp. 705–710.
(2) M. Gerstein in "Seventh Symposium (International) on Combustion," Butterworths Scientific Publications, London, 1959, pp. 903–905.

These results suggested that silanes may be oxidized by a mechanism not available to hydrocarbons, *e.g.*, one involving the availability of 3d orbitals in silicon. To test this hypothesis, various organosilanes were treated with the more reactive allotrope of oxygen, ozone.

We now wish to report that ozone cleaves the Si–Y bond in molecules of the general structure R_3Si–Y, where R is an organic group and Y is an alkyl, trialkylsilyloxy, hydrogen, or hydroxyl substituent. In all cases, the resulting products are hydroxysilanes and siloxanes.

Triethylsilane reacts exothermally with ozone, yielding triethylhydroxysilane as the initial major product after 2 hr. of bubbling a 4% solution of ozone in oxygen through the neat liquid at 24°. The identity of the product was checked by microanalysis and by comparison of physical properties, vapor phase chromatographic behavior, and infrared absorption spectrum with those of an authentic sample of triethylsilanol prepared by the hydrolysis of triethylchlorosilane. After continued ozonization for an additional 6 hr., the product was found by vapor phase chromatography to contain hexaethyldisiloxane, hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, and octaethyltrisiloxane.

Treatment of triethylsilanol with ozone for 12 hr. afforded about 50% yield of hexaethyldisiloxane. Extended treatment of the silanol or hexaethyldisiloxane with ozone gave, in each case, hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, and octaethyltrisiloxane.

Cleavage of a silicon–alkyl bond was observed when ozone was bubbled through tetraethylsilane for 18 hr. at room temperature. The silicon-containing products, as evidenced by vapor phase chromatography, were identical with those obtained from the reaction of triethylhydroxysilane above.

The rates of cleavage by ozone fall in the order: Si–H >> (dehydration of SiOH to siloxane) ~Si–R. Pure oxygen does not cause any of these cleavage reactions to occur significantly at room temperature even after three- to fivefold longer reaction times.

Work is continuing on the elucidation of the mechanistic path, occurrence of intermediates, and the influence of molecular structure in this newly found ozone reaction.

(3) M. Gerstein, O. Levine, and E. L. Wong, *J. Am. Chem. Soc.*, **73**, 418 (1951).

Leonard Spialter, J. Dudley Austin
Chemistry Research Laboratory
Aerospace Research Laboratories
U. S. Office of Aerospace Research
Wright-Patterson Air Force Base, Ohio