(1.5:1) resulted in the formation of IIId, mp 154°, and IIId′, mp 115°, in 5 and 18.6% yields, respectively.

In all of those cases the separation of II from II′ was so difficult that the mixture of II and II′ was used for photolysis. However, in the case of the *p*-anisyl derivative the separation of IIb′ from IIb was successful, so the photolysis of IIb′ as the pure state was monitored. This proved that IIIb′ came from IIb′. Therefore, we could establish the relation that III and III′ came from II and II′, respectively.

Two points are to be noted. (1) This type of rearrangement did not occur thermally.[14] (2) Substituent effects on the product yield were observed. It appears that there is a tendency for the electron-donating substituents to enhance the relative yield of III, while the electron-attracting substituents increase the yield of III′.[15] For example, IIIa arose as a major product by the photolysis of a 2.2:1 mixture of IIa and IIa′, while IIIc′ came out as a major product by the photolysis of a mixture of IIc and IIc′ with almost the same composition (2.3:1) as in the mixture of IIa and IIa′.

Two mechanistic paths a and b may be postulated to account for the formation of III (or III′). In path a, ketene IX (or IX′) formed by the enone–π-methane interaction in the excited state of II (or II′) plays an important role in the rearrangement.[16,17] The photochemical formation of a similar type of ketene from the related bicyclic dienones has been well documented recently.[2–4]

In path b, the photochemically induced cleavage of the O–O bond in II (or II′) is assumed to initiate the reaction, which results in the generation of lactone VII (or VII′). The photocleavage of the O–O bond of epidioxides[7,8] and/or the formation of lactone XI from VI by the thermal cleavage of the O–O bond[14] have been reported.

One of the key points in path b is whether or not the lactone VII (or VII′) rearranges to III (or III′) by photolysis. As the preparation of VII (or VII′) has not been successful, a closely related lactone XI was prepared by the method described by Forbes, *et al.*[14] The photolysis of XI indicated that no sign of the molecular rearrangement was observed, but a hydrogen shift occurred exclusively to give a fully conjugated lactone XII.[14] The formation of XII from XI is rationalized as the photochemically induced hydrogen shift.[18]

From this fact it may not be unlikely to assume that VII (or VII′), if it is once formed, undergoes a rapid photoisomerization to give a conjugated lactone such as VIII (or VIII′) in favor of the formation of intermediate X (or X′) by the bonding at β and β' in VII (or VII′). In all of these points of view we tentatively assume path a to be more favorable, though further studies are necessary to complete the mechanism, particularly to confirm the ketene intermediate and to rationalize the substituent effects observed in this study.

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[14] E. J. Forbes and J. Griffith, *J. Chem. Soc. C*, 575 (1968).

[15] It is considered that the electronic nature of the substituent group in II (or II′) influences the yield of III (or III′). However, it is difficult at present to tell how the substituent affects the rearrangement. One aspect we consider for this is that the substituents may induce some effect on the stability and/or reactivity of intermediate X (or X′) which may arise from IX (or IX′) by the cleavage of the O–O bond and subsequent lactone ring formation.

[16] The ultraviolet absorption spectrum of a mixture of IId and IId′ was measured in alcohol, which indicated that the shoulders of absorption appear at 210 and 290 $m\mu$,[9] and the tail of absorption is extended up to 300 $m\mu$.[8]

[17] For a discussion of the ultraviolet absorption spectrum of fundamental bicyclic enone–π-methane compounds, see O. L. Chapman and D. J. Pasto, *J. Amer. Chem. Soc.*, **82**, 3642 (1960).

[18] R. E. Lutz, P. S. Bailey, C. K. Dien, and J. Riniker, *ibid.*, **75**, 5039 (1953); M. J. Jorgenson and S. Patimterapibal, *Tetrahedron Lett.*, 489 (1970), and references cited therein.

[19] On study leave during 1971–1972 (June) as a Visiting Scientist at Simon Fraser University, Burnaby 2, British Columbia, Canada, whose hospitality, along with that of Professor Y. L. Chow, the author (T. T.) acknowledges.

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New Conformational Species. Matrix Photochemistry of Methyl Propiolate

Sir:

The structure of esters has been a subject of great interest and controversy for more than four decades.[1] Early studies of the dipole moments of simple alkyl esters of the lower carboxylic acids were wholly consistent with the notion that almost all the molecules assumed the trans configuration.[1a–e] Furthermore, Zahn[2] had shown that the moments of many carboxylic esters were independent of temperature over ranges of 140–190° and at temperatures as high as 244°. Microwave spectroscopy[3] and electron diffraction[4] studies have since supported the initial trans formulation for methyl formate. In no case of the acyclic aliphatic carboxylic esters has structural information concerning the cis form been obtained, although recently Krishna[5] has suggested the cis configuration for geranyl formate on the basis of dipole moment measurements.[6] In connection with investigations of matrix-isolated conjugated cabonyl compounds, we have studied the photochemical behavior of methyl propiolate (**1**) in argon at 20.4°K. Williams and Owen have previously reported the microwave spectrum[9] and a vibrational analysis[10] of **1** and from temperature-dependent studies concluded that this ester was present almost exclusively in the trans conformation.

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[1] (a) A. Eucken and L. Meyer, *Phys. Z.*, **30**, 397 (1929); (b) C. T. Zahn, *Phys. Rev.*, **37**, 1516 (1931); (c) C. T. Zahn, *Trans. Faraday Soc.*, **30**, 804 (1934); (d) L. E. Sutton, *ibid.*, **30**, 789 (1934); (e) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936); (f) H. W. Thompson and P. Torkington, *ibid.*, 641 (1945); (g) J. Karpovitch, *J. Chem. Phys.*, **22**, 1767 (1954); (h) D. Tabuchi, *ibid.*, **28**, 1014 (1958); (i) A. J. Bowles, W. O. George, and D. B. Cunliffe Jones, *Chem. Commun.*, 103 (1970); (j) N. L. Owen and N. Sheppard, *Proc. Chem. Soc.*, 264 (1963); (k) R. Huisgen and H. Ott, *Tetrahedron*, **6**, 253 (1959).

[2] C. T. Zahn, *Phys. Z.*, **33**, 730 (1932).

[3] R. F. Curl, *J. Chem. Phys.*, **30**, 1529 (1959).

[4] J. M. O'Gorman, W. Shand, and V. Schomaker, *J. Amer. Chem. Soc.*, **72**, 4222 (1950).

[5] B. Krishna, S. C. Srivastava, and S. V. Mahadane, *Tetrahedron*, **23**, 4801 (1967).

[6] In the case of haloformates and carbonates, positive evidence exists for the presence of a dynamic equilibrium from the temperature dependence of dipole moments.[7] Although some authors[8] have assigned the cis structure to the more stable forms of certain chloro- and fluoroformates, there seems to be disagreement concerning these assignments.[8,9]

[7] S. Mizushima and M. Kubo, *Bull. Chem. Soc. Jap.*, **13**, 174 (1938).

[8] (a) E. Bock and D. Iwacha, *Can. J. Chem.*, **45**, 3177 (1969); (b) E. Bock, D. Iwacha, H. Hutton, and A. Queen, *ibid.*, **44**, 1645 (1968).

[9] G. Williams, N. L. Owen, and J. Sheridan, *Trans. Faraday Soc.*, **67**, 922 (1971).

[10] G. Williams and N. L. Owen, *ibid.*, **67**, 950 (1971).

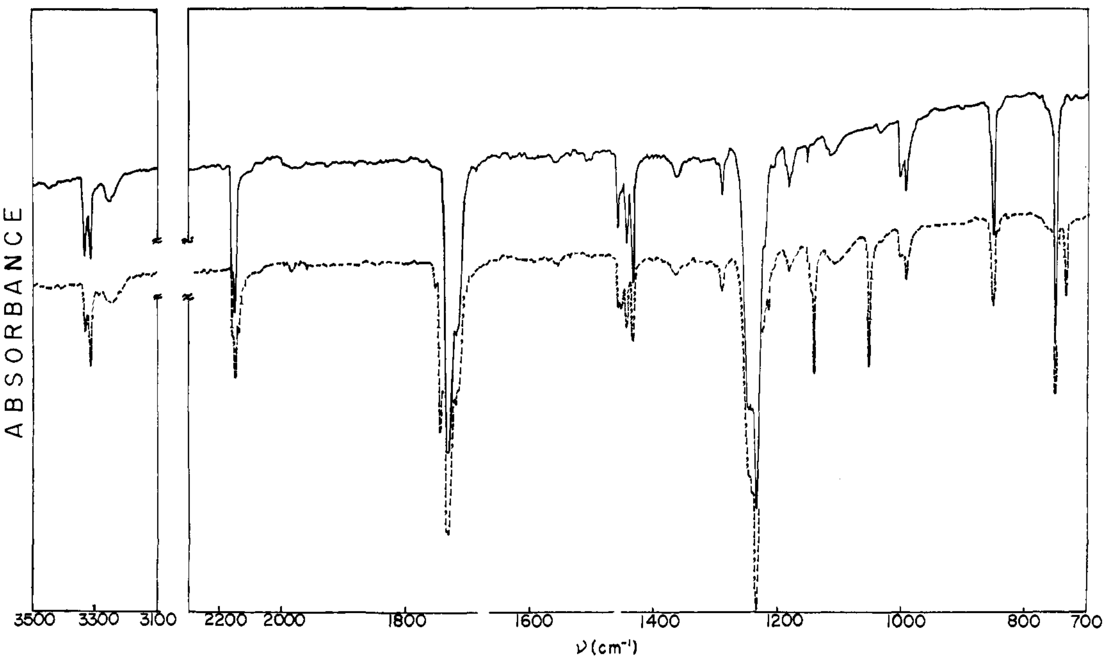
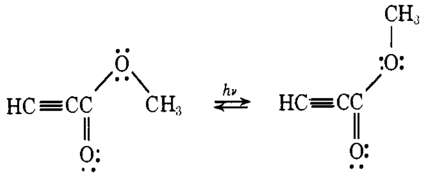


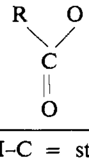
Figure 1. Infrared spectrum of a 52-mm sample of methyl propiolate in argon (M/R = 500) before (——) and after (- - -) a 3-hr irradiation.



trans 1 cis

Irradiation with nickel sulfate filtered mercury lamp light of a 1:500 mole to mole ratio[11] of **1** in argon at 20.4°K produced changes in the spectrum of starting material. A representative spectrum of irradiated **1** is displayed in Figure 1, and the frequencies of new bands which grow at the same rate are listed in Table I.

Table I. New Vibrational Bands Resulting from the Irradiation of *trans*-Methyl Propiolate[a] in an Argon Matrix (M/R = 500)

Frequency, cm^{-1} [b]	Assignment
2140 (w)	C≡C str
1757 (w)	
1749 (s)	C=O str
1453 (m)	Asym deformation of CH_3
1220 (m)	Asym str of C–O
1148 (m)	CH_3 rocking (out of plane)?
1059 (m)	
742 (m)	Bending of  gp (out of plane)

[a] The band at 3316 m cm^{-1} (H–C = str) in starting material showed a progressive increase during the irradiation. [b] s = strong, m = medium, w = weak.

Warming of the matrix to 38°K for 15 min (conditions under which radicals would be expected to couple) and recooling did not result in any detectable loss of the photochemically generated species, whereas trapping of the photolysate externally and redepostion in the cryostat of a room temperature prepared sample of photolysate and fresh argon regenerated the spectrum of starting material. This result rules out photoaggregation as the source of the new bands. (Indeed the narrow line widths of these bands would be inconsistent with their assignment to a polymeric species.) The photoirradiation of **1** in nitrogen under essentially identical conditions gave similar results, indicating that the observed changes were not unique to the argon matrix.

These results are similar to those obtained in our studies of methyl vinyl ketone and acrolein[12] in which photolysis resulted in s-cis–s-trans interconversion. Frequencies attributable to a new species containing ethynyl (HC≡C–) and ester functions ($C(=O)\ddot{O}CH_3$) (see Table I) limit the assignment to a conformer of starting material. The conformational problem in the cases of esters can be reduced to a *two* state situation. Owing to the partial double bond character of the C–O bond, the esters should exist in cis and trans forms. It is proposed that in the present study we are observing the photochemical conversion of the trans conformer of **1** to a new conformer—most probably the cis species. Although vicinal steric interactions between groups bound to the C–O single bond leading to destabilization of the cis form[13] have been earmarked as a major determinant of the position of thermal equilibrium among conformers, the linear ethynyl group should not impose severe restrictions on the motion of the ether methyl group or cause significant deviations from planarity of the cis form of the ester.

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[11] The irradiation of more dilute solutions yielded identical results indicating that the observed effects were due to the photolysis of monomers.

[12] A Krantz, T. D. Goldfarb, and C. Y. Lin, *J. Amer. Chem. Soc.*, **94**, 4022 (1972).

[13] (a) J. Bailey and A. M. North, *Trans. Faraday Soc.*, **64**, 1499 (1968); (b) J. Bailey, S. Walker, and A. M. North, *J. Mol. Struct.*, **6**, 53 (1970). (c) However, see ref 1j for an alternative explanation focusing on electron-pair interaction.

The thermal stability of this new conformer at temperatures up to 38°K is explicable if we assume a barrier to interconversion of a few kilocalories per mole. This stability is not unreasonable in view of (a) the results of Bailey and North[13] who measured barriers between trans and cis conformers to be 8.8 ± 1.4 kcal/mol by ultrasonic relaxation techniques, (b) estimates of the resonance energy of esters,[14,15] and (c) of measurements of the double bond character[4,5] (20%) of the C–O bond in methyl formate.

Studies are underway to determine the barrier to interconversion between the two conformers of **1** by measuring interconversion rates in various matrices at higher temperatures.

Acknowledgment. Acknowledgment is made to the Research Foundation and the Graduate School of the State University of New York and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[14] L. Pauling and J. Sherman, *J. Chem. Phys.*, 1, 606 (1933), estimate resonance energy in esters to be 17–28 kcal/mol.

[15] (a) M. J. Janssen in "The Chemistry of Carboxylic Acids and Esters," S. Patai, Ed., Interscience, New York, N. Y., 1969, p 709, cites a value of 13.5 kcal/mol; (b) M. J. Janssen and J. Sandstrom, *Tetrahedron*, **20**, 2339 (1964).

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Polymer-Protected Reagents. Polystyrene–Aluminum Chloride

Sir:

Insoluble resin techniques offer several advantages in preparative procedures. Resins can be used as diluents to hold reagents from other reagents during a reaction,[1] polymers can be used to hold catalysts during a chemical transformation,[2] and polymers can be used as centers upon which large molecules can be grown.[3-5]

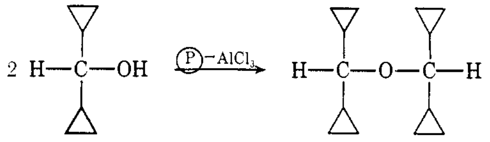
Some time ago, we initiated studies of applications of solid state techniques in organic preparations. In this communication, we report the first use of a tightly bound complex of styrene–divinylbenzene copolymer and anhydrous aluminum chloride, as a mild Lewis acid catalyst for certain organic preparations. The complex of the polymer and $AlCl_3$ provides a shelf-stable acidic material, the active ingredient of which can be called out by an appropriate polymer swelling solvent at the time it is desired.

Polystyrene–divinylbenzene (1.8%) copolymer beads form a water-stable aluminum chloride complex hereafter denoted as Ⓟ–$AlCl_3$. In a typical preparation, 31.0 g (0.46 mol, phenyl residues) of polystyrene–divinylbenzene copolymer beads (1.8%, 50–100 mesh) was added to a 1-l. flask equipped with a stirrer, condenser, and dropping funnel. Carbon disulfide (450 ml) was added followed by 7.5 g (0.06 mol) of anhydrous $AlCl_3$ powder. The mixture was stirred at reflux for 40 min and cooled and 400 ml of cold water was cautiously added to hydrolyze the excess $AlCl_3$. The mixture was stirred until the deep orange color disappeared and the polymer became light yellow. The polymer beads were then filtered and washed with 1 l. of water and successively with 150 ml of ether, acetone, hot isopropyl alcohol, and ether. After these washings, the polymer was dried for 18 hr in a vacuum oven.

Complex formation is demonstrated by the increased color of polymers prepared using higher concentrations of $AlCl_3$, by new bands at 1650 cm^{-1} in the infrared spectrum of the polymer, and by the high general stability of the $AlCl_3$ polymer preparations.[6]

For synthetic purposes, the polymer-bound anhydrous $AlCl_3$ can be released from the polymer by swelling the polymer with certain kinds of solvents. Thus, the $AlCl_3$ can be used to catalyze ether formation and other acid-catalyzed reactions when the polymer holding the reagent is swollen by solvents such as benzene. This is the unique feature of Ⓟ–$AlCl_3$. The polymer protects the easily hydrolyzed Lewis acid until placed in an appropriate solvent where it can be spent in a chemical reaction.

Typical of the reactions of Ⓟ–$AlCl_3$ are its reactions with certain carbinols. For example, dicyclopropylcarbinol, when treated with Ⓟ–$AlCl_3$, produces di(dicyclopropylcarbinyl) ether in yields as high as 81%,[7-9] (eq 1).



(1)

The yield of ether was dependent on the nature of the Ⓟ–$AlCl_3$. The presence of the polymer mediates the effect of the strong Lewis acid catalyst producing higher yields of the desired ether and lower yields of the competing, higher molecular weight side products. In addition, sensitive carbinols react more cleanly with Ⓟ–$AlCl_3$ than they do with $AlCl_3$ directly. Data at 50° for 1:1 mixtures of alcohol and copolymer of different Al content are given in Table I.

The scope of the procedure is demonstrated by the preparation of the mixed ethers, Table II.

Finally, the data in Table III demonstrate the susceptibility of the reaction to the solvent in which the reaction is carried out. Thus, for the reaction of dicyclopropylcarbinol with isopropyl alcohol, much higher product yields are obtained with solvents capable of swelling the polymer. They serve to swell the polymer and make the aluminum chloride more accessible.

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[1] P. Patchornik and M. A. Kraus, *J. Amer. Chem. Soc.*, **92**, 7587 (1970).

[2] A. I. Vogel, "Practical Organic Chemistry," Longmans, London, 1961, p 387.

[3] R. B. Merrifield, Abstracts of Papers, 163rd National Meeting of the American Chemical Society, Boston, Mass., spring 1972.

[4] R. B. Merrifield, *Science*, **150**, 178 (1965).

[5] R. L. Letsinger, M. J. Kornet, V. Mahedevon, and D. M. Jerina, *J. Amer. Chem.* Soc., **86**, 5163 (1964).

[6] For example, 5 g of Ⓟ–$AlCl_3$ prepared as above but not washed with solvents other than water retained 5.28% Al as the chloride. After washing with 150 ml each of water, ether, acetone, hot isopropyl alcohol, and ether, the polymer retained 3.67% Al as the chloride. The 1650-cm^{-1} band was also retained in the polymer after the above wash procedures. In addition, certain Ⓟ–$AlCl_3$ preparations have been left open to the atmosphere for over 1 year without losing either their catalytic activity or the characteristic infrared bands.

[7] H. Hart and J. M. Sandri, *J. Amer. Chem. Soc.*, **78**, 320 (1956).

[8] R. H. Mazur, W. N. White, D. A. Semanov, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[9] Di(dicyclopropylcarbinyl) ether was identified on the basis of its spectral properties and confirmed by independent synthesis: nmr δ 2.78 (2 H, t), 1.10–0.20 (20 H, m); ir 9.02 μ; mass spectrum, *m/e* 95 (100%), 111 (13%), 165 (0.1%), 178 (0.1%).