[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, DU PONT EXPERIMENTAL STATION]

Thermal Stability of Various Olefin–SO_2 Polymers

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Copolymers of SO_2 with ethylene, propylene, butene-2, isobutene and butadiene have been synthesized and pyrolyzed. Degradation of all but butadiene/SO_2 follow first-order kinetics to a first approximation at 200° or above. Random cleavage of propylene/SO_2 seemed to accompany the pyrolysis as it was carried out in these experiments. Pyrolysis of propylene/SO_2 yielded about 85% of the monomers as cracking products.

Introduction

Copolymers formed from simple olefins and SO_2 have been known for a number of years.[1] These products appear to be 1:1 copolymers regardless of the mole ratio of olefin to SO_2 for the polymerization.[1] Another characteristic of these systems is the maximum temperature ("ceiling temperature") above which copolymerization will not take place. This is noted with various olefins and appears to be a value uniquely determined by the olefin in question.[2] It has been widely recognized that the olefin/SO_2 copolymers are thermally unstable at elevated temperatures; however, very few quantitative data on the decomposition are recorded.

We have prepared a series of copolymers and devised a rapid method for measuring the gross rates of decomposition at atmospheric pressure. Decompositions were measured on the ethylene, propylene, butene-2 and isobutylene copolymers. Decompositions of polymers from two olefins with SO_2 are included.

Experimental

Preparation of Polymers.—Polymerizations were carried out both at elevated and reduced temperatures. The media used in various polymer preparations included excess olefin, excess SO_2, toluene and benzene.

In most cases where pressures above atmospheric were encountered, a 500-ml., stainless steel, Parr hydrogenation bomb with rocking agitation was used. In filling the bomb, care was taken to ensure that all air was removed. At the end of a run, pressure was usually released while the bomb was still hot.

In a typical run at elevated temperature, 120 g. of C.P. propylene (above 99% purity by infrared analysis), 20 g. of SO_2, and 0.2 g. of α,α'-azobis-isobutyronitrile initiator were heated at 65–70° for two hours.[3] Yields of polymer of 70–80% were obtained with the product appearing as a white, porous, easily broken cake in the bomb. The polymer was washed five times in a Waring blendor with methanol, filtered and dried for five hours at 75° (1–3 mm.). The polymer showed some tendency to pick up moisture. It was also found difficult to remove all of the uncombined SO_2 unless methanol washing and vacuum drying were employed. Syntheses are recorded in Table I and all runs at 70° were carried out in this manner.

Syntheses at atmospheric pressure (low temperatures) were carried out by photopolymerization in a refrigerated, tubular, vacuum-jacketed reactor similar to the one described in ref. 4. Olefins and SO_2 were condensed into the cold reaction chamber by passing the gases through the inlet line. The initiator, 0.2 g. of α,α'-azobis-isobutyronitrile, has previously been shown to be quite active when irradiated with 3500–3600 Å. light.[4] Irradiation in this region was supplied by four 15-watt General Electric BL-360 fluorescent bulbs mounted in two "Dazor" desk lamp fixtures (Dazor Mfg. Co., St. Louis, Mo.). Air was excluded and agitation accomplished by passing dry N_2 through the inlet tube. It was noted that some polymer could be formed in the absence of added initiators by irradiation of propylene in excess SO_2 with the BL-360 light source. It is well known that ultraviolet light of wave lengths near 3200 Å. or below will initiate polymerization. It is likely that SO_2 serves as the photoinitiator since it absorbs in this wave length region.

TABLE I

PREPARATION OF OLEFIN/SO_2 COPOLYMERS

	Run	Olefin, g.	SO_2, g.	Solvent, g.	Synthesis temp., °C.	Sulfur, % Found	Sulfur, % Calcd.[a]	Yield, g.	First-order k (229°)
1	Ethylene	26	32	Benzene 80	70	34.9	34.8	41	0.00027
2	Propylene	120	32	Propylene	70	30.3	30.2	40–50	.0027
3	Propylene	33	126	SO_2	70	31.1	30.2	83	.0038
4	Propylene	110	40	Toluene 100	−40	30.3	30.2	10	.0030
5	Propylene	40	150	SO_2	−50	31.1	30.2	37	.0020
6	Butene-2	120	40	Butene-2	−25	26.2	26.7	10	.026[e]
7	Isobutene	80	35	Toluene 130	−20	26.4	26.7	8.6	.018
8	Isobutene	120	30	Isobutene	−20	26.7	26.7	9.5	
9	Butadiene	50	40	Toluene 130	−20	27.0	27.1	34	.0014[f]
10	Propylene	42	40	Propylene	70	30.2	[b]	31	
	Butene-2	56		Butene-2					
11	Propylene	42	40	Propylene	−40	27.5	[c]		
	Butene-2	56		Butene-2					
12	Propylene	42	30	Benzene 90	70	31.8	[d]	34	.0012
	Ethylene	28							

[a] Calcd. for a 1:1 olefin/SO_2 copolymer. [b] 30.2% S is calcd. for 1:1 propylene:SO_2. [c] 26.7% S is calcd. for 1:1 butene-2:SO_2. [d] 32.4% S is calcd. for 1:1:2 ethylene:propylene:SO_2. [e] Calcd. for data at 179° and 202°; material foamed at 229°. [f] This material deviated considerably from first-order kinetics.

A few experiments on 3-component copolymers consist-

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[1] (a) F. E. Matthews and H. M. Elder, British Patent 11,635 (1915); (b) D. S. Frederick, H. D. Cogan and C. S. Marvel, THIS JOURNAL, **56**, 1815 (1934); (c) M. Hunt and C. S. Marvel, *ibid.*, **57**, 1691 (1935); (d) H. Staudinger and B. Ritzenthaler, *Ber.*, **68**, 455 (1935).

[2] R. D. Snow and F. E. Frey, THIS JOURNAL, **65**, 2417 (1943).

[3] M. Hunt, U. S. Patent 2,471,959.

[4] M. A. Naylor and F. W. Billmeyer, THIS JOURNAL, **75**, 2181 (1953).

ing of two olefins with SO_2 indicated that both olefins entered the polymer only if the polymerization was carried out at a temperature below the lowest "ceiling temperature" involved. Thus a comparison of sulfur analyses of runs 10 and 11 (Table I) shows that little, if any, butene-2 polymerized at 70° in the presence of propylene, whereas both olefins polymerized at −40°. The "ceiling temperature" for butene-2 is reported as 43–45°.[2] Whether this product was a homogeneous 3-component copolymer or a mixture of separate olefin/SO_2 copolymers was not unequivocally established.

Cracking Propylene/SO_2 Polymer.—Although there are numerous references in the literature indicating that olefin/SO_2 polymers pyrolyze to the original monomers, no reasonably quantitative data were found.

We have pyrolyzed propylene/SO_2 polymer under an atmosphere of N_2 at 280–290°. The apparatus consisted of a flask heated with an electric jacket and attached to a very slow stream of nitrogen. The exit line was connected in series to a trap kept at 10° and a trap at −78°. The system was protected with drying tubes. Results are given in Table II.

TABLE II

CRACKING PRODUCTS FROM PROPYLENE/SO_2 POLYMER

280°, 1 atm. pressure

1	Polymer used	290.0 g.
2	Residue after cracking[a]	25.5 g.
3	Product in 10° trap	12.7 g.
4	Product in −78° trap	238.5 g.

[a] Black solid which was capable of further degradation.

The material from line 3 in Table II was treated with ether and formed a 3-layer system. The lowest layer was a reddish oil, weighed 3.2 g. and gave $n^{20}\text{D}$ 1.3657. The upper layers were combined and distilled giving 1.4 g. of a material boiling 70–90° with a strong sulfide odor and $n^{20}\text{D}$ 1.4062, and a 5.7-g. fraction boiling at 99° with $n^{20}\text{D}$ 1.3375. These data indicate this portion of the cracking products to be mainly water with a small quantity of sulfur compounds.

The material from line 4 in Table II (Dry Ice trap) was fractionated through an all-glass, low temperature still at atmospheric pressure with the following results.

Fraction	B.p., °C.[a]	Yield, g.
1	−48 to −47	96
2	−30 to −10	124[b]
Residue	....	8.5[c]

[a] B.p. of C_3H_5 = −48°; b.p. of SO_2 = −10°. [b] 80% of this fraction distilled at −12 to −10°. [c] Two layers were noted in the residue.

The above data show that 95.4% of the material used was collected as cracking products. Of the polymer degraded to volatile products, 83.4% went to propylene and SO_2 while the rest of the material went to water, unidentified sulfur compounds, etc. The mole ratio of propylene: SO_2 collected in the above fractionation was approximately 1.2 indicating some destruction or loss of SO_2 since the initial polymer was definitely a 1:1 copolymer. The fact that water appeared in the cracking products suggests the possibility of oxidation–reduction reactions between the SO_2 andhydrocarbon portions of the polymers.

Measurement of Rates of Degradation.—Rate curves for the decomposition of the olefin/SO_2 polymers were obtained by following the rate of weight loss of a weighed sample of polymer in an open glass ampule suspended in a vapor bath. Liquid having the desired boiling point was placed in a flask attached to a vapor chamber consisting of a piece of heat resistant glass tubing 1.25″ in diameter and 10″ long. The vapor chamber was enclosed in a second piece of tubing 1⁵/₈″ wide and 10″ long held in place by close fitting asbestos rings at the top and bottom. The upper half of this condenser was divided from the lower half by a third asbestos ring. Two glass sidearms were provided for the upper half of the chamber and were used as inlet and outlet for the air employed in cooling this part of the condenser. This construction enabled operation of the apparatus with a constant height of vapor which was important to the reliability of the results.

Three grams of polymer was placed carefully in the bottom of a piece of 19 mm. tubing sealed at one end. The tubing was then "necked down" to a capillary (1–2 mm.), 3 inches from the sealed end. Care was taken not to heat the polymer during this operation. Glass tips to provide a point of support were sealed onto the capillary about 2.5 to 3 inches up the capillary section. The ampule was then hung by a thin wire from a triple beam balance (from which the pan had been removed) weighing to 0.01 g. It was positioned so that only the capillary neck extended up into the area of the vapor chamber surrounded by the air condenser.

After the ampule was suspended in the vapor chamber, the refluxing bath liquid was heated at a rate such that 5 minutes was required for the vapor ring to move from the bottom of the ampule to 1 inch up on the capillary section. The end of this time was arbitrarily chosen as zero time for determinations of rates of weight loss and as the time required to bring the sample to temperature. The above procedure was adopted since it permitted alignment of the ampule in the vapor chamber without the difficulty of having it stick to the walls as was usually the case when the chamber was wet with refluxing bath. It is essential to keep the vapor ring at a reasonably constant level up on the capillary section of the ampule to minimize weighing errors from liquid condensed on the ampule. Certain limitations are placed on the accuracy of the method by the time required to heat the sample and by the vapor which condenses on the ampule; however, by proper operation, first-order rate constants with a 95% confidence limit of ±16% of the absolute value were achieved.[5]

This technique has been applied to the degradation of other materials which form volatile decomposition products such as polymethylmethacrylate.

Decompositions were carried out at a series of temperatures from 179 to 259°. Materials used in the refluxing bath were distilled prior to use to ensure the correct boiling point and were as follows: *o*-dichlorobenzene (179°), acetophenone (202°), nitrobenzene (210°), diethylene glycol monobutyl ether (229°), diphenyl ether (259°).

It was found that the degradation followed first-order kinetics quite closely over 80–90% decomposition, particularly at temperatures above 190°. Figure 1 illustrates the results on propylene/SO_2. Figure 2 shows the activation energy for this decomposition to be about 32 kcal./mole with rate constants at 210°, 229°, and 259°. In degradations carried out at 170–200°, it appeared that E_{act} dropped considerably below this value, but rates of degradation were slow and experimental errors magnified at the lower temperatures.

Discussion

It appears that in 3-component systems with SO_2 and two different olefins, both olefins will undergo reaction only if the polymerization temperature is kept below the lowest "ceiling temperature" of the individual olefin/SO_2 combinations. This seems reasonable if 1:1 complexes of olefin and SO_2 are involved in the chain-growth step and may also be rationalized on the thermodynamic basis presented by Dainton and Ivin to account for the "ceiling temperature" effect.[6]

It is difficult to determine the detailed mechanism of pyrolyses of the type described here. The reactions take place in most cases in an unfused solid (a few of the polymers melted at the depolymerization temperatures used). However, several interesting results were obtained.

Earlier workers[1c] suggested the possibility that weak links might account for instability in olefin/SO_2 copolymers. An example considered was the sulfinic ester grouping which might result from copolymerization through an S–O linkage rather than by exclusive formation of C–S bonds. We felt that

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(5) This confidence limit was determined by Dr. E. T. Pieski using this apparatus with a different material.

(6) F. S. Dainton and K. J. Ivin, *Proc. Roy. Soc.* (*London*), **212A**, 96 (1952); *Trans. Faraday Soc.*, **46**, 331 (1950).

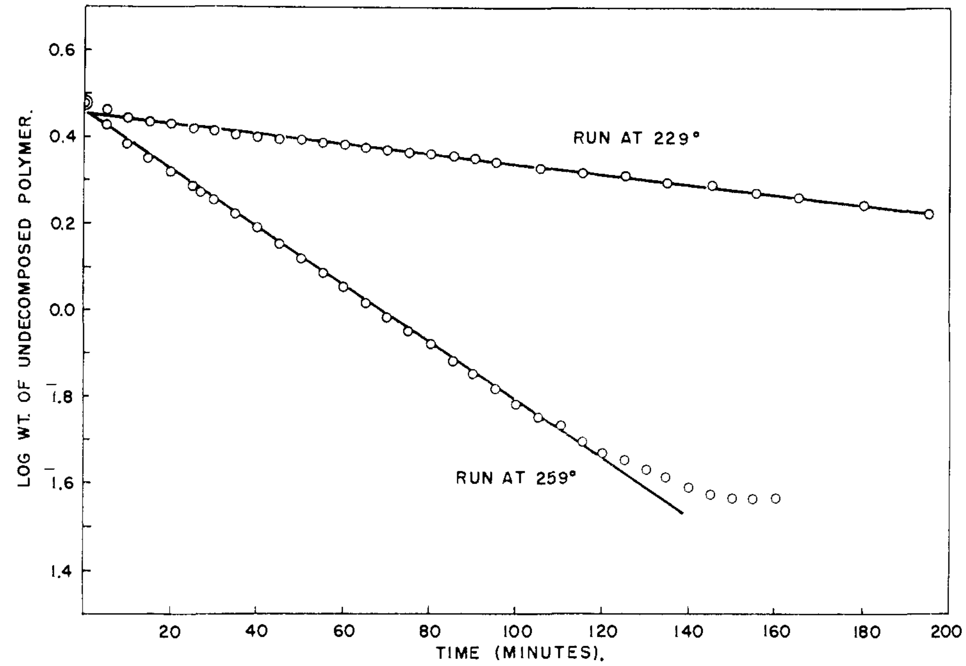

Fig. 1.—First-order decomposition curves for propylene/SO_2 polymer.

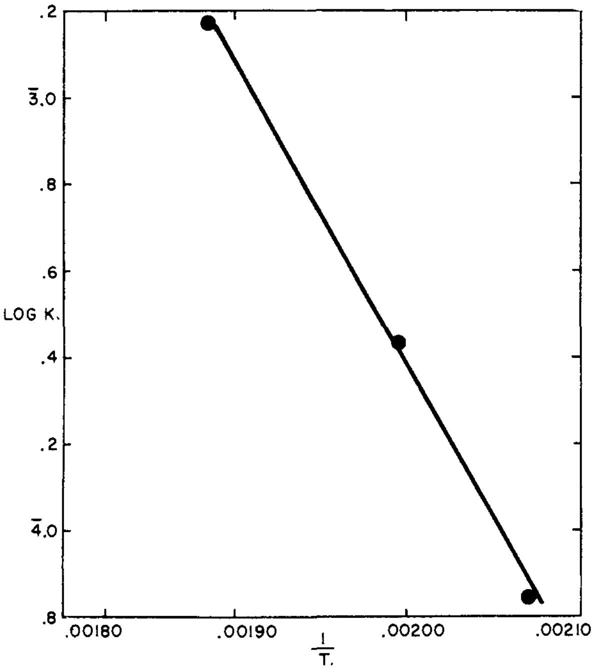

Fig. 2.—Plot for E_{act} decomposition of propylene/SO_2 polymer.

if such were the case, differences in activation energy for formation of these two structures might lead to products of different stability if syntheses were carried out at widely different temperatures or in widely different media. Comparison of runs 2, 3, 4 and 5 of Table I show that this is apparently not the case with propylene/SO_2. The low temperature polymerization in excesss SO_2 (run 5) gave a slightly high sulfur analysis in duplicate syntheses. Since the polymer is somewhat sensitive to liquid SO_2, it is possible that these products were not thoroughly free of unreacted SO_2, although in one case the material was dried 24 hours/10–20 mm./25° followed by 6 hours/2 mm./100°. The relatively small differences in *k* suggest no drastic changes in structure.

In determining *k* by the above procedure, an initial surge in decomposition resulting in a curve in the first portion of the log plot was sometimes observed. This suggested that impurities or by-products of polymerization might influence the degradation. Extraction of propylene/SO_2 copolymer for 18 hours in Soxhlet extractors with water, ethyl acetate, benzene, dioxane, ethanol, and acetone resulted in reduction or disappearance of the initial surge, but the *k*'s were almost unaffected (control k = 0.0026 to 0.0028, extracted products *k*'s = 0.0023 to 0.0030). Trace amounts of acidic material were recovered from the extraction liquids.

Infrared studies were attempted but interference between the sulfone and sulfinic ester groups prevented any distinction of these functions. This work did indicate, however, that butadiene/SO_2 polymer (run 9, Table I) was perhaps as high as 95%, 1,4-adduct.[7]

All of the copolymers from different olefins with the exception of butadiene/SO_2, followed first-order degradation kinetics to a first approximation. The *k*'s for these various compositions are recorded in Table I, runs 1, 2, 6, 7 and 12.

It is interesting to note that the decomposition rates roughly parallel the total number of H atoms on the carbons beta to the sulfone linkage (4 in ethylene, 6 in propylene, 8 in butene-2, etc.). Whether a true β-elimination takes place is yet to be proved.

The effect of heating on molecular weight was examined with propylene/SO_2 copolymer. Molecular weights were followed by determining inherent viscosities of a 0.5% solution of polymer in

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(7) Unpublished results of Dr. C. F. Hammer.

concentrated sulfuric acid. Viscosities were run at 25° in a standard Ostwald viscometer. Care was taken not to heat the polymers while being dissolved.[8] Polymer was heated for various periods of time in an ampule similar to that used for determining weight loss, but fitted with a ground glass joint so that samples could be removed. The inherent viscosity of the heated polymer is plotted against time of heating in Figure 3.

At 229° the precipitous drop in inherent viscosity that accompanies very low weight loss (inherent viscosity is reduced by 50% when weight loss is only about 3%) suggests degradation by random cleavage or by splitting of weak links located randomly in the chain. In this respect the decomposition follows the alkaline hydrolysis of polyacrylonitrile[9] more closely than the pyrolyses of polystyrene[10] or polymethyl methacrylate.[11]

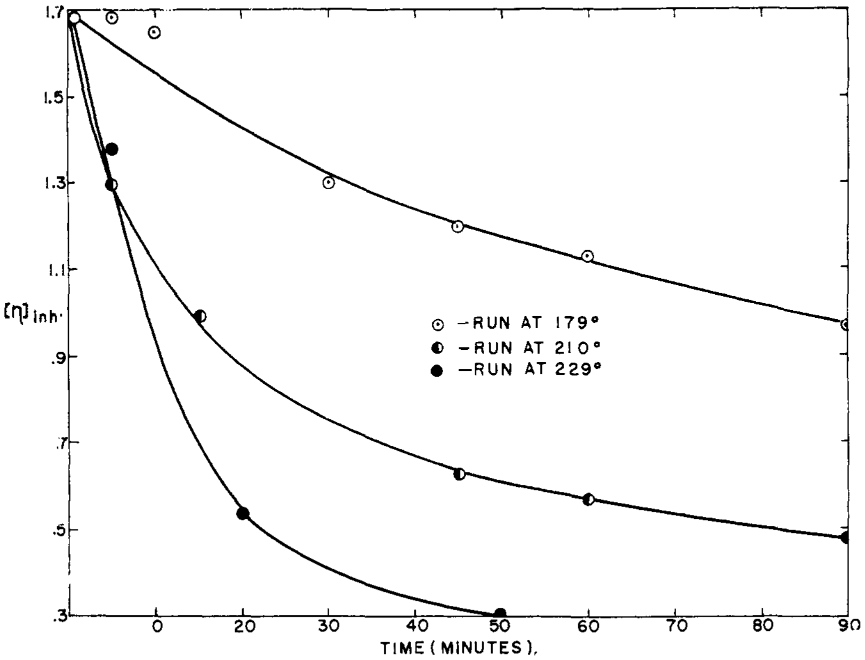

Fig. 3.—Effect of thermal degradation on $(\eta)_{\text{inh}}$ of propylene/SO_2 polymer.

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[8] Inherent viscosity determinations were made by Dr. F. W. Billmeyer.

[9] J. R. McCartney, *Modern Plastics*, **30**, 118 (1953).

[10] H. H. G. Jellinek, *J. Phys. Chem.*, **56**, 707 (1952).

[11] N. Grassie and H. W. Melville, *Proc. Roy. Soc.* (*London*), **199**, 1, 14, 24, 39 (1949).

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[CONTRIBUTION FROM THE ROLLIN H. STEVENS MEMORIAL LABORATORY OF THE DETROIT INSTITUTE OF CANCER RESEARCH AND FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Reactions of Organometallic Reagents with 2-Hydroxymethylenecyclohexanone and Its Isopropyl Ether[1,2]

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The condensation of three organometallic reagents (methylmagnesium iodide, methyllithium and phenylmagnesium bromide) with 2-hydroxymethylenecyclohexanone (I) resulted in 2-alkylidenecyclohexanones (IV and V), presumably by a nucleophilic attack at the hydroxymethylene carbon of the intermediate enolate salt II. The isopropyl ether of 2-hydroxymethylenecyclohexanone (VII) underwent mostly 1,4-addition with methylmagnesium iodide and phenyllithium to give 2-ethylidenecyclohexanone (IV) and 2-(α-isopropoxybenzyl)-cyclohexanone (VIIIb), respectively, while 1,2-addition to VII by methyllithium and lithium aluminum hydride produced cyclohexenecarboxaldehydes (XIa and XIc) related to the androtermone safranal.

2-Hydroxymethylene ketones and their ethers have been used as synthetic intermediates for the introduction of an alkyl group on either of the carbons alpha to the keto group.[3] They have, however, not been employed frequently in condensations with organometallic compounds to introduce alkyl groups at the carbonyl- or hydroxymethylene carbon. Under certain circumstances this reaction could offer promise for the ready preparation of intermediates in the synthesis of terpenes or polycyclic compounds. It was, therefore, made the subject of an exploratory study with 2-hydroxymethylenecyclohexanone and its isopropyl ether.

When an excess of methylmagnesium iodide was treated with 2-hydroxymethylenecyclohexanone (I) there was a copious evolution of methane and the major product was 2-ethylidenecyclohexanone (IV), identified by comparison with an authentic sample.[4] Since I has been shown to react with

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[1] Supported in part by institutional grants to the Detroit Institute of Cancer Research from the American Cancer Society, Inc., the American Cancer Society, Southeastern Michigan Division, and The Kresge Foundation.

[2] This work was abstracted in part from a dissertation submitted by Stewart N. Nickel to the Graduate School of Wayne University in partial fulfillment of the requirements for the degree of Master of Science.

[3] H. K. Sen and K. Mondal, *J. Ind. Chem. Soc.*, **5**, 609 (1928); W. S. Johnson and H. Posvic, THIS JOURNAL, **69**, 1361 (1947); J. W. Cornforth and R. Robinson, *J. Chem. Soc.*, 1855 (1949); A. L. Wilds and C. Djerassi, THIS JOURNAL, **68**, 1715 (1946); F. D. Gunstone and R. M. Heggie, *J. Chem. Soc.*, 1437 (1952); R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, THIS JOURNAL, **74**, 4223 (1952); A. R. Pinder and R. Robinson, *J. Chem. Soc.*, 1224 (1952).

[4] G. Vavon and V. M. Mitchovitch, *Bull. soc. chim.*, [4] **45**, 961 (1929).