675, 708, 849, 873, 903, 917, 954, 1099, 1122, 1176, 1188, 1372, 1456, 1603(wk), 1748(wk), 2933, 3650 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{32}SO_3$: C, 67.31; H, 8.22. Found: C, 67.08; H, 8.19.

On standing, the mother liquor separated colorless plates, m.p. 135–136°, which were dimorphic with the above material. The crystals, m.p. 135–136°, changed to the crystals, m.p. 141–142°, when seeded with the latter in the recrystallization.

Lithium Aluminum Hydride Reduction of the Tosylate XLVI.—The monotosylate (77 mg.) and lithium aluminum hydride (110 mg.) were refluxed in 3 ml. of anhydrous tetrahydrofuran for 5 hr. The mixture was worked up as usual and the product (39 mg.) chromatographed through a column containing 1.5 g. of alumina B (activity III). Elution with petroleum ether yielded 18 mg. of the alcohol LIV as prisms, m.p. 79–80°, which were not reducible over platinum oxide in ethanol solution; infrared spectrum (CCl_4): 907, 957, 1044, 1103, 1261, 1379, 1464, 2950, 3484, 3650 cm.$^{-1}$.

Elution with petroleum ether–benzene (9:1 and later 4:1) yielded 7 mg. of colorless needles, m.p. 69–71° (sintering at 60°); infrared spectrum (CCl_4): 900, 954, 1007, 1131, 1379, 1460, 2959, 3521, 3676 cm.$^{-1}$.

Elution with ether yielded 6 mg. of colorless needles, m.p. 127–129°, pure and mixed with α-maalidiol (XLIV).

Reaction of Monotosylate XLVI with Potassium *t*-Butoxide.—The monotosylate (58 mg., 0.15 mmole) was refluxed in a solution of potassium (60 mg., 1.5 mmoles) in 2.6 ml. of anhydrous *t*-butyl alcohol for 1 hr. The mixture was evaporated *in vacuo*, and the residue worked up by the conventional procedure. The residue was chromatographed through a column containing 1 g. of alumina B (activity II). Elution with petroleum ether yielded 20 mg. of the ketone LV as a liquid; infrared spectrum (CCl_4): 1040, 1139, 1166, 1183, 1357, 1377, 1427(wk), 1464, 1715, 2959 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.51; H, 11.13.

Lithium Aluminum Hydride Reduction of the Ketone LV to the Alcohol LVI.—The ketone (20 mg.) and lithium aluminum hydride (20 mg.) were refluxed in 1 ml. of anhydrous tetrahydrofuran for 4 hr. The mixture was worked up as usual. The alcohol(s) LVI was obtained as a liquid (16 mg.); infrared spectrum (CCl_4): 860, 878, 903, 926, 953, 996, 1022, 1047, 1078, 1107, 1136, 1252, 1374, 1464, 2959 3546, 3690 cm.$^{-1}$.

Cambridge, Mass.

[Contribution from the Polychemicals Department, E. I. du Pont de Nemours & Co., Inc.]

Polynorbornene by Coördination Polymerization[1]

By W. L. Truett, D. R. Johnson, I. M. Robinson and B. A. Montague

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Norbornene has been polymerized to high molecular weight polymers using catalysts derived from lithium aluminum tetraalkyls and titanium tetrachloride. Structural studies on these polymers have shown that a major portion of the polymer chain consists of cyclopentane rings linked in a *cis*-1,3-fashion with *trans*-CH=CH groups. This polymerization has occurred by an unusual ring opening reaction having high stereospecificity.

Introduction

The finding in these laboratories[2–6] of catalysts, designated coördination catalysts, which afforded the facile polymerization of ethylene and other olefins has also provided a means for effecting the polymerization of norbornene (bicyclo[2,2,1]-2-heptene), a monomer which heretofore had not been polymerized by any catalytic method. In general, active catalysts have been prepared from a variety of organometallics with derivatives of Groups IVB to VIB of the Periodic Table. Similar systems have also been disclosed by Ziegler.[7]

This new method of polymerization is being designated as "coördination polymerization"[1–7] as a means of emphasizing and distinguishing its important features from the well-known free radical, cationic and anionic methods. We consider coordination polymerization to involve successive steps of coördination and activation of the monomer at a fixed site on a transition element derivative in a reduced state, followed by a rearrangement (usually with a high degree of stereospecificity) and propagation. The rearrangement and propagation frees the catalyst site for further coördination and activation of monomer. It is believed that the rearrangement step involves a minimum of charge separation and neither carbonium ions nor carbanions in the usual sense are involved.

It is believed that the reaction is more closely related to an SNi type rearrangement rather than an SN2 type displacement. Another important feature of coördination catalysis is found in the stereospecific nature of this polymerization leading to polymer with a high degree of order not likely with other means of polymerization. Other workers in this field of olefin polymerization[8] have also reported on the exceptional regularity found in polymer chains derived from the polymerization of α-olefins using these catalysts.

Discussion

For the work reported here, we have used a catalyst system derived from lithium aluminum tetraheptyl and titanium tetrachloride. At least two kinds of polynorbornene polymers can be made using catalysts derived from these components. Use of less than a molar equivalent of lithium aluminum tetraheptyl for each mole of titanium tetrachloride leads to a rigid, brittle polynorbornene (type A). When a 100% excess of lithium aluminum tetraheptyl over titanium

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[1] Presented at the 130th National Meeting, Am. Chem. Soc., Atlantic City, N. J., September 18, 1956.

[2] E. I. du Pont de Nemours & Co., British Patent 682,420 (November 12, 1952).

[3] A. W. Anderson and N. G. Merckling, U. S. Patent 2,721,198 (October 18, 1955).

[4] A. W. Anderson, *et al.*, French Patent 1,134,740 (December 3, 1956).

[5] E. I. du Pont de Nemours & Co., British Patent 776,326 (September 25, 1957).

[6] A. W. Anderson, *et al.*, U. S. Patent 2,905,645 (September 22, 1959) (Application August 16, 1954).

[7] K. Ziegler, *et al.*, *Angew. Chem.*, **67**, 426 (1955); **67**, 541 (1955); Belgian Patent 533,362 (May 16, 1955) (see Ger. application of November 17, 1953, December 15, 1953, and December 23, 1953).

[8] G. Natta, *J. Polymer Sci.*, **16**, 143 (1955); *Makromol. Chem.*, **16**, 77, 213 (1955); *Angew. Chem.*, **68**, 393 (1956).

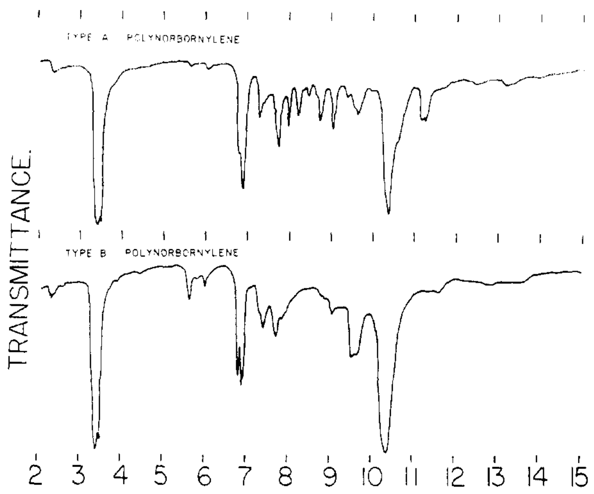


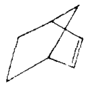
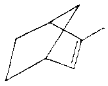
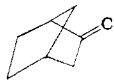
Fig. 1.—Infrared absorption spectra.

tetrachloride is used, a more flexible, tough polymer (type B) is obtained. As part of a broad interest in relating chemical structure to polymer properties, we undertook an investigation of these two types of polynorbornene.

Examination of the infrared spectra, Fig. 1, of these polynorbornene polymers proved fruitful. Since the infrared scan for type B suggested a structure of lesser complexity, most of our attention was devoted to interpretation of this spectrum. The outstanding spectral feature is the very intense band at 10.37 μ. The intensity and position of this band suggested an olefinic carbon–hydrogen deformation such as found in *trans*-olefinic structures.

Although it is probable that the type of unsaturation in polynorbornene could be *trans*, it was necessary to consider the possibility that the presence of *cis*, vinylidene or $R_1R_2R_3$ type unsaturation in a strained bicyclic system might decrease the characteristic wave lengths to a considerable extent. The spectra–structure correlations in Table I show that this does not occur; rather the normal wave lengths are increased in bicyclic systems.[9]

TABLE I

Compound type	Olefinic C–H deformation band, μ
	One or more bands near 14
	One band near 12.50 (only 2 examples)
	Very near 11.40

In order to determine whether the *trans*-olefinic linkage was truly a major component of the polymer structure the intensity of the 10.37 μ band in the polymer spectrum was measured and the unsaturation level was calculated using molar extinction coefficients obtained from the pure standards *trans*-2-pentene and 3-methyl-*trans*-2-pentene. This *semi*-quantitative estimate indicated that the ratio of *trans* units to monomer units in the polymer was about 0.5. Despite the lack of ideal model compounds the data conclusively indicated that *trans* unsaturation was present in major amounts and did not represent end groups. The Experimental section should be consulted for details.

The remainder of the type B polynorbornene spectrum does not furnish much information. Its over-all simplicity is noteworthy. The appearance of a minor amount of absorption at 5.63 μ is of interest. This absorption is in an area characteristic of a strained ring carbonyl group. A search of the literature revealed that it is possible to assign the position of a carbonyl group in the norbornane system with some certainty.[10] Those structures possessing a carbonyl group at the 7-position show absorption at 5.63 μ, while those with a carbonyl group in the 2-position show absorption at 5.71 μ. Thus it is possible that a small portion (probably less than 1%) of our polymer molecule contains the bicyclo[2,2,1]-7-heptanone structure. It is not readily apparent how oxygen could have been introduced into the polymer structure.

The infrared spectrum of type A polynorbornene, while more complex than that for type B, possesses all the bands present in the type B polymer plus bands at 7.25 and 11.25 μ, assignable, respectively, to C-methyl and vinylidene groupings. The greater complexity in the 7–10 μ region is consistent with a generally more complex structure than that of type B.

The indicated presence of unsaturation from our infrared study was most surprising. Prior to this time no case in the literature was known for the addition polymerization of a monomer containing only one double bond leading to a polymer having more than trace amounts of unsaturation. A consideration of the infrared spectra of three model compounds, norbornane, *endo-cis*-2,3-dimethylnorbornane and *trans*-2,3-dimethylnorbornane, showed that these compounds did not possess strong bands in the 10 to 14 μ region. If the norbornene polymerized in a normal fashion, one would expect it to have a spectrum similar to that of the above-noted model compounds.

Since the infrared evidence strongly indicated that in the case of the polymerization of norbornene to type B polynorbornene, the reaction had taken an unusual course, confirmatory chemical evidence was sought as to the presence of unsaturation.

A qualitative chemical proof of the presence of unsaturation in type B polynorbornene was obtained by treatment of low molecular weight polymer, soluble in benzene, with reagents known to attack a double bond. Perbenzoic acid, performic acid and bromine were used for this purpose. In each case, the polymer was examined by infrared before and after reaction. The infrared spectrum of this low molecular weight polymer was essentially the same as that given by high molecular weight polymer. After reaction with a solution of perbenzoic acid, the 10.37 μ band present in the

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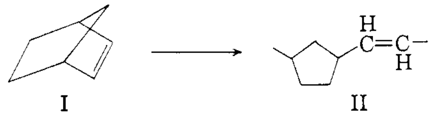
(9) P. R. Schleyer, 130th National Meeting, Am. Chem. Soc., Atlantic City, N. J., September, 1956.

(10) P. Wilder, Jr., and A. Winston, THIS JOURNAL, **78**, 868 (1956).

original polymer spectrum was strongly diminished. A new band, which appeared at 11.20 μ, is in a region where the epoxide structure is expected to absorb. Reaction of the low molecular weight polymer with performic acid gave a similar result in that the 10.37 μ band was removed and additional bands appeared at 5.77 and 8.5–9.5 μ which are characteristic of formate esters. Bromination of the polymer led to a diminution of the 10.37 μ band, but considerable oxidation occurred during the reaction as evidenced by the appearance of a strong band at 5.85 μ which was assigned to a carbonyl. These results with reagents known to attack a double bond confirm the infrared evidence for the presence of unsaturation. Reactions of type A polymer with the same reagents gave parallel results.

Having determined that a major amount of *trans*-unsaturation was present, we were led to assume that a ring-opening reaction had occurred. A possible pattern involved a reaction path of I ⟶ II.

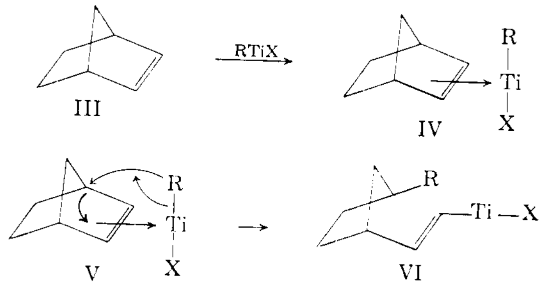


If the polymer possessed structure II, ozonization would be expected to furnish a 1,3-cyclopentanedicarboxylic acid. The actual experiment led to the isolation of an 18% yield of *cis*-1,3-cyclopentanedicarboxylic acid. Since the *cis*-1,3-cyclopentanedicarboxylic acid proved somewhat difficult to crystallize, it was manipulated as the di-*p*-bromophenacyl derivative, m.p. 166–168°. No *trans*-1,3-cyclopentanedicarboxylic acid was isolated, though a search was made for it. It seems reasonable to conclude from the ozonization study that a significant portion of our structure is that of II, and this is further supported by the high crystallinity of the polymer noted below.

On the basis of chemical and infrared evidence we believe that norbornene has polymerized *via* a ring-opening reaction to give polymer chains composed of cyclopentane rings linked in a *cis*-1,3-fashion with *trans*-CH=CH groups. Type B polymer appears to be predominantly this structure, while type A polymer also contains these structures in addition to other polymer units of a more complex and as yet undefined nature.

In view of the current high interest in crystalline polymers it is in order to note that we have prepared polynorbornenes having crystallinities of 5 to 55%. A polymer with 20% crystallinity was shown to have a crystalline melting point of 202° by X-ray diffraction. Another interesting part of the crystallographic work was the finding that the identity period was 11.8 Å. corresponding to two monomer units of structure II. Although it is not possible to categorize this polymer in the popular mode as "isotactic" or "syndiotactic,"[8] the polymerization of norbornene through ring opening must have occurred in a highly stereospecific fashion to result in crystalline polymer.

The occurrence of a remarkably stereospecific polymerization reaction has led us to advance the following mechanism[11]



Recent work in this Laboratory has established that the active catalyst species is at least in part titanium in a low valence state.[12] For simplicity the titanium site has been designated RTiX although it is highly probable that this titanium species is associated with products from the reducing agent or even other titanium compounds.

In the process of norbornene polymerization we believe the following steps are involved: The norbornene nucleus becomes activated by coördination with the reduced titanium center through the π-electrons of the double bond, III → IV. The subsequent rearrangement step is thought of as a concerted process involving a minimum of charge separation. Thus, as the bond between carbon atoms 1 and 2 breaks with these electrons rejoining the double bond, the original carbon-to-titanium bond breaks and a new carbon–carbon bond is formed at the 1-position of the norbornene and a new carbon-to-titanium bond is formed, V → VI. This process regenerates the active titanium center for further coördination and activation of norbornene units. Repetition of this process leads to polymer propagation and formation of high molecular weight polymer. Termination of a polymer chain is thought to occur by transfer with monomer or hydride elimination.

This mechanism accounts for the *cis*-1,3-stereochemistry of the cyclopentane rings in the polymer but does not lend itself to a good understanding of the inversion of the hydrogens on the double bond from *cis* to *trans*. Sterically, of course, the *cis*-ethylenic linkage would be less favored than the *trans*.[13]

Experimental Part[14]

Lithium Aluminum Tetraheptyl.[15]—A mixture of 13 g. (0.34 mole) of lithium aluminum hydride, 285 ml. (2.0 moles) of 1-heptene and 300 ml. of decahydronaphthalene was refluxed under a nitrogen atmosphere; the temperature gradually rose from 115 to 135° over a period of 5 hours, at which time the reaction was complete. The reaction mixture was filtered while hot under nitrogen to remove unreacted solid. Upon cooling, the filtered solution deposited crystals, which were collected, vacuum dried, and dissolved in one liter of xylene. Titration of an aliquot with standard acid gave a concentration of 0.35 to 0.49 molar in lithium aluminum tetraheptyl. Exposure of the solution or solid to air or moisture leads to a rapid loss of activity.

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(11) We are indebted to Professor J. D. Roberts for valuable discussions concerning this mechanism.

(12) D. B. Ludlum, A. W. Anderson and C. E. Ashby, THIS JOURNAL, **80**, 1380 (1958).

(13) A study with molecular models has shown that polymer chains having *trans* linkages are favored over *cis* structures.

(14) Melting points are uncorrected.

(15) This reaction was first carried out in these laboratories by Dr. A. M. Hyson following incomplete synthetic procedures outlined by K. Ziegler, *Angew. Chem.*, **64**, 323 (1952).

Polymerization of Norbornene to Type A Polymer.—The reaction was carried out in glass apparatus in an inert atmosphere. The polymerization vessel was placed in a polyethylene bag of 10-gallon capacity fitted with a two-way stopcock that permitted the bag to be alternately filled with nitrogen and evacuated.[16] A solution of 25 ml. (0.005 mole) of lithium aluminum tetraheptyl in xylene was added to 1.1 ml. (0.01 mole) of titanium tetrachloride in 50 ml. of decahydronaphthalene and the mixture allowed to stand 10 minutes at which time 47 g. (0.5 mole) of norbornene[17] in 94 ml. of a benzene solution was added. After standing 24 hours, three identical reaction mixtures were worked up together using butanol as a precipitating agent with a Waring Blendor. The solid was collected by filtration and washed with acetone to remove catalyst, unreacted monomer and low polymer. Drying at room temperature under vacuum gave 6.5 g. (4.5%) of a white powder which could be pressed to a brittle film at 225°.

Polymerization of Norbornene to Type B Polymer.—The reaction was carried out in an inert atmosphere in the manner noted above. A solution of 84 ml. (0.02 mole) of lithium aluminum tetraheptyl in xylene was added to 1.1 ml. (0.01 mole) of titanium tetrachloride in 50 ml. of decahydronaphthalene and the mixture allowed to stand for 10 minutes whereupon 47 g. (0.5 mole) of norbornene in 94 ml. of benzene solution was added. After standing for 24 hours the polymer was worked up as noted above to give 14.5 g. (31%) of a white powder which could be pressed to a clear, stiff, tough film at 225°.

Reaction of Type A and B Polynorbornene with Perbenzoic Acid, Performic Acid and Bromine.—Benzene solutions of low molecular weight polymer of each type were obtained by benzene extractions of the above polymer preparations using a Soxhlet extractor under a nitrogen atmosphere.

A solution of perbenzoic acid in benzene[18] was prepared but not standardized although it gave an excellent qualitative test for peroxides.

A mixture of 25 ml. of the benzene solution of low molecular weight type B polymer and 25 ml. of the solution of perbenzoic acid in benzene was allowed to stand for 24 hours; the product was precipitated by the addition of methanol, washed with acetone, and vacuum dried. Infrared evaluation of the product before and after reaction indicated reaction with a double bond had occurred. An analogous reaction was carried out with low molecular weight type A polymer with the same result.

A mixture of 50 ml. of performic acid[18] solution and 50 ml. of a benzene solution of low molecular weight type B polymer was allowed to stand for 24 hours and precipitate which had formed was collected by filtration and vacuum dried. Infrared evaluation of the product before and after reaction indicated reaction with a double bond had occurred. An identical reaction was carried out with low molecular weight type A polymer with the same result.

Bromination of low molecular weight type B polynorbornene was achieved by adding in dropwise fashion a solution of bromine (14 g. of bromine dissolved in 100 ml. of benzene) to 25 ml. of the benzene solution of the polymer until a persistent red color developed. The solution was allowed to stand for one hour, the precipitate collected by filtration, washed with methanol and vacuum dried. Infrared evaluation of the product before and after reaction indicated bromination of a double bond had occurred. An identical reaction was carried out with low molecular weight type A polymer with the same result.

Quantitative Determination of the Degree of Unsaturation in Type B Polynorbornene.—The amount of *trans* unsaturation in the polymer was determined by measuring the peak height absorbance of the 10.37 μ band of a carbon tetrachloride solution of low molecular weight type B polynorbornene. The measurements of absorbance intensity of the polymer solution were performed with a Perkin–Elmer model 21 double beam infrared spectrophotometer using sodium chloride optics. A compensation technique employing carbon tetrachloride in the reference beam was used. The solution examined contained 0.01176 g./ml. of polymer. The absorbance per cm. of the 10.37 μ band was 8.30. A molar extinction coefficient of 140 was used in the calculations. This value represents an average measurement obtained in our laboratory using *trans*-2-pentene and 3-methyl-*trans*-2-pentene. These values are in good agreement with those reported in the literature.[19] Calculation of the results indicated 0.47 mole of *trans* unsaturation per polymer chain unit. These data have been interpreted in the Discussion section.

***cis*-1,3-Cyclopentanedicarboxylic Acid.**—This acid was prepared by the oxidation of norbornene using the method outlined by Roberts for the oxidation of *anti*-7-chloro-exo-norbornene,[20] m.p. 121–122° (lit.[21] 121–122°). The acid was further characterized as the di-*p*-bromophenacyl ester, m.p. 166–168°, after crystallization from ethanol.

Anal. Calcd. for $C_{23}H_{20}O_6Br_2$: C, 50.11; H, 3.66. Found: C, 50.20; H, 3.55.

***trans*-1,3-Cyclopentanedicarboxylic Acid.**—This acid was prepared by the isomerization of *cis*-1,3-cyclopentanedicarboxylic acid.[22] A mixture of 4.61 g. of *cis*-1,3-cyclopentanedicarboxylic acid and 100 ml. of concentrated hydrochloric acid was refluxed for 16 hours. The resulting mixture of *cis*- and *trans*-acids was crystallized according to Pospischill to give 0.78 g. of impure *trans*-acid, m.p. 86–88.5° (lit.[22,23] 87–88.5°).

Impure *trans*-1,3-cyclopentanedicarboxylic acid, 0.78 g., m.p. 86–88.5°, was treated with *p*-bromophenacyl bromide to form the di-*p*-bromophenacyl ester. Crystallization of the product from ethanol gave 0.685 g., m.p. 166–168°, either alone or upon admixture with an authentic sample of the di-*p*-bromophenacyl ester of *cis*-1,3-cyclopentanedicarboxylic acid. Evaporation of the filtrate from above and fractional crystallization gave 0.751 g., m.p. 126.5–129°. This is undoubtedly the di-*p*-bromophenacyl ester of *trans*-1,3-cyclopentanedicarboxylic acid.

Anal. Calcd. for $C_{23}H_{20}O_6Br_2$: C, 50.11; H, 3.66. Found: C, 49.9; H, 3.50.

Ozonization of Type B Polynorbornene.—A Welsbach Ozonator, style T19, was used as the source of ozone in this experiment. The ozone was bubbled through a flask containing 3.02 g. of polymer in 300 ml. of carbon tetrachloride at room temperature for two hours. The contents of the flask were added to 50 ml. of water and the mixture refluxed on the steam-bath for one hour. At this point the mixture consisted of three components: a carbon tetrachloride layer, a water layer and a white solid precipitate. The carbon tetrachloride and water were decanted from the white solid precipitate. The carbon tetrachloride and water layers were separated and the carbon tetrachloride layer washed with small portions of water which were combined with the water layer. Evaporation of the carbon tetrachloride solution gave a gum of which 0.54 g. was soluble in sodium bicarbonate, but not in water, and 0.635 g. which was not soluble in sodium bicarbonate; neither of these fractions was further investigated. After standing overnight the original white insoluble precipitate proved to be water soluble, and was combined with the water layer above. Evaporation of the combined water layers gave a solid which infrared examination showed to be identical to *cis*-1,3-cyclopentanedicarboxylic acid. Conversion of this material to the *p*-bromophenacyl ester gave 3.01 g. (equivalent to a 17.5% yield of the acid from ozonization), m.p. 166–168°, either alone or upon admixture with an authentic sample of the di-*p*-bromophenacyl ester of *cis*-1,3-cyclopentanedicarboxylic acid; the infrared scans of the two materials were also identical. Investigation of the filtrates did not indicate that any of the *trans*-1,3-cyclopentanedicarboxylic acid was present.

WILMINGTON 98, DEL.

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(16) This polyethylene dry bag technique has been described. W. L. Truett and D. R. Johnson, *Chem. and Eng. News*, Oct. 21, 1957, p. 52.

(17) C. L. Thomas, *Ind. Eng. Chem.*, **36**, 310 (1944).

(18) D. Z. Swern, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 378.

(19) R. R. Hampton, *Anal. Chem.*, **21**, 923 (1949).

(20) J. D. Roberts, F. O. Johnson and R. A. Carboni, THIS JOURNAL, **76**, 5692 (1954).

(21) S. F. Birch, W. J. Oldham and E. A. Johnson, *J. Chem. Soc.*, 818 (1947).

(22) V. T. Pospischill, *Ber.*, **31**, 1950 (1898).

(23) The melting point of the pure *trans*-acid is 95.5–96.5° as reported by Birch.[21] Preparation of a phenacyl derivative from the impure *trans*-acid demonstrated that isomerization had been incomplete.