oily residue was dissolved in 50 ml. of water. Addition of 5% aqueous potassium iodide precipitated 1.3 g. (92%) of ethylenebis(tributylphosphonium iodide). Recrystallization from a mixture of ethanol and acetonitrile gave material melting at 194–195°.

Anal. Calcd. for $C_{26}H_{58}I_2P_2$: C, 45.49; H, 8.51; I, 36.95; P, 9.04. Found: C, 45.25; H, 8.05; I, 37.05; P. 9.24.

Reaction of Triphenylphosphine with 2-Chloroethylacetate.—A mixture of 50 g. (0.2 mole) of triphenylphosphine and 30 g. (0.25 mole) of 2-chloroethylacetate was stirred at 150° under nitrogen for 2 hr. The mixture was cooled and treated with 50 ml. of acetone and with 100 ml. of ether. The crude product precipitated and was recrystallized two times from a 1,2-dimethoxyethane-nitromethane mixture to obtain 18.1 g. (30%) of ethylenebis(triphenylphosphonium chloride), m.p. 282–285°. An additional recrystallization from 2-propanol gave material melting at 287–289°.

Anal. Calcd. for $C_{38}H_{34}Cl_2P_2$: C, 73.19; H, 5.49; Cl, 11.37; P, 9.95. Found: C, 72.97; H, 5.64; Cl, 11.29; P, 9.76.

The infrared spectrum did not contain carbonyl bands, and the product was identical to material prepared from triphenylphosphine and ethylene dichloride. No attempt was made to isolate the corresponding ethylenebis(triphenylphosphonium acetate).

Reaction of Ethylene(tributylphosphonium Iodide) with Trioctylphosphine and Acetate Ion.—A mixture of 3.45 g. (0.005 mole) of ethylenebis(tributylphosphonium iodide), 3.7 g. (0.01 mole) of trioctylphosphine, 0.2 g. (0.0024 mole) of anhydrous sodium acetate, 15 ml. of methanol, and 20 ml. of 2-propanol was refluxed under nitrogen for 1 hr. The presence of tributylphosphine in the mixture was established by gas chromatography, using an Aerograph Model A-100-C gas chromatograph with a 5-ft. long, 0.25-in. diameter Apiezon L column operated at 204° with a helium flow rate of 60 ml./min. The retention time for tributylphosphine under these conditions was 7.0 min.

Tributylphosphine could not be detected in these reaction mixtures when either acetate ion or trioctylphosphine was omitted. But tributylphosphine was detected when sodium acetate was replaced by 1,1,4,4-tetra-*n*-butyl-1,4-diphosphoniacyclohexane diacetate.

Acknowledgment.—We are indebted to Dr. Robert Stern for first preparing analytically pure di-*n*-butyl-2-acetoxyethylphosphine and to Mrs. Alice T. Tsilibes for some of the experiments with this compound. Analyses were carried out under the direction of Dr. J. A. Kuck and molecular weight determinations were by Mr. E. O. Ernst. We are indebted to Dr. Martin Grayson for his interest and encouragement.

Diels–Alder Reactions. II. The Independence of Reaction Temperature and Mode of Addition in the Isoprene–Methyl Acrylate Diels-Alder Reaction

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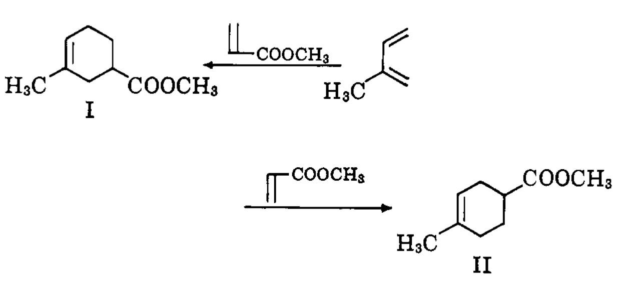
The isoprene–methyl acrylate Diels–Alder reaction was studied at reaction temperatures of 25–350°. No significant differences in the relative amounts of the two structural isomers could be detected by capillary column gas chromatography or infrared absorption spectroscopy analyses. These results are not in agreement with the data published by Nazarov, Titov, and Kuznetsova[1] who claimed that the ratio of 3-isomer to 4-isomer increased with increasing reaction temperature.

The Diels–Alder reaction of isoprene and methyl acrylate is typical of the reaction of an unsymmetrical diene and dienophile. Two structural isomers, the 3-isomer (I) and the 4-isomer (II), may be formed because two modes of addition are possible.[2] Both isomers have been detected in a number of these reactions. Specifically, Alder and Vogt[3] reported that the product of the reaction of isoprene and methyl acrylate contained about 18% of the 3-isomer. Nazarov, *et al.*[4] proved the presence of both structural isomers and later repeated the work to determine more precisely the composition of the product. This investigation was extended to include the effect of the reaction temperature on the mode of addition of this reaction and some other Diels–Alder reactions.



Of particular interest was the claim of Nazarov, Titov, and Kuznetsova[1] that the composition of the product mixture was dependent on reaction temperature. For example, their data indicated the ratio of 4- and 3-isomers of the isoprene–methyl acrylate adduct decreased from 5.1 to 1.4 as the reaction temperature was increased from 20 to 400°. This article did not suggest if the adducts were initially formed and remained at these ratios or whether these ratios were characteristic of a thermally equilibrated mixture. For example, equilibration would be feasible *via* a reverse Diels–Alder reaction.[5]

The latter explanation was initially accepted for two reasons. First, extension of prior work in this Laboratory[6] indicated that the isoprene–methyl acrylate reaction would proceed very rapidly at elevated temperatures and that Nazarov, Titov, and Kuznetsova[1] very likely used a considerably longer reaction time than necessary. Second, the use of an oven temperature as a reaction temperature guide of a highly exothermic reaction is not a sound experimental technique. In

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[1] I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* (Eng. Transl.), 1412 (1959).

[2] The 3- and 4-isomers are often referred to in the literature as the *meta* and *para* isomers, respectively. The latter designation has been avoided because of possible confusion with the nomenclature of aromatic compounds.

[3] K. Alder and W. Vogt, *Ann.*, **564**, 109 (1949).

[4] I. N. Nazarov, A. I. Kuznetsova, and N. V. Kuznetsov, *Zh. Obshch Khim.*, **25**, 88 (1955); *J. Gen. Chem. USSR* (Eng. Transl.), **25**, 75 (1955); *Chem. Abstr.*, **50**, 1623 (1956).

[5] For an excellent review of the stereochemistry of the Diels–Alder reaction, see J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[6] H. E. Hennis, *Ind. Eng. Chem. Process Design Develop.*, **1**, No. 1, 71 (1962).

an expected fast and highly exothermic reaction such as the isoprene–methyl acrylate reaction, the temperature of the reaction mixture may indeed be much higher for some time than the oven temperature would indicate. Thus it was probable that the Russians conducted most of their experiments at essentially the same temperature and then heated the adduct already formed for a period of time.

The expected speed and exothermicity of the isoprene–methyl acrylate reaction was found to be a reality. Fig. 1 shows the reaction temperature and autogenous pressure of a 3-molar run in a one-liter Parr stirred autoclave with the temperature controller adjusted to control mantle temperature at 150°. The temperature plot is the temperature *of the reaction mixture* and this plot clearly indicated the exothermicity of this reaction and the large difference between the mantle and reaction mixture temperatures. The autogenous pressure drop indicates that the reaction is almost complete within a few minutes. It could be concluded from this data that the results of Nazarov, Titov, and Kuznetsova[1] were the consequence of isomerization of the 4-isomer to the 3-isomer.

The analytical method previously used in determining the isomer ratio was a tedious multistep chemical conversion of the adducts to a mixture of isophthalic and terephthalic acids and the separation of these acids *via* their barium salts.[1] It was found in this work that a capillary column gas chromatography unit completely resolved the isomers. Furthermore, pure methyl 4-methyl-3-cyclohexene-1-carboxylate (4-isomer, II) was prepared for an infrared absorption spectroscopy standard by the saponification of the adduct, isolation of the pure 4-acid by crystallization, and methyl esterification of this acid. Thus two analytical methods were available for this work.

Initial experiments were concerned with the attempt to isomerize thermally the adduct previously prepared at low temperature. A mixture of equimolar amounts of isoprene and methyl acrylate were allowed to stay at room temperature for seventy days. The adduct was isolated by distillation in 39% yield, and capillary gas chromatography indicated the presence of 70.3% of the 4-isomer and 29.7% of the 3-isomer. Samples of this product were heated at 120° and 200° for seven hours. Analyses indicated products with 71.8 and 72.2% of the 4-isomer, respectively. The presence of only two peaks representing the two isomers indicated insignificant adduct degradation during this heating. Furthermore, the heating of pure 4-isomer at 198° (reflux temperature) for three hours did not give a detectable trace of 3-isomer. Thus the results of Nazarov, Titov, and Kuznetsova[1] could not be explained on the basis of the thermal equilibration of a kinetically controlled mixture.

The work previously reported[1] on the isoprene–methyl acrylate reaction was then essentially repeated with the added refinements of a stirred autoclave equipped with a special mantle capable of rapid cooling to maintain a constant reaction temperature and with the analytical techniques previously cited. The data collected in this study are tabulated in Table I. No significant differences in product composition due to reaction temperature could be detected. All runs gave an adduct with a gas chromatogram or infrared spectrum consistent with a mixture containing about 70% 4-isomer and 30% 3-isomer.

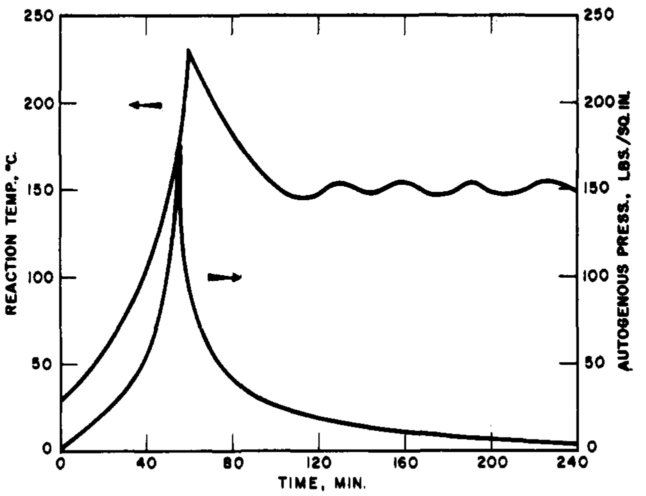

Fig. 1.—The temperature and autogenous pressure of the isoprene–methyl acrylate reaction with the temperature controller set to control at 150.°

The findings of Nazarov, Titov, and Kuznetsova[1] that the product composition of the isoprene–methyl acrylate Diels–Alder reaction is dependent on reaction temperature are not supported by this work. We cannot offer a reasonable answer to this lack of agreement at this time.

Table I

Adduct Composition at Various Reaction Conditions

Reaction Temp., °C.	conditions Time	Yield,[d] %	Analysis, 4-isomer, % Infrared	Gas chromatography[f]
~25[a]	70 days[c]	39	72	70.3
120	6 hr.	69	70	70.4
200	2 hr.	82	69	70.1
350[b]	. . .	0.8[e]	. .	70.8

[a] Room temperature. [b] Gas phase reaction in tubular reactor; reaction time very short. [c] Nazarov, Titov, and Kuznetsova (ref. 1) allowed reaction to proceed 7 months. [d] Distilled product. [e] Product too impure for infrared analysis. [f] All products except 350° run were 99 plus % pure.

Experimental[7]

Isoprene–Methyl Acrylate Reaction Study.—The room temperature isoprene–methyl acrylate reaction was conducted in a corked bottle. The high temperature experiments with the exception of the 350° run were carried out in a Parr series 4500 1-l. medium pressure stirrer type, electrically heated pressure reaction apparatus. The autoclave was equipped with a special heating mantle fitted with water circulating tubes for efficient dissipation of the reaction heat to maintain a constant reaction temperature. The 350° experiment utilized an electrically heated vertically mounted glass tube (19 in. long and 0.75 in. i.d.) packed with glass beads (Propper Mfg. Co., Inc., size 5). The mixed starting materials were conducted through the tube at a rate of 2.5 ml./min.

The heating of the adduct prepared at the low temperature for study of the possibility of isomerization was done in the Parr autoclave and the attempted isomerization of the pure 4-isomer was conducted at the reflux temperature (198°) in a flask equipped with a reflux condenser.

Equimolar amounts of isoprene (Enjay Chemicals Co.), methyl acrylate (Dow Badische Chemical Co.), and a small amount of hydroquinone, and the same purification procedures, were utilized in all the experiments. The purification procedure of the run conducted at 200° is described in detail as typical. Methyl acrylate (86 g., 1.0 mole), isoprene (68 g.,

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(7) All boiling and melting points are uncorrected.

1.0 mole), and 1 g. of hydroquinone were heated at 200° for 2 hr. The crude reaction mixture was fractionated through an 18-in. Vigreux column to yield 126 g. (82%) of a colorless oil, b.p. 85–86° (15 mm.); n^{25}_{D} 1.4606 [lit.[1] b.p. 88–90° (16 mm.), n^{20}_{D} 1.4655].

Methyl 4-Methyl-3-cyclohexene-1-carboxylate (4-Isomer).—The isoprene–methyl acrylate adduct (770 g., 5.00 moles) from combined 150°-reaction temperature runs was caused to react while stirring at 65° with 600 g. (15.0 moles) of sodium hydroxide dissolved in 3 l. of water. The mixture was clear after 2 hr. indicating that the reaction was complete. Concentrated sulfuric acid was added with stirring and cooling until the reaction mixture was acidic (pH 3). Benzene was added to dissolve the precipitated solid product. The organic and aqueous layers were separated and the aqueous solution was extracted with benzene. The combined benzene solutions were water-washed and the benzene was stripped under slightly reduced pressure. The crude product was purified by fractionation through a 6-in. Vigreux column to yield 677 g. (97%) of a mixture of 3-methyl- and 4-methyl-3-cyclohexene-1-carboxylic acid, a crystalline white solid, b.p. 162–164° (37 mm.), m.p. 51–74°.

This mixture of acids was recrystallized (four times) from petroleum ether (b.p. 60–100°) to a constant m.p. 98.5–99° (lit.[8] m.p. 99°). This procedure afforded 269 g. of pure 4-methyl-3-cyclohexene-1-carboxylic acid.

The esterification method of Lorette and Brown[9] was adopted for the preparation of pure methyl 4-methyl-3-cyclohexene-1-carboxylate. 4-Methyl-3-cyclohexene-1-carboxylic acid (140 g., 1.00 mole), methanol (160 g., 5.00 moles), 2,2-dimethoxypropane (208 g., 2.00 moles), and 2 ml. of concentrated hydrochloric acid were heated at the reflux temperature for 3 hr. Low boiling material was removed by distillation under reduced pressure. The residue was diluted with toluene and this solution was washed with water, 5% sodium bicarbonate solution, and once again with water. The toluene was removed by stripping under vacuum (water aspirator), and the crude product was fractionated through an 18-in. Vigreux column to afford 140 g. (91%) of methyl 4-methyl-3-cyclohexene-1-carboxylate, a colorless oil, b.p. 56–57° (2.2 mm.), n^{25}_{D} 1.4600. The capillary column gas chromatogram of the product indicated a single pure compound.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.12; H, 9.16.[10]

Analytical Procedures.—The gas chromatography analyses utilized a Perkin-Elmer Model 154 instrument equipped with 150 ft. of 0.01-in. i.d. stainless steel capillary "R" column coated with Ucon polyglycol LB-550-X, a highly sensitive hydrogen flame detector, and an "O" sample splitting device. Column temperature was not critical; reproducible results were obtained with a column temperature range of 100–175°. A temperature of ~125° was used in this work. Complete resolution of isomers was always achieved and control samples were liberally interspersed with the unknowns to ensure that constant equipment response was obtained.

Carbon disulfide solutions were prepared of the pure 4-isomer and a known mixture of the 3- and 4-isomers utilizing 100 mg. per 5 ml. of carbon disulfide. Infrared absorbance measurements were obtained at both 12.5 μ (4-isomer) and 12.7 μ (3-isomer) in a 1.0-mm. cell with a carbon disulfide blank as the reference for measurements for the standard solutions using a single beam spectrometer. Analytical and interference curves were plotted from the absorbance measurements obtained from the standard solutions. Samples were then prepared as 2% solutions in carbon disulfide, and measurements were made in the same manner. The concentrations of the 3- and 4-isomers were obtained by graphical solutions using the analytical and interference curves.

Acknowledgment.—The author is grateful to Dr. C. B. Roberts for the gas chromatography analyses and to R. T. Scheddel for devising the infrared spectroscopic method of analysis and for performing the measurements.

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(8) E. Lehmann and W. Paasche, *Ber.*, **68B**, 1068 (1935).

(9) N. B. Lorette and J. H. Brown, Jr., *J. Org. Chem.*, **24**, 261 (1959).

(10) Elemental analyses by the staff of Dr. P. H. Boyd of The Dow Chemical Company.

Diels–Alder Reactions of 9-Substituted Anthracenes. VI. 9-Anthryl Acetate, 9-Methoxyanthracene, and 9,10-Dimethoxyanthracene[1]

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9-Anthryl acetate gave only the vicinal type adduct with acrylic acid, and was less reactive in the Diels–Alder reaction than 9-methoxyanthracene. Acrylic acid, acrylonitrile, methyl acrylate, and acrylamide led to the vicinal adducts with 9-methoxyanthracene while allyl alcohol gave the nonvicinal adduct. The acrylic acid adducts of 9-anthryl acetate, 9-methoxyanthracene, and 9,10-dimethoxyanthracene upon treatment with hydrogen iodide underwent a ring opening to give 3-(10-keto-9,10-dihydro-9-anthryl)propionic acid, while the nonvicinal acid prepared by the oxidation of the allyl alcohol adduct gave only ether cleavage as did 9,10-dimethoxy-9,10-dihydro-9,10-ethanoanthracene. The maleic anhydride adducts of 9,10-dimethoxy-, 9,10-diacetoxy- and 9-methoxyanthracene led to (10-keto-9,10-dihydro-9-anthryl)succinic acid. Improved procedures for the preparation of 9-anthryl acetate, 9-methoxy- and 9,10-dimethoxyanthracene have been developed.

9-Anthraldehyde when condensed with monosubstituted dienophiles gave only vicinally substituted Diels–Alder adducts,[3] while 9-cyanoanthracene,[4] 9-anthraldehyde dimethyl acetal,[5] and 9-anthramide[6] gave in some cases both vicinal and nonvicinal adducts with the vicinal adduct, save in one case, predominating.

On the other hand 9-anthroic acid and acrylic acid as well as their salts gave only the nonvicinal adduct[7] and four of the six dienophiles, condensed with 9-nitroanthracene, gave predominantly the nonvicinal adduct.[6]

This indicates that as the substituent on the anthracene becomes more electron withdrawing the more likely it will be to give a nonvicinally substituted adduct. The one case which seems to be an exception for this is where sodium acrylate and sodium 9-anthroate gave the nonvicinal adduct, and this is presumably due to the repulsive effects of the carboxylate ionic moieties.

Since no 9-substituted anthracene bearing an *ortho-para* directing group has been studied in the Diels–

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(2) National Science Foundation summer research participant.

(3) J. S. Meek, B. T. Poon, and S. J. Cristol, *J. Am. Chem. Soc.*, **74**, 761 (1952).

(4) J. S. Meek, J. R. Dann, and B. T. Poon, *ibid.*, **78**, 5413 (1956).

(5) J. S. Meek and J. R. Dann, *J. Org. Chem.*, **21**, 968 (1956).

(6) J. S. Meek, D. R. Wilgus, and J. R. Dann, *J. Am. Chem. Soc.*, **82** 2566 (1960).

(7) K. Alder and K. Heimbach, *Chem. Ber.*, **86**, 1312 (1953).