Reaction of 1,2,3-Trichloro-4,4-difluorocyclobutene (XXI) with Ethoxide Ion.—In a 1-l. three-neck flask, equipped with stirrer, reflux condenser, and addition funnel, was placed 80.0 g (0.414 mole) of a mixture of 94.7% 1,2,3-trichloro-4,4-difluorocyclobutene (XXI, 0.392 mole) and 5.3% 1,4,4-trichloro-3,3-difluorocyclobutene (V, 0.022 mole) in 200 ml of 95% ethanol. The solution was cooled in an ice–water bath, and a solution of 27.3 g (0.414 mole) of potassium hydroxide in 200 ml of ethanol was added dropwise with rapid stirring over a 2-hr period. The reaction mixture was diluted with water and extracted with methylene chloride, and the extracts were washed with water until neutral and dried twice over magnesium sulfate. Rectification through a 315-mm Fenske column gave 43.0 g of product 100% pure by glpc: bp 100° (50 mm); $n^{25}\text{D}$ 1.4438; d^{25}_4 1.3531; molar refractivity, calcd 39.31, found, 39.80.

Anal. Calcd for $C_6H_6Cl_2F_2O$: C, 35.50; H, 2.98; Cl, 34.94; F, 18.73. Found: C, 35.49; H, 3.11; Cl, 35.06; F, 18.54.

The infrared spectrum contained a strong absorption at 1675 cm^{-1}. The nmr spectrum contained a doublet centered at τ 5.05 with a J_{HF} of 0.9 cps, evidence for an allylic proton split by a fluorine nucleus, and a 1:3:3:1 quartet centered at τ 5.45, indicative of a methylene proton on a vinylic ethoxy group. Integration showed the areas of the doublet and the quartet to be in the ratio 1:2.

The total yield of vinyl ether was 59.3 g (0.292 mole, 75%).

Also obtained was 5.5 g (0.027 mole, 12%) of 1,2-dichloro-3-ethoxy-4,4-difluorocyclobutene, identified by its infrared spectrum and glpc retention time.

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Catalytic Actions of Aluminum Chloride on the Isoprene–Methyl Acrylate Diels–Alder Reaction

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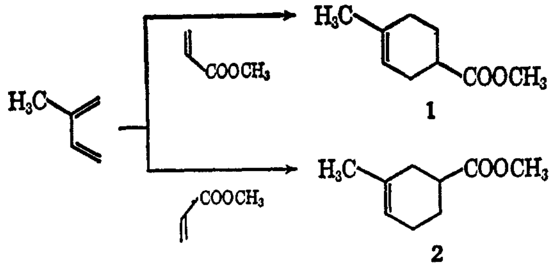
The ratio of methyl 4- and 3-methyl-3-cyclohexene-1-carboxylates (**1** and **2**) formed by the aluminum chloride catalyzed reaction[1] (at 7–12°) of isoprene with methyl acrylate was found to be 95:5. The corresponding ratio for the uncatalyzed reaction (Diels–Alder reaction) was found to be 70:30 (at room temperatures and at 120°) in agreement with the literature.[2] The measurements of the relative rate of butadiene, isoprene, and 2,3-dimethylbutadiene toward methyl acrylate were made to get the partial rate factors (see Figure 1). The aluminum chloride catalyzed reaction is shown to be free from steric complications by inspection of the partial rate factors obtained. A heterolytic two-step mechanism involving rate-determining electrophilic attack of the β-carbon atom of the complexed methyl acrylate on dienes is suggested by the comparison of partial rate factors and an enormous accelerating effect of aluminum chloride.

It recently has been shown that methyl acrylate reacts with 1,3-dienes very rapidly in the presence of anhydrous aluminum chloride to give Diels–Alder condensation products in high yields.[1] The complex formation between aluminum chloride and the acrylate, presumably at the carbonyl oxygen, may polarize the α,β double bond more both to activate the dienophile toward a diene and to make the isomer ratio of the adducts, with an unsymmetrical diene, different from that in the uncatalyzed reaction. Such an effect on orientation has actually been reported by Lutz and Bailey[3] on the reaction of isoprene with methyl vinyl ketone or acrolein under the catalysis of stannic chloride pentahydrate. These workers explained the increased preponderance of the 1,4 isomer in the products by assuming the increased steric retardation against the 1,3-isomer formation where the pendant methyl group of isoprene must come close to the complexed carbonyl group of larger steric requirement.

In the present paper we report the isomer distribution **1**:**2** and the relative rate, k(isoprene):k(butadiene), for the aluminum chloride catalyzed reaction as well as those for the uncatalyzed reaction, as reference of comparison, and present a probable mechanism of the catalyzed reaction.

Results and Discussion

Two groups of workers have reported on the isomer distribution **1**:**2** for the uncatalyzed condensation with some contradictions. Thus Nazarov, *et al.*,[4] reported a ratio of 5.4:1 (16% of **2**) for the room temperature and 3.8:1 (21% of **2**) for the 120° reaction. On the other hand Hennis[2] recently has reported a ratio of 70:30 which was independent of the reaction temperature. This situation induced us to reexamine the ratio.[5]



The analytical procedures adopted here were to dehydrogenate the reaction products and determine the resulting *p*- and *m*-toluates by the infrared absorbance measurements. The dehydrogenation with palladium on carbon in the liquid phase or in solution,

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[1] T. Inukai and M. Kasai, *J. Org. Chem.*, **30**, 3567 (1965).

[2] H. E. Hennis, *ibid.*, **28**, 2570 (1963).

[3] E. F. Lutz and G. H. Bailey, *J. Am. Chem. Soc.*, **86**, 3899 (1964).

[4] I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1412 (1959); *Chem. Abstr.*, **54**, 1409 (1960).

[5] Hennis[2] used the key bands of 12.5 (for **1**) and 12.7 μ (for **2**) for determination of the isomer ratio. We found that the product of the uncatalyzed reaction did not give rise to 12.7-μ absorption, even a shoulder, which according to the literature[2] would show surprising absence of **2**. Since isomer **2** does not seem to have been isolated pure and identified by this author, we could not have full assurance of this assignment of the 12.7-μ band to **2**. The glpc analysis was not convincing for the same reason.

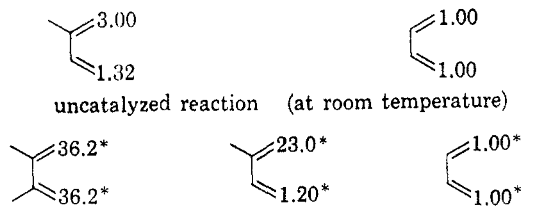


Figure 1. Partial rate factors.

with the technique of immediate purging of hydrogen with inert gases (nitrogen or carbon dioxide), proved not usable, because it led to an almost quantitative disproportionation; a 2:1 mixture of the saturated and aromatized products was formed.

Gas phase dehydrogenation at 320–330° was satisfactory. The possible interconversion of the isomers during the dehydrogenation process *via* dissociation–recombination mechanism was ruled out because first the final analytical result of the isomer ratio was reproducible and dependent on the conditions of condensation reactions, and second pure **1** gave no *m*-toluate by the same procedures as those adopted for the analysis. The infrared determination of the toluate was straightforward.

The isomer distributions are presented in Table I. The results for the uncatalyzed reactions agree with those of Hennis[2] quite well. The relative rates of reaction of butadiene, isoprene, and 2,3-dimethylbutadiene with methyl acrylate were next determined as summarized in Table II.

TABLE I

ISOMER DISTRIBUTIONS OF ISOPRENE–METHYL ACRYLATE REACTIONS

Isoprene–methyl acrylate mole ratios	Temp, °C	Time	Yield, %	**1**:**2** ratio
1.058:1.058[a]	25	41 days	32	69.5:30.5
0.358:0.358[a]	120	6 hr	83	70.0:30.0
0.307:0.303[b]	10–20	3 hr	50	95.0:5.0

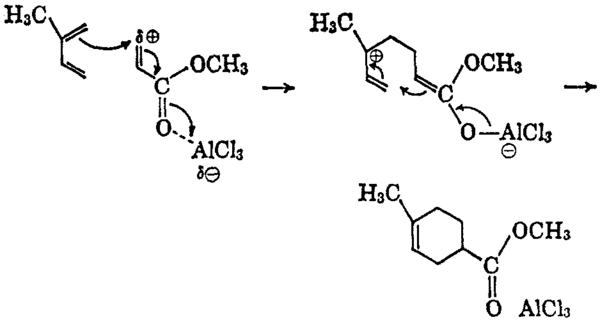
[a] Uncatalyzed reaction; hydroquinone (1 g) was added. [b] The reaction was carried out in 280 ml of benzene in the presence of 0.032 mole of aluminum chloride.

The partial rate factors (prf) calculated from these data are shown in Figure 1. It should be noticed here that the formation of **1**, for example, was assigned to the reactivity of the 1-position of isoprene according to the view that the most electrophilic center (β carbon of methyl acrylate) attacks the nucleophilic positions of the diene component.[6] This view is reasonable for the catalyzed reaction but probably less so for the uncatalyzed reaction (see later discussions). It should also be mentioned that the prf values for the catalyzed reaction are marked with * in order to indicate clearly that they form a separate set.

The Diels–Alder reaction is generally believed to proceed by a single-step mechanism in which the diene and the olefin approach one another in parallel planes in such a mutual orientation that the principle of maximum accumulation of unsaturated centers is satisfied.[7,8] The effects brought about by substituents attached to the reacting unsaturated centers, which were formerly regarded as providing support for the heterolytic two-step mechanism, are explicable by considering the electronic and electrostatic interactions within this transition model.[8a,9] If the aluminum chloride catalyzed reaction were to proceed in a similar way, a steric repulsion between the pendant methyl group of isoprene and the carboxylate group would have a possibility of retarding the formation of **2**, as suggested by Lutz and Bailey[3] for similar cases.[11] In this case, the carboxylate group is now bulkier because of complex formation with aluminum chloride. Interestingly the prf of 2,3-dimethylbutadiene (36.2*) is slightly *larger* than expected from the additivity of the substituent effect (multiplication of prf: 23 × 1.2*), showing that the reaction is free of steric complications. This denies such an explanation as cited above for the depressed proportion of **2**. Consequently, we know that the enhanced reactivity of 1-position relative to 4-position, rather than the depressed reactivity of 4-position, is the reason for the observed effect of the catalyst on the isomer distribution.

That the catalyzed reaction is heterolytic is evident from an enormous acceleration[1] by aluminum chloride. The larger substituent effect of the methyl group in the catalyzed reaction can also be explained on this basis. This is because the contribution of polar effects to the ease and direction of the reaction is likely to be greater in the reaction of a fully grown cationic reagent than in the "largely homolytic" reaction[7] whose characteristics are modified by the polar factors.[12]

The electronic reorganization for the catalyzed reaction may be visualized in eq 1[13] and the substituent effect is explained by comparing the degree of stabilization of the electronic systems **3**, **4**, and **5** (dashed lines). The relation between **3**, **4**, and **5** apparently compares to that between the transition models of



(1)

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(6) G. M. Badger, "The Structure and Reactions of the Aromatic Compounds," Cambridge University Press, London, 1954, p 361.

(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, New York, N. Y., 1953, p 711.

(8) (a) See R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959), for detailed discussion and references of the previously proposed mechanism; (b) S. Seltzer, *J. Am. Chem. Soc.*, **87**, 1534 (1965).

(9) The present authors are not in a position to discuss subtle arguments like one-step or "two-stage" mechanism (see footnotes 8a and 10), but place all the proposed mechanisms into one or the other of two categories, the single-step or two-step mechanism.

(10) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961).

(11) Although such a steric repulsion is within the range of possibility, any estimate of its importance is not feasible because we do not know how far the addends deviate from the parallelism at the transition state. Furthermore the catalyzed reaction may proceed in the Alder *endo*-type or anti-Alder *exo*-type behavior; in the latter case the steric repulsion is quite improbable.

(12) A good account is given in C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 188–189.

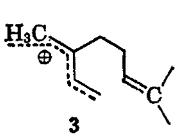
(13) It should be understood that the stereochemical course of the approach of the addends is not implied by this representation.

TABLE II

RELATIVE RATES OF REACTION[a]

Isoprene, mmoles	Butadiene, mmoles	Methyl acrylate, mmoles	$AlCl_3$, mmoles	Benzene, ml	Time	Yield,[b] g	Product[c] ratio	Relative[d] rate
441	815	11.6	0	0	47 days	Trace	1.17	2.16[e]
117.5	1352	11.6	1.14	55	3 hr	$\leq$0.5	1.08	12.18
117.5	1311	34.8	4.86	65	3 hr	1.8	1.14	12.42
117.5	1332	34.8	6.46	70	3 hr	2.7	1.18	11.69
2,3-Dimethylbutadiene	Isoprene							
175.7	176.3	11.8	2.22	90	3 hr.	1.8	2.92	2.99

[a] At 7–12° unless otherwise indicated. [b] Total yield of the condensation products. [c] Mole ratio of the isoprene adduct/butadiene adduct or the 2,3-dimethylbutadiene adduct/isoprene adduct. [d] Relative rate of isoprene/butadiene or dimethylbutadiene/isoprene. [e] At room temperatures.



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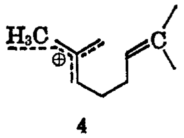

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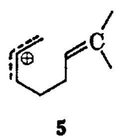

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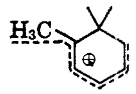
ortho (**6**) and *meta* (**7**) electrophilic substitution of toluene and benzene (**8**), and therefore the order of reactivity is easily explained.



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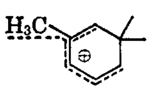

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This will suggest that the reaction involves two electronic reorganization steps which take place in sequence. It has been shown, however, that the aluminum chloride catalyzed addition of anthracenes and 2,3-dimethylnaphthalene to maleic anhydride, dimethyl maleate, and dimethyl fumarate proceeds with retention of configuration of the dienophile substituents in exactly the same way as the uncatalyzed reaction.[14] Therefore it must be assumed that the second step is finished before any rotation around the α,β bond within the dienophile moiety occurs, if the two bond-forming steps are considered to take place one after the other.

Experimental Section

Infrared spectra were recorded on a Nihon Bunko Model DS-402G double-beam spectrophotometer equipped with a grating.

Materials.—The preparation of butadiene, isoprene, 2,3-dimethylbutadiene, and 4-methyl-3-cyclohexene-1-carboxylic acid has been previously described.[1] Methyl 4-methyl-3-cyclohexene-1-carboxylate (**1**) was prepared from the acid by esterification with diazomethane, bp 90–90.5° at 20 mm, $n^{20}D$ 1.4624, $n^{25}D$ 1.4602 (lit.[2] bp 56–57° at 2.2 mm, $n^{25}D$ 1.4600). Methyl *p*- and *m*-toluates were prepared by the usual method, and their purity was checked by infrared absorption and gas–liquid partition chromatography (glpc).

Aluminum Chloride Catalyzed Reactions.—Isoprene was added to a stirred benzene solution of methyl acrylate and anhydrous aluminum chloride at 10–20° as described in the previous paper.[1] For competitive reaction a large excess of isoprene and butadiene was charged in a pressure bottle equipped with a magnetically driven stirrer, and a benzene solution of methyl acrylate and aluminum chloride was added under nitrogen pressure. The reaction was carried out under a pressure of 4 atm.

Uncatalyzed reactions were conducted in the conventional way: the room-temperature reaction in a sealed tube, and the 120° reaction in a stainless steel autoclave.

Analytical Procedures.—The dehydrogenation reactor was a horizontal hard-glass tube (1.8 cm × 45 cm) mounted on a cylindrical electric furnace. The tube was packed with palladium (20 wt %) on asbestos over the middle 30-cm region and was connected to a reactant vessel (vaporizor) and a product trap at the ends. The reactor was heated to 320–330° and the vaporizer to 150–160°. A slow stream of carrier nitrogen was passed through the vaporizer and then the reactor over a period of 7 hr in a run with a 2-g sample. A slow rate and sufficient preheating of the gas was thought to be beneficial to suppress the disproportionation; a 90% conversion to the toluates was achieved by a single passage and recycling was unnecessary. The rest of the product was the starting materials and hydrogenation products. The product was directly dissolved in carbon disulfide (500 mg/10 g of carbon disulfide) for the infrared analysis of methyl *p*- and *m*-toluates. Absorbance measurements were obtained at 758.4 (*para* isomer) and at 749.0 cm^{-1} (*meta* isomer) in a 0.025-mm cell with a carbon disulfide blank as the reference. The isomer ratio for the unknown mixture was read from the calibration curve, $D_{758.4}/D_{749.0}$ *vs.* concentration ratio *para/meta* isomer, obtained from the same measurements on the known mixtures of authentic *p*- and *m*-toluates. Presence of impurities, *i.e.*, the starting materials and hydrogenation products, should be of no harm, since these have negligible absorbance at the key band region.

Compounds **1** and **2** could not be separated by glpc. The ratio of methyl 3-cyclohexene-1-carboxylate to **1** plus **2** and that of methyl 3,4-dimethyl-3-cyclohexene-1-carboxylate to **1** plus **2** were determined by glpc (a 2.7-m PEG column at 165°), using appropriate calibration curves: peak area ratio *vs.* weight ratio. To calculate the relative reactivity from the product ratio use was made of the usual formula $k_a:k_b = \log(1 - P_a/A_0):\log(1 - P_b/B_0)$, where $k_a:k_b$ is the relative reactivity of compound a to b, P_a and P_b are the amounts of the products from a and b, and A_0 and B_0 are the amounts of a and b initially charged.

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(14) (a) P. Yates and P. Eaton, *J. Am. Chem. Soc.*, **82**, 4436 (1960); (b) J. Sauer, D. Lang, and H. Wiest, *Chem. Ber.*, **97**, 3208 (1964).