at 1.25, a 1 H broad singlet at 3.25, and a 5 H multiplet at 7.15 ppm.

Acknowledgments.—The authors thank Mr. Roy Clark of this department for his skillful construction of the dimethylketene generator and the National Science Foundation for support of this research through NSF Grant G-19490.

Aluminum Chloride Catalyzed Diene Condensation. II.[1] Stronger Adherence to the Alder *endo* Rule

TAKASHI INUKAI AND TAKESHI KOJIMA

The Central Research Laboratories, Chisso Corporation, Kamariya, Kanazawa-ku, Yokohama, Japan

Received January 3, 1966

It has been previously reported that aluminum chloride markedly catalyzes the Diels-Alder reactions of acrylates with dienes.[2] The effect of the methyl group in a diene molecule on the rate of the catalyzed and the uncatalyzed reaction was determined to provide an insight into the mechanism of the catalyzed reaction, and a heterolytic two-step mechanism was suggested in a recent article.[1]

Now we report on the stereochemical selectivity in the catalyzed condensation between cyclopentadiene and several dienophiles. Our original interest was to know to what extent the well-known Alder *endo* selectivity[3] would be preserved in this catalyzed modification of the Diels-Alder reaction, since if the reaction does not proceed by the four-center mechanism the stereochemical course of the reaction will not be controlled by the *principle of maximum accumulation of centers of unsaturation* and, therefore the Alder *endo* rule may not be observed in the catalyzed reaction.

The *endo vs. exo* adduct ratios for both the catalyzed and uncatalyzed reactions of cyclopentadiene with methyl acrylate, methyl methacrylate, methyl *trans*-crotonate, dimethyl maleate, and diethyl maleate in benzene at 30° were determined by gas-liquid partition chromatography (glpc) and are listed in Table I. Peak areas were used as the direct measure of the isomeric ratio and the values are probably correct to within a few per cent.[4]

The proportion of the *endo* adduct is enhanced by the catalysis by aluminum chloride in all the reactions now studied. Interestingly even with methyl methacrylate, which preferentially yields the *exo*-methoxycarbonyl adduct in the uncatalyzed reaction,[5] the *endo* adduct is the preferred product in the catalyzed reaction. Consequently we conclude that the catalyzed reaction invariably adheres to the Alder *endo* rule to a greater degree than does the uncatalyzed reaction, which is contrary to what we originally imagined.

TABLE I

endo–exo RATIO OF THE PRODUCTS FROM THE REACTIONS OF CYCLOPENTADIENE WITH VARIOUS DIENOPHILES[a]

Dienophile	Solvent[b]	Catalyst[c]	Reaction time, hr	Ratio[d,e]	
				endo	*exo*
Methyl acrylate	A	U	7.5	80	20
	A	U	...	(83.1	16.9)[f]
	B	U	7.5	78	22
	B	C	0.5	95	5
	B	C	1.0	94	6
Methyl methacrylate	A	U	7.5	34	66
	A	U	...	(33.0	67.0)[f]
	B	U	7.5	31	69
	B	C	0.5	60	40
	B	C	1.0	60	40
Methyl *trans*-crotonate	E	U	24.	64	36
	E	U	...	(62.3	37.7)[f]
	B	U	24.	54	46
	B	C	0.5	94	6
	B	C	1.0	93	7
Dimethyl maleate	D	U[g]	4.0	72	28
	D	U[g]	...	(75	25)[h]
	B	U	5.0	73	27
	B	C	1.0	94	6
	B	C	2.0	94	6
Diethyl maleate	B	U	14.	73	27
	B	C	1.0	96	4
	B	C	2.0	95	5

[a] Reactions at 30° unless otherwise indicated. [b] A, acetonitrile; B, benzene; E, ethanol; D, dioxane. [c] U, uncatalyzed; C, aluminum chloride catalyzed. [d] From glpc peak area assuming equal thermal conductivity of the stereoisomers. [e] The results by previous workers are quoted in parentheses. [f] See ref 5. [g] At 70°. [h] See ref 9.

It is of further interest that the configuration of dienophile substituents is retained in the adduct of the catalyzed reaction too. Thus, the content of 5-norbornene-*trans*-2,3-dicarboxylates in the products from dimethyl and diethyl maleate reactions with cyclopentadiene was less than 0.3% (by glpc) in both the catalyzed and uncatalyzed reactions (even this slight contamination of the *trans* isomer might have been derived from the fumarate impurity in the maleate used).

Our present findings indicate that the catalyzed reaction may not necessarily be regarded as a heterolytic two-step reaction such that the two bond-forming steps take place in sequence. We rather prefer to regard the reaction as having a great deal in common with the uncatalyzed reaction.

To account for the higher *endo* selectivity three considerations come to mind: (1) steric hindrance in the transition states, (2) the enhanced degree of π interaction between the unsaturated centers of the addends, and (3) the polarity effect.

The steric hindrance between the methylene group of cyclopentadiene and the dienophile substituents in the transition state to the *exo* adduct has been invoked to interpret the variation of the *endo vs. exo* adduct ratio from reactions of cyclopentadiene with various dienophiles.[6] Such a steric hindrance may be larger when the dienophile substituent is complexed with aluminum chloride, making the catalyzed reaction more strongly *endo* selective than the uncatalyzed reaction. However, we do not give importance to this effect because the same increased stereospecificity is observed

---

(1) Paper I: T. Inukai and T. Kojima, *J. Org. Chem.*, **31**, 1121 (1966).

(2) T. Inukai and M. Kasai, *ibid.*, **30**, 3567 (1965). See also references cited therein.

(3) M. C. Kloetzel, *Org. Reactions*, **4**, 1 (1948).

(4) See ref 5 for support of this assumption.

(5) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962).

(6) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961), section V.

in the catalyzed reaction of methyl acrylate and piperylene.[7,8] In this case the steric hindrance mentioned above is obviously impossible since the acyclic diene lacks the methylene group under question.

From this analogous behavior of the stereospecificity of the reactions of the cyclic and acyclic dienes we prefer to explain the higher stereoselectivity by a larger π interaction between the unsaturated centers of the addends in the catalyzed reaction than in the uncatalyzed reaction, an explanation which is an extension of the traditional interpretation of the *endo* rule of the Diels–Alder reactions. The dienophile substituents become more electrophilic when complexed with aluminum chloride, and this enhances the rate of condensation (rate effect). At the same time, the complexes orient themselves to the *endo* direction more predominantly by their stronger π interaction with the residual unsaturation of the diene moiety in the transition state (stereochemical effect of the catalysis). This explanation closely parallels that proposed by Sauer, *et al.*,[9] for the stereochemistry of various adducts from dienophiles of varying reactivity.

The third consideration, the polarity effect, may also be a factor. It has been shown by an elaborate study by Berson, *et al.*, that the proportion of the *endo* adduct increases with the increasing polarity of the solvent used and this was explained by assuming a larger dipole moment of the *endo* transition state than the *exo*.[10] Our present results of marked preference of the *endo* adducts correspond to that which would be obtained in the reactions in an extremely polar solvent according to the experimental rule by Berson, *et al.*[5] Since the activated complex of the catalyzed reaction will be formed in the vicinity of the local field of aluminum chloride, which polarizes the reactant and solvent molecules, the polarity effect appears to operate in the right direction. It is difficult to rationalize this on a sound basis, however, because the effects of the dipole moments of the *endo* and *exo* transition complexes on the rate (which are in favor of the formation of the *endo* adduct), and their balance with the opposing effect of dipole induction energy, are subject to substantial uncertainty,[10] particularly in the presence of aluminum chloride.

Experimental Section

Materials.—Cyclopentadiene, bp 40–41°, was obtained by cracking dicyclopentadiene[11] and stored in Dry Ice. Methyl *trans*-crotonate, bp 119–121°, n^{20}_{D} 1.4238, was prepared by esterification of freshly recrystallized *trans*-crotonic acid. Dimethyl maleate, bp 97.5° at 18 mm, and diethyl maleate, bp 118° at 16 mm, were prepared by treating maleic anhydride with the corresponding alcohols in the presence of concentrated sulfuric acid. Methyl acrylate and methyl methacrylate were prepared as described previously.[2] Solvents were purified in the usual way and were anhydrous.

Reactions.—To a suspension of anhydrous aluminum chloride, 6.0 g, in benzene, 100 ml, was added a dienophile in slight excess of the equimolecular amount, and the mixture was stirred in a thermostat at 30° for a while until all the aluminum chloride dissolved. An equimolecular amount of cyclopentadiene in benzene, 50 ml, was added to the solution in 15 min. After reaction periods of 0.5 and 1 hr (or 1 and 2 hr), 50 ml of the reaction mixture was pipetted out onto 50 ml of water, and the benzene layer was washed until neutral, dried with anhydrous sodium sulfate, and concentrated by evaporation under reduced pressure. The concentrate was analyzed by glpc for the isomer ratio.

For the uncatalyzed reaction higher initial concentrations of the reactants, in the range of 2–2.5 *M*, were convenient to achieve sufficient yields of products within several hours.

Analysis of Products.—The analyses were carried out by glpc with an Ohkura Model 1200 instrument. The determinations of the products from methyl methacrylate employed a 2.7 m × 5 mm ϕ copper column packed with 10 wt % 1,2,3-tris(β-cyanoethoxy)propane on Diasolid M (Nihon Chromato Ind., Co. Ltd.) at 85°. The same column packed with 10 wt % Carbowax 6000 on Diasolid M (the same supplier) was used for all others: at 100° for the acrylate and crotonate reaction products; at 180° for the maleate reaction products. The flow rate of helium gas was about 80 ml/min in all cases.

The assignment of the glpc peaks to the *endo* or *exo* isomer was made by comparison of the observed and literature values of the isomer ratio of the uncatalyzed reaction under the same reaction conditions. The agreement between them (Table I) leaves no doubt about this procedure. In the case of diethyl maleate analogy with the methyl ester was resorted to for the identification of the glpc peaks. The *exo* isomer elutes faster than the *endo* and clear separation of the isomers was achieved in all instances.

---

[7] The term *endo* selectivity is a misnomer in referring to reactions of acyclic dienes but is useful for description, because the formation of *cis*-substituted cyclohexenes is mechanistically analogous to the formation of the *endo* adducts from cyclic dienes. The details of the piperylene–methyl acrylate reaction are under investigation and will be shortly published elsewhere.

[8] It should be noted that this may not deny the explanation for the preferred formation of the *endo* adduct in many examples of the Diels–Alder reactions by the steric hindrance to the *exo* orientation. *E.g.*, the predominant formation of the *endo* adduct from cyclopentene and cyclopentadiene seems to be explained by the steric hindrance, because the overlap interaction between the addends in the transition state is thought to be negligible in this instance.[6]

[9] J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).

[10] See ref 5 for a complete discussion.

[11] R. B. Moffett, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 238.

Controlled Oxidation of Organic Compounds with Cerium(IV). II. The Oxidation of Toluenes

WALTER S. TRAHANOVSKY AND L. BREWSTER YOUNG

Department of Chemistry, Iowa State University, Ames, Iowa 50010

Received December 21, 1965

Oxidations of organic compounds with cerium(IV) are potentially interesting since cerium(IV) is an unusually strong, one-electron oxidant. Moreover, unique reactions of cerium(IV) with organic compounds can be expected because of specific coordination properties of the ion with various organic and inorganic ligands. Recently we have reported that ceric ammonium nitrate in 50% aqueous acetic acid converts benzyl alcohols to benzaldehydes in excellent yields.[1] We now wish to report that, under similar conditions, toluenes are oxidized to benzaldehydes.[2] Moreover,

$$\mathrm{ArCH_3} \xrightarrow[\text{50\% aq HOAc}]{\mathrm{Ce(NH_4)_2(NO_3)_6}} \mathrm{ArCHO} \tag{1}$$

$$\mathrm{ArCH_3} \xrightarrow[\text{HOAc}]{\mathrm{Ce(NH_4)_2(NO_3)_6}} \mathrm{ArCH_2OAc} \tag{2}$$

in anhydrous acetic acid, ceric ammonium nitrate oxidizes toluenes to benzyl acetates. Yields of the products from oxidation of various toluenes are shown in Table I.

---

[1] W. S. Trahanovsky and L. B. Young, *J. Chem. Soc.*, 5777 (1965).

[2] Preliminary communication: Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 54S.