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NO. 102

THE EFFECT OF ELECTROSTATIC FIELDS ON REACTING MOLECULES

UNITED STATES NAVAL ACADEMY
ANNAPOLIS, MARYLAND

1979

The Effect of Electrostatic Fields on Reacting Molecules

A Trident Scholar Project Report

by

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ABSTRACT

The Diels-Alder addition of furan to maleic anhydride and 6,6-dimethylfulvene to maleic anhydride in electric fields of 0, 240, and 350 V/cm were studied. It was found that the furan addition was unaffected by the fields, but that the proportion of exo to endo isomers of the 6,6-dimethylfulvene product changed in a qualitatively predictable way.

TABLE OF CONTENTS

		Pages
I.	Introduction	1
II.	Historical	3
III.	Experimental	5-15
	A. Construction of the Reaction Cell	5 - 6
	B. Synthesis of 6,6-Dimethylfulvene	6 - 8
	C. Attempted Synthesis of Benzonitrile Oxide	9-10
	D. Attempted Purification and Analysis of Benzonitrile Oxide	10-11
	E. Addition Reactions of Furan and Maleic Anhydride: Attempted Isolation of Two Isomers	11-13
	F. Addition Reactions of 6,6-Dimethylfulvene and Maleic Anhydride: Isomer Characterization	13-14
	G. Field Studies with 6,6-Dimethylfulvene and Maleic Anhydride	14-15
IV.	Discussion	16-23
	Footnotes	24
	Acknowledgements	25

I. INTRODUCTION

The concept of an electric dipole is a basic one in both chemistry and physics. In the latter area it is known for its role in radiation, its generation of an electric field, and its behavior in an external electric field; it is the last which concerns us here.

The idea of a dipole in chemistry has two basic facets: where it comes from and what it does. The former is concerned with electronegativity and sometimes resonance structures; the latter extends into almost every aspect of chemical behavior, from melting points and solubilities to the mechanisms for involved organic reactions. The chemical effects do have, however, one thing in common: they all operate on the molecular level, each dipole interacting with electric fields generated very near it in space.

This project combines the two views of electric dipoles. It seeks to manipulate electric dipoles by means of an electric field while those dipoles are part of chemicals in the midst of a chemical reaction.

To illustrate the concept, consider two molecules, A-B and C-D (figure 1). Each has an electric dipole, as shown. They add to each other in some reaction which has two possible outcomes: either atom D is far from A, in an overall S-shape, or it is close to A, in an overall C-shape. It is assumed that the resulting

structure is rigid, and the two isomers remain distinct.

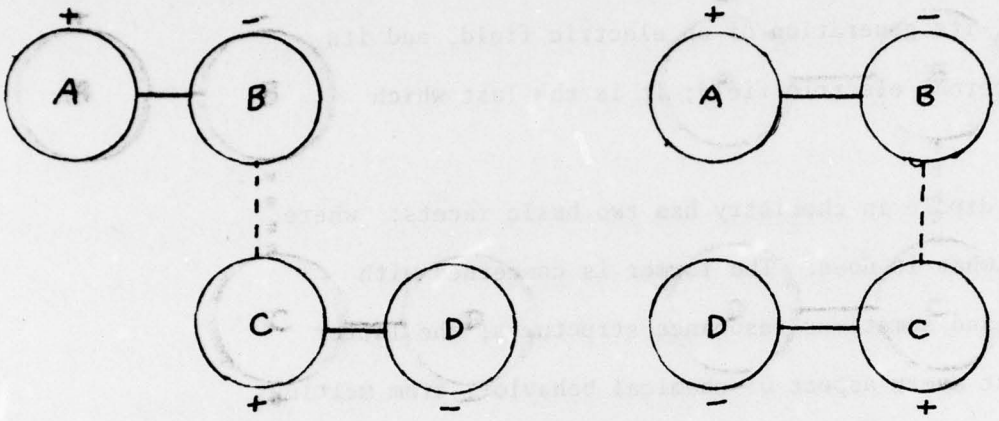

Figure 1. Two-isomer addition of dipolar molecules

Note that in the first configuration, the two dipoles are aligned in the same direction, with the positive atoms (A and C) to the left and the negative atoms to the right. Considering only the dipoles, this is the configuration of lowest energy for a situation in which there is an electric field present, for instance, if a large metal plate were placed to the left of the system and charged negatively and another placed to the right and given an equal positive charge. In the same field the second reacting configuration, producing the C-isomer, must have enough energy to fight the effect of the field in order to exist. In this way it is qualitatively possible to influence the outcome of a chemical reaction by applying an electric field.

II. HISTORICAL

In 1975 P. Gerike[1] reported the results of a study designed to investigate the effects of macroscopic electric and magnetic fields on reacting molecules, specifically reactions that ordinarily produce racemic mixtures of optically active compounds. By applying static electric fields of up to 6800 V/cm and varying electric fields of up to 1200 V/cm, in combination with static magnetic fields of up to 1460 Oe and varying magnetic fields of up to 100 Oe, he was able to produce optical rotations in the product mixture. Although the measured rotations were very small, they seem fairly well supported, indicating that an asymmetric synthesis depending on the fields alone was achieved. Although he suggested some ideas for further explanation of the results, little systematic insight into the phenomenon could be gained, in part due to the instability of the experimental conditions. A physical theory was, consequently, totally lacking.

Prompted by this report, Mead, Moscowitz, Wynberg and Meuwese[2] investigated theoretically the production of optical isomers in uniform and constant magnetic and electric fields. By applying the symmetry operations of reflection and time reversal they showed that both a molecule M and its isomer M* have states of exactly the same energy under those conditions, and thus concluded that it was not possible for one to be produced in preference to the other.

They point out, however, that Gerike's fields were not always constant, even (as Gerike noted) when the variation was unintentional, due to the instability of his field-producing equipment.

In answer to this, Rhodes and Dougherty[3] pointed out that final states of the same energy do not necessarily imply transitional states of the same energy. By assuming a current density (a magnetic moment) in the transitional state, they showed that by applying the same symmetry operations one need not come out with transitional states of the same energy, as the interaction of the current density vector $\bar{j}$ with the magnetic field will not, in general, be of the same energy as the interaction of the reflected current density $\bar{j}^*$ with the field. They went on to show that $\bar{j}$ cannot be simply the adiabatic response of the molecule to the applied magnetic field if asymmetric synthesis is to occur; it must be either a nonadiabatic response or a permanent magnetic moment. In these cases it was shown that an applied electric field along with the applied magnetic field could indeed lead to transition states of different energies, and, hence, produce an asymmetric synthesis. Making a calculation with reasonable values for each of the variables involved, however, they found that such a scheme would lead to only 0.3 ppm excess of one isomer at room temperature.

III. EXPERIMENTAL

A. Construction of the Reaction Cell

The first practical consideration was the construction of a place in which reacting molecules could be subjected to uniform electric fields of known intensity. This was accomplished by cementing five pieces of glass together in the form of a box, 10 cm. by 10 cm., by 1 cm. thick, and adding two rather larger brass plates on the outside (figure 2). A screw and nut assembly on each of these allowed the attaching of leads to the voltage source, a Jackson Model 607D, kindly provided by the Electrical Engineering Department.

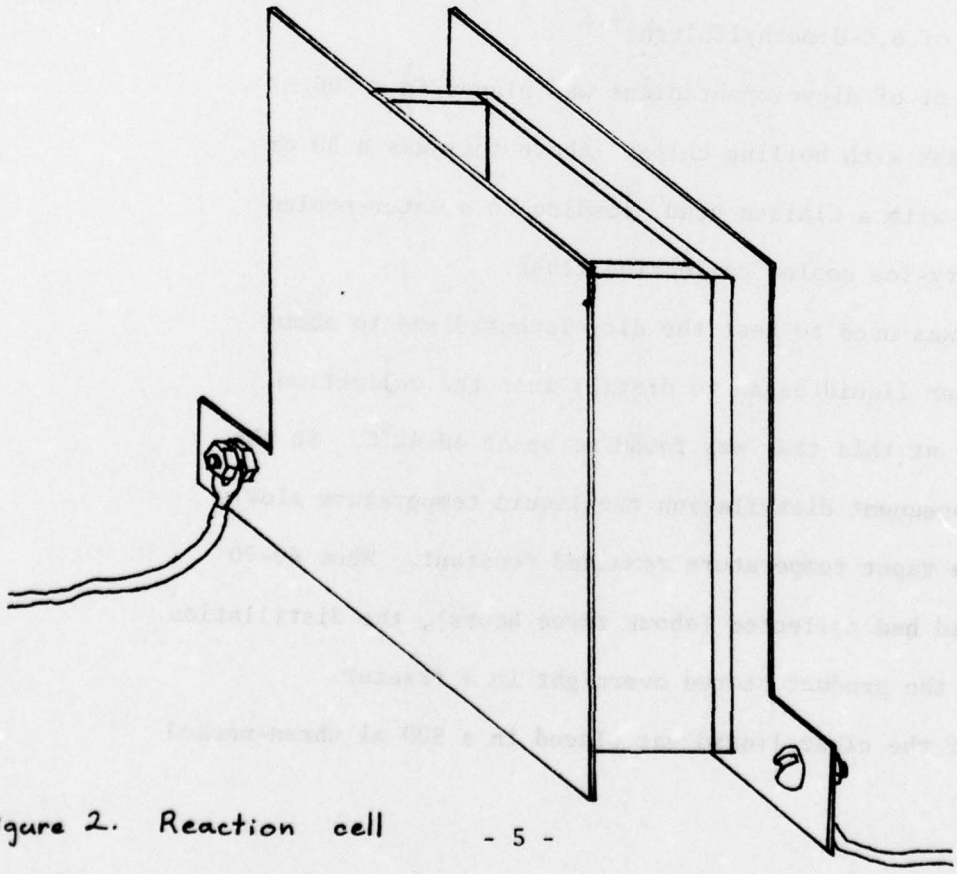

Figure 2. Reaction cell

Major problems were encountered with the cement. Several types of glass sealer and silicone-based cement were used, as well as a marine epoxy; none lasted for more than two weeks before leakage occurred with ethyl ether, the solvent for the earliest furanmaleic anhydride experiments. Only the marine epoxy lasted for more than four days in benzene, remaining intact for almost six. This required the rebuilding of the cell about every three reactions in benzene. This did allow, however, the modification of the cell at times, such as the adding of wood insulation on the outside. This last was deemed necessary as the potential used went over 100V.

B. Synthesis of 6,6-dimethylfulvene[4,5]

About 200 ml of dicyclopentadiene was placed in a 500 ml round-bottomed flask with boiling chips. Above this was a 50 cm distilling column with a Claisen head, leading to a water-cooled condenser and a dry-ice cooled collecting flask.

A mantle was used to heat the dicyclopentadiene to about 140°C, when a clear liquid began to distill into the collection flask. The vapor at this time was found to be at 40-42°C. In the course of the subsequent distillation the liquid temperature slowly rose to 170°; the vapor temperature remained constant. When 60-70 ml of clear liquid had collected (about three hours), the distillation was stopped, and the product stored overnight in a freezer.

33.84g of the clear liquid was placed in a 500 ml three-necked

flask with 29.82g of acetone. 10 ml of 20% KOH in ethyl alcohol was added dropwise over about two minutes, with stirring. Initially the solution turned yellow, then darkened and took on a slight greenish tint; as it darkened to a medium brown a fine white precipitate formed. After about five minutes the color was a very dark coffee-brown, the precipitate had disappeared, and the flask had become quite warm.

After fifteen minutes, 100 ml each of methylene chloride and water were added to the mixture. Two layers formed: the lower layer was light orange, the upper one dark orange to brown. The latter was determined to be aqueous and was discarded. The organic portion was washed with two 100 ml portions of water, after which it was much lighter, almost yellow. It was then transferred to a 250 ml Ehrlenmeyer flask and dried with $CaCl_2$.

A simple distillation apparatus was assembled, with a water bath as heater and the collection flask cooled in icewater. A light yellow liquid was collected at vapor temperature 39-48^{o}C, liquid temperature 52-68^{o}. At this point a drop in vapor temperature signalled a change in vapor composition. Flasks were changed, an aspirator vacuum drawn, and the hot water bath replaced with a microburner. The second fraction was collected at vapor temperature 61-65^{o}, appearing in the collection flask as a clear orange liquid. This was stored in a freezer between uses.

Purity was tested with a Gow-Mac gas chromatograph with a Carbowax 20-M column at 145°C. This showed one large peak and one small peak, the latter of extremely variable size; this was probably an air peak, and in no case was larger than 5% of the other peak.

Identity was tested by comparison of NMR with a known spectrum. Two singlet peaks appear, at δ 2.2 and 6.5, with relative areas of 3 and 2, respectively. This indicates a very large contribution from a resonance structure (figure 3) with aromatic character, the peaks being due to ring hydrogens on one hand and methyl group hydrogens on the other. (Compare the NMR spectrum of furan)

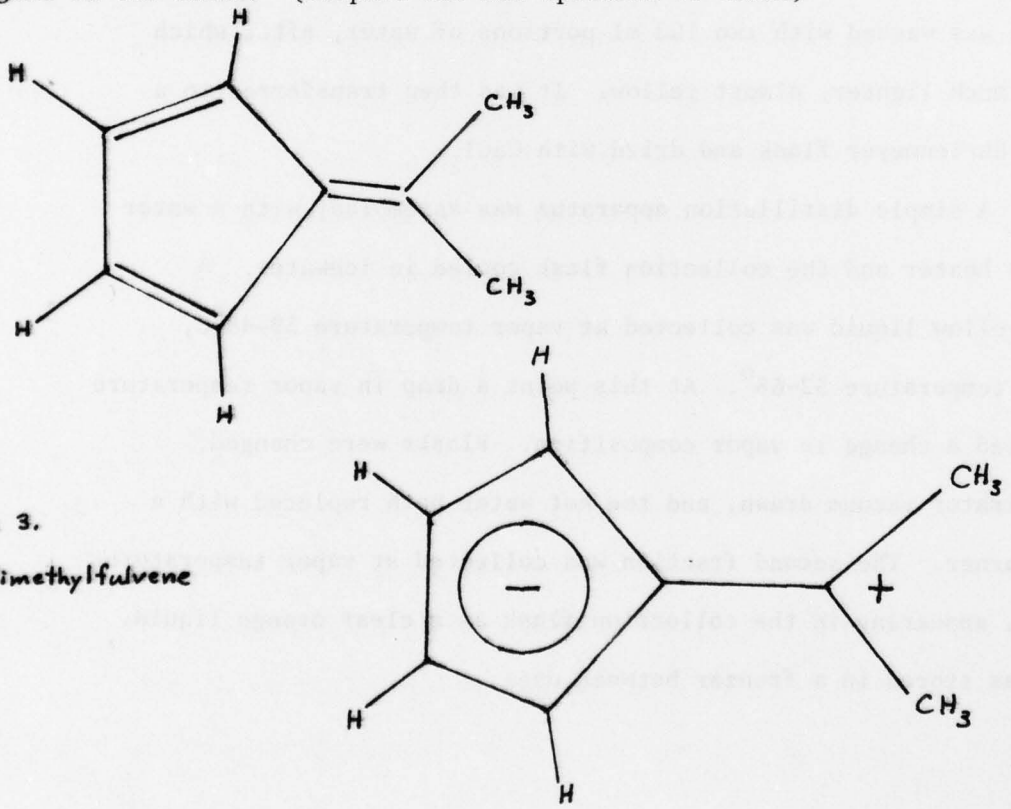

Figure 3.
6,6 - dimethylfulvene

C. Attempted Synthesis of Benzonitrile Oxide

6.71g of hydroxylamine hydrochloride was slurried in 175 ml of ethyl ether; 11.77g benzaldehyde and 5g pyridine were added, and the mixture left stirring at room temperature.

Three days later no solid was visible, and a viscous, green liquid layer had formed at the bottom. The mixture was extracted with 50 ml water, and the aqueous layer discarded. The organic layer was then washed with two 50 ml and one 100 ml portions of water. It was subsequently dried in a 250 ml Ehrlenmeyer flask over $CaCl_2$.

After several hours drying, the clear, slightly green-tinted liquid was transferred to a 500 ml round-bottomed flask and Cl_2 gas was bubbled through it. The solution turned immediately a deep green; in another five minutes a white solid formed on the container walls, and the flask became warm to the touch. After 20 minutes of Cl_2 treatment the color began to turn yellowish, and the amount of solid seemed to decrease. In another five minutes the color was entirely brown-gold and the flask was no longer noticably warm.

After a total of 50 minutes of Cl_2 addition no change had been noted since the 25 minute mark. Cl_2 addition was stopped, an aspirator vacuum drawn, and a warm water bath added to heat the mixture. No noticable evaporation occurred.

After several weeks of storage at room temperature a growth of large, clear crystals was noted in the mixture. These were

recrystallized twice from benzene, giving a melting point of 123-4°C.

D. Attempted Purification and Analysis of Benzonitrile Oxide

Several methods for purification of the precursors to benzonitrile oxide in the above attempted synthesis were tried, as well as several methods for analysis of the substance(s) along the way. The major ones are noted below.

Thin-layer chromatography of the initial product (end of the second paragraph of the above synthesis) on SiO_2 strip with hexane as the elutant showed two spots. On the same strip with methylene chloride one of the spots had essentially the same rate of diffusion as the CH_2Cl_2, but no new spots appeared.

After treatment with Cl_2, TLC's of the product (again on SiO_2 strips) showed five separate spots with methylene chloride and three with hexane; none of these was identifiable with the faster moving spot noted before Cl_2 treatment.

At this point a column chromatographic separation was attempted. A column of SiO_2 was made up with chloroform as the solvent, and a maximum amount of the chlorinated product was dissolved in 10 ml of $CHCl_3$. The column was eluted at first with chloroform; after ten fractions (about 250 ml) were taken off, the column was changed over slowly to acetone, and two more fractions (totalling about 40 ml) were eluted.

TLC's of these fractions showed faint single spots on the first four fractions and the 12th and 13th, and nothing at all on the rest. These could be tentatively identified with two of the spots on the TLC of the mixture, but evaporation of the fractions yielded far too small a volume of product to test further.

NMR's were taken at various stages. Before chlorination the spectrum showed (in addition to the ethyl ether peaks) a broad aromatic signal at δ 7.2-7.8, with singlets at δ 8.3, 10.0, and 10.6. Some of these could be tentatively identified with pyridine, and some with benzaldehyde, but not with any certainty, and the difficulty of separation made any clearer spectrum unobtainable.

After chlorination but before the attempted evaporation the NMR showed the aromatic peaks as before, with a very broad peak at δ 9.0-9.3 (center 9.2) and a sharp one at 9.9.

The clear crystals found at the end showed two distinct aromatic peaks, at δ 7.4-7.6 and 8.0-8.3, and one broad peak at 11.9-12.2 (center 12.0). This last looked promising, but the assignment of a peak at 12.0 to a hydroxamic acid chloride is unprecedented, all available examples occurring at δ 8.5-9.0.

E. Addition Reactions of Furan and Maleic Anhydride: Attempted Isolation of Two Isomers

3.08g of maleic anhydride were dissolved in 100 ml of ethyl ether, and 2.00g of furan added. The mixture was then left to react at room temperature.

One day later a TLC of the reaction mixture, on SiO_2 with methylene chloride, showed three spots. The same reaction after five days showed five spots, none in the same position as any in the earlier TLC. A TLC of the reacting materials using the same substrate and elutant showed that maleic anhydride moves essentially with the CH_2Cl_2, while the furan does not move at all.

After six days of reaction the mixture was placed in a 500 ml round-bottomed flask and an aspirator vacuum drawn. The volume was reduced to about 10 ml, at which time crystals began to appear and the vacuum was disconnected. These crystals melted 105-109°C, and upon purification (recrystallization from ether) melted 110-111°. An NMR of these crystals showed three peaks: singlets at δ 3.4, 5.5, and 6.7. The areas integrated to 1:1:1. These data are in accordance with the assumed product.

A chromatographic column was run on the residue to attempt to isolate the other isomer of the product. The column was SiO_2 with benzene as the liquid phase and elutant. Ten fractions of about 50 ml each were obtained; the first five showed a faint, identical spot upon testing with TLC, the rest nothing at all. Upon evaporation none of the fractions yielded a detectable amount of solid.

Essentially the same reaction as the above was run, this time inside the electric cell, with a 240 V potential between the plates. After five days the voltage source was disconnected and an

NMR of the reaction mixture run, as well as TLC. The results were identical with those outlined above.

The same reaction was run under the same conditions several times, varying the solvent from ether to benzene to acetone. In each case the NMR's and TLC's produced were identical to those reported above.

F. Addition Reactions of 6,6-Dimethylfulvene and Maleic Anhydride: Isomer Characterization

1.98g of 6,6-dimethylfulvene in 10 ml of benzene was added to 80 ml of a saturated solution of maleic anhydride in benzene (about 10 g/l), and allowed to react overnight at room temperature. Then the mixture was placed in a 500 ml round-bottomed flask and an aspirator vacuum drawn; a heating mantle was added after about five minutes. When the volume had been reduced to about 10 ml the heat and vacuum were withdrawn; at this point a significant amount of green-clear crystals had formed.

The slurry was filtered, the crystals thus obtained subsequently recrystallized from benzene four times. This gave a white solid, melting at 133-6°C. The NMR showed four peaks: a very large singlet at δ 1.6, a smaller singlet at 3.0, and two close triplets at 3.9 and 6.4. The integration gives areas of 3:1:1:1, respectively. This is consistent with the exo isomer of the product, since in that case the hydrogens α to the anhydride group (identified as those at 3.0) would not be expected to be split by the others according

to the Karplus curve. By analogy with similar compounds the peaks at 3.9 and 6.4 are identified with the bridgehead and double-bond hydrogens, respectively; the large singlet has the area and shift consistent with the methyl hydrogens.

The reaction was repeated, and this time an NMR run of the slurry without purification. The spectrum was overall very similar, except that the peaks at 3.9 and 6.4 became more split and a nearly flat-topped quartet appeared at δ 3.5. Integration showed that, if this were added to the area of the 3.0 peak, the result was equal to either of the two downfield peaks and one third of the methyl peak. The splitting on the new peak was in accordance with the Karplus prediction for the endo isomer; thus both isomers could be characterized by NMR data.

G. Field Studies with 6,6-Dimethylfulvene and Maleic Anhydride

80 ml of saturated maleic anhydride in benzene was placed in the electric reaction cell, and the chosen voltage (0,240,350) applied. 10 ml of a solution of 1.00g of 6,6-dimethylfulvene in benzene was added dropwise over five minutes, and the reaction allowed to proceed at room temperature for about 12 hours.

At the end of this time the field was removed and the solution transferred to a 250 ml single-necked round-bottomed flask. An aspirator vacuum and a hot water bath were applied; in 40-60 minutes the flask was dry, with a deposit of solid

product on the walls. This was dissolved in about 5 ml of deuterated chloroform and placed in an NMR sample tube. The areas of the two distinct α hydrogen peaks were then integrated to give the ratio of isomers.

IV. DISCUSSION

In order to more clearly understand the processes involved in this project, let us look once again at figure 1. The difference in energy between the two configurations which is due to the imposed field is simply the difference in energy between molecule B-C lined up with the field and lined up against the field; this is, in a vacuum:

$$E = 2dqD$$

just twice the product of the charge of B-C's dipole, the separation of the dipole, and the electric field strength at the dipole. With a dipole of normal molecular dimensions and a 240 V/cm field, this energy is:

$$E = 1.1 \times 10^{-3} \text{ kcal/mole}$$

in units customarily used by chemists.

Now let us consider the reaction itself. For a multitude of reasons the two configurations will probably not be of equal energy even in the absence of an applied field. The actual difference in energy can be calculated, if the relative amount of each produced in the reaction is known, by the Boltzmann distribution expression. For a reaction which normally produces a 39:61 ratio of isomers, this difference is:

$$E = -kT \ln (n / N_t)$$
$$= 0.28 \text{ kcal/mole}$$

Now, suppose that it is desired to change the proportion of isomers through the imposition of an electric field. To reach a proportion

of 33:67, the barrier must be made to be:

$$E = 0.43 \text{ kcal/mole}$$

In other words, an additional 150 calories per mole must be added to the energy barrier. This is 135 times the amount of energy available under the conditions of the first calculation; thus it appeared from such simple models that the project was impossible from the start.

But to actually test the possibility, a reaction was needed. The first one subjected to field studies was the Diels-Alder addition of furan to maleic anhydride (figure 4). Each of the reactants has a

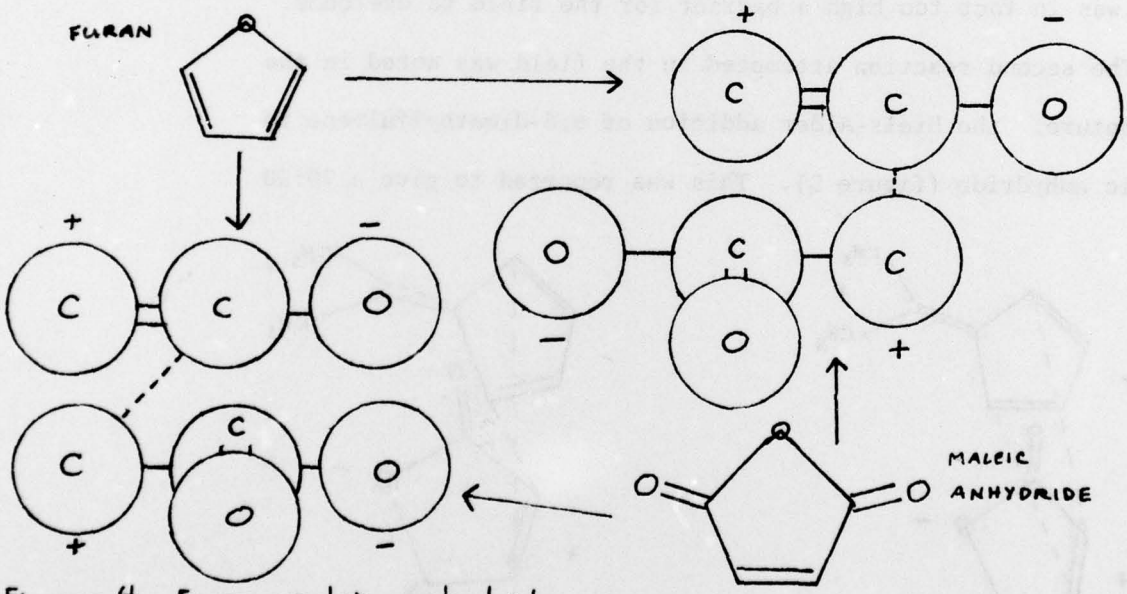

Figure 4. Furan-maleic anhydride

dipole, due to the electronegativity of oxygen, and the bicyclic product formed retains the configuration imposed by the transition state. This reaction had the advantage of using off-the-shelf

chemicals, and proceeding without special conditions. It had the great disadvantage of being very regiospecific; only one isomer, the field-inhibited endo form, has ever been reported from this reaction in the literature.[6] This implies an energy barrier between isomers much higher than that found in the above calculation; in fact, assuming as much as 5% of the total product could have been exo without being detected (a doubtful assumption in itself; one or two percent would be more realistic) the barrier would be about 1.74 kilocalories per mole. As noted in the experimental section, this was in fact too high a barrier for the field to overcome.

The second reaction attempted in the field was noted in the literature: the Diels-Alder addition of 6,6-dimethylfulvene to maleic anhydride (figure 5). This was reported to give a 70:30

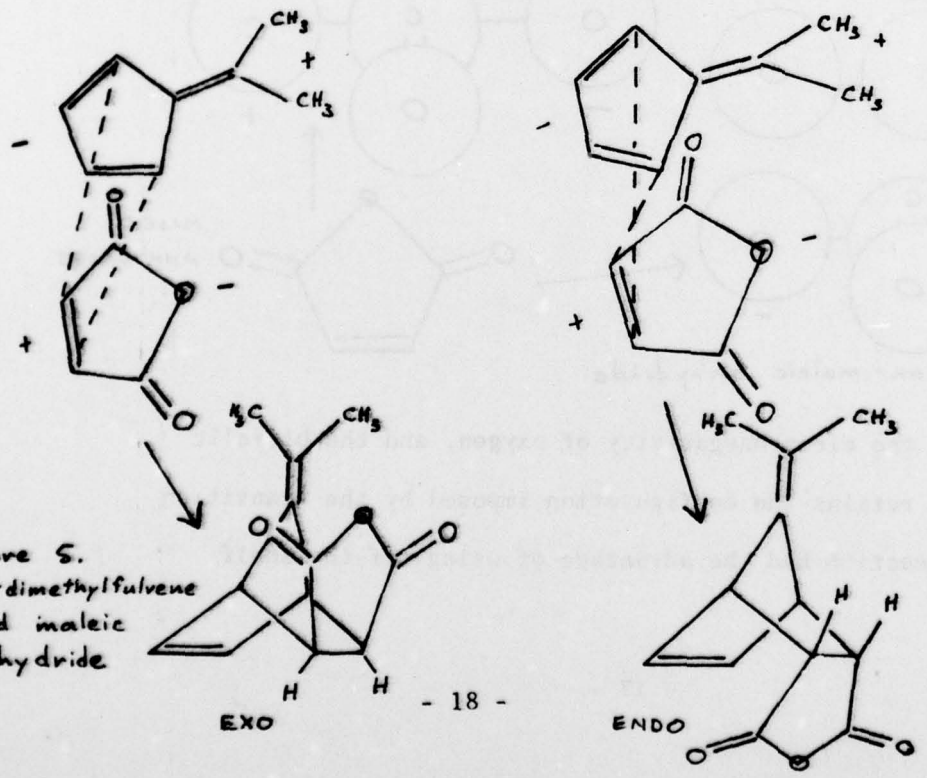

Figure 5. 6,6-dimethylfulvene and maleic anhydride

ratio of products[7], and thus was a more suitable reaction; however, it did involve the synthesis of the fulvene compound. The dipole of this molecule, it should be noted, is a result of a resonance structure (figure 3), and is quite sizable.

After synthesis of the fulvene, the following results were obtained:

Reaction Number	Field (V/cm)	% Field-Favored	Boltzmann Barrier
35	0	62	283 cal/mole
36	0	60	237
38	0	61	274
43	0	62	283
46	0	63	312
37	240	68	435
47	240	68	435
48	240	67	410
50	350	72	557
55	350	73	573

These are plotted in figure 6.

A third reaction which appeared to be suitable for study was the addition of benzonitrile oxide to a class of compounds including benzofuran[8] (figure 7). The dipole here is electronegative in nature, and both of the product isomers were reported in the literature in comparable yields. This, however, necessitated the synthesis of the benzonitrile oxide. This probably was accomplished, but purification to the quality necessary for quantitative studies was never accomplished.[9]

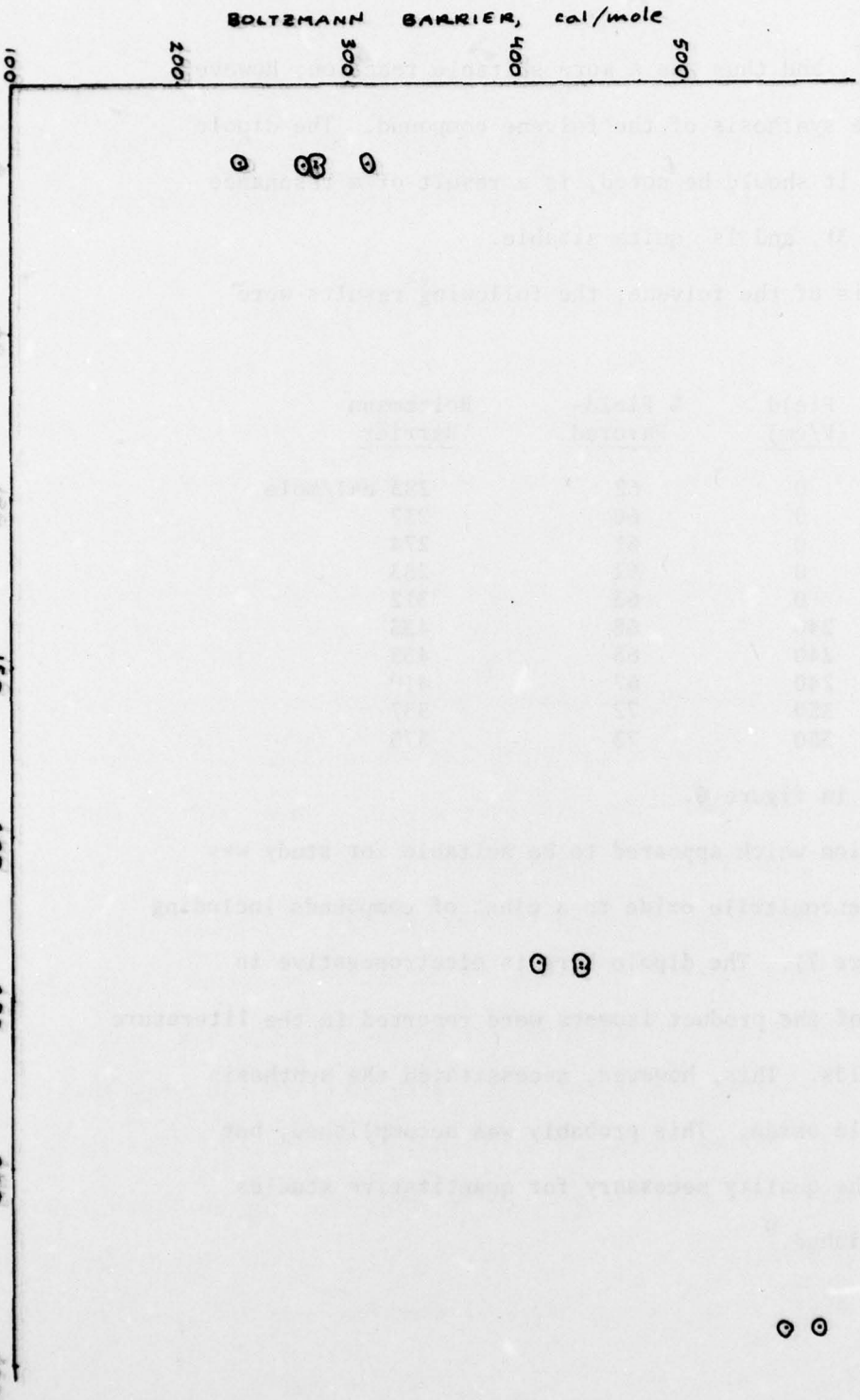

FIGURE 6. FIELD STRENGTH VS. ENERGY BARRIER

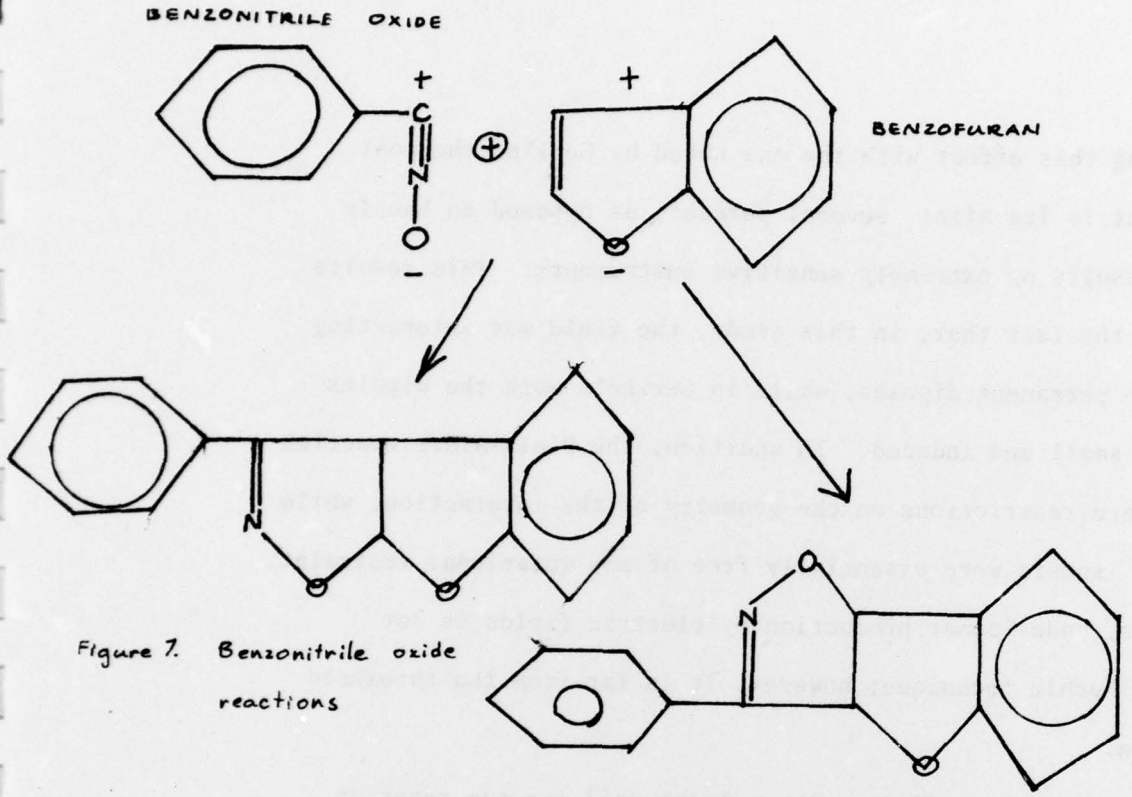

Figure 7. Benzonitrile oxide reactions

Returning to the most significant results of the study: an effect was observed, one that should not have been. One of the calculations must be in error. The most probable answer lies in the calculation for dipole-field energy. Recall that the calculation involved assumed a vacuum around the dipole; during the actual reaction this was not the case. All reactions were run in some kind of solvent; in those that changed with the field this was benzene. It turns out to be extremely difficult, if not impossible, to predict quantitatively the behavior of this system from current theory if the solvent is included, and the experimental results show that excluding the solvent introduces large errors.

Comparing this effect with the one noted by Gerike, the most striking fact is its size: several percent, as opposed to barely noticable results on extremely sensitive instruments. This results partly from the fact that, in this study, the field was interacting with sizable permanent dipoles, while in Gerike's work the dipoles were rather small and induced. In addition, the Diels-Alder reaction imposes severe restrictions on the geometry of the interaction, while the optical isomers were essentially free of any rotational restraint. As it stands, endo-isomer production by electric fields is not truly a synthethic technique; however, it is far from the threshold of detection.

As a matter of serendipity, the solvent used for the reaction might turn out to have been the best for this purpose. Benzene is easily polarizable, and in such a state can effectively magnify the imposed field, while it has no permanent dipole, which would tend to shield reactant dipoles from the effects of the field. Some further study along these lines is needed to verify or disprove this idea.

One thing did appear that was not at all looked for. Referring to figure 6 and the table of data, note that simply increasing the field by 46% (from 240 to 350 volts/cm) increased the induced energy barrier by 92%. In other words, the adding a little more field had a large effect. This could be due to a cumulative polarization effect, but the mechanism is at best speculative. Data

from many more field strengths are needed to clarify this phenomenon.

The outlook for more investigation is promising, in this surprising field that has received so little prior attention.

FOOTNOTES

[1]P. Gerike, "A New Absolute Asymmetric Synthesis," Naturwissen-Schaften, 62, 38 (1975)

[2]A. Moscowitz, C. A. Mead, H. Wynberg and F. Meuwese, "The Influence of an Electric and Magnetic Field in Chemical Reactions," Tetrahedron Letters, 12, 1063 (1977)

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[8]P. Caramella, G. Cellerino, K. N. Houk, F. M. Albini and C. Santiago, "Selectivity in Cycloadditions. 6.Cycloadditions of Nitrile Oxides to Benzofuran, Regiochemistry," Journal of Organic Chemistry, 43, 15, 3006 (1978)

[9]Note that no purification data is available for the literature report, which involved only the identification of several products of the reaction.

ACKNOWLEDGEMENTS

It would be a travesty of justice to fail to mention at least the major contributors to the success of this project: Dr. T. E. Bitterwolf, for his gentle words of encouragement and motivation; Mr. Charles Robertson, to whom the reaction cell owes it (repeated) existence; Associate Professors J. W. Schultz and O. L. Jones, during whose lectures in physical chemistry some of my most constructive daydreaming was done; Assistant Professor W. R. Roberts, a contact to a different world, if not a real one; my academic advisor, Professor E. R. Pinkston, and my project advisor, Associate Professor C. F. Rowell, about whom much must need pass unsaid; and chronologically last, but most to be thanked for this report itself, Mrs. Edna Iaquinta of the magic typewriter.

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Furan resins.
Dimethylfulvene.

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The work synthesizes some model compounds whose structure provides a dipole for interaction with electric field.

The Diels-Alder addition of furan to maleic anhydride and 6,6-dimethylfulvene to maleic anhydride in electric fields of 0, 240, and 350 V/cm were studied, and they were set to react in a cell in which a static electric field was maintained. - It was found that the furan addition was uneffected by the fields, but that the proportion of exo to endo isomers of the 6,6-dimethyl-

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fulvene product changed in a qualitatively predictable way. The details are described in the papers.

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