action products was first surmised by comparison of their glpc retention times with those of likely reference compounds on the following column substrates: silicone rubber SE-30, polyester (Reoplex) and fluorinated ester (Zonyl E-7).[41] With use of the disk-integrated areas of the glpc signals, a synthetic mixture of reference substances could then be prepared such that its glpc matched that of the reaction material, assuming peak areas were proportional to molar concentration. Final substantiation of the composition of the product was through infrared and nmr spectral correlation with the synthetic mixture. The yield of hydrocarbon was determined by direct weight in the larger experiments or by calibration curves of glpc peak area *vs.* mmoles of selected knowns in the smaller ones. The yield was corrected for recovered aldehyde which eluted at longer retention time in the 1.5-hr reactions. For complete data and details of these determinations, the dissertations of L. L. M. and J. F. Z. should be consulted.

Acknowledgment.—This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of this fund. We deeply appreciate the assistance of the following people who determined many of the nmr spectra: Drs. R. S. Bly and R. K. Bly (University of South Carolina); Dr. R. R. Sauers (Rutgers); and Dr. S. J. Lapporte (Chevron Research Corporation), as well as the analytical department of G. D. Searle and Company, Skokie, Illinois.

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[41] We are indebted to Dr. H. E. Simmons of the Du Pont Co. for the generous gift of Zonyl E-7 ester (Jan 1963).

The Formation of Aromatic and Pseudo-Aromatic Compounds in Radiofrequency Discharges

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The formation of aromatic and pseudo-aromatic compounds from nonaromatic species has been observed in a 28-Mc electrodeless discharge. Cyclohexadiene when excited yields an emission spectrum characteristic of benzene and benzene can be isolated in the products. Evidence is presented for the conversion of 1,3-cyclopentadiene to the cyclopentadienide anion and indene to the indenide anion.

Emission spectra of organic molecules have been obtained for some time by the use of electrical discharges,[1] but the technique has not received wide usage and little attention has been paid to the chemical reactions that result.

A large percentage of the work that has been done can be attributed to the efforts of Schüler and coworkers using high frequency, high voltage discharges through organic vapors between internal metal electrodes.[2]

The use of radiofrequency electrodeless discharges for the excitation of the emission spectra and the initiation of chemical reactions with organic molecules appears to be more promising.[3] The use of microwave frequencies (2450 Mc) results in extensive fragmentation.[4] Aside from the obvious advantages associated with the absence of internal electrodes, this technique allows for the continuous variation of excitation frequencies and power levels to obtain optimum conditions.

The emission spectra of a variety of organic compounds were obtained using a 28-Mc electrodeless discharge. With nonaromatic molecules sharp line fragmentation spectra consisting of CH, C_2, and other diatomic molecules were usually obtained. In the case of aromatic compounds, emission spectra of the entire molecule or a modified molecule were obtained. These emission spectra or fluorescence spectra are related to the corresponding absorption spectra in a crude mirror image fashion.[5] This relationship varies from quite precise in some cases to rather crude in others. The emission spectra of benzene and toluene were found to rather precisely mirror the absorption spectra of these molecules, while fluorobenzene was quite different. In all instances, however, the absorption and emission spectra coincided at the $0 \rightarrow 0$ band.

It was found that some nonaromatic compounds when subject to the 28-Mc discharge emitted continuous spectra of the type characteristic of aromatic molecules. Both 1,3- and 1,4-cyclohexadiene emitted a benzene spectrum which could be identified by previously recorded data.[6,7]

No benzene was found in the original dienes as analyzed by gas chromatography but the vapors which had been passed through the discharge showed appreciable amounts of benzene indicating that benzene was formed from the dienes in the discharge. The amount of benzene formed from 1,4-cyclohexadiene (6%) was somewhat greater than that formed from the 1,3-diene (2%). On the other hand, when 1,3-pentadiene vapor was subjected to the 28-Mc discharge, a fragmentation spectrum mainly arising from diatomic molecules was obtained. 1,3-cyclopentadiene, however, was found to emit an aromatic-type continuous emission spectrum and one of the purposes of this research was to establish the origin of the continuous spectra for nonaromatic compounds.

Experimental Section

Determination of Emission Spectra.—Radiofrequency power was supplied by a Johnson Viking II radiofrequency transmitter equipped with a Heathkit Model VF-1 variable frequency oscillator capable of operation over the range 1750 kc to 28 Mc. A frequency of 28 Mc was employed throughout this work.

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[1] A. W. Stewart and C. L. Wilson, "Recent Advances in Physical and Inorganic Chemistry," Longmans, Green and Co., London, England 1946.

[2] H. Schüller, *Spectrochemica Acta.*, **4**, 85 (1950).

[3] G. W. Robinson, *J. Chem. Phys.*, **22**, 1384 (1954).

[4] A. J. McCormack, S. C. Tong, W. D. Cooke, *Anal. Chem.*, **37**, 1470 (1965).

[5] H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., p 539.

[6] R. K. Asundi and M. R. Padyhe, *Nature*, **156**, 368 (1945).

[7] S. Leach, *J. Chem. Phys.*, **51**, 556 (1954).

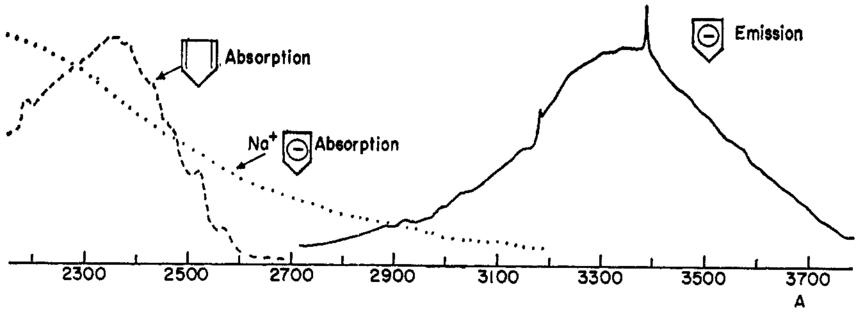

Figure 1.—Absorption spectra of cyclopentadiene and sodium cyclopentadienide and emission spectrum of cyclopentadienide anion .

The discharge tube consisted of a horizontal 11-mm-outside-diameter Pyrex tube with a quartz window sealed onto the end. Energy was coupled into the tube by a loosely fitting external copper coil. In operation, the tube was evacuated then back filled with the organic vapor. The pumping rate was adjusted so that a pressure of 0.1 to 0.2 mm was maintained. Light from the quartz window was focused into a Jarrel-Ash 0.5-m scanning monochrometer equipped with an RCA IP-28 photomultiplier tube.

Materials.—Eastman Blue Label dicyclopentadiene was chromatographed on alumina to remove moisture and then cracked under dry nitrogen to 1,3-cyclopentadiene which was collected and stored at −80° until used. Columbia Chemicals Co. indene and indan were chromatographed on alumina and then distilled *in vacuo* with a dry nitrogen bleed. Columbia 1,3- and 1,4-cyclohexadiene were chromatographed on alumina to remove traces of benzene; gas chromatography and ultraviolet spectroscopy showed the treated dienes to be benzene free. Eastman dimethoxyethane was treated overnight with lithium aluminum hydride and then distilled from this material under a dry nitrogen atmosphere.

Ultraviolet Spectra. A. Cyclopentadienide Anion.—A glove box was flushed with prepurified grade nitrogen and desiccated with phosphorus pentoxide for several days prior to use. The following operations were carried out in the glove box: two 100-ml volumetric flasks were filled just below capacity with freshly distilled dimethoxyethane. To one flask was added 12.0 μl (0.23 mmole) of cyclopentadiene. After temperature equilibrium the flasks were diluted to volume and a piece of sodium metal (0.4 to 0.5 g) cut free from surface oxide was added to each. The sodium metal was crushed in the flasks to increase the surface area and the reaction rate. Stoppered 0.1-cm quartz cells were filled and sealed in the glove box.

Spectra were recorded at 2-hr intervals using a Cary Model 14 recording spectrophotometer and the reaction was judged complete when the cyclopentadiene maximum disappeared and two successive spectra showed no significant change.

The anion spectrum showed gradually increasing absorption from 3100 to 2200 A. Measurements could not be made below this wavelength owing to low solvent transmission. Since no maxima were observed, the molar absorptivity was calculated at an arbitrarily selected wavelength, 2200 A, and was found to be 8200.

B. Indenide Anion.—The procedure used in this case is the same as that described above with the following exceptions: A concentration of 60 μl of indene per 100 ml was used. Attempts to form the indenide anion using sodium metal were unsuccessful and, therefore, the more active sodium–potassium alloy was used. Approximately 0.08 to 0.10 g of the alloy was added to each flask. Only partial conversion to the anion was realized, however, before the alloy became inactive. The addition of more alloy did not bring about complete conversion.

Solutions of the anion in dimethoxyethane were a red-purple color and were characterized by a broad, low energy maximum centered at approximately 3650 A and an additional, more intense maximum near 2950 A. Any additional maxima which may have been present were obscured by the absorption of the unreacted indene present in solution.

Investigations of Trap Contents.—The products from the discharge tube were trapped at low temperatures. Trap contents were allowed to warm slowly to room temperature then transferred to a stoppered sample vial. Residual material was washed into the vial with ether. Samples were chromatographed on an F & M Model 609 gas chromatograph with a hydrogen flame detector. Positive identification of components was accomplished by turning off the flame, condensing the desired component on a chilled glass plate, and determining the ultraviolet absorption spectrum in 95% ethanol solution.

Concentrations were determined by comparison of the experimental areas with those obtained from appropriate synthetic mixtures. A 6-ft., 9% dioctyl phthalate on Fluoropak-80 column was used for the separation of the isomeric cyclohexadienes from benzene and for the determination of indene in indan.

Results and Discussion

Passage of 1,3-cyclopentadiene through the discharge gave in intense featureless spectrum with a broad maximum centered at 3350 A as shown in Figure 1. A single sharp line which appears at 3380 A has been observed experimentally[8] and predicted theoretically[9] to be present in the cyclopentadiene radical spectrum. An additional, less intense line observed in the cyclopentadiene radical spectrum[8] but not predicted theoretically[9] was not detected in the present case. The presence of the weak 3380-A line superimposed on the background spectrum indicates that a small, but measurable concentration of cyclopentadiene radicals was formed in the discharge. The intense background spectrum cannot, however, be attributed to this radical.

There are several possible species which could account for the observed spectrum: fragments obtained from the cyclopentadiene molecule, the corresponding cation molecule, and the cyclopentadienide anion.

Since there was no evidence of diatomic molecular emission and the emitted spectrum differed so markedly from other fragmentation spectra such as 1,3-pentadiene, the first explanation could be easily discarded.

The 1,3-cyclopentadiene cation, unlike the anion, would not be aromatic and is inherently less likely to form in the discharge. Additionally, attempts to obtain emission spectra from notably stable cations were unsuccessful. Thus, the spectrum obtained from 1,3,5-cycloheptatriene was a combination of the molecular spectra obtained from benzene and toluene rather than a spectrum attributable to the stable, aromatic tropilium cation. Other compounds such as 1-propane and allyl chloride which could form relatively stable cations gave decomposition spectra similar to those obtained from nonaromatic molecules. This instability is probably due to the highly energetic collisions which would occur with positively charged ions in the electron-rich discharge. Thus, it is unlikely that the 1,3-cyclopentadiene cation, which would not be expected to possess unusual stability, would give a characteristic spectrum.

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(8) B. A. Thrush, *Nature*, **178**, 155 (1956).

(9) H. C. Longuet-Higgins and K. L. McEwen, *J. Chem. Phys.*, **26**, 719 (1957).

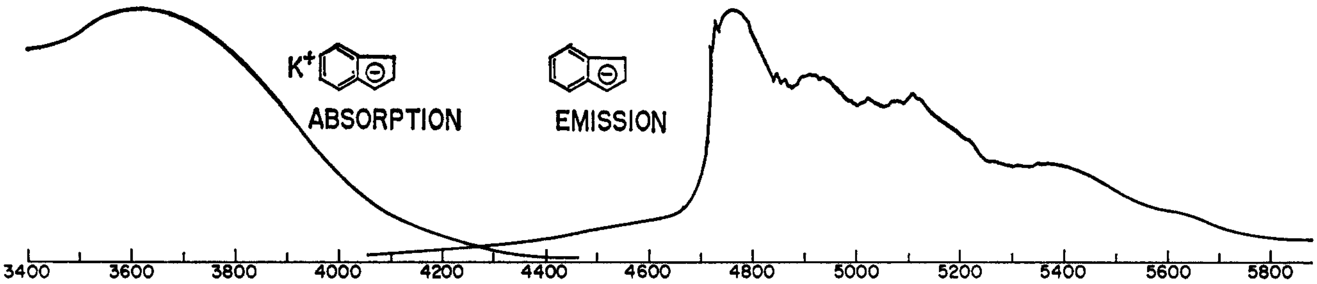

Figure 2.—Absorption spectrum of potassium indenide and emission spectrum of indenide anion.

Consideration of the cyclopentadienide anion favors its assignment as the species reasonable for the emission spectrum obtained from 1,3-cyclopentadiene. This anion, as a pseudo-aromatic molecule, would be expected to possess unusual stability and, like many aromatic molecules, to give rise to a molecular emission spectrum.

The absorption spectrum of the cyclopentadienide anion could provide evidence of the assignment of the emission spectrum to this anion if a mirror image relationship existed between the two. No absorption spectrum of the cyclopentadienide anion could be found in the literature, although several theoretical predictions of the position of the first maximum are to be found.[8,10,11] Each of these calculations predict a lowest energy maximum in the region of 2000 to 2100 A. The experimentally determined spectrum of sodium cyclopentadienide confirms these predictions (Figure 1). No maxima were observed above 2200 A and, because of poor solvent transmission, measurements could not be made at shorter wavelengths. The anion spectrum is, however, characterized by gradually increasing absorption in the region 3100 to 2200 A. Since no maximum was observed, a molar absorptivity at 2200 A was calculated by dividing the absorbance at this wavelength by the product of the molar concentration and the cell thickness and was found to be 8200.

As shown in Figure 1, the cyclopentadienide anion spectrum extends to longer wavelengths than the spectrum of the neutral diene, and overlaps with the emission spectrum in the region of 3060 A. This observation, together with the previously discussed facts, indicated the emission spectrum obtained on passage of 1,3-cyclopentadiene through the 28-Mc discharge is that of the cyclopentadienide anion.

The five-membered ring present in the indene molecule presents a situation analogous to the cyclopentadiene ring and formation of the indenide anion would result in a fully aromatic molecule.

Theoretical calculations have predicted a lowest energy maximum for the indenide anion at 3740 A.[10] The position of the lowest energy maximum in the potassium indenide spectrum was determined experimentally in dimethoxyethane solution and found to be in reasonably close agreement with the predicted spectrum; the experimental maximum appears at 3660 A.[12] Therefore, the emission spectrum of the indene anion, which should occur at lower energy than the absorption maximum, should be well within the visible region.

Two distinct emission spectra were obtained when indene vapor was excited in a 28-Mc field. A short wavelength maximum which appears in the 2700- to 3600-A region is due to the neutral indene molecule and is related in a "mirror image" fashion to the lowest energy maximum in the indene absorption spectrum. A longer wavelength maximum of lower intensity in the 4200- to 5800-A region was obtained from indene. This spectrum has previously been observed by Schüler from both indene and indan.[13] Since both molecules give the same spectrum it was assigned to a common unspecified free radical and designated as the "C-spectrum."

In the present investigation, this same "C-spectrum" was obtained from indene. Indan, however, afforded, in addition to this spectrum, additional emission at lower energy which was not present in the indene spectrum or reported by Schüler. The origin of this emission was not investigated.

The same type of relationship was found to exist between the indene and indan visible emission, and the lowest energy maximum in the indenide anion absorption spectrum (Figure 2) as had been described previously for the cyclopentadienide anion absorption and emission spectra (Figure 1). This relationship suggests the visible emission to be due to the indenide anion.

This assignment would be rendered uncertain since both indene and its saturated analog, indan, gave rise to the same emission spectrum; however, investigation of the trap contents obtained when indan was passed through the 28-Mc discharge revealed that 4% of the material recovered had been converted to indene and disclosed that this material was the largest single component, other than indan, present. It is, therefore, understandable that both molecules could afford the same emission spectrum since the indene molecule is common to the two discharges.

Conclusions

The assignment of the emission spectrum obtained from 1,3-cyclopentadiene to the aromatic anion is based on a number of interrelated observations: acyclic dienes underwent decomposition whereas the isomeric cyclohexadienes were converted to the closely related aromatic structure, benzene, which did afford a spectrum. No continuous emission spectrum would, therefore, be anticipated from the neutral 1,3-cyclopentadiene molecule, but its conversion to the aromatic

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(10) N. S. Ham, *J. Chem. Phys.*, **32**, 1445 (1960).

(11) J. Koutecky, P. Hochman, and P. Michl, *ibid.*, **40**, 2439 (1964).

(12) The use of sodium potassium alloy for the generation of metallic salts has been found to give the potassium salt.

(13) H. Schüler, L. Reinbeck, and R. Köberle, *Z. Naturforsch.*, **7a**, 428 (1952).

cyclopentadienide anion would be anticipated. This interpretation was supported by the agreement between the emission spectrum and the cyclopentadienide absorption spectrum.

A small concentration of cyclopentadiene radicals was shown to be present by the appearance of a line assigned to this radical;[8] however, the radical does not account for the major portion of the spectrum. Extensive decomposition of the 1,3-cyclopentadiene molecule did not take place since fragment spectra characteristic of this type of decomposition were not observed. The possibility that the spectrum could be attributed to a cation molecule was eliminated by the failure of more stable cations to afford characteristic molecular spectra.

The related indene molecule presents a situation analogous to that in 1,3-cyclopentadiene. Indene gives an intense visible emission spectrum which is related to the indenide anion absorption in the same manner as was observed for the cyclopentadiene system.

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The Structures of the Photolysis Products of Carvonecamphor

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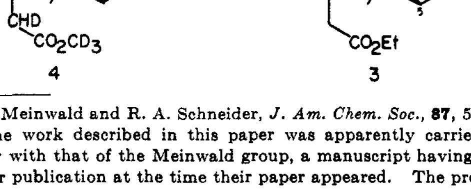
Evidence is presented which establishes the structure **3** for the ultimate product of the irradiation of carvone in ethanolic solution. Degradation of **3** to the ketone **9** provides a substance which on the basis of infrared and nuclear magnetic resonance spectra establishes both the ring structure and stereochemistry of the photoproduct. Independent syntheses of the hydrocarbons **18** and **19** are described, and the values of the chemical shifts of the bridge methyl groups in these compounds are used to support the stereochemistry assigned to **3**.

A recent publication by Meinwald and Schneider[1] concerning the synthesis and reactions of carvonecamphor prompts us to submit our own observations in this area.[2]

We had observed that, upon irradiation in ethanol, carvone (1) was converted through the intermediacy of the known[3,4] tricyclic ketone 2 to a saturated bicyclic ester. The corresponding methyl ester was formed on irradiation of carvone in methanol solvent. When the photolysis of 2 was carried out in perdeuteriomethanol, an ester was obtained which contained no deuterium in the ring portion of the molecule, in agreement with data obtained by Meinwald in similar experiments.[1] On the basis of mechanistic reasoning,[5] the perdeuteriomethanol ester was assigned structure 4 and the ethyl ester structure 3. In this communication we describe further experiments which define absolutely the ring structure and stereochemistry of these esters.



It was felt that definitive evidence for the stereochemistry of 3 could be obtained on the basis of long-range spin coupling between the proton on C_5 and the *endo*-C_6 proton,[6] if indeed 3 represents the correct stereochemistry of the compound. Unfortunately, the signals for both of the protons are obscured by those of the two methyl groups; so it was decided to degrade 3 in the hope of obtaining compounds in which these signals would be open to observation, and at the same time provide a basis for comparison with synthetic materials.

Schmidt degradation[7] of the acid 5, obtained either by hydrolysis of 3, or by direct irradiation of 1 in aqueous solution, gave a high yield of the amine 6, which was converted to the exocyclic olefin 8 by pyrolysis of the amine oxide[8] of the tertiary amine 7.[9] Oxidation of the olefin to the corresponding ketone 9 was effected in good yield by means of a potassium permanganate–sodium periodate mixture.[10,11] The infrared spectrum of this ketone showed an absorption maximum at 5.67 μ, a value to be expected for a strained cyclopentanone ring.[12] Several attempts were made to reduce the

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[1] J. Meinwald and R. A. Schneider, *J. Am. Chem. Soc.*, **87**, 5218 (1965).

[2] The work described in this paper was apparently carried out concurrently with that of the Meinwald group, a manuscript having been completed for publication at the time their paper appeared. The present paper describes data complementary to Meinwald's, and which allows the same conclusions to be drawn regarding the structures and means of formation of the compounds involved.

[3] G. Ciamician and P. Silber, *Ber.*, **41**, 1928 (1908).

[4] G. Büchi and I. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957).

[5] G. Quinkert, *Angew. Chem.*, **77**, 229 (1965); O. L. Chapman, "Advances in Photochemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, p 365.

[6] J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961).

[7] H. Wolff, *Org. Reactions*, **3**, 307 (1946).

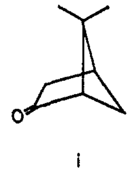
[8] A. C. Cope and E. Ciganek, *Org. Syn.*, **39**, 40 (1959).

[9] M. L. Moore, *Org. Reactions*, **5**, 301 (1949).

[10] R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

[11] J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 2857 (1960).

[12] The ketone i shows λ_{max} 5.69 μ.[11] The absorption maximum of **9** also eliminates the alternative ring systems ii and iii, since a bicyclo[2.2.0]-butanone structure ii would be expected to show λ_{max} ~5.62 μ [W. G. Dauben and R. M. Coates, *ibid.*, **86**, 2490 (1964)], while a bicyclo[3.1.0] hexanone system would show λ_{max} no lower than a normal cyclopentanone (5.73–5.75 μ) [T. Norin, *Acta Chem. Scand.*, **15**, 1676 (1961)].



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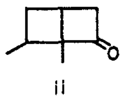

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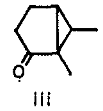

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