simplest models of the phosphorescent state are planar and based on the assumption that the aromatic bonds (1.40 Å.) are changed to two double bonds (1.33 Å.) and four single bonds (1.54 Å.). No change of the hydrogens relative to the carbons is assumed. Only the vibrations[2] $\nu_1 = 992$; $\nu_6 = 606$; $\nu_8 = 1596$ cm.$^{-1}$ are to be considered. Assuming that the angles of 120° are maintained, one obtains $\nu_1 = 5$; $\nu_6 = 0$; $\nu_8 = 10$. The high value of ν_8 is not in accord with the data. On the assumption that the C–C–C angle on the carbons 1 and 4 is equal to the tetrahedron angle,

TABLE I

trans-DIBROMOETHYLENE $\nu_1 = 1578$; $\nu_2 = 1060$ cm.$^{-1}$

Band no.	1	2	3	4
$\nu_1\nu_2$	01	10	11	20
Calcd.	..	1578	2638	3156
Obs.	1060	1700	2600	3260

TABLE II

NAPHTHALENE, $\nu_1 = 1378$; $\nu_2 = 512$

Band no.	1	2	3	4	5	6
$\nu_1\nu_2$	01	10	11	20	30	40
Calcd.	512	1378	1890	2756	4134	5512
Obs.	500	1470	1880	2850	4250	5600

TABLE III

β-CHLORONAPHTHALENE, $\nu_1 = 1384$; $\nu_2 = 518$; $\nu_3 = 273$

No.	1	2	3	4	5	6	7	8	9	10
$\nu_1\nu_2\nu_3$	001	010	011	100	101	110	111	112	200	201
Calcd.	273	518	791	1384	1657	1900	2175	2448	2768	3041
Obs.	280	500	800	1320	1550	1810	2150	2350	2700	2900

No.		11	12	13	14	15	16	17	18	19
$\nu_1\nu_2\nu_3$		210	211	212	221	301	310	311	312	410
Calcd.		3286	3559	3804	·4077	4425	4670	4943	5216	6054
Obs.		3170	3400	3600	3800	4300	4500	4700	5000	6000

the values $\nu_1 = 5$, $\nu_6 = 2$, $\nu_8 = 3$ are obtained. Actually all bands can be represented by means of these frequencies, all except the first band by various combinations, too numerous to be listed here. The agreement gains more significance by the fact that only two frequencies are independent as accidentally $\nu_1 + \nu_6 = \nu_8$.

A model in which the hydrogens 1 and 4 move out of the plane to occupy tetrahedron corners furnishes $\nu_5 = 10$; $\nu_{10} = 8$. The spectrum does not support this model.

Thus the somewhat more detailed, though still crude, application of the Franck–Condon principle confirms the quinoid model of Lewis and Kasha, and especially their assumption that the hydrogens do not appreciably move with respect to the carbons.

(3) Regarding the other substances investigated by Lewis and Kasha, vibration data are insufficient even for an approximate analysis. But the spectra of several substances can be safely correlated with two or three vibration fre-

(2) Cf. E. B. Wilson, Jr., *Phys. Rev.*, **45**, 706 (1934); K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943).

quencies. A few remarks are to be made on three of these substances.

The first frequency of *trans*-dibromoethylene (Table I) is well known as the stretching frequency of the ethylene bond. The second frequency has not been found among the five totally symmetric frequencies.[3] One is forced to conclude that the phosphorescent molecule has a lower symmetry than the symmetry C_{2h} of the ordinary molecule. If the assumption is made that the center of symmetry is maintained, the frequency 1060 must be correlated to the one frequency of the class B_g permitted in the Raman spectrum. This vibration consists essentially of an out-of-plane movement of the hydrogens.

Both Raman lines of naphthalene (Table II) are polarized; the vibrations therefore are totally symmetric.

The Raman frequencies of β-chloronaphthalene (Table III) have been taken from Magat's compilation.[4] A comparison with the spectra of the halogen derivatives of naphthalene indicates that the excited vibrations are not due to the halogen. The change of the aromatic bonds into double and single bonds seems to be the main cause of the distortion also in this case.

The authors are greatly indebted to Professor G. N. Lewis for advice and information.

(3) "Annual Tables of Constants and Numerical Data," vol. 11 (1931–1934), section 26, "Raman Effect" by M. Magat, Gauthier-Villars, Paris, 1936.

(4) Ref. 3, Vol. 12 (1935–1936), section 26, issue 15, Herman and Cie, Paris, 1937.

DEPARTMENT OF CHEMISTRY
THE STATE COLLEGE OF WASHINGTON
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Chloromaleic Anhydride in the Diene Synthesis

BY MARTIN E. SYNERHOLM

The observation has been made that chloromaleic anhydride will react readily in a Diels–Alder condensation with propenyl phenols or phenol ethers[1] with loss of hydrogen chloride, yielding dihydronaphthalene derivatives. More tests have now been made in order to ascertain whether this addition–dehydrohalogenation is typical of the behavior of chloromaleic anhydride toward conjugated dienes. It is shown that the

(1) Synerholm, THIS JOURNAL, **67**, 345 (1945).

expected addition occurs with cyclopentadiene, anthracene or butadiene. In these cases, there is no elimination of hydrogen chloride, even at elevated temperatures.

The greater reactivity of the double bond in chloromaleic anhydride than in diethyl chloromaleate is demonstrated by the fact that under conditions favorable for rapid condensation of the anhydride with anthracene, the ethyl ester–anthracene mixture gives almost complete recovery of unchanged anthracene.

The condensation of tetraphenylcyclopentadienone and chloromaleic anhydride takes place with loss of hydrogen chloride and carbon monoxide to form tetraphenylphthalic anhydride. The usual preparation of this dye intermediate involves the condensation of maleic anhydride with tetraphenylcyclopentadienone followed by dehydrogenation using bromine or sulfur.[2] A simplification of the procedure and a material shortening of the reaction time are effected by the use of chloromaleic anhydride. The yield and purity of the product are practically unaltered.

Experimental

Condensation of Chloromaleic Anhydride with Cyclopentadiene.—Thirteen grams (0.098 mole) of chloromaleic anhydride and 6.6 g. (0.10 mole) of freshly distilled cyclopentadiene in 50 ml. of benzene were allowed to stand at room temperature overnight. The mixture was diluted with 100 ml. of petroleum ether (30–60°) and, after standing for several hours, was filtered. The yield of colorless crystalline product melting at 161° was 15 g. (75%). *Anal.* Calcd. for $C_9H_7O_3Cl$: Cl, 17.9. Found (Parr bomb): Cl, 18.0.

Condensation of Chloromaleic Anhydride with Anthracene.—Ten grams (0.075 mole) of chloromaleic anhydride and 13.5 g. (0.076 mole) of anthracene (Eastman Kodak Co.) were refluxed one hour in 50 ml. of xylene. On cooling, 13 g. (56%) of colorless crystals melting at 155° was obtained. One recrystallization from toluene raised the melting point to 157°. *Anal.* Calcd. for $C_{18}H_{11}O_3Cl$: Cl, 11.4. Found (Parr bomb): Cl, 11.3.

Condensation of Chloromaleic Anhydride with Butadiene.—Seventeen grams (0.128 mole) of chloromaleic anhydride and 9 g. (0.166 mole) of butadiene were mixed in 50 ml. of benzene. After standing stoppered for one week at room temperature, the mixture was diluted with 100 ml. of petroleum ether and, after standing overnight, was filtered. The colorless granular precipitate was recrystallized from toluene to which a few drops of glacial acetic acid had been added. The yield was 4.2 g. (16% based on chloromaleic anhydride). *Anal.* Calcd. for $C_8H_9O_4Cl$ (free acid): Cl, 17.3. Found (Parr bomb): Cl, 17.3.

Attempted Condensation of Diethyl Chloromaleate with Anthracene.—Eight grams (0.039 mole) of diethyl chloromaleate and 6 g. (0.034 mole) of anthracene in 25 ml. of xylene were refluxed five hours. On cooling, 4.5 g. of anthracene (m. p. 211–214°; mixed with original anthracene, m. p. 213°) crystallized. Concentration of the filtrate yielded an additional 0.5 g. of unchanged anthracene.

Preparation of Tetraphenylphthalic Anhydride.—Twenty grams (0.052 mole) of tetraphenylcyclopentadienone and 7.3 g. (0.055 mole) of chloromaleic anhydride (Eastman Kodak Co. practical) in 25 ml. of bromobenzene were refluxed for one hour. The mixture was cooled to 0°

and filtered. The crystals of tetraphenylphthalic anhydride, which were washed first with a little cold bromobenzene, then with petroleum ether (30–60°), weighed, after drying in air, 19.5 g. (83%) and melted at 288°. The addition of 100 ml. of petroleum ether to the filtrate produced 2.7 g. of additional material melting at 278–282°.

BOYCE THOMPSON INSTITUTE FOR PLANT RESEARCH, INC.
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The Purification and Biological Potency of Natural d,γ-Tocopherol

BY LEONARD WEISLER, JAMES G. BAXTER AND MARION I. LUDWIG

The vitamin E activity of natural d,γ-tocopherol as measured by the Evans resorption sterility test has been observed by the Biological Department of these Laboratories to decrease as more highly purified specimens became available. This note describes the preparation and assay of the purest specimen we have yet prepared.

Early preparations were reported[1] to have about one-third the potency of α-tocopherol. In 1939 a sample was prepared from corn oil in this Laboratory and found by assay in the General Mills Laboratories to have less than one-fifteenth the potency of α-tocopherol. We attributed the low potency to decomposition of the sample since γ-tocopherol (as palmitate) was found at the same time to be one-ninth as potent as α-tocopherol. More recently a preparation from mixed vegetable oils (mainly cottonseed), after separation of α-tocopherol by chromatography,[2] had one-twelfth the potency of natural d,α-tocopherol[3] which appeared to support the oxidation hypothesis.

In the past year, however, C. D. Robeson and K. Meng of this Laboratory have repeatedly chromatographed supposedly pure γ-tocopherol from cottonseed oil and obtained preparations of decreased potency. Meng obtained one having as little as one-twenty-fifth the potency of α-tocopherol. This suggested that the chromatographic separations previously made might have been incomplete and that our best γ-preparation might have contained small amounts of α-tocopherol. It further suggested the possibility that pure γ-tocopherol has no biological activity as measured by the resorption sterility test. The activity of the synthetic tocopherol is still under investigation.[4]

We have recently prepared γ-tocopherol from a soybean oil distillate which contained only small amounts of α- in the mixed tocopherols, making the chromatographic separation more efficient. The details were as follows:

(1) Emerson, Emerson, Mohammad and Evans, *J. Biol. Chem.*, **122**, 99 (1937).

(2) Baxter, Robeson, Taylor and Lehman, THIS JOURNAL, **65**, 918 (1943).

(3) Joffe and Harris, *ibid.*, **65**, 925 (1943).

(4) Harris, Jensen, Joffe and Mason, *J. Biol. Chem.*, **156**, 491 (1944).

(2) *Org. Syntheses*, **23**, 93 (1943); Dilthey, Thewalt and Trösken, *Ber.*, **67**, 1962 (1934).