tilled oxalyl chloride was added. The reaction commenced immediately and the product had gone into solution after about 15 minutes. After another 20 minutes, the solvents were removed under vacuum and the last traces of oxalyl chloride were removed by adding more dry chloroform and distilling off under suction. A portion of the **ester acid chloride (XIX)** thus obtained on treatment with methanol and working up the reaction in the usual way gave the parent diester XVIII, as shown by melting point and mixture melting point determination. The oily acid chloride XIX was taken up in 50 cc. of anhydrous ether and treated with an excess of a dry ethereal solution of diazomethane. The evolution of nitrogen was instantaneous. After one hour the ether was removed under vacuum to give a solid diazoketone which was used without any purification. A solution of the diazoketone in 20 cc. of methanol was heated under gentle reflux and small portions of freshly precipitated silver oxide (1 g. in all) were added over a period of one hour. After the evolution of nitrogen had practically ceased, silver metal was removed by filtration. Methanol was removed under suction and the residual oil was dissolved in benzene. Colloidal silver was best removed by passing through a short column of alumina. Benzene was removed and the semi-solid mass left was crystallized twice from methanol as white prismatic crystals, m.p. 87–88.5°. Mixture melting determination with the diester obtained from X showed no depression. The diester thus obtained was also hydrolyzed to the dicarboxylic acid X according to the procedure already described; melting point and mixture m.p. 215–216°.

Oxidation of the Adduct 2-Methyl-7-methoxy-1,2-cyclopentenophenanthrene-3′,4′-dione (VI) with Alkaline Hydrogen Peroxide.—The mother liquors from the separation of the adduct V were concentrated. All attempts at crystallization through chromatography or evaporative distillation under high vacuum were unsuccessful. Two grams of the crude adduct VI was oxidized by excess of alkaline hydrogen peroxide in a manner similar to that used for the adduct V. The original brown color of the alkaline solution was changed to light yellow after the oxidation was complete. The cooled solution on treatment with hydrochloric acid gave an oily product which was redissolved in a dilute solution of potassium bicarbonate. This solution was extracted with ether to remove the insoluble material and then treated with hydrochloric acid to give a semi-solid mass. This was filtered, washed and dried; yield 0.8–0.9 g. The dry product after two crystallizations from ethyl acetate as a white powder had a m.p. 220–221°, yield 0.3–0.4 g. This proved to be **2-methyl-2-carboxy-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene-1-acetic acid (XXII)**. Heer and Miescher,[8] who prepared this dicarboxylic acid in a different manner, reported a m.p. 210–212°. A mixture of a sample provided by Dr. Miescher and our sample had a m.p. 216–218°. The dicarboxylic acid on treatment with hydrogen chloride in acetic acid was recovered unchanged. The dicarboxylic acid on treatment with acetic anhydride was converted to the corresponding **anhydride XXIII** which after crystallization from benzene–petroleum ether as white needles had m.p. 148–149°; literature[8] m.p. 147–148°.

The mother liquors from the crystallization of the dicarboxylic acid XXII were evaporated to dryness. The oily residue was treated with diazomethane and the diester thus obtained was distilled under high vacuum to yield a brown viscous oil. This was saponified with excess 20% potassium hydroxide solution. The semi-solid acid thus obtained was reconverted to the dimethyl ester and evaporatively distilled under high vacuum. Hydrolysis of the ester thus obtained gave the dicarboxylic acid XXII as a semi-solid mass, which after drying and crystallization from ethyl acetate had a m.p. 218–220°, and showed no depression in m.p. when mixed with an authentic sample of XXII obtained as above; yield 90–100 mg.

Partial Dehydrogenation of 2-Methyl-2-carboxy-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene-1-acetic Acid (XXII) to 2-Methyl-2-carboxy-7-methoxy-1,2,3,4-tetrahydrophenanthrene-1-acetic Acid (XXIV).—Two hundred mg. of the hexahydrodicarboxylic acid XXII was dissolved in about 20 cc. of purified xylene, 200 mg. of 10% palladium–charcoal was added and the mixture heated under a gentle reflux for about 30 to 40 minutes. The catalyst was filtered off and xylene removed under vacuum. The residue on trituration solidified. It was recrystallized from a mixture of xylene–acetic acid into glistening prismatic crystals, m.p. 229–231°. Bachmann, Cole and Wilds,[11] who prepared this acid by a different route, reported a m.p. 230–231°. A mixture melting point determination of our sample with that provided by Professor Bachmann showed no depression.

Conversion of 2-Methyl-2-carboxy-7-methoxy-1,2,3,4,9,-10-hexahydrophenanthrene-1-acetic Acid (XXII) to 1,2-dimethyl-7-methoxy-phenanthrene (XVII) was carried out in a manner similar to that described for the isomeric dicarboxylic acid X. The identity of 1,2-dimethyl-7-methoxyphenanthrene from the two sources was checked through determination of mixed melting point, which showed no depression, and comparisons of their infrared spectra which were identical.

NEW DELHI, INDIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Arylation of Unsaturated Systems by Free Radicals. VII. The Meerwein Reaction. V.[1] Further Arylations of Maleimides. Ultraviolet Spectra of Arylmaleimides, Arylmaleic Anhydrides and Arylmaleo- and Fumaronitriles

BY CHRISTIAN S. RONDESTVEDT, JR., MAX J. KALM AND O. VOGL

RECEIVED JUNE 11, 1956

Arylation of maleimide and N-isopropylmaleimide by diazonium salts in the presence of cupric ion produces α-arylmaleimides and α-aryl-N-isopropylmaleimides. The yields are generally higher in arylations of the N-isopropyl derivative, chiefly because of the more favorable physical properties of aryl-N-isopropylmaleimides. Their ultraviolet spectra and those of related compounds are reported and discussed.

α-Arylmaleimides can be formed in a single operation by the arylation of maleimide with diazonium salts in the presence of cupric ion.[2] It appeared from two experiments that N-substituted (especially N-isopropyl) maleimides might generally give higher yields of arylated product than unsubstituted maleimide. Because of our interest in arylmaleic anhydrides,[3] which can be prepared in high yield by hydrolysis of arylmaleimides followed by cyclization,[2] we have tested this tentative conclusion by arylating N-isopropylmaleimide with a series of diazonium salts. Further information was sought concerning the effects of nuclear substitution on the yields in the Meerwein reaction.

The reactions were conducted by the methods de-

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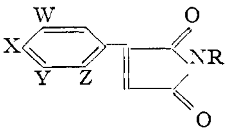
(1) Paper IV, O. Vogl and C. S. Rondestvedt, Jr., THIS JOURNAL, **78**, 3799 (1956).

(2) C. S. Rondestvedt, Jr., and O. Vogl, *ibid.*, **77**, 2313 (1955).

(3) C. S. Rondestvedt, Jr., and A. H. Filbey, *J. Org. Chem.*, **19**, 119 (1954).

TABLE I

α-ARYLMALEIMIDES

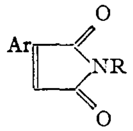


W	X	Y	Z	R	Yield, %	M.p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Crystn. solvent[m]
H	H	H	Cl	H	..	123–124	$C_{10}H_6ClNO_2{}^a$	57.85	57.97	2.91	2.85	A
H	H	H	Cl	*i*-Pr	36	127–129[b]	$C_{13}H_{12}ClNO_2$	62.53	62.10	4.84	4.74	...
Cl	H	H	H	*i*-Pr	36[c]	68–70	$C_{13}H_{12}ClNO_2$	62.53	62.75	4.84	4.81	E–P
H	Cl	H	Cl	H	..[d]	163–164	$C_{10}H_5Cl_2NO_2{}^e$	49.62	49.70	2.08	2.12	A
H	Cl	H	Cl	H	43[f]	200-202 dec.	$C_{10}H_6Cl_3NO_2{}^{g,h}$	43.12	43.13	2.17	2.37	A
H	Cl	H	Cl	*i*-Pr	26	77.5–78.5[i]	$C_{13}H_{11}Cl_2NO_2$	54.95	55.29	3.90	3.79	E-P
Cl	H	H	Cl	*i*-Pr	54[j]	101.5–102.5	$C_{13}H_{11}Cl_2NO_2{}^k$	54.95	55.27	3.90	3.93	E-P
H	H	H	H	*i*-Pr	27[l]	89.5-90.5	$C_{13}H_{13}NO_2$	72.54	72.67	6.09	5.94	E-P
H	H	H	Br	*i*-Pr	41	138–139[b]	$C_{13}H_{12}BrNO_2$	53.08	53.35	4.11	4.08	...
H	NO_2	H	H	*i*-Pr	19	126.7-128.0	$C_{13}H_{12}N_2O_4$	59.99	60.06	4.65	4.62	EA
H	CH_3O	H	H	*i*-Pr	41	133–134.5	$C_{14}H_{15}NO_3$	68.55	68.41	6.17	6.11	EA-C

[a] % N calcd. 6.75; found, 6.78. [b] B.p. at 0.4 mm. [c] 70% before crystn. [d] By dehydrohalogenation of pure α-2,4-dichlorophenyl-β-chlorosuccinimide. [e] % N calcd. 5.79; found, 6.01. [f] Plus 13% of mixture with preceding cmpd. [g] α-2,4-Dichlorophenyl-β-chlorosuccinimide. [h] % N calcd. 5.03; found, 4.91. % Cl calcd. 38.19; found, 38.42. [i] Dimorphic, also 70–71°. [j] 82% before crystn. [k] % Cl calcd. 24.96; found, 24.71. [l] 72% before crystn. [m] A = alcohol; E = ether P = petroleum ether (30–40°); EA = ethyl acetate; C = cyclohexane.

TABLE II

ULTRAVIOLET SPECTRA OF ARYLMALEIMIDES



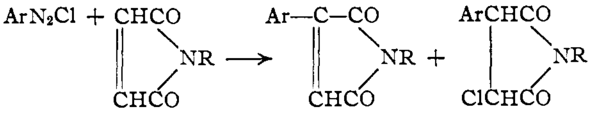
λmax, mμ (10^{-3} ε)

Band	R	Ar = H	C_6H_5	p-$CH_3C_6H_4$	p-$CH_3OC_6H_4$	p-BrC_6H_4	p-ClC_6H_4	p-ClC_6H_4	p-$ClC_6H{}^d$
1	H	280 (0.44)	329 (5.4)	342 (7.0)	365 (9.5)	334 (6.4)	332 (5.3)	344 (4.9)[b]	....
	$(CH_3)_2CH$	301 (0.52)	342 (3.5)	....	374 (8.0)	....	344 (4.4)	342[a](3.5)[c]	338 (3.4)
2	H	230[a](5.0)	259 (8.8)	268 (7.2)	271[a](5.3)	264 (7.8)	259 (7.3)	274 (10.0)[b]	....
	$(CH_3)_2CH$	231[a](4.8)	270 (9.4)	....	286 (6.5)	....	274 (10.5)	294 (9.5)[c]	266 (8.7)
3	H	222[a](11.5)	229[a](12.8)	234[a](13.5)	232 (16.2)	230 (15.8)	228 (14.8)	229 (15.6)[b]	....
	$(CH_3)_2CH$	223[a](10.8)	223 (12.4)	....	234 (14.4)	....	228 (13.7)	230 (22.6)[c]	229 (19.8)
4	H	216 (13.4)	221 (13.2)	226 (14.4)	....	....	....	....	....
	$(CH_3)_2CH$	217 (12.3)	....	....	....	....	....	....	....

Band	R	m-ClC_6H_4	o-ClC_6H_4	o-BrC_6H_4	p-$O_2NC_6H_4$	2,4-$Cl_2C_6H_3$	2,5-$Cl_2C_6H_3$	p-$BrC_6H_4{}^e$	p-$CH_3OC_6H_4{}^f$
1	H	....	315 (2.7)	....	319 (14.2)	318 (3.7)	....	359 (7.9)	394 (8.2)
	$(CH_3)_2CH$	337 (2.6)	324 (2.0)	316 (1.5)	326 (5.8)	328 (2.7)	303 (1.4)	....	....
2	H	....	259 (5.6)	....	268 (24.4)	262[a](6.4)	....	321 (5.4)	332 (5.7)
	$(CH_3)_2CH$	270 (8.7)	269 (6.1)	270 (4.7)	274 (19.0)	272 (7.3)	269 (5.2)	....	....
3	H	....	242[a](7.6)	....	....	244[a](10.4)	....	308 (5.2)[g]	270[a](9.9)
	$(CH_3)_2CH$	233[a](11.0)	244[a](6.5)	245[a](5.6)	....	222[a](16.1)	246 (9.9)	....	....
4	H	....	216 (16.8)	....	216 (19.5)	219 (18.0)	....	234 (23.2)	232 (21.3)
	$(CH_3)_2CH$	218[a](13.7)	216 (16.3)	219[a](15.4)	216 (12.5)	220 (16.6)	224(20.5)	....	....

[a] Shoulder. [b] N-Ethyl. [c] N-Phenyl. [d] Also β-methyl; compound is *p*-chlorophenyl-N-isopropylcitraconimide. [e] Compound is α,β-bis-*p*-bromophenylmaleimide. [f] Compound is α,β-bis-*p*-methoxyphenylmaleimide. [g] Also shoulder at 267 (10.4).

scribed previously.[2,4] In most examples, the crude products appeared to be mixtures of the α-arylmaleimide I and the α-aryl-β-chlorosuccinimide II.[2,5] Occasionally II was isolated directly. Usually, the crude mixture was treated at once with 2,6-lutidine or 2,4,6-collidine to convert the II to I. To remove the substantial amounts of "diazo resins" which contaminated the product, it was passed in benzene solution through a column of activated alumina. The results obtained in the preparation of various new arylmaleimides are given in Table I. In some cases, the product obtained appeared to be a mixture of I and II, and attempted dehydrohalogenation caused decomposition.



I II

No justification can be found in these data or in our earlier results[2] for the often-quoted statements that yields are invariably better when the diazonium

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(4) C. S. Rondestvedt, Jr., and O. Vogl, THIS JOURNAL, **77**, 3401 (1955).

(5) Note that in ref. 2, structure III is incorrect; the chlorine should be on the β-carbon, not on the α-carbon.

salt contains electron-attracting substituents and that the yields decrease in the order $p > m > o$.[6,7] In this work, there was no trend with position of the substituent. The only definite conclusion is that an *ortho*-nitro group is harmful, since no product could be obtained from *o*-nitroaniline with either maleimide or N-isopropylmaleimide.

Ultraviolet Spectra

The spectra of maleimide, N-isopropylmaleimide, and the various arylmaleimides are recorded in Table II. Maleimide itself exhibits four bands: (1) a moderate-intensity band at 280 mμ (0.44),[8] (2) and (3) shoulders at 230 (5.0) and 222 mμ (11.5) of increasing intensity and (4) a high-intensity band at 216 mμ (13.4). N-Isopropylmaleimide has bands corresponding closely in position and intensity to bands 2–4 of maleimide, but the long wave length band is shifted markedly to 301 mμ.

The effect of an α-aryl group may be considered in terms of alteration of the basic maleimide pattern by the substituent. The phenyl group has little effect on the position or intensity of the short wave length bands 3 and 4. On the other hand, the longer wave length bands 1 and 2 are shifted dramatically (30–50 mμ) toward the red and intensified (7–10-fold for band 1).

The influence of substituents in the aryl group can be examined by comparing the individual bands with the unsubstituted phenylmaleimides. Band 1 is shifted bathochromically by most of the *para*-substituents, the shift increasing from bromine and chlorine (2–5 mμ) to methyl (13 mμ) and methoxyl (32–36 mμ). The intensities rise in the same order. By contrast, the *p*-nitro group causes a hypsochromic displacement (10–16 mμ) accompanied by a hyperchromic effect especially marked in the N-unsubstituted compound.

Band 1 is shifted slightly to shorter wave lengths in the only *meta*-substituted compound examined—*m*-chlorophenyl-N-isopropylmaleimide.

ortho-Substituents cause a pronounced hypsochromic displacement of band 1, the shift being slightly greater with *o*-Br than with *o*-Cl. The 2,4-dichlorophenylmaleimides display band 1 in the position expected from the sum of the effects of *o*-Cl and *p*-Cl, but the *m*-Cl in 2,5-dichlorophenyl-N-isopropylmaleimide causes an anomalous hypsochromic displacement of 21 mμ.

Band 2 is not nearly so sensitive to substituents in the aryl group. Its intensity is generally slightly decreased, but the only significant changes in its position occur with *p*-methyl, *p*-methoxy and *p*-nitro substituents.

Band 3 is intensified but not shifted by *para*-substituents. The *m*-Cl shifts it bathochromically 10 mμ. *ortho*-Halogens, on the other hand, roughly halve the intensity but shift it bathochromically. 2,4-Dichloro-N-isopropylmaleimide is anomalous in that band 3 scarcely moves, and it is more intense than in the parent compound; this may result from poor resolution, however, since here band 3 appears only as a shoulder.

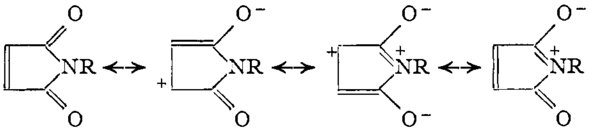
Band 4 is intensified somewhat by most substituents, but it is not appreciably changed in position. The absence of band 4 from many of the spectra may result from a slight hypsochromic displacement to wave lengths inaccessible to our spectrophotometer.

Comparing the N-isopropyl compounds with N–H compounds, we see that in the former, band 1 appears at some 10 mμ longer wave length than in the latter, but it is less intense. Band 2 is shifted the same amount by the isopropyl group, but the intensities are reversed. Bands 3 and 4 are not altered by N-alkyl groups, except for the above-mentioned anomaly with 2,4-dichlorophenyl-N-isopropylmaleimide. N-Ethyl is very similar to N-isopropyl. N-Phenyl is quite different, however. In the one case available, band 1 appears as a shoulder at the same position as in the N-isopropyl compound, but band 2 is shifted bathochromically 20 mμ with little change in intensity; band 3 is not shifted but its intensity is nearly doubled.

An added α-methyl group, as in *p*-chlorophenyl-N-isopropylcitraconimide, shifts bands 1 and 2 hypsochromically 6–8 mμ. Band 3 is not displaced but its intensity is increased 50%.

The data described above permit tentative conclusions concerning the structural features responsible for the absorptions observed. In maleimide and N-isopropylmaleimide, bands 3 and 4 doubtless represent the α,β-unsaturated carbonyl absorption (structure III) which characteristically appears near 225 mμ (the "K-band" resulting from π-π conjugation).[9] Although bands 1 and 2 might be called the absorption of the imide system –CO–NH–CO–, they are better attributed to the entire "aromatic" ring system. It should be noted that succinimide is transparent above 260 mμ and has only a weak maximum at 243 mμ (0.092) and a shoulder in the end absorption region at 218 mμ (0.187).[10] Benzene displays intense "ethylenic" absorption at 203 mμ (7.4) (the "E-band") and weaker "aromatic" absorption at 250 mμ (0.2) (the "benzenoid" or "B-band").

One may thus visualize maleimide as a hybrid of the unperturbed structure and resonance structures III–V. Evidence for the participation of doubly



III IV V

bonded nitrogen structures has been found in the infrared spectra of cyclic amides,[11] and these structures should be more probable with maleimides because of the ring symmetry. The bathochromic shift caused by N-alkylation is doubtless a result

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[6] For example, see E. Müller, *Angew. Chem.*, **61**, 179 (1949).

[7] K. B. L. Mathur, *et al.*, *J. Ind. Chem. Soc.*, **32**, 465 (1955), and previous papers.

[8] Parenthetical figures following a wave length represent 10^{-3} ε.

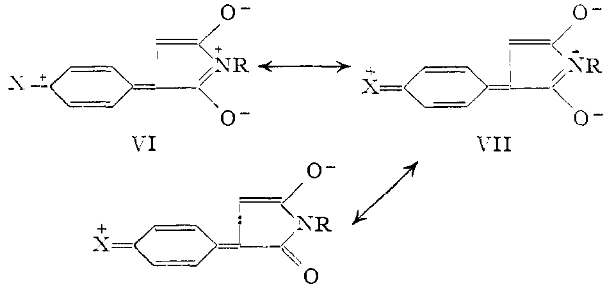
[9] Compare, for example, $CH_3COCH{=}CHCOCH_3$, λ_{max} 226 mμ (14.5). The terminology is that of E. A. Braude, *Ann. Repts. Progr. Chem.*, **42**, 105 (1945). Many of the comparison data are taken from this compilation.

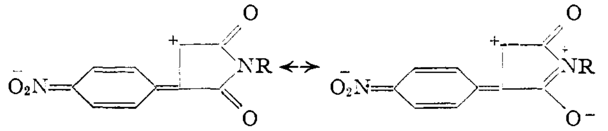
[10] Measured in 95% ethanol. *Cf.* L. J. Saidel, *Nature*, **172**, 955 (1953); J. P. Polya and T. M. Spotswood, *Rec. trav. chim. Pays-Bas*, **68**, 576 (1949); H. Ley and W. Fischer, *Ber.*, **46**, 328 (1913). The last authors report the spectra of a few maleimide derivatives, not those studied in the present work; their curves cover only a portion of the range we have studied.

[11] H. Lenormant, *Bull. soc. chim. France*, 33 (1948).

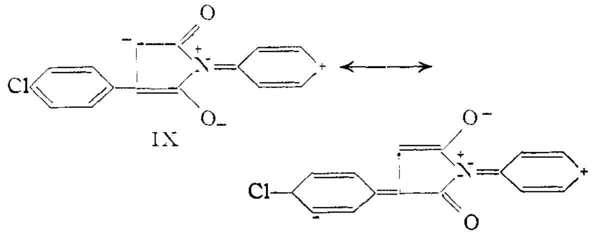
of the increased availability of electrons on nitrogen; it might also be caused by the absence of hydrogen bonding of the type known for amides with a hydrogen on nitrogen.

The bathochromic shift of band 1 caused by the phenyl group reflects the conjugation of the new chromophoric group with the maleimide ring (structure VI). The further shifts caused by auxochromes are attributable to structures like VII. The pronounced hypsochromic shifts caused by *ortho* substitution must then result from steric hindrance to coplanarity which diminishes resonance in the sense of structure VI.[12] This conclusion is further supported by the absence of fluorescence in the *ortho*-substituted compounds. A lesser amount of hindrance is presented by the β-methyl group in p-chlorophenyl-N-isopropylcitraconimide. The p-nitro group demands an electronic drift away from the maleimide ring VIII, and the extra energy manifests itself in the observed hypsochromic shift.


VI VII


VIII

The interpretation of band 2 is not so clear. It is influenced by resonance, since it is shifted toward the red by introduction of the phenyl group and further shifted by auxochromes. However, it does not respond to steric hindrance, except from an α-methyl group, and nitro also causes a bathochromic shift.


IX X

The position of band 3 seems to respond more to the inductive effects of the ring substituents than to resonance; its intensity appears to be resonance-influenced. Thus in the chlorophenyl-N-isopropylmaleimides, the bathochromic shifts increase as the chlorine atom is moved closer to the maleimide ring. In the *ortho*-halogen compounds, the intensity is greatly diminished, as is the resonance.

Band 3 is the most intense in p-chlorophenyl-N-phenylmaleimide, while in the same compound, band 2 is not intensified but is rather markedly displaced. This suggests that resonance structures such as IX and X are quite important.

The spectra of available arylmaleic anhydrides and arylmaleo- and fumaronitriles were measured and are recorded in Tables III and IV.

TABLE III

ULTRAVIOLET SPECTRA OF ARYLMALEO- AND FUMARONITRILES IN ETHANOL

Nitriles	λ_{max}, mμ (10^{-3} ϵ)
Phenylmaleo-[a]	.... 229 (10.0); 296 (15.2)
Phenylfumaro-[a]	.... 230 (9.7); 297 (15.0)
p-Chlorophenylmaleo-[b]	221 (8.9); 233 (11.5); 306 (19.6)
p-Chlorophenylfumaro-[b]	220 (13.2); 233 (10.2); 302 (12.7)
p-Methoxyphenylmaleo-[c]	226 (8.9); 243 (11.9); 339 (22.2)
p-Methoxyphenyl-fumaro-[c]	225 (13.0); 244 (11.1); 339 (16.0)
Di-p-chlorophenylmaleo-[b]	223 (17.9); 242[d] (12.0); 334 (17.6)

[a] Samples furnished by Dr. D. W. Hein (reference 13). [b] Described in reference 1. [c] Samples furnished by Prof. Leonard E. Miller. [d] Shoulder.

Three intense bands are found in the spectra of the nitriles. With unsubstituted phenyl, the short wave length maximum lies beyond the accessible range of the instrument, appearing only as end absorption. In general, the positions of all the bands are independent of the stereochemistry but are dependent on the ring substituent. The intensities (except for unsubstituted phenyl) are not greatly influenced by the ring substituent but are markedly affected by the stereochemistry; the longest wave length band is more intense with the *cis*-dinitriles and the shortest wave length band is more intense for the *trans* compounds. As with the imides, a methoxyl group causes a pronounced bathochromic shift; all of the bands are affected, the displacement being greatest with the long wave length band. Phenylmaleo- and phenylfumaronitrile[13] exhibit practically identical spectra. By way of comparison, maleonitrile displays steadily rising absorption from 258 mμ (0.009) to 237 mμ (2.3), with no definite maxima or even shoulders in the region reported. Fumaronitrile has a weak shoulder at 292 mμ (0.004) and a more intense shoulder at 232 mμ (11.7), with no well-defined maxima.[14]

Maleic anhydride exhibits a broad weak band in the region 270–310 mμ (0.013)[8] and a strong maximum at 208 mμ (8).[16] Succinic anhydride has only weak absorption from 219–255 mμ.[16a] Phenylmaleic anhydride has three strong bands. The long wave length band, at a longer wave length than in phenylmaleimides, is very markedly shifted toward the red and intensified by *para* substituents,

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[12] A discussion of the manifestation of steric inhibition of resonance in ultraviolet spectra is given by W. R. Remington, THIS JOURNAL, **67**, 1838 (1945).

[13] W. F. Beech and H. A. Piggott, *J. Chem. Soc.*, 423 (1955); W. C. Schneider, THIS JOURNAL, **77**, 2796 (1955); D. W. Hein, *ibid.*, **77**, 2797 (1955).

[14] E. Ruppol, *Bull. classe sci.*, *Acad. roy. Belg*, **21**, 236 (1935); **22**, 1166 (1936). Note that in the first paper, the presumed maleonitrile and citracononitrile are actually maleimide and citraconimide.[15] Ruppol's second paper gives the spectrum of authentic maleonitrile, m.p. 32.2–32.6°.

[15] P. Bruylants and J. Jennen, *ibid.*, **22**, 1141 (1936); J. Jennen, *ibid.*, **22**, 1169 (1936); *cf.* H. Mommaerts, *ibid.*, **27**, 579 (1941).

[16] (a) S. Menczel, *Z. physik. Chem.*, **125**, 208 (1927); (b) A. Wassermann and A. Smakula, *ibid.*, **155**, 366 (1931); W. G. Barb, *Trans. Faraday Soc.*, **49**, 143 (1953).

TABLE IV

ULTRAVIOLET SPECTRA OF ARYLMALEIC ANHYDRIDES IN ISOÖCTANE[a]

Aryl	λ_{max}, mμ (10^{-3} ϵ)
Phenyl	216[b](9.6); 240[b](3.2); 312 (10.2)
p-Tolyl	222[b](11.7); 246 (3.9); 328 (14.6)
p-Chlorophenyl	224 (12.2); 245 (4.5); 322 (14.5)
p-Methoxyphenyl	229 (12.4); 248[c](5.9); 256 (4.8); 353 (19.1); 370[c](13.2)
m-Methoxyphenyl	216[b](13.6); 255 (5.0); 261 (5.0); 310 (8.4); 353 (2.6)
o-Methoxyphenyl	216 (13.7); 249 (5.0); 254 (5.0); 302 (1.2); 350 (5.8)
α-Naphthyl	222 (81.3); 259 (7.7); 370 (7.3); 390[c]
β-Naphthyl	224 (69.5); 274 (13.8); 285 (14.6); 330 (23.6); 374 (9.4); 389[c]
Di-*p*-methoxyphenyl	215 (13.8); 235 (15.8); 266 (8.8); 326 (8.1); 340 (9.0); 389 (13.4)

[a] Described in references 2 and 3 and this paper. [b] Beginning of end absorption plateau. [c] Shoulder.

the effects paralleling but being greater than those of the corresponding *p*-substituted phenylmaleimides. A *m*-methoxyl does not affect this band, while a hypsochromic shift is caused by *o*-methoxyl. A fourth band at still longer wave lengths appears in all of the methoxy compounds and the naphthylmaleic anhydrides.

The middle band in the anhydrides is less sensitive to substitution. It is split into a doublet in the methoxy compounds. The shifts of 19 mμ in α-naphthyl- and about 40 mμ (doublet) in β-naphthylmaleic anhydride are unexpectedly large.

The short wave length band appears in some cases as a definite peak, in others only as end absorption. *para*-Substituents cause bathochromic shifts, with some intensification, while *ortho*- and *meta*-methoxyl intensify but do not shift this band. This peak in the two naphthyl compounds is noteworthy for its extremely high intensity.

Experimental

Arylation of Maleimides.—The amine dissolved in three equivalents of dilute hydrochloric acid was diazotized at 0° by dropwise addition of sodium nitrite solution. The filtered diazonium solution was adjusted to *p*H 3 (Beckman *p*H meter) with saturated sodium acetate solution and added to a solution of 1.0–1.5 moles of the maleimide in acetone.[17] The cupric chloride (0.15 mole) was added, followed by enough acetone to make the solution homogeneous. Exothermic evolution of nitrogen usually began at once. A cooling bath was used to moderate the initial reaction, following which the mixture was allowed to warm to room temperature and stirred until nitrogen evolution had ceased. The acetone was then evaporated at reduced pressure.

The product, if solid, was collected, washed with water and then dissolved in benzene; if liquid, it was extracted into benzene. A moderate excess of 2,6-lutidine was added to the dried solution and the mixture was warmed gently to initiate dehydrohalogenation. More vigorous heating usually caused decomposition. When no more lutidine hydrochloride separated, the mixture was washed with water, dilute sulfuric acid and water, then dried and evaporated at reduced pressure.

The residue, if liquid, was subjected to vacuum distillation. If solid and amenable to crystallization, it was recrystallized. Otherwise, it was dissolved in a minimum amount of benzene and passed through a column of activated alumina. In most cases, the "diazo resins" were retained at the top of the column, and the progress of the product through the column could be followed by its fluorescence under ultraviolet light. (The *ortho*-substituted compounds did not fluoresce.) The eluate was then evaporated and the residue was recrystallized.

The details of the successful experiments are recorded in Table I. Brief descriptions of experiments which did not give pure products are given below. They represent single trials, and it is likely that further study will give much improved results. For example, the use of excess maleimide and the employment of milder dehydrohalogenation conditions (perhaps a stroger base at lower temperatures) would undoubtedly be helpful.

α-*m*-**Chlorophenylmaleimide.**—The product from 0.1 mole each of *m*-chloroaniline and maleimide was crystallized from benzene (Norit), giving 8.55 g. (41%) of light yellow product, m.p. 139.5–141.5°. It was evidently a mixture of the arylmaleimide and the arylchlorosuccinimide, as shown by analysis.

Anal. Calcd. for $C_{10}H_6ClNO_2$: C, 57.85; H, 2.91. Calcd. for $C_{10}H_7Cl_2NO_2$: C, 49.21; H, 2.89. Found: C, 53.47; H, 2.94.

When the product was refluxed with 2,6-lutidine for 1 hr. and poured into dilute sulfuric acid, it could not be purified.

α-**2,5-Dichlorophenylmaleimide.**—The product from 0.1 mole each of amine and maleimide was crystallized from benzene, yielding 12.4 g. (51%) of a white solid, m.p. 163.5–165°, again a mixture.

Anal. Calcd. for $C_{10}H_5Cl_2NO_2$: C, 49.62; H, 2.08. Calcd. for $C_{10}H_6Cl_3NO_2$: C, 43.12; H, 2.17. Found: C, 45.72; H, 2.39.

Refluxing with 2,6-lutidine gave a product which could not be purified.

α-*m*-**Bromophenyl-N-isopropylmaleimide.**—From 0.1 mole of each reagent there was obtained only 53% of the theoretical nitrogen. Treatment of the residue with lutidine with gentle warming gave 38% of the theoretical amount of lutidine hydrochloride. Filtration through 300 g. of alumina yielded an orange oil which solidified on cooling. On attempted recrystallization from ether–petroleum ether, the product separated as an oil which ultimately solidified after standing in a refrigerator for several weeks; white crystals, 3.7 g., m.p. 245–250°. From its high melting point, it was judged to be α,β-bis-*m*-bromophenyl-N-isopropylmaleimide, so it was not further investigated. Probably the use of excess maleimide and purification by distillation would have given the desired product.

The 4,4'-Biphenylene-bis-(N-isopropylmaleimide).—A strongly fluorescent product was obtained from 0.07 mole of benzidine and 0.14 mole of N-isopropylmaleimide. The theoretical amount of nitrogen was collected. The product was treated with 0.28 mole of 2,6-lutidine. The resulting material was too insoluble in benzene to permit alumina treatment. Of the many solvents tried for recrystallization, only ethyl acetate–cyclohexane gave yellow crystals, m.p. 225–255°, which seem to be a mixture of mono- and diarylated products resulting from reaction with one or both amino groups.[18]

α-*o*-**Nitrophenyl-N-isopropylmaleimide.**—The crude product from 0.15 mole of *o*-nitroaniline and 0.225 mole of N-isopropylmaleimide was treated with 0.3 mole of 2,6-luti-

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(17) In most of the examples reported in Table I only 1.0 mole of the maleimide was used. With *p*-methoxy-, *p*-nitro- and *o*-bromobenzenediazonium chlorides, 1.5 moles of the maleimide was used. It is likely that many of the other yields reported would have been greatly improved with the larger amount of maleimide. Often the yield of product after lutidine treatment was much higher than the yield of crystallized material, and it was suspected in some of these examples that contamination by the diarylated maleimide was responsible for the difficulties encountered in crystallization.

(18) Only a few examples of the use of diamines in the Meerwein reaction have been reported by E. Müller, ref. 6, and S. Malinowski and S. Benbenek, *Roczniki Chem.*, **27**, 379 (1953); *C. A.*, **49**, 1034h (1955). In our hands, the reaction of tetrazotized 2,2'-diaminobiphenyl with maleimide likewise gave a product which could not be purified.

dine. The resulting material was distilled, giving a green-yellow liquid, 17.9 g., b.p. 51–53° (0.9 mm.). The residue was tarry. The distillate appears to be a mixture of nitrobenzene and N-isopropylmaleimide, judging from analysis and refractive index.

A similar experiment with maleimide also failed.

***α-p*-Chlorophenylmaleic Hydrazide.**—Since maleic hydrazide was insoluble in aqueous acetone, dimethyl sulfoxide was used as the organic solvent.[19] The mixture obtained from 0.15 mole of each reagent was treated with 0.3 mole of 2,6-lutidine, but no lutidine hydrochloride separated. The only product isolated was a small amount of unreacted maleic hydrazide.

***α*-(2,4-Dichlorophenyl)-*β*-chlorosuccinimide.**—The reaction of 0.1 mole each of amine and maleimide yielded 11.5 g. of white product, m.p. 196–198° dec. Recrystallization from alcohol gave pure material, m.p. 200–202° dec. The mother liquor yielded 3.2 g., m.p. 173–185° dec., of a mixture of this product and 2,4-dichlorophenylmaleimide (see below), which mixture could be dehydrohalogenated readily to the pure material.

***α*-2,4-Dichlorophenylmaleimide.**—Treatment of the above chlorosuccinimide (1 g.) with 10 ml. of 2,6-lutidine with gentle warming gave a quantitative yield of α-2,4-dichlorophenylmaleimide.

***o*-Methoxyphenylmaleic Anhydride.**—The crude product from maleimide and *o*-anisidine was hydrolyzed directly with aqueous alkali, and the arylmaleic acid was cyclized thermally.[2] The *o*-methoxyphenylmaleic anhydride was isolated by distillation, b.p. 140° (0.2 mm.), and purified by crystallization from methylene chloride, m.p. 135–136°.

Anal. Calcd. for $C_{11}H_8O_4$: C, 64.70; H, 3.95. Found: C, 64.61; H, 4.13.

***m*-Methoxyphenylmaleic Anhydride.**—A similar procedure with *m*-anisidine gave *m*-methoxyphenylmaleic anhydride, m.p. 146–147°.

Anal. Calcd. for $C_{11}H_8O_4$: C, 64.70; H, 3.95. Found: C, 65.04; H, 3.88.

Ultraviolet Spectra.—All spectra were measured on a Cary recording spectrophotometer at approximately 10^{-4} *M* concentration. The maleimides and nitriles were dissolved in 95% ethanol, the anhydrides in Phillips Spectro Grade isooctane. The extinction coefficients calculated by Beer's law are believed accurate to within 5%.

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[19] Unpublished experiments have shown that the *p*-nitrophenylation of coumarin proceeded in 26% yield with dimethyl sulfoxide solvent, compared to 40–45% in acetone. Hence dimethyl sulfoxide may prove to be a useful solvent for Meerwein reactions in some cases.

[CONTRIBUTION FROM ORGANIC CHEMISTRY SECTION, BALLISTIC RESEARCH LABORATORIES]

Further Studies of the Cleavage of 3-Alkoxypropionitriles with Lithium Aluminum Hydride[1]

BY LOUIS M. SOFFER, MANFRED KATZ AND ELIZABETH W. PARROTTA

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The direct addition reduction of 3-alkoxypropionitriles by lithium aluminum hydride in ether results in 5–10% cleavage at high hydride concentrations (molar ratio of hydride to nitrile, MRHN $\geqslant$ 1) and 52–66% cleavage at low concentrations (MRHN $<$ 1). Reduction in ether by reverse addition, as well as reductions in tetrahydrofuran by both direct and reverse addition lead to high cleavage over a wide MRHN range. Explanations are offered for the varying amounts of hydrogen and parent alcohol produced.

The direct addition (DA) reduction[2] of 3-alkoxypropionitriles with excess lithium aluminum hydride in ether results in 5–10% yields of the parent alcohol, whereas 70–95% yields are obtained from an identical reduction in tetrahydrofuran. The agreement in yields of hydrogen and of alcohol in ether was explained in terms of a reaction of hydride with a hydrogen atom from the α-carbon of the alkoxypropionitrile to produce hydrogen gas and an unstable organoaluminohydride species which cleaved to yield alcohol. This sequence was not satisfactory when applied to the results in tetrahydrofuran because of the excess of hydrogen over alcohol obtained in this solvent. This paper describes additional experiments made at various molar ratios of hydride to nitrile (MRHN) and utilizing both DA and RA procedures.

Results and Discussion

As shown in Table I, runs 1–3, essentially the same yields of hydrogen, alcohol and unsplit amine were obtained at MRHN of 1.1 and 2.0. As the MRHN was lowered below 1, however, there was a surprising increase in the yield of alcohol at the expense of unsplit amine, with a much smaller increase in the amount of hydrogen. It is interesting (runs 5 and 6) that nearly identical results were obtained at MRHN of 0.4 and 0.3, with the only difference being in the amount of alkoxypropionitrile undergoing reaction. In these runs the amount of alcohol produced was greater than the amount of hydride initially present. Therefore, under these conditions, alcohol must result from an additional process to that described above; a probable one is the reaction of one or more of the organoaluminohydride species[3] present with alkoxypropionitrile.

In RA reductions (runs 7–12), where alkoxypropionitrile was present in excess for a considerable portion of each reaction, cleavage was dominant with high yields of hydrogen at all MRHN. This may be attributed to the increasing amount of abstraction arising from the more polar environ-

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[1] L. M. Soffer and E. W. Parrotta, THIS JOURNAL, **76**, 3580 (1954).

[2] Direct addition means that the nitrile was added to the hydride solution. Reverse addition (RA) is the opposite procedure: L. M. Soffer and Manfred Katz, *ibid.*, **78**, 1705 (1956).

[3] For example, $ROCH_2C^{\ominus}HC{\equiv}N$-complex (or reduced version), $ROCH_2CH_2CH{=}N$-complex, $ROCH_2CH_2CH_2N$-complex and RO-complex.