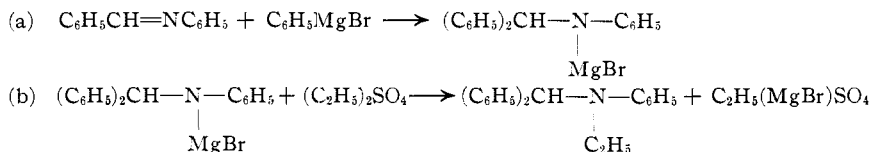


separating the ether layer and drying with sodium sulfate, the ether was removed by distillation from a water-bath; the final product was a thick, clear oil which darkened on standing; d_4^{20} 1.06; n_D^{25} , 1.597.

Analyses. Calc. for $C_{21}H_{21}N$: N, 4.88. Found: 4.91, 5.06.

The probable mechanism of these reactions follows.



The analysis and the calculated refractive index are in agreement with the formula $(C_6H_5)_2CHN(C_2H_5)C_6H_5$. To further establish its identity the compound was prepared by known reactions and was found to boil at the same temperature, 191° at 5 mm. pressure. This was done according to the method of Busch and Rinck⁵ by adding $1/4$ mole of benzalaniline to $1/4$ mole of phenyl magnesium bromide and working up in the customary manner to give *o*-phenylbenzylaniline, $C_6H_5NHCH(C_6H_5)C_6H_5$. This amine was found to boil at 165° at 5 mm. pressure. Its hydrochloride was prepared by passing dry hydrogen chloride into a cold mixture of ether and ethyl alcohol from which the salt was precipitated directly in a pure condition melting at 199° . The hydrochloride was then heated directly with one molecular equivalent of diethyl sulfate for 6 hours at $110-120^\circ$. The amine was set free by sodium hydroxide, taken up in ether, washed with water, dried over sodium sulfate and then distilled. As previously mentioned, the boiling point agreed with that of the compound made by treating the organomagnesium halide directly with diethyl sulfate.

Summary

1. A study has been made of the reaction between diethyl sulfate and organomagnesium halides having the MgX group on carbon, oxygen and nitrogen.
2. In all cases the MgX group has been replaced by an ethyl group.
3. The yields of reaction products in several experiments are decidedly good. In addition to its value for synthetic purposes the reaction is recommended as a reliable method for the determination of the mechanism of certain reactions.

AMES, IOWA

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

CERTAIN TRIPHENYLMETHANE DYES¹

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The preparation in a pure state of a number of dyes of the malachite green series was undertaken as a part of a study of the bactericidal action of dyes in general. In the course of these studies we have had occasion

⁵ Busch and Rinck, *Ber.*, **37**, 2691 (1904); **38**, 1761 (1905).

¹ Presented at the Annual Meeting of the American Chemical Society, September, 1921.

to prepare a number of new members of this group and to make new observations on others. Although this work has been discontinued while still incomplete, we wish to present in brief tabular form the results of the chemical work as far as it has been carried. In a number of cases where the chlorides and sulfates proved too soluble for convenient manipulation, the nitrates were found to be of service because of their more sparing solubility and greater tendency to crystallize. Such substances as malachite green and brilliant green may be readily isolated and purified in this form. This is also true of the furfural analog of malachite green recently described as the zinc double chloride, the oxalate and the chloroplatinate by Renshaw.²

TABLE I
LEUCO COMPOUNDS

Derivative of Leuco mala- chite green	Preparation	Crystalline form	Melting point ° C.	Formula	Analyses		Remarks
					Calc. N %	Found N %	
<i>m</i> -Acetam- ino-	From the -NH ₂ deriv. with acetic anhydride	Faintly green- ish rhombs from 85% al- cohol	154.5-155.5	C ₂₃ H ₂₉ ON ₃	10.85	11.14	Crystallized with diffi- culty
<i>m</i> -Uramino-	From the -NH ₂ deriv. with KNCO in acetic acid	Delicate need- les from alco- hol	194-196	C ₂₁ H ₂₅ ON ₄	14.43	14.43	
<i>p</i> -Diethyl- amino-	From Mich- ler's hydrol and diethyl- aniline	Cream-colored needles from benzene-alco- hol	142-144.5	C ₂₇ H ₃₃ N ₃	10.47	10.63	
<i>o</i> -Chloro- <i>p</i> - dimethyl- amino-	From Mich- ler's hydrol and <i>m</i> -chloro- dimethylaniline	Flat, tan need- les from tol- uene-ligroin	170-171.5	C ₂₃ H ₂₀ N ₃ Cl	10.31	10.55	
2-Hydroxy- 5-phenyl- azo-	From the <i>o</i> - OH comp. and diazotized aniline in al- kaline solu- tion	Lenticular platelets from benzene	186-187	C ₂₇ H ₃₀ ON ₄	12.44	12.62	Did not yield a crystalline dye on oxi- dation
2-Hydroxy- 5-(<i>p</i> -meth- oxy-phen- ylazo)-	Using diazo- tized <i>p</i> -anisi- dine	Ochreous prisms from benzene	187-188	C ₃₀ H ₃₂ O ₂ N ₄	11.67	11.79	Purified with difficulty Did not yield a crys- talline dye when oxi- dized

The dyes were prepared in the usual way by oxidation of the leuco compounds with lead peroxide. The leuco compounds, in turn, were prepared either from the corresponding aldehyde and dialkyl aniline, or from the benzohydrol and substituted aniline.

² Renshaw, THIS JOURNAL, **44**, 864 (1922).

TABLE II
DYES

Derivative of Malachite green	Salt	Crystal form	H ₂ O of cryst.	Decompn pt. (anhydrous) ° C.	Formula	Analyses				Color with conc. H ₂ SO ₄	
						Calc. N H ₂ O % (anhydr.)	Found N % (anhydr.)	H ₂ O %	Carbinol		
Unsubstituted	nitrate	olive platelets	1 mol.	130-135	C ₂₂ H ₂₆ O ₈ N ₃ ·H ₂ O	4.4	10.73	4.48	10.42	minute crystals.	orange
<i>p</i> -Methyl-	chloride	blue green leaflets	4	160	C ₂₁ H ₂₇ N ₂ Cl ₄ H ₂ O	15.98	7.40	16.30	7.84	needles	orange
<i>o</i> -Chloro-	Cl ⁻	voluminous threads	...	intumesces 170° with preliminary softening	C ₂₃ H ₂₄ N ₂ Cl ₂	...	7.02	...	6.80	octahedra	orange
<i>p</i> -Chloro-	NO ₃ ⁻	green hairs, golden luster	3.5	m. 120-175	C ₂₃ H ₂₁ O ₃ N ₃ Cl ₃ · ¹ / ₂ H ₂ O	12.90	9.88	13.06	10.17	minute cryst.	bright orange
<i>p</i> -Nitro-	Cl ⁻	purple needles	5.5	150-155	C ₂₂ H ₂₀ O ₂ N ₃ Cl _{1.5} · ¹ / ₂ H ₂ O	19.48	10.25	19.14	10.15	minute platelets	bright orange
<i>p</i> -Acetyl-methylamino-	NO ₃ ⁻	green needles, metallic luster	0.5 to 1	193-196	C ₂₆ H ₃₀ O ₄ N ₄ ·H ₂ O	3.75	12.11	2.70	12.35	prisms	orange
<i>o</i> -Chloro- <i>p</i> -dimethylamino-	Cl ⁻	olive needles	3.5	185-190	C ₂₅ H ₂₉ N ₄ Cl ₂ · ³ / ₂ H ₂ O	12.48	9.51	11.96	9.92	rhombs	bright orange
<i>m</i> -Uramino-	NO ₃ ⁻	olive-green needles	4	185	C ₂₄ H ₂₇ O ₄ N ₃ ·4H ₂ O	13.82	15.58	13.53	15.39	thin platelets	bright orange
<i>o</i> -Hydroxy-	Cl ⁻	bronze-diamond platelets	0	195 with preliminary softening	C ₂₂ H ₂₅ ON ₂ Cl	...	7.36	...	7.16	rhombs	dull greenish-blue
<i>p</i> -Hydroxy-	Cl ⁻	hairs	...	185-190	C ₂₁ H ₂₅ ON ₂ Cl	...	7.36	...	7.20	reddish needles	yellowish-orange
<i>o</i> -Methoxy-	NO ₃ ⁻	bronze needles	...	?	C ₂₄ H ₂₇ O ₄ N ₃ ·H ₂ O	4.10	9.99	4.12	9.71	leaflets	olive-brown
<i>m</i> -Methoxy-	carbinol	beveled hexagonal plates	...	147-149.5	C ₂₁ H ₂₃ O ₂ N ₂	...	7.45	...	7.60		brown, with olive reflex
<i>p</i> -Methoxy-	Cl ⁻	blue leaflets	...	125-140	C ₂₄ H ₂₇ ON ₂ Cl	...	7.10	...	7.16	needles	orange
<i>o</i> -Ethoxy-	carbinol	needles	...	178-180	C ₂₅ H ₃₀ O ₂ N ₂	...	7.18	...	7.44		blue
<i>p</i> -Ethoxy-	Cl ⁻	needles leaflets	...	150 with preliminary softening	C ₂₅ H ₂₉ ON ₂ Cl	...	6.85	...	6.95	rhombs	orange
3,4-Methylenedioxy-	Cl ⁻	bronze hairs	4	155-160	C ₂₄ H ₂₅ O ₂ N ₂ Cl ₄ ·H ₂ O	14.98	6.86	14.13	7.01	micro-crystals	wine-red
<i>o</i> -Hydroxyacetic-acid	ether anhydride	grass-green platelets	0	170-175	C ₂₅ H ₂₆ O ₃ N ₂	...	6.97	...	7.18		wine-red with olive reflex
Furo-	NO ₃ ⁻	olive-green hairs, bronze luster	5	190	C ₂₁ H ₂₅ O ₄ N ₃ ·5H ₂ O	19.10	11.02	18.93	11.02		brown-purple
Brilliant green	NO ₃ ⁻	brassy aggregates	1	140-210	C ₂₇ H ₃₅ O ₃ N ₃ ·H ₂ O	3.87	9.40	3.66	9.52		orange-brown