reaction mixture was allowed to stand at room temperature for about forty hours. Most of the alcohol was removed under reduced pressure and the residue was warmed at 50–60° for four hours with 150 cc. of 5% sodium hydroxide solution. This solution was cooled and acidified with dilute sulfuric acid. The organic material was extracted with ether, dried over anhydrous sodium sulfate and distilled.

The yield of 3-methyl-Δ^2-cyclohexenone was 3 g. (12.5%), b. p. 86–88° at 14 mm.; n^{20}D 1.4940.

The 2,4-dinitrophenylhydrazone after three crystallizations from alcohol melted at 172.5–173°.

Anal. Calcd. for $C_{13}H_{14}O_4N_4$: N, 19.30. Found: N, 19.31.

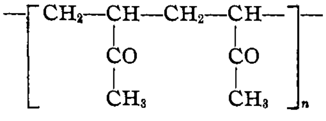
The semicarbazone was also prepared and it melted at 201–201.2° which agrees with the melting point previously reported.[13]

Some Reactions of Other Fractions of the Distillate from Pyrolysis.—Fraction II from the pyrolysis mixture reacted with 2,4-dinitrophenylhydrazine to give a product melting at 138–146° but it could not be purified to give a chemical individual.

Fraction III was heated with selenium to 300–320° for seven hours. After cooling the melt was extracted with 10% sodium hydroxide solution and the solution was filtered. On acidifying the filtrate a light colored, ether-soluble powder with a marked phenolic odor was obtained. The powder did not melt sharply and no pure products were isolated.

Summary

Evidence has been presented to show that the polymer of methyl vinyl ketone has the "head to tail" structure



$$-\left[CH_2-\underset{\underset{CH_3}{|}}{\underset{CO}{\underset{|}{CH}}}-CH_2-\underset{\underset{CH_3}{|}}{\underset{CO}{\underset{|}{CH}}}-\right]_n-$$

URBANA, ILLINOIS RECEIVED OCTOBER 18, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 164]

Condensations by Sodium. XI. Trimethoxytrixenylcarbinol and Comparisons of Colors of Some Carbonium Salts in this Series

BY AVERY A. MORTON AND WILLIAM S. EMERSON

Tris-[4′-methoxytrixenyl]-carbinol has now been prepared by the reactions represented in the equation

$$3CH_3OC_2H_4C_2H_4Br + 6Na + (C_2H_5)_2CO_3 \longrightarrow (CH_3OC_6H_4C_6H_4)_3CONa + 3NaCl + 2NaOC_2H_5$$

Besides demonstrating the effectiveness of sodium as an agent in the preparation of large size triarylcarbinols, our purpose[1] was to observe qualitatively the effect on color, and therefore presumably on basicity, of introducing an additional phenyl group between the functioning and influencing groups. We are now able to state that the order of the effect of substituents as observed in the triphenylmethane series by Baeyer and Villiger[2] and by Ziegler and Boye,[3] namely, MeO > CH_3 > H, is preserved in the trixenylmethane series and that the parent member of this series, trixenylcarbinol, is a far stronger color producing substance than the corresponding carbinol of the triphenylmethane series. In general the basic characters of the two series of carbinols are parallel, the introduction of the methoxy group causing a considerable increase in the basicity of both.[4]

The Hardy[5] color analyzer is particularly well adapted to measurements of this kind. This instrument measures the transmission T, of light through solutions at definite wave lengths, 100% T meaning that the transmission is the same as that of a colorless blank solution and 0% indicating that the color is so intense that no light of that wave length passes. The amount of color is proportional to log $1/T$. Results are mechanically plotted, a typical set of curves being shown in Fig. 1. All of the data are summarized in Table I. Visually at the very low acid concentration of 0.000667 triphenylcarbinol showed no color, trixenylcarbinol was a faint pink, trimethyltrixenylcarbinol was a strong purple, and trimethoxytrixenylcarbinol was an intense blue. The trimethoxy derivative, indeed, becomes colored at or near the neutral point in cold glacial acetic acid.

We are particularly grateful to Professor Hardy

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(1) See Morton and Emerson, THIS JOURNAL, **59**, 1947 (1937).

(2) Baeyer and Villiger, *Ber.*, **35**, 1189 (1902).

(3) Ziegler and Boye, *Ann.*, **458**, 229 (1927).

(4) See Kolthoff, THIS JOURNAL, **49**, 1218 (1927); Lund, *ibid.*, 1346, for the effect of introducing methoxy groups in triphenylcarbinol.

(5) Hardy, *J. Optical Soc. Am.*, **18**, 96 (1929); **25**, 305 (1935).

TABLE I

PER CENT. TRANSMISSION AND MAXIMUM ABSORPTION OF VARIOUS CARBINOLS IN ACETIC ACID CONTAINING SULFURIC ACID

	Per cent. transmission of solution at concentrations of				
Carbinol concn. × 10^5	= 7.47	7.47	7.47	7.18	Wave length at max. absorp.
Acid concn. × 10^3	= 34.8	3.60	.360	.0667	
Carbinol	%	%	%	%	
Triphenyl	77.0	99.5	100		414
Trixenyl	0	12.5	81.0	94.5	542
Trimethyltrixenyl	0	0	24.5	64.0	575
Trimethoxytrixenyl	0	0	0	7.5	638
Trixenyl		34.5[a]			
Trixenyl		56.5[a]			

[a] Concentration of carbinol in these two experiments was 3.74 and 1.87 × 10^{-5}, respectively.

for his aid and advice in the colorimetric measurements.

Experiments

4-Bromo-4'-methoxybiphenyl.—4-Hydroxybiphenyl was methylated with dimethyl sulfate and then brominated according to the directions of Bell.[6]

Tris-(4'-methoxytrixenyl)-carbinol.—After 5 g. of bromoethoxybiphenyl, 1 ml. of diethyl carbonate, and 40 ml. of anhydrous thiophene-free benzene had been heated to boiling in a 1-liter, 3-necked flask provided with a reflux condenser and mechanical stirrer, 1 g. of sodium sand was added and the mixture was refluxed for two hours before cooling and decomposing with 10 ml. of methanol followed by 100 ml. of water. When the benzene had been evaporated on the steam-bath, the remaining volatile material was removed by steam distillation. After filtration, the ether soluble–petroleum insoluble material was obtained from the residue by extraction. It was crystallized once from xylene and ligroin and then twice from glacial acetic acid. After drying for two hours in a vacuum at 100° the bluish-white needles melted at 188–189°; yield 1 g. (27.5%).

Anal. Calcd. for $C_{40}H_{34}O_4$: C, 83.0, H, 5.88. Found: C, 82.5, 82.7; H, 6.04, 6.04.

Colorimetric Measurements.—Solutions were made by dissolving the carbinol in Mallinckrodt reagent grade of glacial acetic acid and diluting to the concentration (mol per liter) given in the tables. Sulfuric acid solutions were made from a standard solution prepared by dissolving C. P. concentrated acid whose normality had been measured in glacial acetic acid, and then diluting to the concentrations, normality per liter, recorded. Transmissions were measured in the Hardy color analyzer using a cell 1 cm. in thickness.

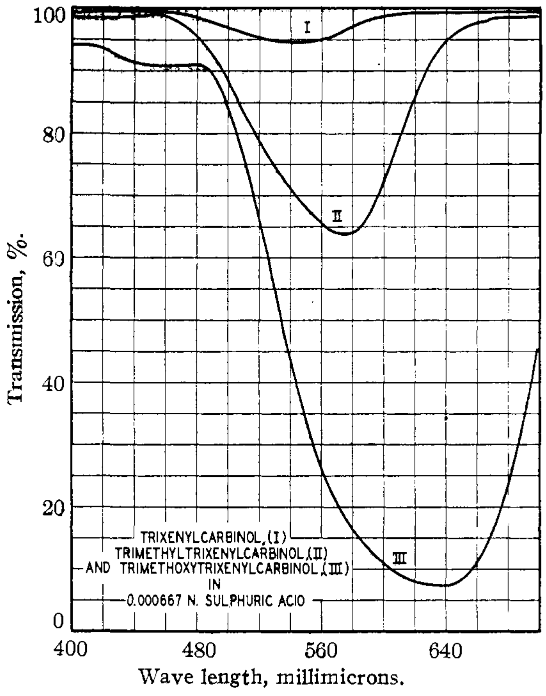

Fig. 1.

Conclusions

Trimethoxytrixenylcarbinol has been prepared by means of the sodium condensation synthesis for tertiary carbinols.

Judged by the appearance of color in a solution of sulfuric in acetic acid, the order of strength of carbonium bases in this series is trimethoxytrixenylcarbinol > trimethyltrixenylcarbinol > trixenylcarbinol > triphenylcarbinol.

CAMBRIDGE, MASS.

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[6] Bell, *J. Chem. Soc.*, 1071 (1930).