

## Synthesis of Novel N-Substituted Dimethylmaleimidyl Esters and Their Applications as Plasticizers for Poly(Vinyl Chloride)

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### Abstract

Three N-(hydroxyphenyl) dimethylmaleimides were directly prepared in good yields (81-86)% from the reaction of dimethylmaleic anhydride with amino phenols.

The prepared imides were esterified to the corresponding benzoates, methacrylates and cinnamates via their reaction with different acid chlorides in the presence of triethylamine.

The prepared esters were tested as plasticizers for PVC via preparing of thirty six samples of PVC with the prepared esters in certain weight ratio followed by recording their softening points. Comparison the results with the universal plasticizers for PVC (DOP) and (DBP) indicated that the prepared esters in general have high plasticizing efficiency.

### Introduction

The shortage of rubber in would war II produced an urgent need for new plasticizers, thus a rapid growth of plasticizer industry had started from that time. great number of plastisizers found wide applications with many polymers especially PVC(1-5), since PVC is unique in its acceptance of large amounts of plasticizers . Which caused gradual change in physical properties of PVC from rigid solid to flexible plastic which can be used in a wide variety of applications(6,7). In the present work nine novel N-substituted dimethylmaleimidyl esters are prepared via esterification of the corresponding N-(hydroxyphenyl) dimethylmaleimides by using different acid chlorides in the presence of triethylamine.

The new esters are tested as plasticizers for PVC plastic and in general they show high plasticizing efficiency.

### Experimental

1. Melting points were determined on Gallen Kamp Capillary melting point apparatus.

2. IR spectra were recorded on a Shimadzu FTIR 8000.

3. U.V spectra were recorded on Shimadzu UV-VIS recorder spectrophotometer UV-160.

4. Softening points were determined on Thermal Microscope Reichert Thermover, SP1, 160.

### 1-Preparation of N-(hydroxyphenyl) 2,3-dimethylmaleimides [1-3]

The titled compounds were prepared according to literatures(8,9) with minor modifications:

To a solution of (0.01 mole) of 2,3-dimethylmaleic anhydride in (25 ml) of acetone (0.01 mole) of ortho, meta or p-aminophenol dissolved in (25 ml) of acetone was added dropwise with stirring and cooling. After keeping it for overnight at room temperature the solvent was evaporated to dryness and the residue was dissolved in (10 ml) of chloroform followed by filtration. The imide was precipitated with petroleum ether b.p. (40-60)°C then purified by recrystallization from cyclohexane.

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Table (I) lists melting points, percent yields and spectral data of the prepared imides.

### 2- Preparation of N-dimethylmaleimidyl phenyl benzoates [4-6]

The titled compounds were prepared according to literature procedures<sup>(10,11)</sup> with some modifications:

In a suitable round bottomed flask fitted with a pressure-equalized funnel (0.01 mole) of N-(hydroxyphenyl)-2,3-dimethylmaleimide was dissolved in (40 ml) of dry acetone. (0.01 mole) of triethylamine was added to this solution followed by dropwise addition of (0.01 mole) of benzoyl chloride with stirring and cooling then stirring was continued for another (7 hrs) before filtration. The filtrate was evaporated under reduced pressure then residue was extracted with water and chloroform. The organic layer was dried and the solvent was evaporated to produce a brown oil which was recrystallized from petroleum ether b.p. (60-80)°C. physical properties and spectral data of the prepared benzoates are listed in Table (II).

### 3- Preparation of N-dimethylmaleimidyl phenyl methacrylates [7-9]

The titled compounds were prepared by the same procedure used in the preparation of benzoate esters [4-6] except using of methacryloyl chloride instead of benzoyl chloride.

The prepared esters were purified by recrystallization from petroleum ether b.p. (60-80)°C.

Physical properties and spectral data of the prepared methacrylate esters are listed in Table (III).

### 4- Preparation of N-dimethylmaleimidyl phenyl cinnamates [10-12]

The titled compounds were prepared by the same procedure used in the preparation of benzoate esters [4-6] except using of cinnamoyl chloride instead of benzoyl chloride.

The prepared esters were purified by recrystallization from petroleum ether b.p. (60-80)°C.

Physical properties and spectral data of the prepared cinnamates are listed in Table (IV).

### 5- Testing of The Prepared Esters as Plasticizers for PVC

Four samples from each ester were prepared by mixing and grinding a constant weight (1 gm) of PVC with four different weights of the prepared ester (plasticizer) (0.1, 0.2, 0.3 and 0.4 gm) respectively. Slides were prepared from the thirty six plasticized samples then softening points were recorded on (Thermal Microscope) apparatus.

The same manner was applied using (DOP) and (DBP) plasticizers. The results were used for comparison. All results are listed in Table (V).

### Results and Discussion:

In continuation of our research program directed towards the synthesis of novel imidyl esters having high plasticization efficiency for PVC, a new series of dimethylmaleimidyl esters including benzoates, methacrylates and cinnamates have been prepared.

Preparation of three N-(hydroxyphenyl)-2,3-dimethylmaleimides by condensation of 2,3-dimethylmaleic anhydride with ortho, meta and p-aminophenols.

Literatures<sup>(10, 11)</sup> revealed that this reaction proceeds by the one step mechanism and the cyclic imide was formed under elimination of water after

mixing of amine with anhydride in acetone for (24 hrs.).

The second step includes esterification of the prepared imides [1-3] to the corresponding benzoates, methacrylates and cinnamates respectively via treatment with benzoyl, methacryloyl and cinnamoyl chlorides in the presence of triethylamine.

IR spectra of the prepared imides revealed a clear strong absorption band in the region  $(3317-3332)\text{cm}^{-1}$  which was assigned to stretching vibration of phenolic  $(\text{OH})^{(12)}$ , while this band was not observed in IR spectra of the prepared esters.

The absence of this band in IR spectra of the prepared esters and presence of new absorption bands at  $(1722-1786)\text{cm}^{-1}$  and  $(1130-1207)\text{cm}^{-1}$  which were attributed to ester  $(\text{C}=\text{O})$  and ester  $(\text{C}-\text{O})$  respectively are good proofs for the success of esterification reaction.

On the other hand U.V. spectra of the prepared esters revealed absorptions at wave lengths  $(290-310)\text{nm}$  which attributed to  $(\pi \rightarrow \pi^*)$  transitions in benzene ring which was in conjugation with both maleimidyl ring and the attached benzoate, methacrylate or cinnamate groups.

Tables (I-IV) list physical properties and spectral data of the prepared compounds while Figures (1-6) Show IR and U.V. spectra for some of them. The final step of this work involved testing the

ability of the prepared esters for plasticization of PVC.

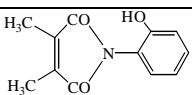
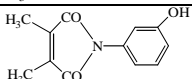
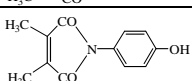
Thirty six samples were prepared. The softening points were recorded the results indicated that the prepared esters caused a clear depression in PVC softening point and the depression increased with increasing of plasticizer concentration.

The incorporated plasticizer in a polymer have many points of attachment along the polymer chains through the formation of secondary molecular forces between its molecules and polymeric chains especially when there is a good compability between them and this will mask the centers of forces for polymer-polymer intermolecular attraction and this decrease the orientation of the crystalline phase which inturn reduced modulus, softening points and tensile strength with increasing of elongation and flexibility<sup>(13-15)</sup>.

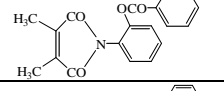
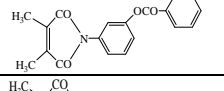
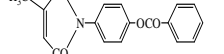
Plasticization efficiency of the prepared plasticizers were tested by comparison the results with (DOP) and (DBP) the universal plasticizers for PVC.

The results indicate that all the prepared esters are good plasticizers for PVC and they are more efficient than both (DOP) and (DBP). All the results of this study are listed in Table (V) and softening curves of the prepared esters are shown in Figures (7-9).

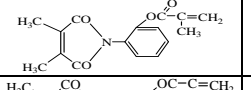
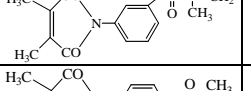
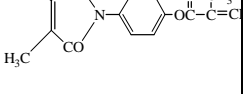
**Table (I) Melting points, Percent yields and spectral data of dimethylmaleimides**

Comp. No.	Compound structure	Yield %	Melting point °C	U.V $\lambda_{\text{max}}$	Major IR absorptions, $\text{cm}^{-1}$		
					$\nu\text{O}-\text{H}$ phenolic	$\nu\text{C}=\text{O}$ Imide	$\nu\text{C}-\text{N}$
1		86	150-151	285	3317	1697	1404
2		85	128-129	284	3332	1697	1396
3		81	166-168	285	3323	1687	1411

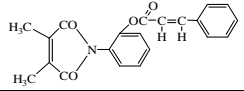
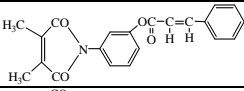
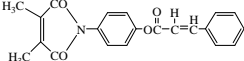
**Table (II) Melting points, Percent yields and spectral data of N-dimethylmaleimidyl phenyl benzoates**

Comp. No.	Compound structure	Yield%	Melting point °C	U.V $\lambda_{\max}$	Major IR absorptions, $\text{cm}^{-1}$		
					$\nu\text{C}=\text{O}$ Ester	$\nu\text{C}=\text{O}$ Imide	$\nu\text{C}-\text{O}$ Ester
4		84	108-110	290	1772	1705	1145
5		87	98-99	295	1758	1695	1190
6		89	112-114	291	1786	1701	1172

**Table (III) Melting points, Percent yields and spectral data of N-dimethylmaleimidyl phenyl methacrylates**

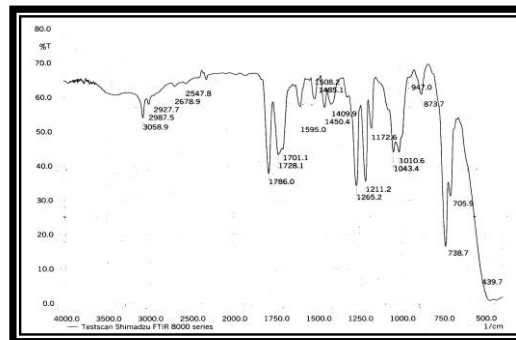
Comp. No.	Compound structure	Yield%	Melting point °C	U.V $\lambda_{\max}$	Major IR absorptions, $\text{cm}^{-1}$		
					$\nu\text{C}=\text{O}$ Ester	$\nu\text{C}=\text{O}$ Imide	$\nu\text{C}-\text{O}$ Ester
7		85	Oil	300	1760	1712	1142
8		90	Oil	305	1760	1704	1195
9		73	oil	310	1762	1704	1188

**Table (IV) Melting points, Percent yields and spectral data of N-dimethylmaleimidyl phenyl cinnamates**

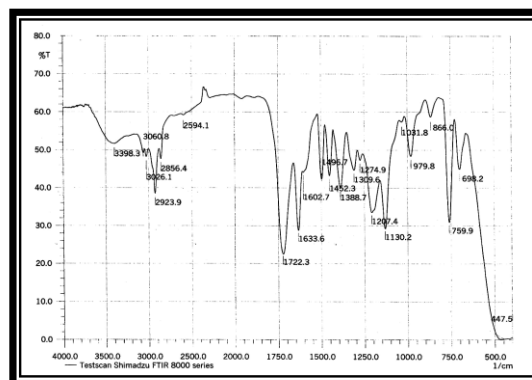
Comp. No.	Compound structure	Yield %	Melting point °C	U.V $\lambda_{\max}$	Major IR absorptions, $\text{cm}^{-1}$		
					$\nu\text{C}=\text{O}$ Ester	$\nu\text{C}=\text{O}$ Imide	$\nu\text{C}-\text{O}$ Ester
10		70	Oil	291	1725	1650	1200
11		74	58-60	290	1722	1634	1130 1207
12		82	71-72	291	1728	1650	1180

**Table (V) Effect of different weight ratios of plasticizers on PVC softening point**

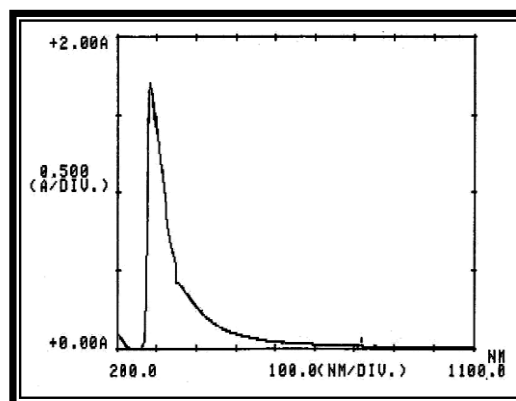
Comp. No.	Weight ratio of plasticizer to (1gm) of PVC	Softening point °C
4	0.1	120-136
	0.2	115-122
	0.3	105-114
	0.4	92-102
5	0.1	132-148
	0.2	124-135
	0.3	113-120
	0.4	107-115
6	0.1	140-148
	0.2	129-141
	0.3	121-133
	0.4	116-122
7	0.1	145-165
	0.2	135-141
	0.3	127-136
	0.4	113-120
8	0.1	151-167
	0.2	139-148
	0.3	128-140
	0.4	117-127
9	0.1	155-168
	0.2	140-151
	0.3	126-137
	0.4	114-125
10	0.1	160-171
	0.2	147-155
	0.3	130-141
	0.4	110-120
11	0.1	165-177
	0.2	150-160
	0.3	133-148
	0.4	117-127
12	0.1	130-136
	0.2	119-128
	0.3	108-116
	0.4	95-105
DOP	0.1	185-210
	0.2	175-195
	0.3	160-180
	0.4	150-170
DBP	0.1	185-208
	0.2	180-195
	0.3	165-187
	0.4	150-170



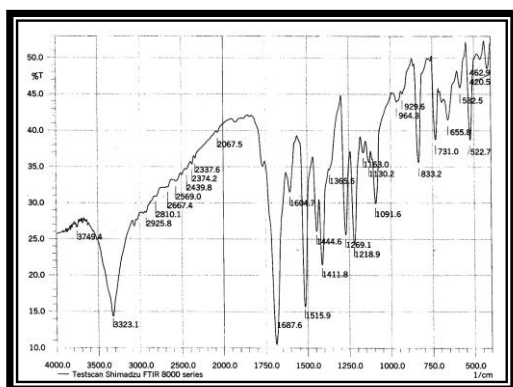
**Fig.(2) IR spectrum of compound [6]**



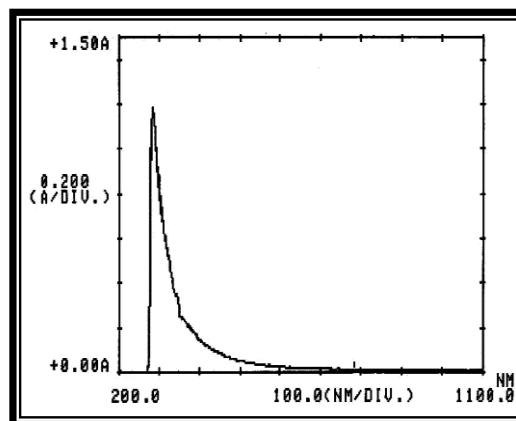
**Fig.(3) IR spectrum of compound [11]**



**Fig.(4) U.V. spectrum of compound [5]**



**Fig.(1) IR spectrum of compound [3]**



**Fig.(5) U.V. spectrum of compound [9]**

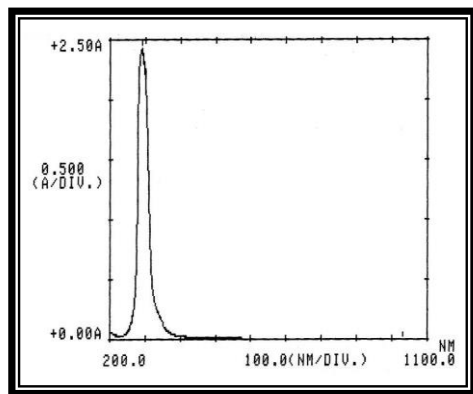


Fig.(6) U.V. spectrum of compound [12]

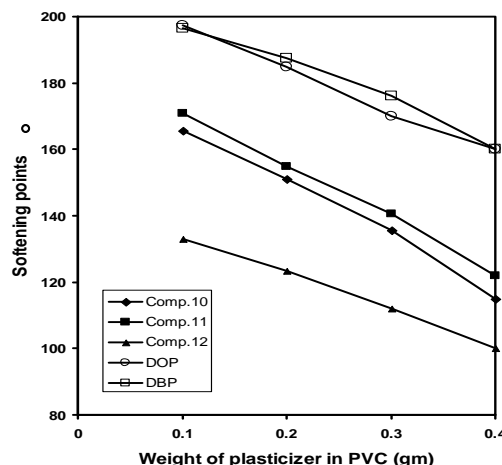


Fig.(9): Softening curve of cinnamate esters compared with (DOP) and (DBP)

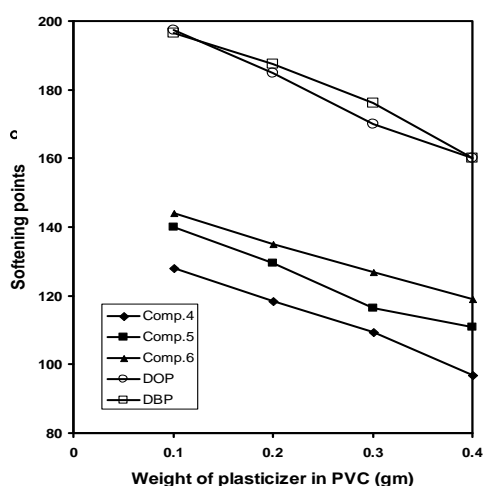


Fig.(7): Softening curve of benzoate esters compared with (DOP) and (DBP)

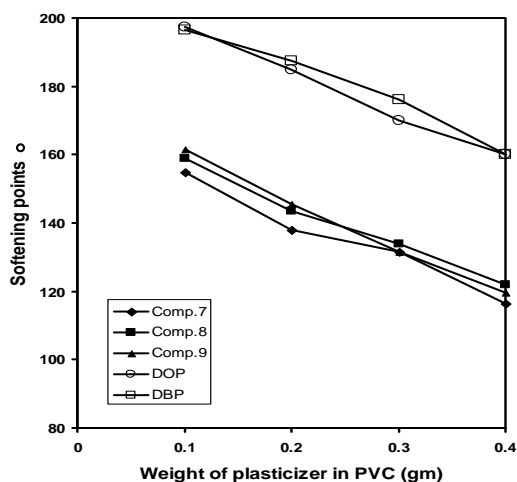


Fig.(8): Softening curve of methacrylate esters compared with (DOP) and (DBP)

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## تحضير استرات N- معوض ثنائي مثيل مالي ايميديل جديدة وتطبيقها كملدنات لبولي (كلوريد الفايثيل)

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### الخلاصة:

تضمن البحث تحضير ثلاثة من مركبات N-(هيدروكسي فنيل) ثنائي مثيل مالي ايميدات بمنتوج جيد (81-86%) وذلك من خلال تفاعل ثنائي مثيل انهيدريد الماليك مع مركبات امينو فينول. ادخلت الايميدات المحضرة في تفاعل استرة لغرض تحويلها الى استرات البنزوات، الميث اكريلات والسينامات المقابلة وذلك من خلال تفاعلها مع كلوريدات حوامض مختلفة بوجود ثلاثي اثيل امين. تم اختبار قابلية الاسترات المحضرة على تلدن PVC وذلك من خلال اعداد ستة وثلاثون نموذج من PVC مع الاسترات المحضرة وفق نسب وزنية محددة ثم قياس درجات التلدن لجميع هذه النماذج. اوضحت المقارنة بين النتائج المستحصلة مع النتائج في حالة استخدام الملدنات العالمية لبولي كلوريد الفايثيل وهما (DOP) و (DBP) على التوالي بان الاسترات المحضرة عموماً ذات كفاءة عالية في تلدن PVC.