

Study on 1-4 Cycloaddition Reaction. I. Synthesis and Optimization of New Adduct Using Diels–Alder Reaction

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ABSTRACT: The present investigation has been achieved in accordance with the Diels–Alder reaction (1,4 cycloaddition) to produce a new halogenated bicyclic adduct. *ortho*-Bromoallylbenzoate is a new dienophile that was prepared in a pure form, and its structure was confirmed. The Diels–Alder syntheses of hexachlorocyclopentadiene and the new dienophile were studied to determine the optimum condensation reaction conditions under a temperature range of 90–160°C, reaction times of 1–8 h, and molar diene/dieno-

phile ratios from 1:1 to 5:1 as a consequence. The optimum conditions reached were a temperature of 140°C, an initial diene/dienophile molar ratio of 3:1, and a duration time of 6 h. The maximum stoichiometric yield under these optimum conditions (82.5%) was obtained. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2331–2338, 2003

Key words: halogenation; IR spectroscopy; NMR; esterification

INTRODUCTION

The use of the Diels–Alder reaction for the synthesis of a six-membered ring system has served as the basis for the design of a large number of efficient syntheses.^{1–3} In this reaction cycloienes are reacted with dienophiles and form adducts simply by mixing the components at room temperature or by gentle warming. However, in cases with either unreactive dienes or dienophiles more vigorous conditions may be necessary.^{4,5} The Diels–Alder reaction is reversible and many adducts dissociate into their components at quite a low temperature.^{3,5} In these cases better yields are obtained by using an excess of one of the reactants or a solvent from which the adduct readily separates.³ Although cyclopentadiene is more reactive than an acyclic diene in which the double bonds are constrained in a planar cisoid form, Veliev and Guseinov found that its fully chlorinated derivative, hexachlorocyclopentadiene (HCP), can add to certain dienophiles under certain conditions.⁶ It was found that HCP readily adds to the olefinic bonds of the conjugated system, for example, maleic anhydride and acrylonitrile. Similarly, HCP condenses with allylic dienophiles and halogenated olefins only at elevated temperatures.^{5,6}

Comparative studies were carried out in order to compare the reaction reactivities of halogenated dienophiles that undergo a reaction with HCP.⁷ It is

concluded that halogenated dienophiles undergoing a reaction with HCP under the described conditions must have at least one hydrogen atom on each of the double bonded carbons.⁸

Because of the great importance of Diene synthesis in industry,^{7–9} we had to continue the work conducted in previous studies. Thus, the aim of this work is to produce a new bicyclic adduct containing a halogen atom and allyl-ester group, which may be used to improve numerous industrial materials.

EXPERIMENTAL

Materials

The HCP (diene) details are as follows: boiling point = 239°C/753, density at 25°C = 1.7179 mL, molecular weight = 272.7 g, viscosity at 35°C = 5.04 cP, and n_D^{25} = 1.5626.

Methods

IR spectroscopy

The IR spectrum was carried out was carried out at the Egyptian Petroleum Research Institute using a FTIR spectrometer at wavelengths of 500–4000 cm^{-1} and a transmittance of 20–100%.

NMR measurements

Proton NMR spectra were measured in deuterated CH_3Cl containing tetramethyl silane as an internal

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standard and recorded on a Varian EM-390 90-MHz NMR spectrometer at Cairo University.

Thin layer chromatography

A 0.25-mm layer of silica gel (30 g with 60 mL H₂O) was spread over a 20 × 20 cm glass plate, and 100 mL of hexane-acetone (1:1) solvent was used in a Shardon TM chromatography tank. The dimensionless R_f value is calculated using experimental data from the following ratio⁷:

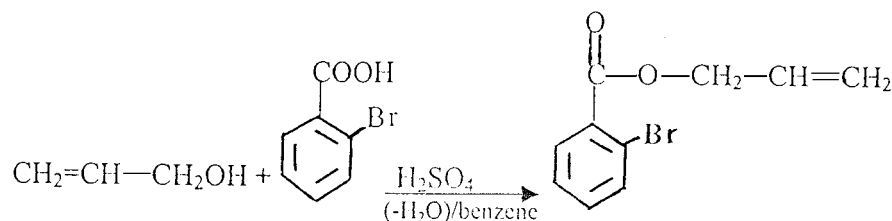
R_f

$$= \frac{\text{distance of compound from origin to center of spot}}{\text{distance from origin line to front origin}}$$

Elemental analysis

The elemental analysis was carried out at Cairo University Microanalytical Center, Giza, Egypt.

Synthesis of *o*-bromoallylbenzoate



A mixture of about 0.5 mol of *o*-bromobenzoic acid,⁸ about 2.5 mol of absolute allyl alcohol, concentrated sulfuric acid, and benzene as a solvent were put in a three-necked round-bottom flask in a water bath. The flask was attached to a trap for removing water (Dean-Stark) and a thermometer.

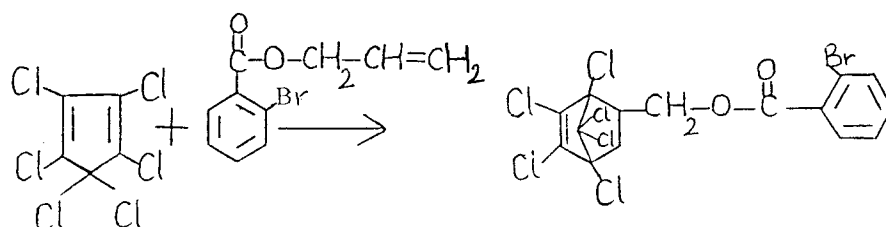
The mixture was kept at 80–85°C for several hours so that all the proposed quantity of water was removed from the reaction mixture. The product was cooled, washed several times with cold water, and then washed several times with a dilute sodium bicarbonate solution. This ester solution was dried by an-

hydrous magnesium sulfate and filtered, and all the undesirable materials were distilled off. The new ester was collected at 160°C at 15 mmHg with a 48–50% yield by weight.

The new ester has the following properties: average molecular weight = 239.43 g (theor. = 240.98 g); color: yellowish brown crystals; melting point = 148–150°C; solubility: soluble in CCl₄ and xylene (cold), ether and benzene (hot), not soluble in H₂O.

The IR spectra and the elemental analysis of the proposed ester are given in Figure 1 and Table I, respectively.

Synthesis of (1,2,3,4,7,7) hexachloro-5-(*o*-bromomethylbenzoate)-bicyclic (2,2,1) heptene-2



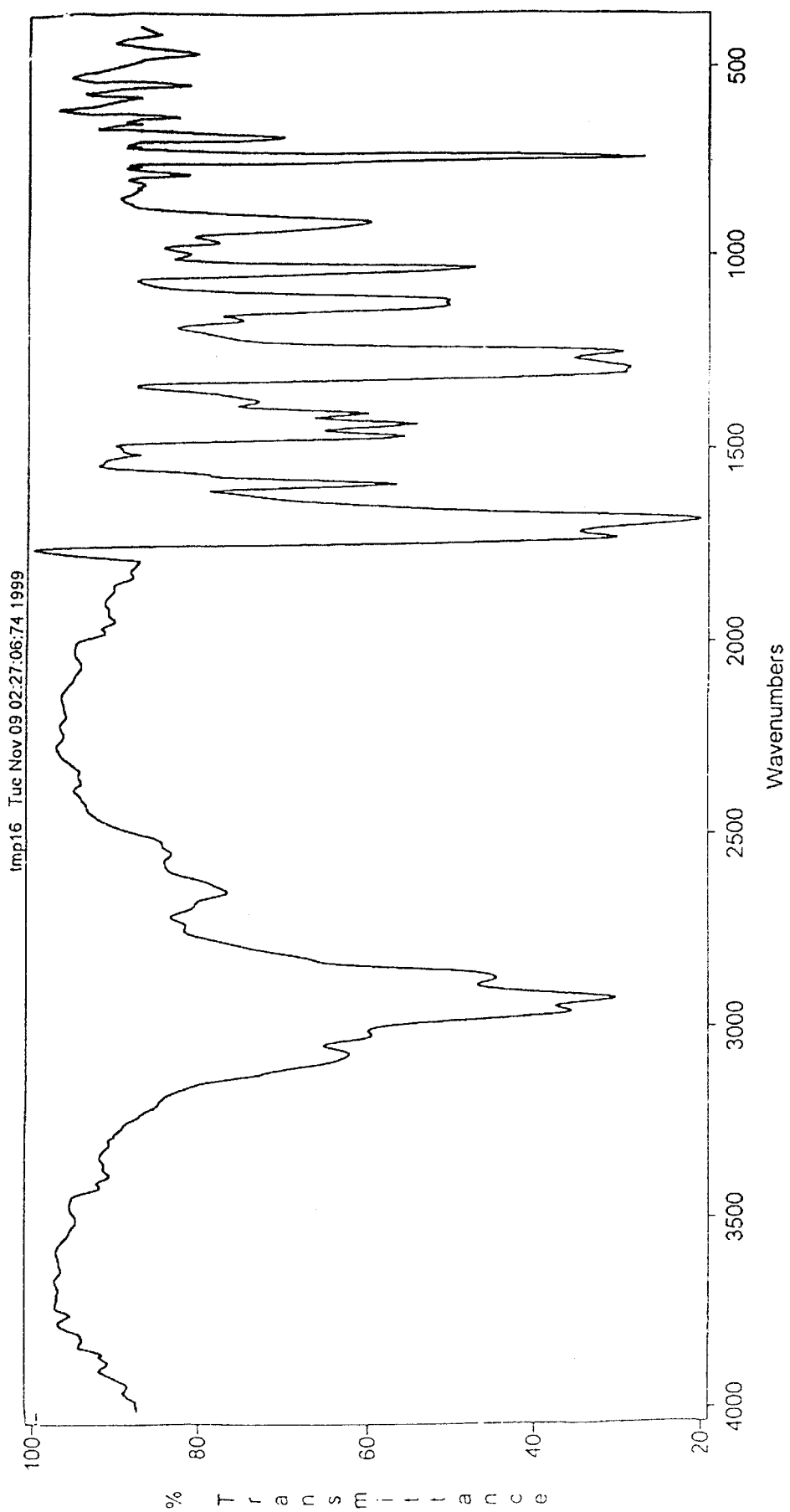


Figure 1 The IR of *o*-bromoallylbenzoate.

TABLE I
Elemental Analysis of Proposed Dienophile and Adduct

Compound	Element			
	C		H	
	Theor. (%)	Found (%)	Theor. (%)	Found (%)
Ester (dienophile)	50.00	51.50	3.75	4.90
Adduct	35.01	35.92	1.75	1.74

The reaction takes place through the following steps⁸:

1. A blend of 0.75 mol of HCP and 0.25 mol of dienophile (*o*-bromoallylbenzoate) is made. A 3:1 ratio of the reactants is mixed together in a dry test tube, which is tightly closed and put into an oil bath at a fixed temperature of 140°C and a fixed duration time of 6 h.
2. The tube is then cooled and opened. The weight of the adduct is determined after separation of the unreacted materials using subatmospheric pressure (20–32 mmHg).
3. The adduct is then purified by recrystallization using DMF.
4. The same procedure is repeated with another new test tube at each 10°C interval rise of the temperature of the reaction from 90 to 160°C.
5. The previous reactions take place without using solvents or catalysts.
6. In order to determine the optimum conditions at which the maximum yield is obtained, the previous trend is repeated to study the effect of the variation of molar ratios of the diene/dienophile from 1:1 to 5:1 at a fixed temperature of 140°C and a fixed duration time of 6 h and a fixed molar ratio of 3:1 diene/dienophile at a fixed temperature of 140°C and a duration time of 1–8 h.

By studying the preceding factors (temperature, molar ratio, and time), the optimum conditions are achieved as given in Tables II–IV.

The structure of the new pure adduct was confirmed by the average molecular weight of 514.2 g, the IR spectra (Fig. 2), ¹H-NMR analysis (Fig. 3), and elemental analysis (Table I).

TABLE II
Effect of Temperature on Diels–Synth of HCP with *o*-Bromoallylbenzoate

	Temp. (°C)							
	90	100	110	120	130	140	150	160
Yield (wt %)	28.3	42	58.1	67.8	77.8	82.5	78	71.6

Fixed criteria: the molar ratio of diene dienophile is 3:1 and the reaction time is 6 h.

TABLE III
Effect of Reaction Time on Diels–Synth of HCP with *o*-Bromoallylbenzoate

	Reaction Time (h)							
	1	2	3	4	5	6	7	8
Yield (wt %)	30.5	47.6	60.5	70	77.2	82.5	82	82.1

Fixed criteria: 140°C and a diene dienophile molar ratio of 3:1.

The synthesis of bicyclic compounds containing substituents such as halogen atoms, ether, ester groups, and aromatic rings could be considered as a basic rule for the production and improvement of many synthetic materials.^{7,8} HCP and its derivatives are very interesting materials to use for these purposes.

The success of such considerations is of importance in studying this related research, which seeks to prepare a new allylic halogen ester to synthesize a new halogenic bicyclic adduct. This could open a promising field for future development.

RESULTS AND DISCUSSION

Determination of optimum reaction conditions: effect of reaction temperature

The study of the effect of temperature on the product yield was carried out at 90–160°C at a fixed reaction time of 6 h and a fixed reactant ratio of 3:1 diene (HCP)/dienophile (*o*-bromoallylbenzoate). Figure 4 shows that the product yield increases with increasing temperature up to 140°C, at which a maximum yield of 82.5 wt % was obtained (Table III). Studies show that the adduct formation is a combination or association reaction in which new bonds are involved.^{3,4} These bonds need heating to be activated. The optimum temperature for this activation seems to be 140°C. From Table II it is found that the yield percentage obtained at 100°C is about 40% of that of the theoretical yield under the same conditions (6-h reaction time, 3:1 diene/dienophile molar ratio). Raising the reaction temperature from 120 to 140°C, it was found that the actual yield was increased, but not greatly. Above 140°C, the actual yield gradually decreased. This indicates that raising the temperature

TABLE IV
Effect of Molar Ratio Diene/Dienophile on Diels–Synth of HCP with *o*-Bromoallylbenzoate

	Molar Ratio Diene/Dienophile				
	1:1	2:1	3:1	4:1	5:1
Reactants (g)	12.82	19.64	26.46	33.28	40.1
Yield (wt %)	35	61.5	82.5	82	82

Fixed criteria: 140°C and a duration time of 6 h.

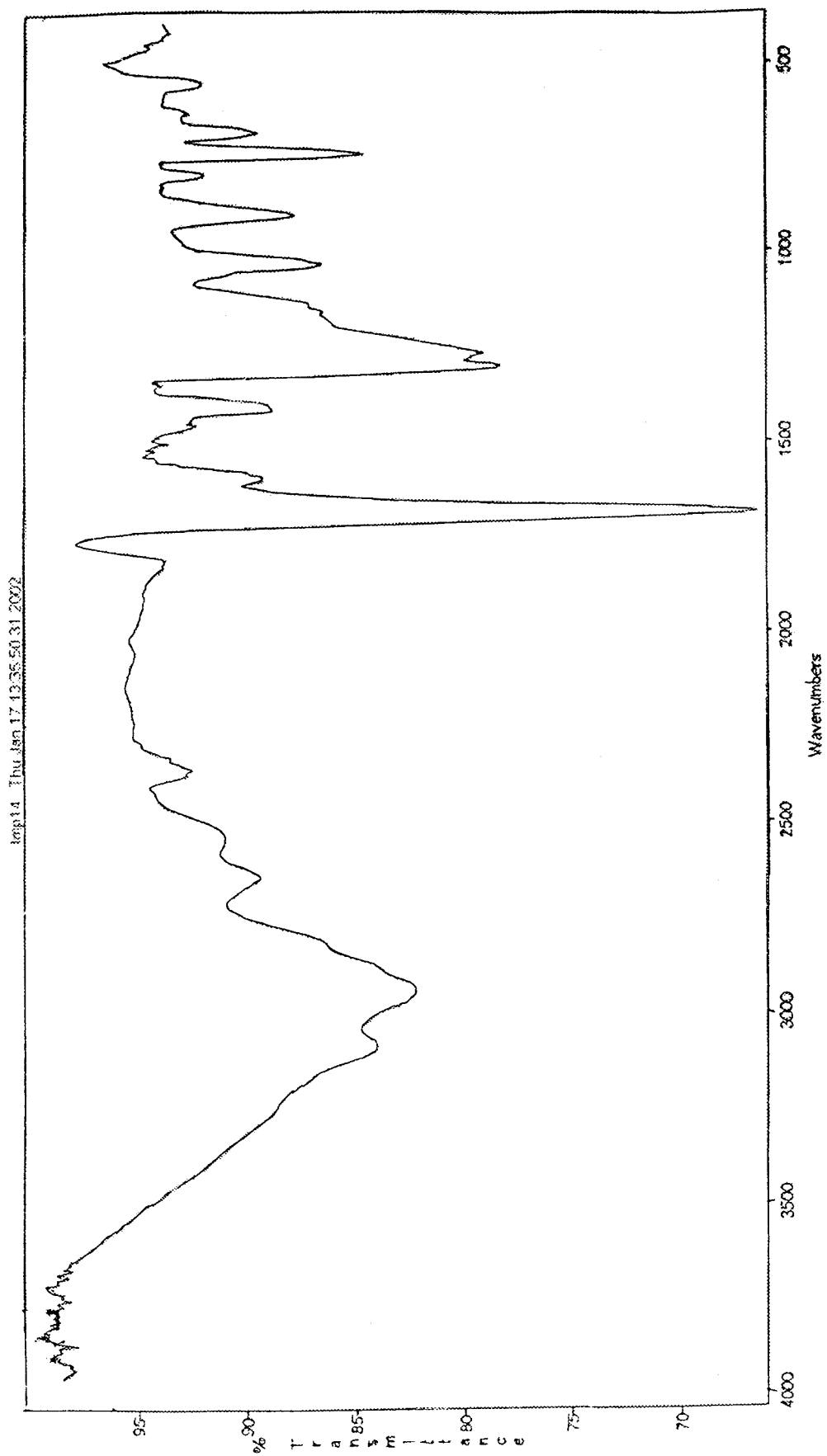


Figure 2 The IR of the adduct.

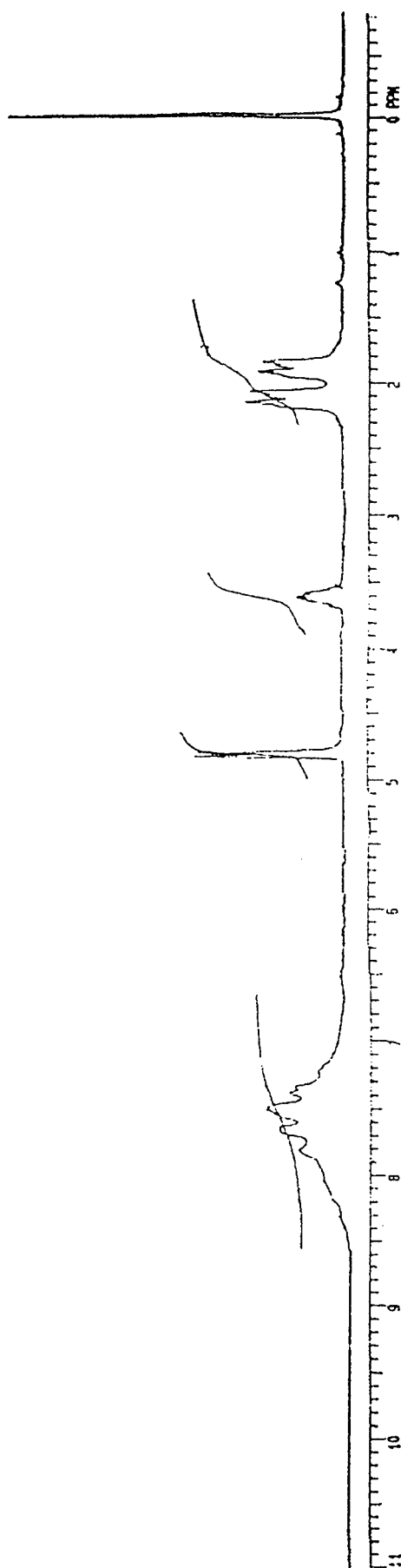


Figure 3 The NMR spectrum of the adduct.

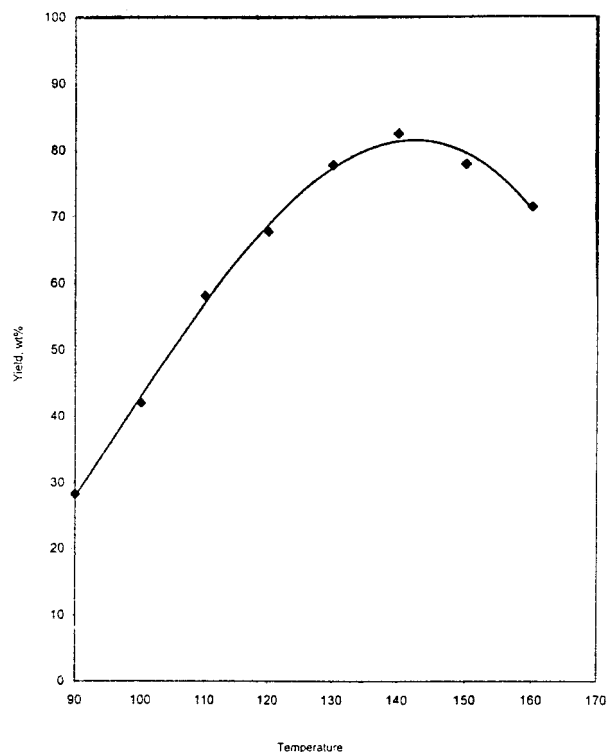


Figure 4 The effect of the temperature on the Diels-Synth of HCP with *o*-bromoallylbenzoate.

accelerates the reversible reaction,^{3,4} yet it still accelerated the adduct formation; hence, the actual yield percentage was steadily slowed down. Further increasing the temperature sharply decreases the yield percentage. This may be due to the formation of by-products.^{8,10-12}

Effect of reaction duration

The effect of the reaction time on the product yield was studied over 1–8 h with a fixed 3:1 reactant ratio of diene/dienophile and a fixed reaction temperature of 140°C (Table III). In the first hour a very active reaction (about 30% of the theor. yield) was obtained. Under these conditions there is much concentration of the diene and enough dienophile to proceed with the reaction.

Figure 5 shows that, at an interval of 4–6 h, the yield increases with the increase of the reaction time but slowly. Under these conditions there is a decrease in the concentration of the dienophile and the reaction medium, and the diene concentration is always present in excess. This indicates a pseudo-first-order reaction with respect to the dienophile.

A further increase in the reaction time above 6 h has no effect on the product yield. This may be due to formation of side reactions.^{8,10-12}

Effect of initial molar ratio

The effect of the reactant ratio (diene/dienophile) on the product yield was studied over the range of 1:1–5:1

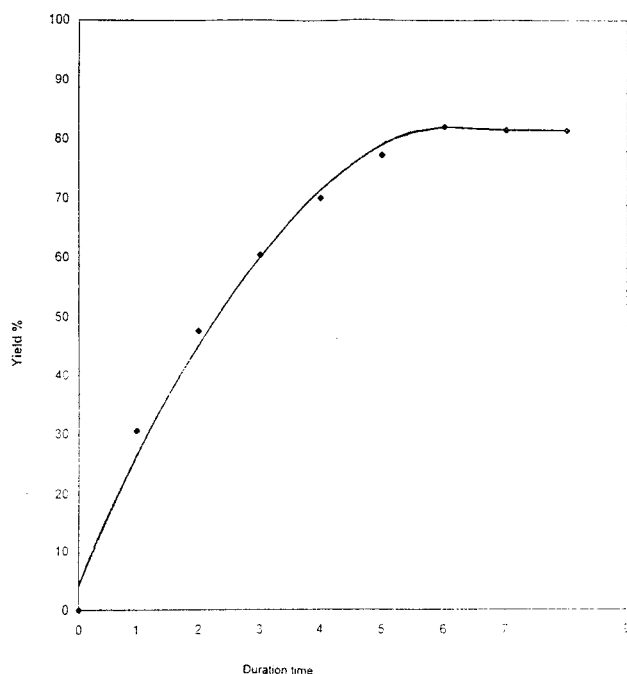


Figure 5 The effect of the reaction time on the Diels-Alder reaction of *o*-bromoallylbenzoate.

molar ratios with a fixed reaction time of 6 h and a reaction temperature of 140°C (Table IV). It was found that, at an equimolar ratio of the reactants (1:1), about 35% of the theoretical yield was obtained. When doubling the initial molar concentration, about 60% of the yield was obtained. The maximum yield of 82.5% was achieved at a 3:1 ratio of diene/dienophile (Fig. 6). It could be concluded that the excess diene in the reaction medium increases the rate of the reaction. A further excess of the concentration of diene has no effect on the rate or the yield of the reaction.^{8,10-12}

The diene synthesis of HCP and *o*-bromoallylbenzoate is a Diels-Alder reaction, the reaction is exothermic, and it takes place under pressure and without using any solvent.

The new dienophile (*o*-bromoallylbenzoate) was prepared and characterized by its average molecular weight and by IR. The Figure 1 absorbance could be due to *o*-aromatic disubstitution at 750 cm⁻¹; the allylic ester structure at 1125–1200 cm⁻¹; the carbonyl group at ~1700–1730 cm⁻¹; the terminal double bond at ~1910 cm⁻¹; and the aromatic C–H, C=C, and C–Br at about 3020, 1588, and 650–740 cm⁻¹, respectively.

The new adduct was confirmed by its average molecular weight and by elemental analysis (Table I). The IR spectrum of the adduct gave the transmission absorbances that are attributable to carbon halogens (stretching) at 580–700 cm⁻¹; ester C=O (stretching vibration) at 1680 cm⁻¹; aromatic C=C and C–H (stretching vibrations) at 1500–1600 and 2940 cm⁻¹, respectively; and ortho disubstituted aromatic at 740 cm⁻¹.

The ¹H-NMR spectrum of the new proposed adduct is presented in Figure 3. The presence of peaks was observed at δ 1.8–2.2 ppm (doublet of doublet) and δ 3.5–3.8 ppm (multiple) due to the bicyclic protons. This indicated that the reaction between the diene and dienophile was carried out and a bicyclic compound formed as a Diels-Alder reaction (1-4 cycloaddition). The ¹H-NMR peaks at δ 4.6–4.8 ppm (doublet) and δ 7.0–8.3 ppm (multiple) were due to protons of CH₂O and the ortho aromatic disubstitutions, respectively.

The optimum conditions for the diene synthesis of HCP and *o*-bromoallylbenzoate at which the maximum yield represents 82.5% of the possible stoichiometric yield are a diene/dienophile molar ratio of 3:1, a reaction time of 6 h, and a reaction temperature of 140°C.

From the study of the chemical structure of the new adduct, it could be seen that the bromine atom in the dienophile molecule is a deactivator substituent, which has both mesomeric and inductive effects (+M and –I), but the inductive effect predominates. Thus, its –I decreases the electron density on the terminal olefinic double bond, thereby increasing the reactivity of the dienophilic olefin. In addition, the presence of 6 chlorine atoms in the diene molecule decreases the electron density on its double bonds.¹³ At the same time the presence of the bromine atom at the ortho position in the dienophile molecule has a great steric effect. All these limiting conditions explain the difference of the yield in this work from others,¹¹ although

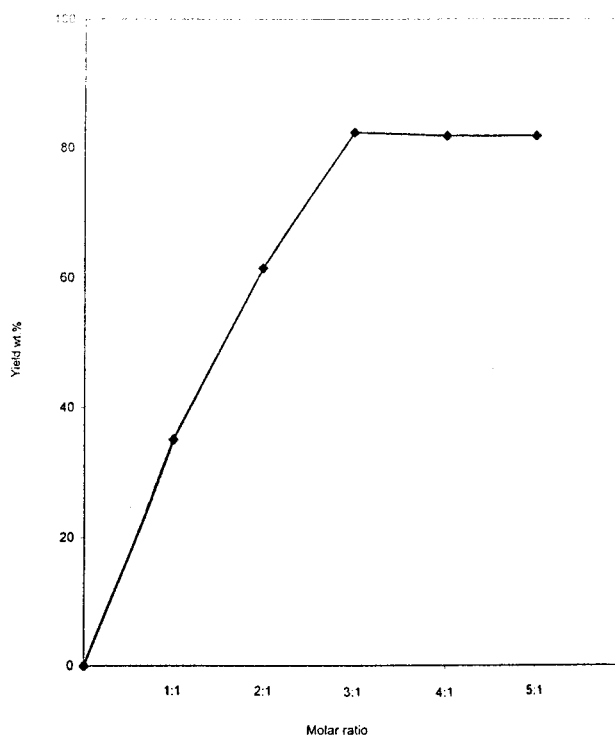


Figure 6 The effect of the molar ratio of HCP with *o*-bromoallylbenzoate.

all the dienophiles are of the same allylic structure. This means that the kinds and positions of the substituents in the dieneophilic molecules have a great influence on the electron density of the terminal alkenyl double bonds and therefore on the reactivity of the dieneophilic olefin. This is in concordance with several studies.^{4,8,11}

The presence of a high percentage of halogen atoms in the new bicyclic adduct can be used in the future as a fire retarding modifier for many polymeric materials.

CONCLUSION

The following conclusions were drawn from the results of this study.

1. A new dienophile (*o*-bromoallylbenzoate) was prepared and its structure was confirmed.
2. The condensation reaction of HCP with *o*-bromoallylbenzoate was studied as a Diels–Alder 1,4-cycloaddition reaction.
3. The reaction was exothermic and took place without using a catalyst or solvent.
4. The structure of the new adduct was confirmed.
5. The optimum conditions at which the maximum yield (82.5%) obtained were found to be a temperature of 140°C, a 3:1 molar ratio of diene/dienophile, and a duration time of 6 h.
6. The kind and position of the dienophilic molecule play a great role in the maximum yield.

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