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Synthesis of Some 2,4-Hexadiyne and their Polymers

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Abstract

Diacetylene monomers 2, 3 and 4 were synthesized using Hay coupling procedure. They subjected to γ-ray irradiation resulted into polymer formation compound (8) while compounds (3a-c) were unsuccessful towrd topochemical polymerization. The corresponding acid chloride compound (5) was then condensed with diamine affording polyamide 6 and 7. The above symmetrically substituted 1,3-diynes together with their polymers have been characterized by combination of spectral methods IR,^{1}H NMR, C^{13}NMR and are discussed.

الخلاصة

يتضمن البحث تحضير عدد من المركبات ثنائية الاستيلين وقد جرى تعريض هذه المركبات (والتي تمثل مونومرات) لاشعة كاما حيث تحول المركب (4) الى البوليمر المقابل بينما لن تنتج المركبات (3a-c) بسبب عدم توفر ظروف البلمرة بسبب تركيب هذه المونومرات الذي لا يتيح لها من الترتيب بشكل بلوري ترتيبا مناسبا لتقنية البلمرة بالحالة الصلبة. كما تضمن البحث تحضير بولي اميدات (المركبات 6 و 7) عن طريق تقنية البلمرة التكثيفية وتم تشخيص المركبات اعلاه من خلال اطياف الـ ^{1}HNMR و ^{13}CNMR و IR.

Introduction

It was established that for diacetylene to undergo polymerization, the molecules in the parent monomer crystal packed in a ladder like fashion (Fig.l), such that the ends of one triple bond system are separated from an adjacent triple bond system by a distance (D) <0.4 nm. Polymerization occurs by the successive tilting of each molecule along the ladder, with the minimum of movement of all atoms from their lattice sites. An additional requirement is that the angle (9) between the diacetylene rod and the translational axis is approximately 45. These requirements were developed as a " least motion principle" which maintains the mode of parcting of the side groups R, the specific volume and the lattice symmetry throughout the reaction (2).

The chain repeat distance (Ca 4.9) and the bond length together with angles of the polymer backbone were found similarly(3) . It was found that substituted diacetylene may have as many as five different modifications of which only one may have the desired reactivity (4). Since no theory or predictive aid has been produced for the identification of which packing modes and conditions lead to reactivity for a given molecule, the development of suitable polymerizable monomers has been left to the intution of the experimental chemist(6).

There is a limited work in the literature for the polycondensation reactions of diacetylen compounds(7,8) so poly amides 6 and 7 were prepared in this work as new poly 2,4-hexadiyne-l,6-diamides.

The importance of polydiacetylene syntheses comes from the brood applications in industry and medicine, Among the industrial applications are the use of diacetylene polymers as Time-Teperature indicators(9) , Photographic and photocopying formulations(10),Ultrafast light sharpener(11) and other optical applications(12,13).The meantime medical applications of polydiacetylenes are associated with designing a usable biosensors for detection and recognition of the more important biological events like dibetic, influenza virus and other microbial infection associated with lipids and peptides in humanbeing(14 -1 9).

Experimental

The IR spectra were recorded on Perkin Elmer 580 and 1600 instruments ^{1}HNMR spectra were recorded on Bruker WP 200 (200.13 MHz) spectrometer. C^{13} NMR were recorded on a Bruker WP 200 (50.323 MHz) spectrometer at Heriot-Watt University Edinburgh, U.K. Hetachi R-24 spectrometer of the Chemistry Department , Mosul University was also used in ^{1}HNMR measurements.

Compound (2) was prepared according lo previous work [(20)]. Melting points were measured using Electrothermal type 9300 instrument.

Preparation of 2, 4-hexadiyne-l, 6-bis phenylacetate (3a)

Phenyl acetyl chloride (3.0 gm., 0.02 mol.) was added to a solution of 2,4-hexadiyne -1,6-diol (1.1 gm., 0.01 mol.) in dry benzene (10 ml) with stirring. The mixture was then refluxed for 4 h. and the reaction quenched by pouring the mixture into water (80 ml). The organic layer was extractedwith benzene(2x20 ml). The combined organic fractions were washed with 5% sodium carbonate solution (5 ml) then with water (5 ml), followed by drying over anhydrous magnesium sulphate. After removal of most of the solvent the mixture was chromatographed on silica gel, eluting with 80/20 mixture of 40-60 petroleum ether/ether). To this solution small amount of 40-60 petroleum ether was added to initiate the crystallization and stored in cold box for 12 h. A white crystals of compound (3 a) was obtained (60% yield), m.p. 52 °C.

Preparation of 2, 4-Hexadiyne-l, 6-bis salicylate (3b)

Salicoyl chloride was prepared according to the well known procedure , 2,4-hexadiyne-l,6-diol (3.3 g, 0.03 mol.) was dissolved in dry benzene (50 ml.), salicoyl chloride (9.0 g, 0.06 mol) was then added. The reaction mixture was refluxed for 3h. Then it was left to stand for 12h. The solvent was evaporated and the final product was crystallized from water / acetone gave yellow crystals of 2,4-hexadiyne-l,6-disalicylate (3b), 80% yield, mp 78-80 °C.

Preparation of 2, 4-hexadiyne-l, 6-diacetate (3c)

Acetyl chloride (1.6 g, 0.02 mol.) was condensed with 2,4-hexadiyne-1,6-diol (1.1 g., 0.01 mol.) in a a similar procedure as before . Recovery of2,4-hexadiyne-l,6-diacetate was affected by distillation (105 °C, 3 Torr) to yield 70% of clear liquid.

Synthesis of 2,4-hexadiyne 1,6-dioylchloride (5)

Compound (4) , Ig, (0.001 mol.) and phosphorous penta chloride (2 g., 0.002 mol.) were mixed in flask fitted with reflux condenser and Calcium chloride tube. The reaction mixture was shaken from time to time. The reaction immediately started with the evolution of hydrogen chloride. After the reaction has been completed . The final compound was treated with dry ether after evaporation of the resulted phosphorous oxychloride under reduced pressure gave oily product compound (5), 0.82 g 70% yield.

Preparation of poly (2, 4-hexadiyn-l, 6-dioyl piprazine (6) by interfecial poly condensation in stirred system(22).

Piperazine (1.72 g., 0.02 mol.) dispensed as standardized 10% aqueous solution) and sodium hydroxide (0.8 g., 0.02 mol. Dispensed as 20% standard solution) in water (100 ml.) . A solution of2,4-hexadiyne-1,6-dioyl chloride (6.18 gm, 0.01 mol.) in 1, 2-dichloro ethane (60 ml.), (distilled from phosphorous pentoxide) was added rapidly with vigrous stirring . Stirring was continued for further 15 min. The precipitated polymer was washed with methanol (twice) then with water and left to dry at room temperature for 7 days gave black to deep red product (4.6 g.), 70% yield. The polymer was insoluble in most of the common organic solvent, m.p >250 °C.

Preparation of poly (2,4-hexadiyne-l,6-dioyl hexa methylene diamine), (7) by interfecial poly condensation in stirred system (22):

In 250 ml conical flask equiped with mechanical stirrer was placed a solution of hexamethylene diamine (1.16 g., 0.01 mol) and Sodium hydroxide (0.8 g.) in water (100ml)..Asolutionof2,4-hexadiyne-l,6 -dioyl chloride (2.06 g., 0.01 mol) in dichloroethylene (60 ml) . After the mixture has been stirred for 30 min., the polymer was collected on fritted glass filter , and washed with water then it was left to dry at room tempeature for 72 h., it gave dark polymer 70% yield m.p > 250 °C . The polymer was insoluble in any organic solvent.

Polymerization of 2, 4-hexadiyn-l, 6-dioic acid (4)

Exposure of the title compound to gamma radiation (50 M rad) caused the diacetylene monomer to polymerise and turn a red in colour , but with low yield convertion. The compound was exposed to γ-ray for further 50 M rad which showed more polymerization of the remaining monomers in the sample. Extraction with acetone did remove unreacted monomer. The resulted polymer (8) was insoluble in most of common organic solvents, the conversion ratio was 60%.

Results and Discussion

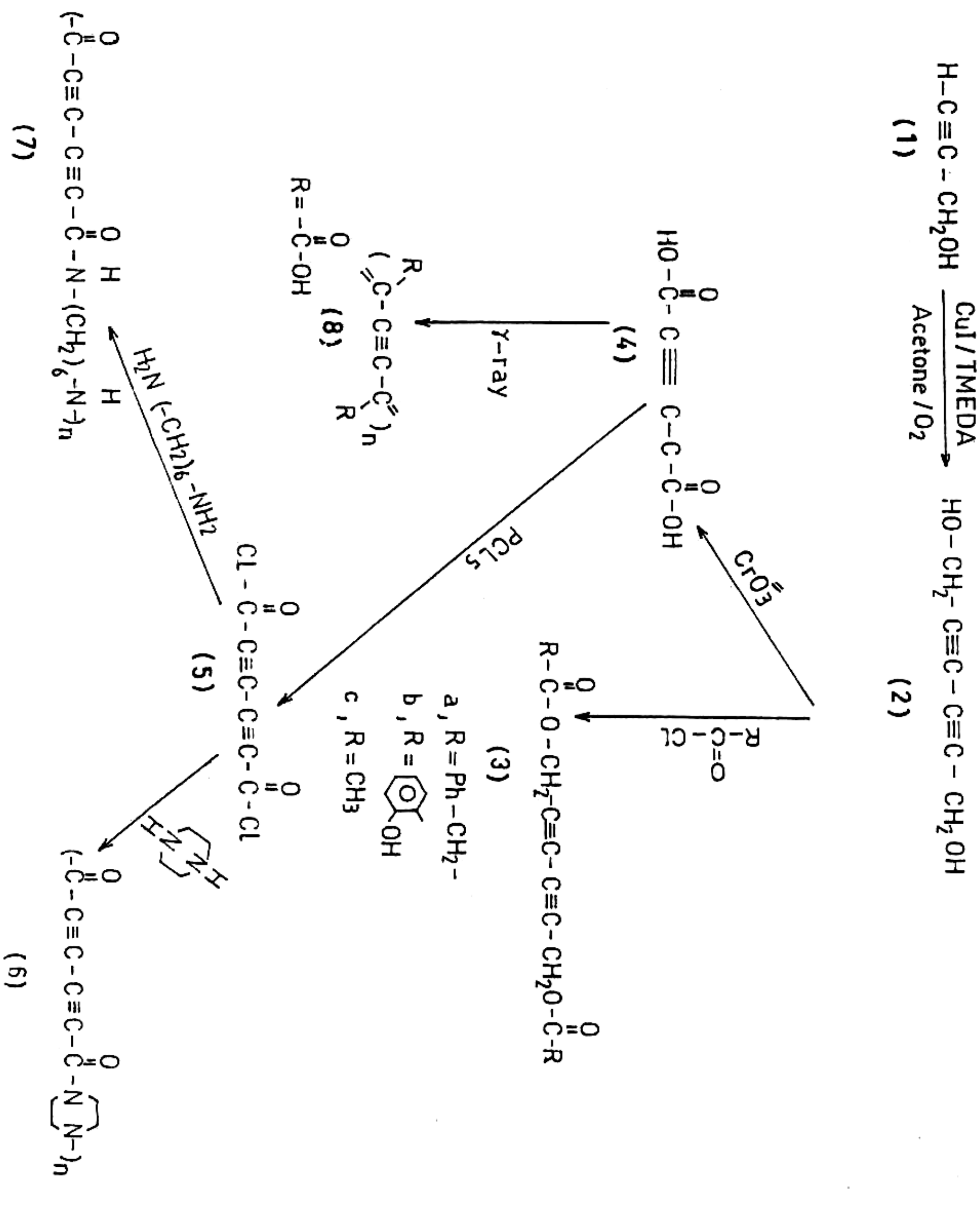
Attempted polymerzation of 2,4-hexadiyne-1,6-diphenyl [acetate (3a), salicylate (3b)]

It was previously reported that many carboxylate ester of 2,4-hexadiyne-l,6-diol could be polymerized in solid state polymerization[23,24] compound (3 a, scheme 1) is one of the esters that has not been polymerized . It was also published (25) that 2,4-hexadiyne-l, 6-dibenzoate could not be polymerized in soild-state polymerization . The attention to polymerize compound (3 a) comes from the fact that the CH_2 group might give further flexibility to the side chain to have good packing . But polymerization of the above compound was unsuccessful although 2,4-hexadiyne-l,6-diphthalate had been polymerized[26]. The combination of IR and NMR Spectral methods gave satisfactory character, Table (1). The IR indicates the carboxylate group which absorbed at 1740cm^{-1} ,The phenyl (C=C) stretching appred at 1600 cm^{-1} . ^{1}HINMR also shows 6.55 ppm. for phenyl protons and 4.3 ppm assigned to CH_2O-protons.

2,4-Hexadiyne-l,6-disalicylate (3b, Scheme 1) was prepared by condensation of salicoylchoride with 2,4-hexadiyne-l,6-diol under anhydrous condition (listed in the experimental part) . The reactivity of this compound has been examined toward topo-chemical polymerization, but polymerization of this type was unsuccessful . The compound has been satisfactory characterized by a combination of spectral methods (IR, ^{1}H and ^{13}CNMR), Table (1).

The IR spectrum indicates the presence of salicylate linkage absorbed at ν 1690 cm^{-1} and 3250 cm^{-1} for the phenolic O -H stretching .

The band absorbed at ν 2100 cm^{-1} assignable to the acetylenic stretching mode. The C^{13}NMR shows the signal resonating at 7.9-7.0 ppm assigned to the aromatic protons while at 51.5 ppm related to CH_2 protons , ^{13}CNMR spectrum also gave farther evidence for the character of the disalicylate which shows resonating signals at 169 ppm assignable to (C=0), 137-118 ppm for phenyl carbons and two types of acetylenic signals resonating at 76.1,70.62ppm.


H−C≡C − CH2OH
(1)
CuI / TMEDA
Acetone / O2
HO−CH2−C≡C−C≡C−CH2OH
(2)
CrO3
R−C(=O)−Cl
R−C(=O)−O−CH2−C≡C−C≡C−CH2O−C(=O)−R
(3)
a, R = Ph−CH2−
b, R = −C6H4−OH
c, R = CH3
HO−C(=O)−C≡C−C≡C−C(=O)−OH
(4)
γ-ray
(=C(R)−C≡C−C(R)=)n
(8)
R = −C(=O)−OH
PCL5
CL−C(=O)−C≡C−C≡C−C(=O)−CL
(5)
H2N (-CH2)6-NH2
(−C(=O)−C≡C−C≡C−C(=O)−N(H)−(CH2)6−N(H)−)n
(7)
HN NH
(−C(=O)−C≡C−C≡C−C(=O)−N N−)n
(6)

Scheme (1)

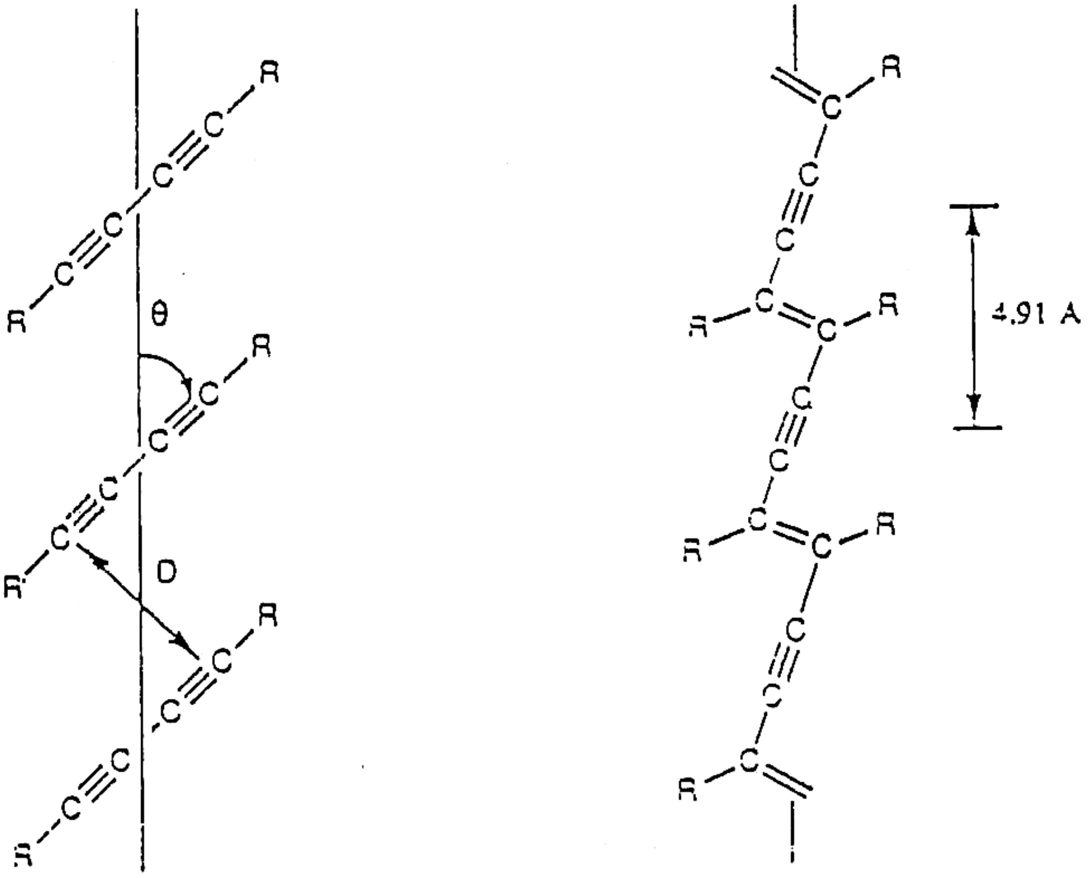


Fig. (I): Postulated Backbone Conformation of Polydiacetylenes

Attempted polymerization of 2,4-hexadiyne-l,6-diacetate(3c)

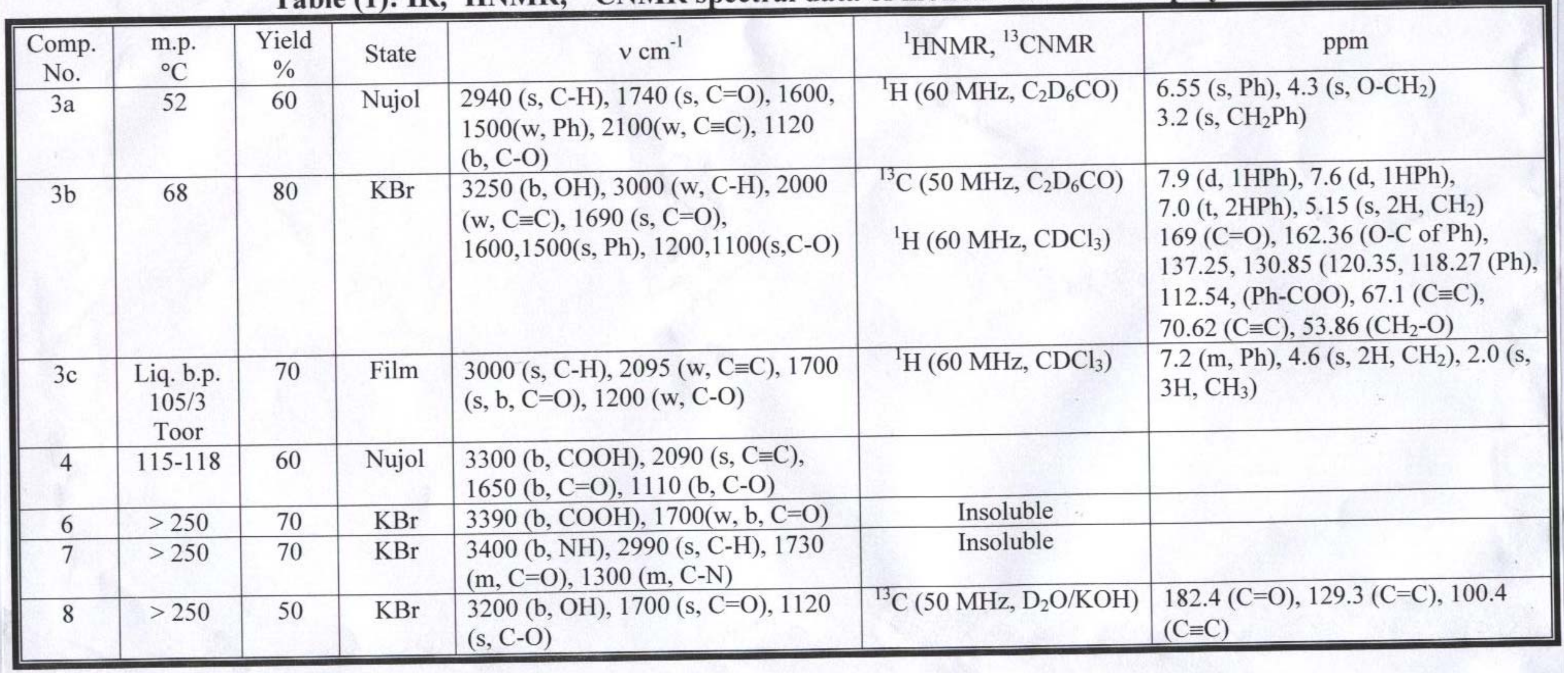
In a procedure similar to that mentioned above 2,4-hexadiyn-l, 6-diacetate was also prepared , but the resulted compound is oil at ambient temperature it could not be polymerized in solid-state polymerization , but it might polymerize at 0°C or below. The combination of IR and NMR spectral methods (Table 1) gave satisfactory character.

The poly condensation polymerization in stirred system of 2,4-hexadiyne -1,6-dioylchoride and piperazine afforded a dark polymer precipitated as spongy mass, Drying in an air atmosphere resulted in the transformation of the polymer into hard solid material which was insoluble in common organic solvents. The infrared absorption spectral data of the polymer are presented in Table(1) and are detailed there in.

Using the previously mentioned polymerization process [22]. 2.4-Hexadiyn-l,6-dioyl chloride was condensed with hexamethylene diamine, the resulted polymer (6) scheme (1) was also as spongy mass and transformed into hard and dark solid material . The IR spectral data of the polymer are presented in Table (1) and are detailed there in.

The polymer (8) ,shown in scheme (1) was polymerized in the solid state under γ-irradiation[20] to give red-solid . Unreacted monomer was recovered as reported in the experimental part . The polymer was insoluble in common organic solvents, but gave water soluble potassium salt. The spectral data is in accord with anticipated poly eneyne[27]. ^{13}CNMR Spectrum (Table 1) of its potassium salt in aquous solution shows comparable resonating signals at 100.4 and 129.3 ppm assignable to C=C and C=C carbons respectively together with the carbonyl resonance at 182.4 ppm. The above observation supporting and give resonable evidence for the eneyne structure of the polymer backbone[28] .

Table (1): IR, ^{1}HNMR, ^{13}CNMR spectral data of monomers and their polymers



Comp. No.	m.p. °C	Yield %	State	ν cm^{-1}	^{1}HNMR, ^{13}CNMR	ppm
3a	52	60	Nujol	2940 (s, C-H), 1740 (s, C=O), 1600, 1500(w, Ph), 2100(w, C≡C), 1120 (b, C-O)	^{1}H (60 MHz, C_2D_6CO)	6.55 (s, Ph), 4.3 (s, O-CH_2) 3.2 (s, CH_2Ph)
3b	68	80	KBr	3250 (b, OH), 3000 (w, C-H), 2000 (w, C≡C), 1690 (s, C=O), 1600,1500(s, Ph), 1200,1100(s,C-O)	^{13}C (50 MHz, C_2D_6CO) ^{1}H (60 MHz, $CDCl_3$)	7.9 (d, 1HPh), 7.6 (d, 1HPh), 7.0 (t, 2HPh), 5.15 (s, 2H, CH_2) 169 (C=O), 162.36 (O-C of Ph), 137.25, 130.85 (120.35, 118.27 (Ph), 112.54, (Ph-COO), 67.1 (C≡C), 70.62 (C≡C), 53.86 (CH_2-O)
3c	Liq. b.p. 105/3 Toor	70	Film	3000 (s, C-H), 2095 (w, C≡C), 1700 (s, b, C=O), 1200 (w, C-O)	^{1}H (60 MHz, $CDCl_3$)	7.2 (m, Ph), 4.6 (s, 2H, CH_2), 2.0 (s, 3H, CH_3)
4	115-118	60	Nujol	3300 (b, COOH), 2090 (s, C≡C), 1650 (b, C=O), 1110 (b, C-O)		
6	> 250	70	KBr	3390 (b, COOH), 1700(w, b, C=O)	Insoluble	
7	> 250	70	KBr	3400 (b, NH), 2990 (s, C-H), 1730 (m, C=O), 1300 (m, C-N)	Insoluble	
8	> 250	50	KBr	3200 (b, OH), 1700 (s, C=O), 1120 (s, C-O)	^{13}C (50 MHz, D_2O/KOH)	182.4 (C=O), 129.3 (C=C), 100.4 (C≡C)

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