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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

New Method for Synthesis of Aromatic Diimide Dicarboxylic Acid Diallyl Esters

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Abstract—New method is suggested for synthesis aromatic diimide dicarboxylic acid diallyl esters from the corresponding acids under the action of allyl halides in aprotic polar solvents in the presence of anhydrous K_2CO_3.

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It is known that allyl resins produced from allyl monomers are construction materials possessing exclusive electrical and mechanical properties at room temperature. However, their application had been restricted by their poor heat resistance, because shape and size preservation at elevated temperatures is highly important for quite a number of electrical products [1]. To improve the heat resistance of allyl resins, amide groups were introduced into the backbone [2], which improved the heat resistance of target products, but final articles were nonmachinable.

Later, allyl monomers with aryl imide groups of varied structure were synthesized in [3] and easily machinable heat-resistant allyl polymeric materials were produced from these monomers. Similarly, new aryl imide-containing diallyl monomers and heat-resistant machinable polymeric materials based on these monomers were obtained [4].

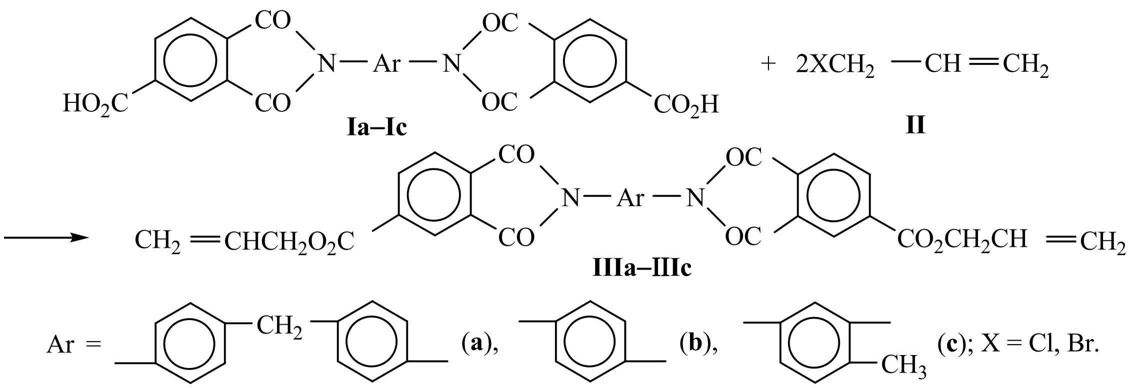
It is known that the carboxy group of aromatic imidocarboxylic acids has a higher reactivity in nucleophilic substitution reactions [5–7]. Therefore, potassium salts of these acids [8], or acid themselves in the presence of catalysts [9], can enter into a reaction with an excess amount of epichlorohydrin to form glycidyl ethers in high yield (80–90%). Aryl imide-containing bisallyl esters have been synthesized from *N*-allyl-4-phthalimidocarboxylic acid and various aliphatic and arylaliphatic dihalide compounds [2]. A new method is suggested on the basis of these data for synthesis of diallyl esters of fully aromatic diimide dicarboxylic acids, which have been synthesized previously only from chloranhydrides of the corresponding acids and allyl alcohol [3, 4]. The diallyl esters were synthesized by the reaction of aromatic diimidodicarboxylic acids with allyl halides in the presence of anhydrous K_2CO_3 (Scheme 1).

The starting aromatic bis(imidocarboxylic) acids (**Ia–Ic**) were synthesized by the methods described in [4, 10–12] in 75–90% yield. Aromatic diimide dicerboxylic acid bisallyl esters (**IIIa–IIIc**) were obtained using the above scheme by heating of bis(imidocarboxylic) acids (**Ia–Ic**) with an excess amount of an allyl halide in such aprotic solvents as *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) in the presence of K_2CO_3 as an acid acceptor.

The composition and structure of bisallyl esters (**IIIa–IIIc**) synthesized by the new method were characterized by IR and ^{1}H NMR spectra and elemental analysis data.

The IR spectra of compounds **IIIa–IIIc** contain absorption bands at 725, 1725, and 1785 cm^{-1}, characteristic of aromatic imide rings. The absorption bands at 1640 and 3200–3700 cm^{-1} can be assigned to, respectively, the C=C allyl double bond and C–H bonds. The absorption peak at 1720 cm^{-1}, characteristic of the C=O ester group appears combined with the imide absorption. The characteristic absorption bands observed in the IR spectra of compounds **IIIa–**

Scheme 1.



IIIc are in good agreement with the data previously obtained for similar compounds [4].

The ^{1}H NMR spectra of bisallyl esters **IIIa–IIIc** contain signals with chemical shifts of 7.00–8.50 ppm, characteristic of aromatic protons. In addition, the chemical shifts of 6.00–6.16, 5.25–5.50, and 4.82–4.96 ppm can be attributed to, respectively, =C–H, $=CH_2$, and $–CH_2–$ protons of the allyl group. The chemical shifts of 3.26–3.38 and 2.00–2.25 ppm are characteristic of protons of the $–CH_2–$ group in compound **IIIa** and protons of $–CH_3$ in compound **IIIc**. These characteristic chemical shifts occur in the ^{1}H NMR spectrum of bisallyl ester **IIIc** (see the figure). The chemical shifts observed for the synthesized bisallyl esters (**IIIa–IIIc**) are also in good agreement with published data [4].

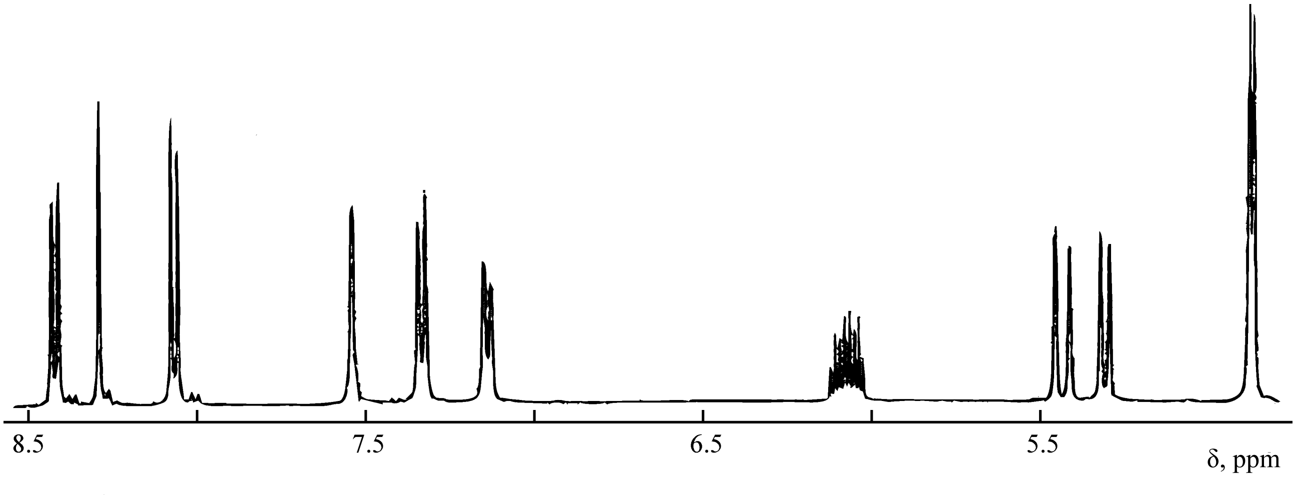
EXPERIMENTAL

All the starting substances were used without additional purification: allyl bromide (Fluka), 4,4'-diaminodiphenylmethane (Merck), 1,4-diaminobenzene (Merck), 2,4-diaminotoluene (Merck), trimellitic anhydride (Merck), *N,N*-dimethylacetamide (Merck), *N,N*-dimethylformamide (Merck), and K_2CO_3 (Merck).

***N,N*'-Bis(4-carboxyphthalimido)-4,4'-diphenylmethane (Ia)** was produced by condensation of trimellitic anhydride (TMA) (20 mmol) with 4,4'-diaminodiphenylmethane (10 mmol) in DMF (50 ml) by the previously described method [4, 10–12]. Yield 90%, mp 370°C (from DMAc) (according to published data [12], mp 372°C).

***N,N*'-Bis(4-carboxyphthalimido)-1,4-benzene (Ib)** was produced by condensation of TMA (20 mmol) with 1,4-diaminobenzene (10 mmol) in DMF (45 ml) [4, 10–12]. Yield 87%; mp 435–438°C (from DMAc) (according to published data [113], 428–430°C).

***N,N*'-Bis(4-carboxyphthalimido)-2,4-toluene (Ic)** was produced by condensation of TMA (20 mmol)



^{1}H NMR spectrum of *N,N*'-bis(4-allyloxycarbonylphthalimido)-2,4-toluene (**IIIc**) in DMSO-d_6. (δ) Chemical shift.

with 2,4-diaminotoluene (10 mmol) in DMF (45 ml) [4, 10–12]. Yield 75%, mp 368–370°C (from DMAc) (according to published data [12], 371°C).

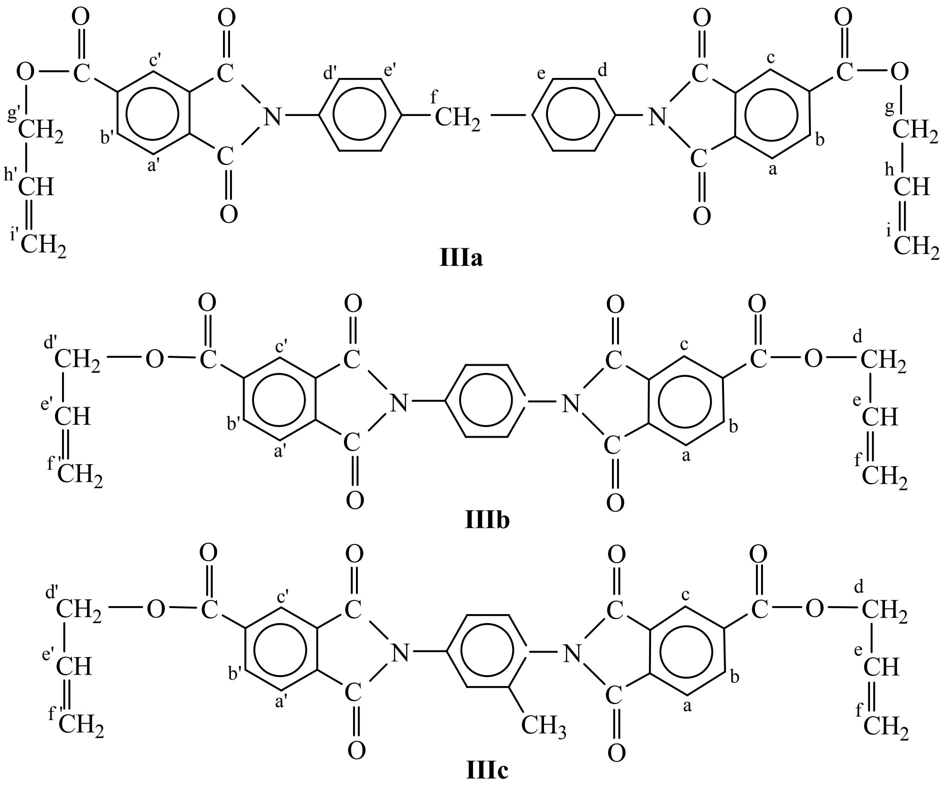
***N,N'*-Bis(4-allyloxycarbonylphthalimido)-4,4'-diphenylmethane (IIIa).** A reaction vessel with a magnetic rabble, thermometer, reflux, and Dean–Stark apparatus was charged with a solution of 2.18 g of compound **Ia** (4 mmol) in 40 ml of DMAc and with 1.10 g of anhydrous K_2CO_3 (4 mmol). The mixture was agitated for 15 min at room temperature, 8 ml of toluene was added, and the resulting mixture was heated on a water bath at 125–130°C until water ceased to be released. After water was removed, 2 ml of allyl bromide (sixfold excess) and about 50 mg of KI was added. The agitation of the reaction mixture was continued for 4 h at a temperature of 130°C. After the reaction was complete, the mixture was cooled to 50–60°C and poured into 300 g of icy water acidified with hydrochloric acid. The resulting yellowish white precipitate was filtered off, washed on the filter with water and then with acetone, and dried in air and then in a vacuum. Yield of dry raw product 2.20 g (88%); mp 278–280°C. On being recrystallized from DMAc, product **IIIa** had the form of fine light yellow grains. Yield 2.10 g (84%); mp 282–284°C. Found, %: C 71.24, 71.30; H 4.26, 4.30; N 4.39, 4.42. $C_{37}H_{26}N_2O_8$. Calculated, %: C 70.92, H 4.18, N 4.47.

IR spectrum, cm^{-1} (KBr): 1785, 1725, and 725 (imide group); 1640 (C=C of the allyl group); 3600–3200 (C–H); and 1720 (C=O of the ester group is overlapped by the absorption of the imide group).

^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 8.42–8.48 d ($H_b + H_{b'}$, 2H), 8.30–8.36 s ($H_c + H_{c'}$, 2H), 8.08–8.12 d ($H_a + H_{a'}$, 2H), 7.42–7.48 (two overlapped doublets, $H_d + H_{d'}$, 4H), 7.38–7.42 (two overlapped doublets, $H_e + H_{e'}$, 4H), 6.2–6.16 m ($H_h + H_{h'}$, 2H), 5.30–5.46 d.d ($H_i + H_{i'}$, 4H), 4.86–4.94 d ($H_g + H_{g'}$, 4H), 4.08 s ($H_f + H_{f'}$, 2H).

***N,N'*-Bis(4-allyloxycarbonylphthalimido)-1,4-benzene (IIIb)** was produced by the reaction of compound (**Ib**) (5 mmol) with allyl bromide (5 ml) (sixfold excess) in DMAc (80 ml) in the presence of anhydrous K_2CO_3 (5 mmol) by the method for synthesis of compound **IIIa**, described above. Yield of yellowish white unpurified dry product 73%; mp 294–296°C (with decomposition). On being recrystallized from DMF, product **IIIb** had the form of grayish white

Scheme 2.



fine grains. Yield 68%; mp 308–310°C (with decomposition). Found, %: C 67.34, 67.32; H 3.83, 3.85; N 5.14, 5.18. $C_{30}N_{20}N_2O_8$. Calculated, %: C 67.16; H 3.76; N 5.22.

IR spectrum cm^{-1} (KBr): 1785, 1725, and 725 (imide group); 1640 (C=C of the allyl group); 3600–3200 (C–H); 1720 (C=O of the ester group is overlapped by the absorption of the imide group).

^{1}H NMR spectrum, δ, ppm: 8.42–8.50 d ($H_b + H_{b'}$, 2H), 8.32–8.38 s ($H_c + H_{c'}$, 2H), 8.10–8.14 d ($H_a + N_{a'}$, 2H), 7.60–7.66 s (protons of the C_6H_4 group, 4H), 6.05–6.15 m ($H_e + H_{e'}$, 2H), 5.30–5.50 d ($H_f + H_{f'}$, 4H), 4.90 d ($H_d + H_{d'}$, 4H).

***N,N'*-Bis(4-allyloxycarbonylphthalimido)-2,4-toluene (IIIc)** was produced by the reaction of compound **Ic** (2 mmol) with allyl bromide (2 ml) (sixfold excess) in DMAc (20 ml) in the presence of anhydrous K_2CO_3 by the method for synthesis of compound **IIIa**, described above. On being recrystallized from DMAc, product **IIIc** had the form of fine yellowish gray ball-shaped crystals. Yield 75%; mp 287–288°C. Found, %: C 67.86, 67.90; H 4.16, 4.12; N 4.98, 4.96. $C_{31}H_{22}N_2O_8$. Calculated, %: C 67.63, H 4.03, N 5.09.

IR spectrum, cm^{-1} (KBr): 1785, 1725, and 725 (imide group); 1640 (C=C of the allyl group); 3600–3200 (C–H); 1720 (C=O of the ester group is overlapped by the absorption of the imide group); 2930–2910 and 1385–1375 (CH_3–Ar).

^{1}H NMR spectrum, δ, ppm: 8.40–8.48 d ($H_b + N_{b'}$, 2H), 8.30 s ($H_c + H_{c'}$, 2H), 8.05–8.10 d ($H_a + H_{a'}$, 2H), 7.50–7.60 s (1H), 7.40–7.48 d (1H) and 7.10–7.18 d (1H) are aromatic protons of the $(CH_3)C_6H_3$ group (a total of 3H), 6.0–6.14 m ($H_e + H_{e'}$, 2H), 5.30–5.50 d.d ($H_f + H_{f'}$, 4H), 4.84–4.90 d ($H_d + H_{d'}$, 4H), 2.00–2.60 s (protons of the CH_3 group, 3H).

The structures of the synthesized compounds **IIIa–IIIc** are shown in Scheme 2.

CONCLUSIONS

(1) A new method for synthesis of aromatic diimide dicarboxylic acid diallyl esters was developed.

(2) Three allyl esters: *N,N'*-bis(4-allyloxycarbonylphthalimido)-4,4'-diphenylmethane, *N,N'*-bis(4-allyloxycarbonylphthalimido)-1,4-benzene, and *N,N'*-bis(4-allyloxycarbonylphthalimido)-2,4-toluene were synthesized by the new method and characterized.

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