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ARYNIC SPECIES; EFFECT OF SUBSTITUENTS ON THE REACTIVITY OF MONOSUBSTITUTED DEHYDROBENZENES[1]

F. GAVIÑA*, S. V. LUIS, A. M. COSTERO
Departamento de Química Orgánica, Colegio Universitario de Castellón
Universidad de Valencia, Castellón de la Plana, Spain.

and

P. GIL
Departamento de Química Orgánica, Facultad de Farmacia
Universidad de Granada, Granada, Spain

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Abstract - Evidence is presented demonstrating the existence of free dehydrobenzenes in the thermal decomposition of diaryliodonium-2-carboxylates, and that o-benzyne itself and its 4-methyl-, 4-chloro-, 4-bromo- and 4-nitro-derivatives are generated from insoluble polymer-bound precursors and trapped by a second solid phase in Diels-Alder reactions. Lifetimes for these elusive species are determined.

Since highly reactive arynic intermediates have been widely studied since the initial work by Roberts[2], Wittig[3] and Huisgen[4], the characteristic reactivity of these species and the methods for their generation are well known[5]. However, data about their stabilities and lifetimes are rare, being mainly limited to gaseous o-benzyne itself. Ebel and Hoffman[6] described a lifetime shorter than 20 milliseconds for o-benzyne generated by thermal decomposition of bis-o-iodophenyl mercury at 700ºC in an argon atmosphere, while Schafer and Berry[7] calculated a lifetime of some hundreds of microseconds for the same intermediates from time-resolved ultraviolet and mass spectra of photoionizated decomposition of benzenediazonium 2-carboxylate. Mazur and Jayalekshmy[8], in their delayed trapping experiments, reported of a polymer-bound o-benzyne which has lifetime higher than one minute. But in this case, results are related to the pseudodilution effect in the polymeric matrix, as shown by the fact that intermediate persistence time is affected by crosslinking and functionalization degree.

Up to now, there have been no data about the stability of o-arynes as free species in solution, although it has been suggested that the surprisingly high selectivity of benzyne in some reactions[9] implies an appreciable lifetime for this intermediate. In this sense, studies about the effects of substituents on the stability of o-arynes have been carried out by considering that a higher degree of selectivity is most likely a consequence of a higher stability. Thus, Huisgen and coworkers[10] reported that -I substituents (electron withdrawing groups) decrease the selectivity, whereas the reverse occurs with + I substituents (electron releasing groups)[5a].

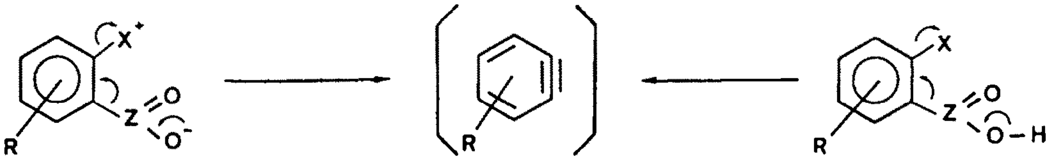
On the other hand, Bielh and coworkers[11] concluded in their work that both, + I and -I substituents make less stable these intermediates and Zoltewicz and Bunnett[12] suggested that a 4-methyl substituent decreases the intermediate's stability

The three phase test[13] has been used to demonstrate the existence of reactive intermediates as free species in solution. Recently, we showed how a modification of this method permits lifetime determinations for those reactive species[14].

This paper reports the application of this method in order to demonstrate the generation of monosubstitued o-benzynes in heterolytic fragmentation reactions, showing the influence of substituents on the kinetic stability of these intermediates by lifetime determinations.

Methods and results

The first step in our work was the synthesis of polymeric precursors able to yield o-arynic species by heterolytic fragmentation 1,4[15] as outlined in Scheme I

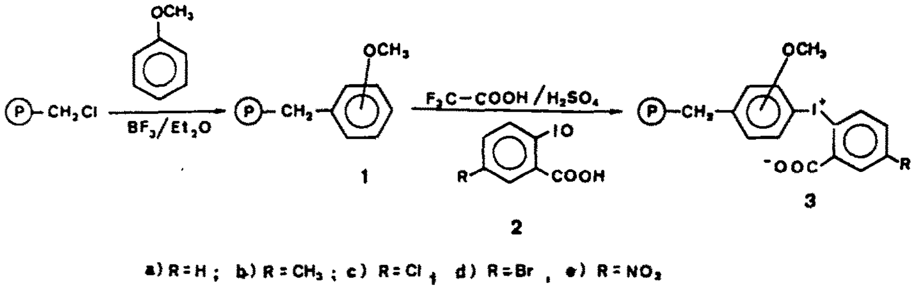


SCHEME I

This reaction requires the presence of a ZO_2^- or ZO_2H group, where Z is generally in ortho respect to a good leaving group as diazonium[16], aryliodonium [17, 18,19], halogene[20], triazene[21], etc. The polymer-bound leaving group tested was aryliodonium. One of the most important advantages of the use of this type of reaction for the generation of o-arynic species is the fact that these are thermal proccesses occurring without any reagent except the solvent. This simplifies the practical work up and eliminates the formation of side products. This feature has also permitted the use of thermogravimetric analysis[1a] to study these processes, showing that thermogravimetry can be an important tool in polymeric reagents work.

Polymeric diaryliodonium-2-carboxylates. Diaryliodonium-2-carboxylates have been described as useful precursors for the generation of o-benzyne[17-19], 4-methyl-benzyne[22] and 4-nitro-benzyne[23]. They are easily obtained by acid-catalysed condensation of an 2-iodoso-benzoic acid with benzene. In polystyrene-divinylbenzene copolymers, the aromatic moiety is able to react in many electrophilic aromatic substitution reactions, such as chlorosulphonation[24], nitration[25], etc, but attempts to obtain a suitable polymeric o-benzyne precursor by condensating such polymers with an iodosobenzoic acid or its derivatives under acid conditions were unsuccesful.

The synthesis of polymeric diaryliodonium-2-carboxylates, 3, was accomplished as shown in Scheme II. The first step was the formation of



SCHEME II

activated aromatic nuclea on the polymer beads by reaction of a Merrifield's resin (2% crosslinked, 3.5 mequiv Cl/g) with anisole and BF_3/Et_2O complex. Ortho and para substitution must occur in 1, since the reaction between anisole and benzyl chloride afforded an equimolecular mixture of ortho and para-(methoxyphenyl) phenylmethane. Condensation of 1 with o-iodosobenzoic acids was then feasible under mild conditions with F_3CCO_2H/H_2SO_4. Neutralization with triethylamine afforded 3, the IR of which presented a carboxylate band at 1600-1635 cm^{-1}. o-Iodosobenzoic acids, 2, were easily synthetized in excellent yields by oxidation of the related o-iodobenzoic acids with potassium persulfate in sulfuric acid, followed by hydrolysis.

Non isothermal thermogravimetric analysis of polymers 3 is shown in Figure 1, together with that for Merrifield's resin (M), methoxylated polymer 1

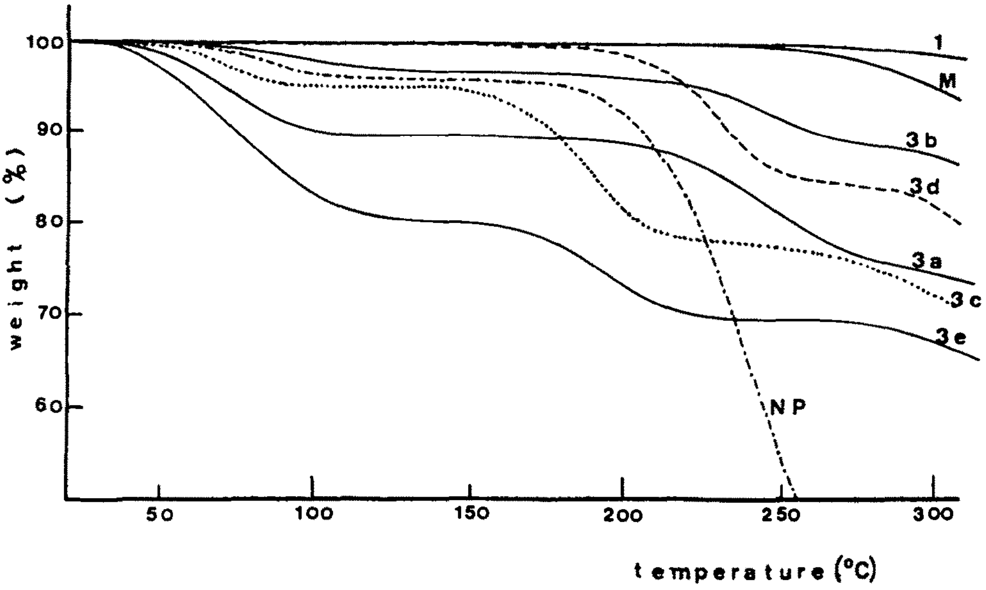


Fig. 1

and diphenyliodonium-2-carboxylate (NP). For compounds 3, there is always a first weight loss starting at c. a. 50ºC, which can be assigned to moisture and solvents retained by polar groups inside the polymer bead. This fact must be considered when calculating polymers functionalization by weight increase. In this way, calculations of functionalization degrees for polymers 3 are given in Table I, where yields are referred to chloromethylated resin.

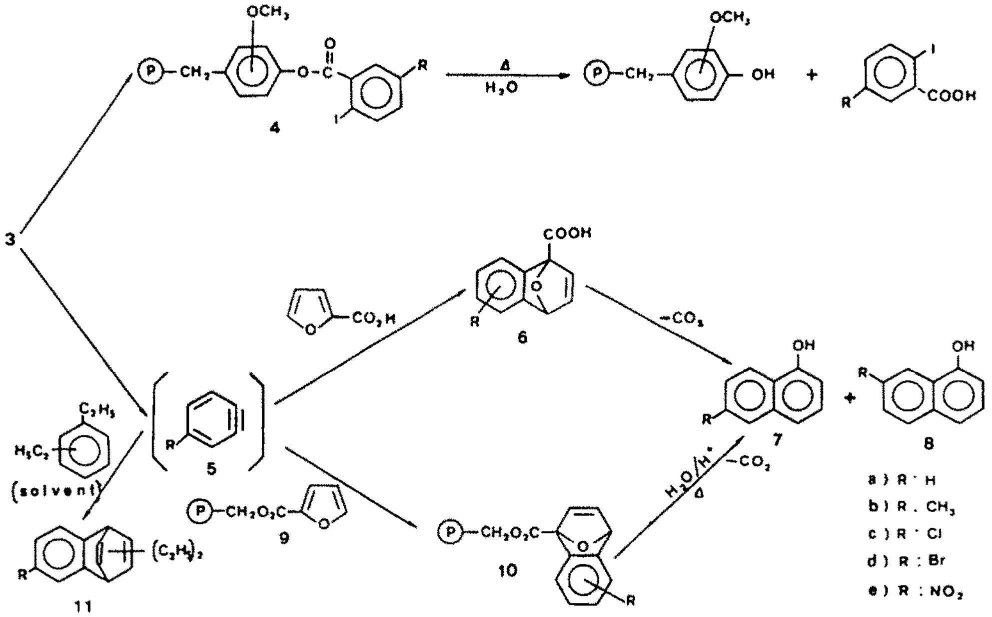
TABLE I

Functionalization degrees and thermic decomposition of polymer-bound precursors

Polymers 3	R	Functionalization degree (Mequiv/g)	Yields from Merrifield's resin (%)	Decomposed/Rearranged functional groups when polymers are heated at 200ºC
a	H	1.28	78	97.4 / 1
b	CH_3	0.52	33	98.8 / 1
c	Cl	1.07	71	29.9 / 1
d	Br	0.74	55	19.2 / 1
e	NO_2	0.76	61	46.1 / 1

Decomposition of functional groups in these polymers occurs at about 200ºC, as with the non polymeric diphenyliodonium-2-carboxylate. This process seems likely to take place through benzyne and CO_2 loss. Thus, when thermal decomposition of polymers 3 was carried out in a solution of furoic acid in refluxing diethylbenzene (Scheme III), an almost equimolecular mixture of 6- and 7-substituted 1-naphthols, 7 and 8, was obtained in a 20-30% yield. The naphthols were identified by spectroscopic analysis and mass spectra as well as by comparison with authentic samples. These results can be explained through a Diels-Alder reaction of a 4-substituted o-benzyne (5) with 2-furoic acid to afford a mixture of 6- and 7-substituted 1,4-epoxy-1,4-dihydro-1-naphthoic acids (6), which in these conditions experiment a concerted process with a CO_2 loss, to yield the respective naphthols, 7 and 8.

A quantitative thermogravimetric study in this range suggests that only a part of functional groups are decomposed in a fragmentation process. IR analysis of polymers after being heated showed disappearance of carboxylate bands and the presence of a weaker one at about 1720 cm^{-1}, So, as described[18] for non polymeric analogous compounds, side reaction must be a rearrangement to 4, as shown in Scheme III. In fact, after hydrolysis and work-up as usual, 5-substituted-2-iodobenzoic acids could be isolated from these polymers. Competition between heterolytic fragmentation and rearrangement is affected by the nature of R groups in 3. Thus, when R was hydrogen (3a) or methyl (3b), fragmentation was by far the main process, but when R was an electron-withdrawing group (3 c-e; R= Cl, Br, NO_2) side reaction increased in its importance. The fragmentation/rearrangement ratio could be calculated from thermograms and results, under these conditions, are also given in Table I



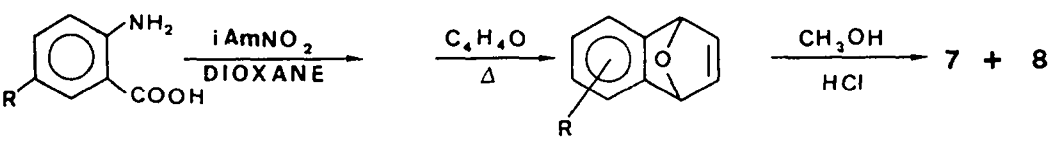
SCHEME III

<u>Trapping agent</u>. A polymeric trapping agent related to furoic acid was the polymeric ester of 2-furancarboxylic acid, 9[13b]. Thermal decomposition of diphenyliodonium-2-carboxylate in the presence of 9 in diethylbenzene yielded a polymer 10a (R=H), from which 1-naphthol was obtained after saponification followed by acidification (Scheme III). This suggests that 9 can act as a good dienic trapping agent for o-arynes.

<u>The three phase test</u>. Since 1974[13a] the Three Phase Test has been a useful tool in the study of different intermediates. Its main advantage is the impossibility of direct reaction between precursors and trapping agents. This feature is especially important in arynic chemistry where trapping by nucleophiles or dienes has been used to support the intermediacy of such species, but where a mechanism of addition-elimination by direct reaction between precursor and trapping agent, as the first step, may sometimes account for the formation of adducts[5c].

Three phase tests were accomplished when suspensions of polymer-bound furoate, 9, and a polymeric diaryliodonium-2-carboxylate (3) were heated and stirred. After hydrolysis of polymeric adduct, 10a (R=H) followed by acidification, 1-naphthol was obtained, showing the transference of the o-benzyne moiety. Mixtures of 6- and 7-substituted 1-naphthols were obtained when precursors were 3 b-e. These results agree with the liberation of an arynic intermediate from the polymer-bound precursor and its reaction with the polymeric trapping agent.

Reference Compounds. For comparative purposes, mixtures of 6- and 7-substituted 1-naphthols (R= H, CH_3, Cl, Br, NO_2) were prepared by the route outlined in Scheme IV. This was performed by decomposition of an diazotized anthranilic acid in the presence of furan, to afford an 1,4-epoxy-1,4-dihydro-naphthalene, which when heated with MeOH/HCl[3] gave a mixture of substituted 1-naphthols in an overall yield of 7-30 % after purification. Spectral properties (IR, NMR and MS) of mixtures were in accord with those expected for isolated isomers and separation was not attempted.



SCHEME IV

Lifetime measurements. We have recently reported that the Three Phase Test can be adapted for lifetime determinations of free intermediates in solution, through separation of the resins to a constant distance and introduction of a variable flow of the liquid phase by using the so-called "Polyphasic Dynamic Reactor" (PDR)[14].

We applied this method to determinate the lifetime of the monosubstituted o-benzynes we studied before, by means of the three phase test. For that, a polymeric precursor for a specie 5 and polymeric furoate (9)as trapping agent were used. A flow of solvent at 185ºC was produced and adjusted by the use of a peristaltic pump. For o-benzyne, trapping by 9 (as shown by formation of 1-naphthol after hydrolysis of polymeric adduct) was detected only for run-times shorter than 5.0 ± 0.3 s. and lifetime for this intermediate in these conditions must be stated in this value. Results for monosubstituted o-arynes are given in Table II. The shortest run-time that could be obtained in our experiences was 3.3 s. and even in that case, transference of 4-methyl o-benzyne could not be detected. The three phase test implies that an intermediate is liberated from a polymer-bound precursor and passes through the solvent to a second polymer in which it is trapped and this process needs at least 0.2 s to be completed[26]. Thus, trapping of methyl o-benzyne on the three phase test, without separation of polymers, as in PDR, implies that its lifetime is at least in the range of some tenths of a second, and can be stated a value of

TABLE II

Lifetimes of o-arynic species in solution

Arynes (5)	Lifetimes (s)
o-benzyne (a)	5.0 ± 0.3
4-Methyl-1,2-benzyne (b)	$<$ 3.3
4-Chloro-1,2-benzyne (c)	6.7 ± 0.3
4-Bromo-1,2-benzyne (d)	5.4 ± 0.3
4-Nitro-1,2-benzyne (e)	7.2 ± 0.3

0.2 - 3.3 s.

It is obvious that those values for the lifetimes are depending on the ability to detect the trapped species. In our experimental conditions they mean that, at those times, 97% of molecules have been too reactive to reach the trapping agent. As we used the same conditions in all the cases, we can utilize lifetimes comparison as a way to compare reactivities.

Results in Table II show that lifetimes of o-arynic species in solution, for the experimental conditions outlined are longer than the lifetime calculated for gaseous o-benzyne generated in drastic conditions. However, as expected, these lifetimes are not as long as those determined for polymer-bound o-benzyne, whose immobility on the polymeric matrix may mainly explain its reduced reactivity. o-Arynes seem to behave like electron-rich intermediates, thus electron withdrawing groups stabilize these species and electron releasing groups make more reactive species when compared to o-benzyne itself.

It can be adduced that arynes may be formed, as indicated in Scheme I, in a concerted manner, but they may result from two or more elementary steps, including several intermediates, so that the significance of the numbers in Table II will remain uncertain. But solution analysis after these experiments showed only aryne-solvent adduct 11[27] (Scheme III) without any carbonylic groups. These results and the ones from thermogravimetric studies indicate that numbers in Table II must indeed correspond to o-arynes lifetimes.

Conclusions

Monosubstituted o-benzynes are generated by thermal decomposition of benzoic acids with the electrofugal group aryliodonium at 2-position.

We have demonstrated how the lifetime of o-arynic intermediates in solution can be stated in some seconds in the absence of any trapping agent except the solvent (diethylbenzene). Kinetic stability of these species is affected by substituents. Electron withdrawing groups seems to stabilize them and the reverse is found for intermediates with electron releasing groups. It is in agreement with the conclusions of Zoltewicz and Bunnett[12] and shows that arynes selectivity is not a direct consequence of their stability.

The polyphasic dynamic reactor (PDR) has come to be a very important tool for comparative studies within a family of compounds

EXPERIMENTAL SECTION

General methods for working with polymeric reagents and multiphase systems, including PDR lifetimes measurements, have been described[14]. Anthranilic acids were comercially available or prepared by methods described in the literature. Iodobenzoic acids (known compounds) were prepared by diazotization and then reaction with KI, from anthranilic acids.

Preparation of 2-iodosobenzoic acids (2). General method

The crude iodobenzoic acid (8 mmol) was stirred in 8 ml conc. H_2SO_4 in an ice bath to obtain a clear solution or a homogeneous suspension. 3g (11 mmol) of potassium persulfate were slowly added so that temperature was kept below 5ºC. Then, the mixture was stirred for one additional hour and poured into iced water. The solid was filtered, washed with water and acetone and dried to constant weight. Recrystallization was accomplished in boiling water.

2b, 2c and 2d are new compounds. 2a[28] and 2e[23] are known compounds, but references to some of their physical or spectroscopic properties are lacking.

2-iodosobenzoic acid (2a)- Yield: 85 %, IR (KBr): 2900, 2410, 1610, 1582, 1560, 1339 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.2-7.9 (m, 4H) m.p.: 221 ± 0.3ºC. Anal. calcd. for $C_7H_5IO_3$: C, 31.82; H, 1.89; I, 48.11; Found: C, 31.58; H, 1.90; I, 47.93.

5-Methyl-2-iodosobenzoic acid (2b)- Yield: 82 %. IR (KBr): 3500, 2400, 1620, 1590, 1570, 1312 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.2-7.9 (m, 3H), 2.46 (s, 3H). m.p.: 210-212ºC (d). Anal. calcd. for $C_8H_7IO_3$: C, 34.53; H, 2.52; I, 45.68. Found: C, 34.36; H, 2.56; I, 45.28.

5-Chloro-2-iodosobenzoic acid (2c) - Yield: 70 %. IR (KBr): 2930, 2410, 1610, 1560, 1325 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ : 7.5-8.0 (m, 3H) m.p. 199-201ºC (d). Anal. calcd. for $C_7H_4ClIO_3$: C, 28.14; H, 1.34; I, 42.55; Found: C, 28.15; H, 1.41; I, 43.02.

5-Bromo-2-iodosobenzoic acid (2d) - Yield: 94 %. IR (KBr): 2880, 2420, 1610, 1570, 1550, 1325 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ : 7.5-8.1 (m, 3H). m.p.: 226-228ºC (d). Anal. calcd for $C_7H_4BrIO_3$: C, 24.49; H, 1.17; I, 37.03; Found: C, 24.55; H, 1.15; I, 37.42.

5-Nitro-2-iodosobenzoic acid (2e)- Yield: 91 % IR (KBr): 2900, 2410, 1618 1590, 1565, 1524, 1352, 1325 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ : 7.2-8.5 (m, 3H) m.p.: 224-226ºc (d) Anal. calcd. for $C_7H_4INO_5$: C, 27.18; H, 1.29; I, 41.10. Found: C, 26.93; H, 1.31; I, 40.87.

Preparation of a polymer with methoxyphenyl groups (1)

Chloromethylated resin (6 g., 19.0 mequiv Cl) was suspended in 75 ml dioxane containing 15 ml of anisole and 1 ml BF_3/Et_2O complex and refluxed for 72 h. The resin was then filtered, washed with methanol, dioxane, methylene chloride and acetone and dried to give 7.3 g. of 1 (2.8 mequiv/g) Quantitative transformation of functional groups was showed by weight increase and complete disappearance of C-Cl band at 665 cm^{-1}. IR (KBr) 1505, 1435, 1240 cm^{-1}.

Polymeric Diaryliodonium-2-carboxylates (3). General Method

Polymer 1 (1 g, 2.8 mequiv.) was stirred in a solution of 8.4 mequiv of the 2-iodosobenzoic acid (2) in 20 ml F_3CCO_2H and 0.5 ml conc. H_2SO_4 at about 50ºC for 96 h. Then, the red resin was filtered and washed with acetic acid and with $EtOH/CH_2Cl_2$ until neutral pH. After this, resin was treated with a mixture of Et_3N/CH_2Cl_2 1/5 (v/v) at room temperature for 1 h, filtered and washed with EtOH, CH_2Cl_2 and acetone and dried to constant weight, yielding polymers 3.

IR (KBr, cm^{-1}): 3a: 1603, 1484, 1448, 1246, 1012, 691; 3b: 1602, 1485, 1242, 1110, 690; 3c: 1615, 1540, 1320, 805, 790, 732, 690; 3d: 1620, 1540, 1320, 1250, 718, 690; 3e: 1630, 1520, 1338, 813, 718, 692.

Non isothermal thermogravimetries of these resins are shown in Figure 1 Calculations of functionalization from weight loss between 180 and 275ºC are given in Table I

Thermal decomposition of polymers 3, in the presence of furoic acid

In a typical procedure, polymeric diaryliodonium-2-carboxylate (3a) (0.36 g, 0.4 mequiv) and furoic acid (0.143 g, 1.3 mequiv) were refluxed in 20 ml diethylbenzene and 1 ml methylglycol for 24 h. After filtering and washing with CH_2Cl_2 and ether, IR of the resin showed no carboxylate bands and the presence of a weak C=O band at 1720 cm^{-1}. The filtrate was extracted with a dilute solution of $NaHCO_3$ and the organic phase was chromatographied on silica gel to give 13 mg (0.09 mmol, 23 % yield) of 1-naphthol, identical with an authentic sample.

When instead of 3a, substituted diaryliodonium-2-carboxylates (3 b-e) were used, the product was a mixture of 6- and 7-substituted 1-naphthols, also identical with authentic samples. Al least in one case (b), NMR supported that both isomers were formed in roughly equivalent amounts (It showed two alike bands for 6- and 7-methyl groups).

Non isothermal thermogravimetries of polymers 3 after these reactions still showed a weight loss between 200 and 275ºC. Quantitative studies indicated fragmentation/rearrangement ratios given in Table I

Trapping agent test

1.7 g (4.98 mmol) of diphenyliodonium-2-carboxylate[17,18,19] and 0.7 g (1.9 mequiv) of 9[13b] in 12 ml diethylbenzene and 12 ml methylglycol were stirred for 30 h at 120ºC. Then, the resin was filtered and washed with water and EtOH, giving 10. IR: 1720, 1580, 1470, 1450, 1390, 1290, 1225, 1165, 1100 cm^{-1}.

10 was hydrolysed with a 5 % solution of NaOH in H_2O/EtOH 1/1 (v/v) giving a yellow liquid which was filtered from the resin, concentrated and acidified, giving furoic acid and 1-naphthol (62 %)

Three Phase Tests

Polymeric diaryliodonium-2-carboxylates (3, 0.2 mequiv) and polymeric furoate (9, 0.9 mequiv) separated by porous plates and suspended in diethylbenzene, were refluxed for 24 h. After work-up and saponification of the trapping resins as described above, 1-naphthol when precursor was 3a and mixtures of 6- and 7-substituted 1-naphthols, when precursors were 3 b-e were obtained.

Distillation of diethylbenzene solutions after three phase tests provided a small amount of adducts 11:

11a - IR: 1605, 1460, 1011, 920, 760, 720, 680 cm^{-1}. ^1H NMR (CCl_4) δ : 7.15-7.60 (m, 4H), 6.1-6.6 (m, 3H), 4.6-4.8 (m, 1H), 2.3 (q, 4H), 0.91 (t, 6H). MS, m/e 210, 209, 195, 181, 156, 152

11b - IR (KBr): 1605, 1560, 1405, 760, 730, 670 cm^{-1}. ^1H NMR (CCl_4) δ : 6.8-7.3 (m, 3H), 6.2-6.5 (m, 3H), 4.6-4.8 (m, 1H), 2.6 (s, 3H), 2.2 (m, 4H), 0.9 (t, 6H). MS, m/e: 224, 223, 209, 195, 170, 166.

11c - IR (KBr): 1585, 1572, 1260, 812, 760, 732 cm^{-1}. ^1H NMR (CCl_4) δ : 7.2-8.0 (m, 3H), 6.1-6.6 (m, 3H), 4.6-4.8 (m, 1H), 2.4 (m, 4H), 0.92 (t, 6H). MS, m/e 246, 244, 231, 229, 217, 215, 181.

11d - IR (KBr): 1585, 1380, 1065, 812, 778, 730 cm^{-1} ^1H NMR (CCl_4) δ : 7.3-8.5 (m, 3H), 6.1-6.7 (m, 3H) 4.6-4.8 (m, 1H), 2.3 (m, 4H) 0.95 (t, 6H). MS, m/e 290, 288, 275, 273, 261, 259, 181.

11e - IR (KBr): 1618, 1565, 1520, 1352, 1310, 805, 730 cm^{-1}. ^1H NMR (CCl_4) δ : 7.5-8.8 (m, 3H), 6.2-6.8 (m, 3H), 4.8-5.0 (m, 1H), 2.3 (m, 4H), 0.99(t,6H). MS, m/e 255, 254, 240, 226, 209, 181

Preparation of 1-naphthols. General method

A mixture of 2 ml of furan and 5 ml (0.037 mol) of isoamyl nitrite was added dropwise for a period of 15 min. over 30 ml of refluxing chloroform. At the same time, but over 2 h., a solution of 78 mequiv. of furan and 20 mequiv of 5-substituted anthranilic acid in 20 ml dioxane was also added. Temperature was kept at about 70ºC and after the addition was finished, the reaction was continued for an additional hour. The mixture was concentrated to give an oil, which was treated with a 10 % solution of KOH and extracted with two 50 ml portions of hexane. The organic phase was washed with water and dried over anhydrous $MgSO_4$. The solvent was then evaporated to give a compound which was refluxed for 10 min. in 20 ml methanol with 2 ml conc. HCl. The solution was concentrated and extracted with ether. The ether solution, after drying over $MgSO_4$, was distillated, giving a mixture of naphthols 7 and 8.

In this way, the following mixtures were obtained:

6- and 7-methyl-1-naphthol (7b and 8b): IR (KBr, cm^{-1}): 3290, 3060, 2980, 2920, 1605, 1570, 1380, 1370, 1265, 1185, 820; ^1H NMR (CCl_4) δ: 6.7-8 (m, 6H), 2.65 (s, 1.5 H), 2.55 (s, 1.5 H); MS m/e 158, 157, 130, 129, 128, 115.

6- and 7-chloro-1-naphthol (7c and 8c). IR (KBr, cm^{-1}): 3320, 1585, 1572, 1375, 1352, 1260, 1085, 812, 732 cm^{-1}; ^1H NMR (CCl_4): δ: 6.5-8.0 (m); MS m/e 180 178, 151, 149, 115, 114.

6- and 7-Bromo-1-naphthol (7d and 8d): IR (KBr, cm^{-1}): 3330, 1580, 1380, 1350, 1260, 1075, 812, 778, 735; ^1H NMR (CCl_4) δ : 6.8-8.5 (m); MS m/e 225, 223, 115, 114.

6- and 7-nitro-1-naphthol (7e and 8e): IR (KBr, cm^{-1}): 3400, 1580, 1525, 1330, 1310, 1270, 780, 735; ^1H NMR ($(CD_3)_2CO$) δ : 7.0-9.0 (m); MS m/e 189, 158, 115, 84, 64, 46.

PDR lifetime measurements

Lifetime measurements were made as described[14] by using a polymeric precursor and polymeric furoate as trapping agent in a series of experiments. The solvent was diethylbenzene at 190ºC and the reaction time 7 h. After each experiment, the polymeric trapping agent was saponified and the solution tested for the presence of the adequate naphthol (comparative TLC, CH_2Cl_2/ether 2/1 v/v). This presence showed the transfer of the arynic moiety and a lifetime for the intermediate higher than the run-time.

Accuracy of this procedure allowed us to detect 1 mg naphthol as a minimum. It means that when no naphthol appears in TLC, less than 3 % of reactive intermediate has been transfered to trapping polymer.

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