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Generation of Benzyne in the Thermal Decomposition of 2-Carboxyphenyl *p*-Toluenesulfonate

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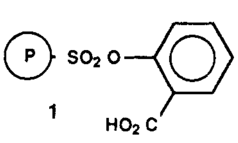
The scope and the mechanism of the generation of 1,2-dehydrobenzene in the thermal decomposition of 2-carboxyphenyl *p*-toluenesulfonate and its salts (**3**) have been studied. 1,2-Dehydrobenzene, which can be trapped with dienic or nucleophilic reagents, is formed in a nonconcerted process with the intermediacy of a species $C_6H_4CO_2$ (**11**) (probably benzoxet-2-one). A complex mixture of disalicylide, trisalicylide, and some other polysalicylides is formed, in the absence of trapping agents, by polymerization of this intermediate.

Heterolytic fragmentation of arenecarboxylic acids or metalated arenes ortho-substituted with nucleofugic leaving groups are two of the more common procedures for the generation of *o*-arynic species.[1] A variety of leaving groups have been used in these processes. Halogens are usually selected as leaving groups for the generation of dehydroarenes from ortho-metalated compounds, while the diazonium group is normally used when the precursor is an arenecarboxylic acid derivative. *p*-Toluenesulfonate and related groups have been often used as leaving groups in heterolytic fragmentation reactions. Accordingly, the preparation of *o*-benzyne from phenyl benzenesulfonate by treatment with lithium tetramethylpiperidide was studied a few years ago,[2] and the generation of arynes from aryl tosylates or similar leaving groups has become a useful procedure in this field.[3] Recently[4] we described the generation of *o*-dehydrobenzenes from polymeric 2-carboxyaryl benzenesulfonates, the presence of the intermediates being demonstrated by the use of the three-phase test.[5] However, the generation of arynes from those polymer-bound precursors was much less efficient than when using other polymeric benzoic acid derivatives.[6,7] In the preparation of polymeric 2-carboxyaryl benzenesulfonates from chlorosulfonated resins, only a minor part of the chlorosulfonyl groups is transformed into the desired functionality (**1**) (0.3–0.6 mequiv/g), and sulfonic acids (**2**) are present as the main functionality (>3 mequiv/g) in the final polymer. Such a situation would clearly affect the efficiency of the aryne generation[8] as well as the mechanisms of thermal decomposition, and limits the utility of three-phase techniques.



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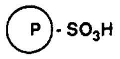

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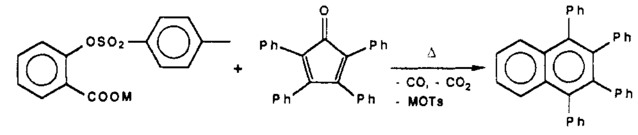
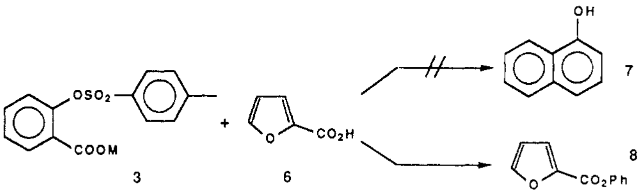
Scheme I



3 **4** **5**

a) M = H, b) M = Na, c) M = K

Scheme II



3 **6** **7** **8**

Table I. Thermal Decomposition of Compounds 3 in the Presence of Tetracyclone (4)

precursor	M	temp, °C	time, h	adduct (%)[a]
3a	H	300	1	**5** (12)
3b	Na	300	1	**5** (17)
3c	K	300	1	**5** (18)
3b	Na	260	1	**5** (8)

[a] Yields after isolation and purification. No attempt was made to optimize yields.

In the present work, we report further studies on the scope and mechanisms of the generation of *o*-dehydrobenzene from 2-carboxyphenyl *p*-toluenesulfonate.

Results and Discussion

2-Carboxyphenyl *p*-toluenesulfonate (**3a**, M = H) was synthesized by reaction of salicylic acid with *p*-toluenesulfonyl chloride. Sodium and potassium salts (**3b**, M = Na; **3c**, M = K) were prepared by reaction of stoichiometric quantities of acid **3a** and sodium or potassium hydroxide. The generation of *o*-dehydrobenzene in the thermal decomposition of this acid (**3a**) and its salts (**3b,c**) was clearly indicated by trapping the intermediate with tetracyclone, a suitable dienic trap for *o*-arynic species. When compounds **3a–c** were heated at 300 °C for 1 h in a nitrogen atmosphere in the presence of tetracyclone (**4**, a slight excess of diene was used), 1,2,3,4-tetraphenylnaphthalene

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(1) (a) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967. (b) Reinecke, M. G. Five Membered Hetarynes in *Reactive Intermediates*; Abramovitch, R. A. Ed.; Plenum Press: New York, 1982; Vol. 2, pp 367-526. (c) Reinecke, M. G. *Tetrahedron* **1982**, *38*, 427-498. (d) Nefedov, O. M.; D'Yachenko, A. I.; Prokof'ev, A. K. *Russ. Chem. Rev.* **1977**, *46*, 941-965.

(2) Fleming, I.; Mah, T. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1577-1579.

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(4) Gaviña, F.; Luis, S. V.; Ferrer, P.; Costero, A. M.; Gil, P. *Tetrahedron* **1986**, *42*, 5641-5648.

(5) (a) Rebek, J., Jr. *Tetrahedron* **1979**, *35*, 723-731. (b) Gaviña, F.; Costero, A. M.; Luis, S. V. *Reactive Polymers* **1989**, *10*, 189-206.

(6) Gaviña, F.; Luis, S. V.; Costero, A. M.; Gil, P. *Tetrahedron* **1986**, *42*, 155-166.

(7) Luis, S. V.; Gaviña, F.; Ferrer, P.; Safont, V. S.; Torres, C.; Burguete, M. I. *Tetrahedron* **1989**, *45*, 6281-6296.

(8) For instance, **4** was found to decompose to an appreciable extent in the presence of sulfonic resins at temperatures below 200 °C.

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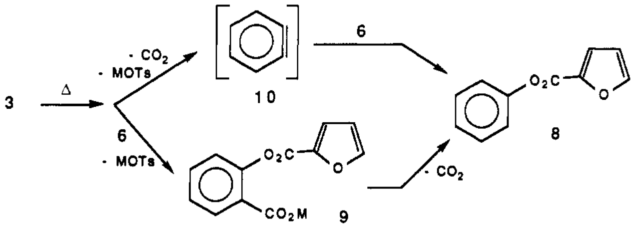
Table II. Thermal Decomposition of Compounds 3 in the Presence of 2-Furoic Acid (6)

precursor	M	temp, °C	time, min	adduct (%)[a]
3a	H	250	30	**8** (48)
3b	Na	250	30	**8** (53)
3c	K	250	30	**8** (60)

[a] Yields after isolation and purification.

Scheme III



was formed via carbon monoxide extrusion from the initial adduct. The yields ranged from 10 to 20% (Table I) and were similar for the acid **3a** and its salts **3b** and **3c**.

As shown in the last entry in Table I, temperature has a marked effect on the yield of adduct **5**, and pyrolyses are better carried out at temperatures of about 300 °C. However, it has to be noted that some decomposition of tetraphenylcyclopentadienone (**4**) is observed at high temperatures.[9] The results in Table I suggest that generation of *o*-dehydrobenzene in the thermal decomposition of **3a** or its salts (**3b,c**) is more efficient than pyrolysis of related *o*-halobenzoates,[10d] but the efficiency is low when compared with some other precursors, such as diaryliodonium-2-carboxylates, from which yields of ca. 60% have been reported.[7,11]

2-Furoic acid (**6**) was also checked as a trap for the intermediate *o*-benzyne generated from compounds **3**. This diene has been shown to react with *o*-dehydrobenzenes in moderate yields to give 1-naphthols (**7**) via 1,4-epoxy-1,4-dihydro-1-naphthoic acids as the initial adducts.[6,7] Rather surprisingly, no 1-naphthol was detected, but high yields of phenyl furoate (**8**), the expected product for nucleophilic reaction of furoic acid with *o*-benzyne, were obtained as shown in Table II.

Trapping of *o*-benzynes with carboxylic acids and alcohols has been reported to occur in fair yields,[7,12] and reaction of *o*-dehydrobenzenes with metal carboxylates is thought to play an essential role in the pyrolysis of *o*-halobenzoates.[10] Differences for compounds **3a–c** cannot be considered very significant since partial proton exchange between furoic acid (in excess) and carboxylates **3b** and **3c** can occur. The absence of dienic trapping of *o*-benzyne by **6** as well as the high yields of ester **8** as compared with yields for adduct **5** are remarkable. The formation of phenyl furoate by a nonarynic route (Scheme III), via intermediate **9**, would explain these results in a simple way.

However, direct nucleophilic attack by **6** on the *p*-toluenesulfonates **3** to give ester **9** is not likely as shown by the fact that ester formation did not take place when furoic acid was heated with phenyl *p*-toluenesulfonate or 4-nitrophenyl *p*-toluenesulfonate under conditions similar to the ones of experiments listed in Table II. In the same way, decarboxylation (at appreciable rates) of compounds like **9** requires higher temperatures.[10] Thus, the participation of a nonarynic route via nucleophilic substitution and decarboxylation, as outlined in Scheme III, seems to be excluded as an important pathway. Alternatively, the high yields of ester **8** can be explained by assuming that carboxylic acids facilitate thermal fragmentation of **3** to give intermediate **10**. Support for this assumption was obtained when **3a** was heated at 200 °C for 30 min in a nitrogen atmosphere with benzoic acid as nucleophilic trap (10 times in excess). Phenyl benzoate was formed in 27% yield, even though decomposition of **3a** required more than 10 h in the absence of benzoic acid. Decomposition of **3a** was shown to be appreciable in the presence of furoic acid even below 150 °C. Thus, phenyl furoate was isolated in low yield when a mixture of **3a** and **6** was refluxed in xylenes for 3 days.

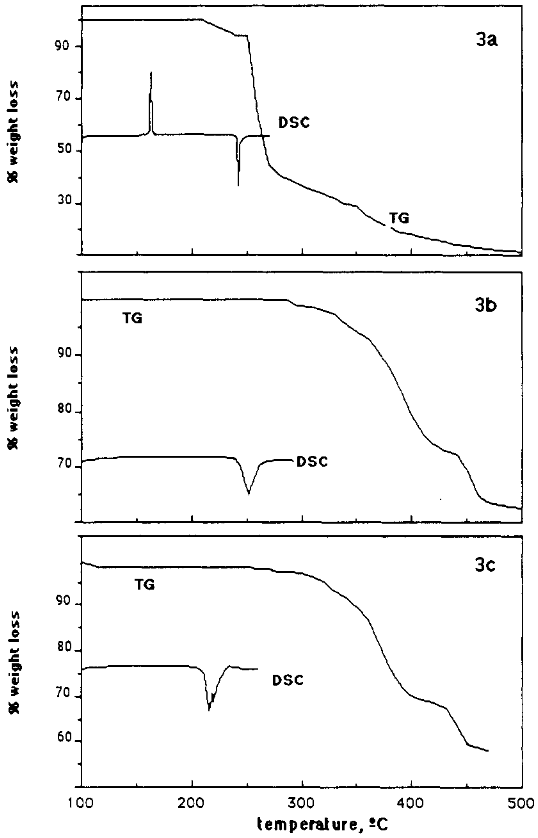


Figure 1. TG and DSC curves for compounds **3a–c**.

Thermal analysis (TG and DSC curves) of *p*-toluenesulfonates **3** is shown in Figure 1. For the free acid **3a**, melting is observed at 165 °C and a further exothermic reaction occurs at 242 °C. For the sodium salt (**3b**) the exothermic process takes place at 252 °C and for the potassium salt (**3c**) at 216–221 °C. At higher temperatures (above 300 °C) decomposition and volatilization of products occurs with violence and DSC curves cannot be accurately obtained. Thermogravimetric analyses are very similar for salts **3b** and **3c** with no appreciable weight loss below 300 °C. At temperatures of about 500 °C, 61–63% of the initial weight still remains for **3c**, corresponding to the calculated value for potassium *p*-toluenesulfonate; a similar result is obtained for the sodium salt **3b**. Accordingly, the resulting solids were identified as sodium (from **3b**) or potassium (from **3c**) *p*-toluenesulfonates. The situation is more complicated for the acid **3a** where de-

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(9) McNelis, E. *J. Org. Chem.* **1965**, *30*, 4324–4326.

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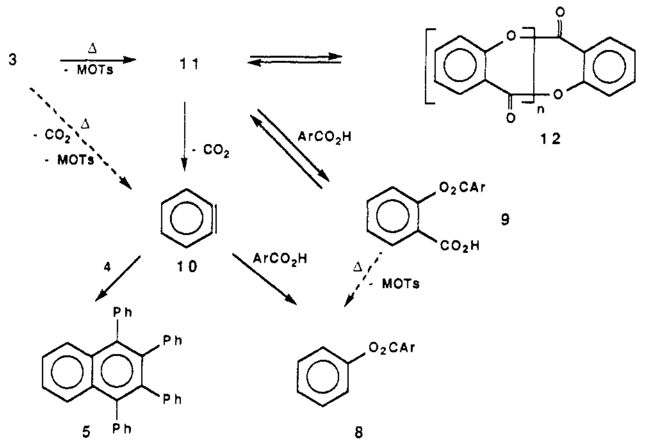
(12) Stiles, M.; Miller, R. G.; Burckhardt, U. *J. Am. Chem. Soc.* **1963**, *85*, 1792–1797.

Scheme IV

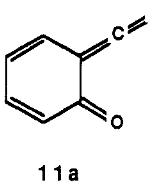


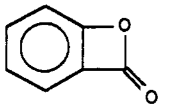
composition of the *p*-toluenesulfonic acid initially formed can also occur at relatively low temperatures.[4,13]

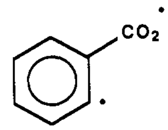
Simultaneous thermal and infrared analysis of **3c** allowed us to follow the decomposition process. An initial reaction was observed in the course of which carboxylate bands disappeared and ester bands (ca. 1730 cm^{-1}) formed, as well as the ones characteristic for metal *p*-toluenesulfonates in the 1000–1300-cm^{-1} region. At 170 °C complete decomposition takes 20 h, and no weight loss ($\leq 2\%$) was detected. At 350 °C carboxylate groups disappear in the first 15 min and the ester bands initially formed cannot be observed after heating 40 min at that temperature, the final residue being potassium *p*-toluenesulfonate.

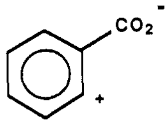
When a sample of **3a** was heated at 170 °C (or refluxed in diglyme) for 20 h in a nitrogen atmosphere in the absence of any trapping agent and the residue was extracted with an organic solvent, a nearly quantitative yield of potassium *p*-toluenesulfonate was obtained as the insoluble solid. The soluble part was a complex mixture of oligosalicylides where trisalicylide and a polymer were the main components. Separation of the mixture was difficult, but samples of pure trisalicylide[14] could be isolated after column chromatography on silica.

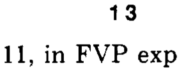
The interpretation of the whole set of experimental data requires the consideration of the intermediacy of benzoxet-2-one or a related species $C_6H_4CO_2$ (**11**) (Scheme IV). The fact that initial decomposition occurs with no appreciable weight loss implies that generation of *o*-benzyne (**10**) by a concerted fragmentation process (with simultaneous formation of MOTs and CO_2 loss) does not take place or, at least, it is a minor reaction. The intermediacy of species $C_6H_4CO_2$ (**11**) in the generation of arynic intermediates is well documented.[1,15] The ketoketene and benzoxet-2-one structures (**11a,b**), as well as the biradical and betainic ones (**11c,d**) have been considered as intermediates whose occurrence in the thermolysis of diaryliodonium 2-, 3-, and 4-carboxylates has been demonstrated by means of the three-phase test.[7] Thus, according to Scheme IV, thermal decomposition of compounds **3** gives rise to benzoxet-2-one or a related species **11** which can evolve through decarboxylation to *o*-dehydrobenzene (**10**) or by oligomerization to form disalicylide (**12**, $n = 1$), trisalicylide (**12**, $n = 2$), and some other polysalicylides (**12**, $n > 2$). Oligomerization to give polysalicylides or related structures can be considered a characteristic reaction of benzoxet-2-ones and similar compounds.[16] In our experiments, at least at moderate temperatures ($\leq$ 300 °C), oligomerization of **11** seems to be much faster than decarboxylation to **10**. However, transformation of **11** to **12** is reversible at higher temperatures. This equilibrium, as well as the initial process, would be facilitated by the presence of acidic compounds. So, benzyne **10** is slowly formed via **11** and can be trapped by dienes or nucleophiles to give adducts **5** and **8**. Benzoxet-2-one could also react with carboxylic acids to form salicylic acid derivatives **9**, but, as was mentioned, decarboxylation of these compounds cannot be considered an important route in the formation of aromatic esters **8**. Thermal reversibility of the conversion of **11** into **9** also must be considered: for instance, FVP of 3-acetoxy-2-naphthoic acid has been reported to yield naphtho[2,3-*b*]oxet-2-one as the major product,[16] and thermolysis at 300–350 °C of acetylsalicylic acid was described to afford disalicylide and trisalicylide in fair yields.[14a] The failure of 2-furoic acid to give cycloadduct is probably related to the role of acidic compounds promoting the thermal fragmentation of **3** to **10**. According to this role, some kind of interaction between the carboxylic group of 2-furoic acid and functional groups in **3** (and/or **12**) is to be expected. This situation would affect the reactivity of 2-furoic acid, increasing its nucleophilicity and decreasing its dienic character toward the intermediate **10** which is being formed. In this way, a simple explanation can be offered for the differences observed between precursors **3** and the related polymer-bound **1**, from which a low yield of 1-naphthol has been reported.[6] For the polymeric precursor **1**, the fragmentation to benzyne is most likely promoted by sulfonic groups (**2**) present in excess in the resin and not by furoic acid. Thus, the reactivity of this trapping agent is much less affected and cycloaddition can occur.


11a


11b


11c


11d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In agreement with the sequence outlined in the Scheme IV, the mass spectrum of **3c** introduced at 300 °C showed two of the most prominent peaks at *m/e* 120 (91%) and 92 (98%) corresponding to the benzoxet-2-one fragment and the carbonylcyclopentadiene **13** which is considered to be formed from **11**, in FVP experiments, by CO loss followed by a Wolff-type ring contraction (see ref 16). The expected molecular peaks for disalicylide, trisalicylide, and

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(13) Bothe, N.; Dorscher, F.; Klein, J.; Widdecke, H. *Polymer* **1979**, *20*, 850–854.

(14) (a) Baker, W.; Ollis, W. D.; Zealley, T. S. *J. Chem. Soc.* **1951**, 201–208. (b) Edgerley, P. G.; Sutton, L. E. *J. Chem. Soc.* **1951**, 1069–1074.

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tetrasalicylide at *m/e* 240 (83%), 360 (13%), and 480 (1%) can be also observed, as well as peaks at 275 (88%), 395 (12%), and 515 (1%) which could correspond to fragments of linear oligomers with tosylate as the terminal group.[17]

Finally, evidence for the generation of *o*-dehydrobenzene in the thermolysis of trisalicylide was obtained. When trisalicylide (**12**, *n* = 3) was heated at 300 °C in an inert atmosphere in the presence of tetracyclone (**4**), tetraphenylnaphthalene (**5**) was formed in low yields. Compound **5** could not be detected at lower temperatures (refluxing in xylenes or nitrobenzene). Similarly, when trisalicylide was heated at 250 °C for 15 min in the presence of 2-furoic acid, phenyl furoate (**8**) was isolated in 27% yield.

Conclusions

1,2-Dehydrobenzene (**10**) is generated in the thermolysis of 2-carboxyphenyl *p*-toluenesulfonate (**3a**) and its sodium and potassium salts (**3b** and **3c**) at temperatures of 250–300 °C. The concerted fragmentation with simultaneous decarboxylation and MOTs formation seems to be at best a very minor pathway. Instead, benzyne is generated through the intermediacy of a species $C_6H_4CO_2$ (**11**), most likely benzoxet-2-one. Intermediate **11** easily dimerizes, trimerizes, and polymerizes to afford the respective polysalicylides (**12**, *n* = 1, 2, 3, ...). In our experimental conditions, decarboxylation of **11** to **10** is slow as compared with the oligomerization process, but the latter is reversible so that 1,2-dehydrobenzene can be formed by thermolysis of either **3** or **12**. The presence of acidic compounds seems to promote both thermal decomposition processes. Trapping of *o*-benzyne with dienic or nucleophilic reagents affords the corresponding adducts in low to good yields. According to these yields, compounds **3** behave as better *o*-benzyne precursors than the related metal *o*-halobenzoates,[10] but they do not seem to be as useful as the two most common thermal sources for this intermediate, phenyldiazonium-2-carboxylate and diphenyliodonium-2-carboxylate. The absence of dienic reaction of 2-furoic with **10** is remarkable when compared to the results obtained with some other precursors.[4,6,7] In this respect, it has to be noted that the nature of the precursors and reaction conditions was demonstrated to play an important role in the reactions of thiophenes as traps for benzyne.[15] In our case, the participation of the carboxylic group of **6** in the thermal decomposition of **3** or **12** to **10** seems to favor the action of 2-furoic acid as a nucleophile and not as a diene. Differences between precursors **3** and the polymer-bound precursor **1**, as is for instance the lower temperature of thermolysis for **1**, indicate the importance of factors associated with the polymeric backbone such as the presence of additional groups, the microenvironment of the reactive sites, and the pseudodilution effect.[18] Thus, the additional sulfonic groups (**2**) in the resin functionalized with precursor **1** would greatly influence the generation process, according to the general effects observed for acidic compounds on the thermolysis of precursors **3**, and would also affect the trapping process. On the other hand, the immobilization of the precursor in the polymeric matrix will always favor dissociative processes over the associative ones.[19] In some cases, the conjunction of these factors can even produce changes in the mechanisms involved, and this must be considered when using polymer-bound reagents in mechanistic studies.

Experimental Section

2-Carboxyphenyl *p*-Toluenesulfonate (3a). 2-Hydroxybenzoic acid (20 g, 0.145 mol) was dissolved in a solution of NaOH (11.6 g, 0.29 mol) in 100 mL of water. *p*-Toluenesulfonyl chloride (27.6 g, 0.145 mol) was then added in small portions. When addition was complete, stirring at room temperature was continued overnight. The solid formed was filtered and redissolved in a NaOH aqueous solution and the resulting solution carefully acidified with diluted HCl. The precipitate was filtered and washed with boiling water. On cooling, unreacted 2-hydroxybenzoic acid was recovered from the filtrate. After drying the remaining solid, pure **3a** (a single spot by TLC) was obtained (11.4 g, 27%): mp 165–171 °C; IR (KBr) 3070, 2862, 2654, 2530, 1698, 1601, 1592, 1413, 1371, 1298, 1276, 1194, 1171, 1080, 908, 880, 861, 769, 725, 546 cm^{-1}; ^{1}H NMR (CD_3OD) δ 7.0–7.9 (m, 8 H), 2.43 (s, 3 H); MS *m/e* (rel abundance) 292 (22), 275 (8), 155 (36), 139 (6), 121 (39), 120 (100), 92 (32), 91 (61), 81 (12), 65 (67). Anal. Calcd for $C_{14}H_{12}O_5S$: C, 57.5; H, 4.1. Found: C, 57.6; H, 4.2.

Preparation of Salts 3b and 3c. Sodium and potassium salts derived from **3a** were prepared by reaction of the foregoing 2-carboxyphenyl *p*-toluenesulfonate with an aqueous solution of NaOH or KOH containing the stoichiometric quantity of base. The solid was washed with a few milliliters of water and acetone and vacuum dried at 80 °C: IR (KBr) 3068, 2970, 1606, 1565, 1380, 1196, 1168, 1084, 887, 823, 778, 737, 663, 566 cm^{-1}.

Thermolysis of 3c in the Presence of Tetraphenylcyclopentadienone (4). The potassium salt of 2-carboxyphenyl *p*-toluenesulfonate (**3c**) (0.342 g, 1.04 mmol) and tetraphenylcyclopentadienone (**4**) (0.5 g, 1.30 mmol) were mixed and heated under nitrogen in an oil bath at 300 °C for 1 h. The resulting solid was extracted with benzene, the solution was evaporated, and the residue was chromatographed on silica to give 1,2,3,4-tetraphenylnaphthalene (0.079 g, 18%) identical with an authentic sample, mp 205 °C (lit.[11] mp 203–206 °C). The same procedure was used for thermolyses of compounds **3a–c**.

Thermolysis of 3c in the Presence of 2-Furoic Acid (6). **3c** (0.84 g, 2.55 mmol) and 2-furoic acid (**6**) (1.438 g, 12.8 mmol) were mixed and heated under nitrogen in an oil bath at 250 °C for 30 min. The resulting mixture was extracted with benzene; the solution was evaporated and the residue chromatographed on silica to afford phenyl furoate as an oil which solidified upon standing (0.28 g, 60%): mp 37 °C; IR (neat) 3141, 3070, 3020, 1740, 1571, 1474, 1397, 1301, 1199, 1096, 1018, 759, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.6–7.7 (m, 1 H), 7.2–7.4 (m, 6 H), 6.5–6.7 (m, 1 H). Anal. Calcd for $C_{11}H_8O_3$: C, 70.2; H, 4.3. Found: C, 70.1; H, 4.2. No 1-naphthol could be detected. The same procedure was used for related thermolyses of compounds **3a–c**.

Thermolysis of 3c in the Absence of Trapping Agents. (a) A sample of **3c** (0.544 g, 1.65 mmol) was heated at 170–180 °C for 20 h. The residue (0.533 g) was extracted with CH_2Cl_2 and the undissolved solid was filtered off and dried to afford slightly impure potassium *p*-toluenesulfonate (0.35 g). The salt was identical with a sample prepared by neutralization of *p*-toluenesulfonic acid with KOH: IR (KBr) 3020, 2908, 2863, 1590, 1392, 1179, 1123, 1032, 1005, 808, 680, 563 cm^{-1}. The soluble extract was a complex mixture with two major products. Pure samples of both were obtained by chromatography on silica. The first one yielded 2-hydroxybenzoic acid as the only product after saponification with KOH–MeOH–H_2O, and was shown to be trisalicylide by comparison with an authentic sample:[14] mp 200–204 °C (lit.[14] mp 197–203 °C); IR (KBr) 1725, 1597, 1482, 1448, 1285, 1244, 1211, 1122, 1076, 1030, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.1–7.9 (m). The second one was a sticky compound which upon saponification afforded 2-hydroxybenzoic acid and

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[17] The mass spectrum of **3a** could be obtained at low probe temperatures and showed the expected fragmentation pattern. The molecular peak at *m/e* 292 is appreciable (22%) as well as the M^+ – OH fragment (8%) at *m/e* 275, and peaks at *m/e* 155, 139, 91, and 64 can be assigned to fragmentation of the tosyl moiety. The base peak corresponds to the fragment $C_6H_4CO_2$ (*m/e* 120), and accordingly the peak at *m/e* 92 (120 – CO) is also important (32%).

[18] Kraus, M. A.; Patchornik, A. *Isr. J. Chem.* **1978**, *17*, 298–303.

[19] A clear example of the importance of some of these factors is found in the report of Mazur and Jayalekshmy of the generation of a polymer-bound *o*-benzyne which could be trapped even after a delay time of several minutes: Mazur, S.; Jayalekshmy, P. *J. Am. Chem. Soc.* **1979**, *101*, 677–683.

a small amount of *p*-toluenesulfonic acid. It was considered to be a linear polysalicylide with *p*-toluenesulfonate as terminal group: IR (KBr) 1726, 1596, 1480, 1447, 1372, 1283, 1246, 1197, 1156, 1121, 1045, 744, 686 cm^{-1}. Some other polysalicylides seemed to be present, but only small impure samples could be obtained. Very similar results were obtained after refluxing a sample of **3c** in diglyme for 19 h.

(b) The mass spectrum of **3c** introduced at 300 °C (probe temperature) showed, in agreement with the preceding results, the following peaks: *m/e* (rel abundance) 515 (1), 480 (1), 396 (4), 395 (12), 361 (4), 360 (13), 277 (8), 276 (16), 275 (88), 248 (10), 242 (4), 241 (16), 240 (83), 197 (9), 196 (18), 169 (11), 168 (18), 157 (11), 156 (10), 155 (100), 139 (16), 121 (28), 120 (91), 92 (98), 91 (99), 77 (12), 76 (11), 65 (59), 64 (79), 63 (73).

Attempted Esterification of 2-Furoic Acid with Phenyl *p*-Toluenesulfonate. 2-Furoic acid (0.5 g, 4.46 mmol) and phenyl *p*-toluenesulfonate were mixed and heated under nitrogen at 250 °C for 4 h. After that period, both starting materials were recovered unchanged and the formation of phenyl furoate could not be detected.

Thermolysis of Trisalicylide in the Presence of 2-Furoic Acid. Trisalicylide (0.8 g, 2.2 mmol) and 2-furoic acid (1 g, 8.9 mmol) were mixed and heated under nitrogen at 250 °C for 15 min. The resulting mixture was dissolved in benzene and subjected to column chromatography on silica to give 0.11 g (0.6 mmol, 27%) of phenyl furoate.

The Metal-Ammonia Reduction of Mono- and Dinaphthylbenzenes

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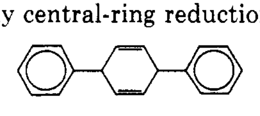
The metal-ammonia reduction of 1- and 2-phenylnaphthalene (**9** and **10**, respectively), 1,3-bis(1-naphthyl)benzene (**5**), 1,3-bis(2-naphthyl)benzene (**6**), 1,4-bis(1-naphthyl)benzene (**7**), and *m*-quinquephenyl (**8**) has been investigated. **9** affords a mixture of isomeric dihydro products together with 1-phenyl-1,2,3,4-tetrahydronaphthalene, and the effect of metal, temperature, and quenching methods on the product distribution is reported. **10** provided only a single dihydro (1,4-) isomer plus a tetrahydro product. Both **5** and **7** provided a number of dihydro, tetrahydro, hexahydro, and octahydro products. On the other hand, **6** afforded high yields of a single tetrahydro product with lithium, and exclusively an octahydro product when 5-7 mol of sodium was used. In contrast to the terphenyls, which seem to have a propensity for inner-ring reduction, none of the naphthyl benzenes showed any tendency to reduce in the central benzene ring. *m*-Quinquephenyl reduced in two rings with no evidence for reduction in the central or outer rings.

Although the metal-ammonia reduction behavior of a large number of benzene and polynuclear aromatic compounds has been investigated,[1,2] relatively little attention has focused on compounds with multiple aromatic rings connected by active (π) or inactive (CH_2) spacers. One exception is a report on the isomeric terphenyls.[3] *p*-Terphenyl reacts with alkali metals in anhydrous ammonia to provide both central-ring reduction (**1**), and outer-ring reduction (**2**) products. The yield of **1** ranges from ca. 25 to 75% and is largely a function of the particular metal used with the ratio of outer- to inner-ring reduction decreasing in the series Ca > K > Na > Li. On the other hand, the isomeric *m*-terphenyl and *o*-terphenyl provide only central-ring reduction (**3** and **4**, respectively).



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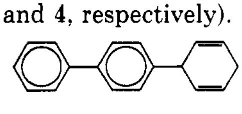

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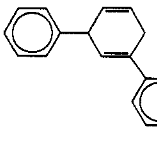

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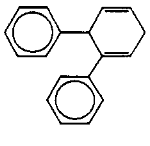

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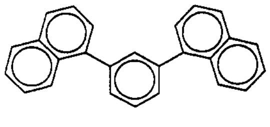
An aim of this study was to learn if the tendency for central-ring reduction, as observed with the terphenyls, would also prevail in multiple ring systems where (a) the outer rings have greater electron affinity (e.g. **5-7**) or (b) there are more than three rings (e.g. **8**). However, the investigation of **5-7** required a thorough understanding of the reduction behavior of the simpler cases, the isomeric phenylnaphthalenes.

Table I. Metal-Ammonia Reduction of 1-Phenylnaphthalene (9)[a]

entry	metal (mmol)[b]	temp, °C	% composition[c] 11	12	13
1	Li (2.5)	-78	34	58	7
2	Li (5)	-78	31	-	69
3	Li (10)	-78	30	-	70
4	Li (10)	-33	30	-	69
5	Na (2.5)	-78	25	69	6
6	Na (5)	-78	28	48	24
7	Na (2.5)	-33	25	53	5
8	Na (10)	-33	26	16	58
9[d]	Na (2.0)	-33	10	30	30

[a] Reactions inverse quenched after 1 h by pumping into aqueous ammonium chloride. [b] Millimoles of metal per millimole of hydrocarbon. [c] By GC; difference from 100% represents unreacted starting material. [d] Results from ref 4.



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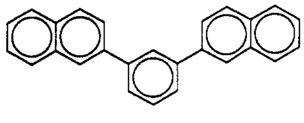

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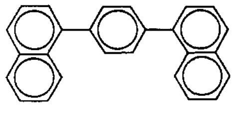

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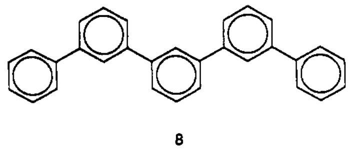

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