centrations of these solutions were in the range 0.3–0.5 M. Apart from 4-*p*-OCH_3, the cations did not exhibit significant variations in chemical shifts with changes of temperature, superacids, or concentrations. In the case of 4-*p*-OCH_3 the variation may be due to equilibration with an O-protonated or Lewis acid associated species.

Acknowledgment. We are grateful to Professor D. G. Farnum for communicating his results for **4** and to Professor H. C. Brown for communicating the results for **5** and **6** to us prior to publication. M.J.J. acknowledges a Commonwealth Postgraduate Award.

Registry No. **3** (Z = 4-OCH_3), 76481-14-6; **3** (Z = 4-CH_3), 76481-15-7; **3** (Z = 4-F), 51804-43-4; **3** (Z = 4-Cl), 76481-16-8; **3** (Z = 3-CH_3), 76481-17-9; **3** (Z = H), 76481-18-0; **3** (Z = 3-F), 76481-19-1; **3** (Z = 3-Cl), 76481-20-4; **3** (Z = 3-CF_3), 76481-21-5; **3** (Z = 3,5-Cl_2), 76481-22-6; **3** (Z = 4-CF_3), 76481-23-7; **4** (Z = 4-OCH_3), 76481-24-8; **4** (Z = 4-CH_3), 76481-25-9; **4** (Z = 4-F), 51804-53-6; **4** (Z = 4-Cl), 76481-26-0; **4** (Z = 3-CH_3), 76481-27-1; **4** (Z = H), 52873-73-1; **4** (Z = 3-F), 76481-28-2; **4** (Z = 3-Cl), 76481-29-3; **4** (Z = 3-CF_3), 76481-30-6; **4** (Z = 3,5-Cl_2), 76481-31-7; **4** (Z = 4-CF_3), 76481-32-8; **4** (Z = 3,5-$(CF_3)_2$), 76481-33-9; **7** (Z = 4-OCH_3), 17138-75-9; **7** (Z = 4-CH_3), 22975-57-1; **7** (Z = 4-F), 76481-34-0; **7** (Z = 4-Cl), 76481-35-1; **7** (Z = 3-CH_3), 76481-36-2; **7** (Z = H), 1565-71-5; **7** (Z = 3-F), 76481-37-3; **7** (Z = 3-Cl), 76481-38-4; **7** (Z = 3-CF_3), 76481-39-5; **7** (Z = 3,5-Cl_2), 76481-40-8; **7** (Z = 4-CF_3), 76481-41-9; **7** (Z = 3,5-$(CF_3)_2$), 76481-42-0; **8** (Z = 4-OCH_3), 76481-43-1; **8** (Z = 4-CH_3), 29480-17-9; **8** (Z = 4-F), 76481-44-2; **8** (Z = 4-Cl), 29480-19-1; **8** (Z = 3-CH_3), 76481-45-3; **8** (Z = H), 29480-18-0; **8** (Z = 3-F), 76481-46-4; **8** (Z = 3-Cl), 76481-47-5; **8** (Z = 3-CF_3), 76481-48-6; **8** (Z = 3,5-Cl_2), 76481-49-7; **8** (Z = 4-CF_3), 76481-50-0; **8** (Z = 3,5-$(CF_3)_2$), 76481-51-1; 3-[4-(trifluoromethyl)phenyl]-2-pentene, 76481-52-2; 3-(3,5-dichlorophenyl)-2-pentene, 76481-53-3; 2-[3,5-bis(trifluoromethyl)phenyl]-2-chloroadamantane, 76498-69-6.

Stevens-Type Rearrangement of Open-Chain Analogues of Reissert Compounds. Evidence for Participation by Radical Intermediates

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The thermal rearrangements of the conjugate bases (**2**) of *N*-benzyl open-chain analogues of Reissert compounds give products formally derived from two competing [1,2] rearrangement–elimination reactions. The products of the major sequences of reactions are deoxybenzoins and benzonitriles, while those of the minor sequence are α-benzamidostilbenes. The results are compatible with a radical pair mechanism involving initial homolysis of the conjugate base **2** followed by two possible modes of radical recombination (Schemes I and II).

Although base-catalyzed rearrangements of Reissert compounds derived from quinoline and isoquinoline have been observed,[1,2] there have been no reports of analogous rearrangements for open-chain Reissert analogues other than a brief mention of this in our recent paper covering synthetic uses of such compounds.[3] We report here examples of several base-catalyzed rearrangement reactions of open-chain analogues of Reissert compounds and present evidence in support of a mechanism involving initial homolysis of each conjugate base, with two subsequent modes of radical pair recombination.

Open-chain analogues of Reissert compounds **1a–j** have been prepared by known methods.[3,4] The anions **2a–j** of these Reissert analogues have been generated by treatment of **1a–j** with sodium hydride in tetrahydrofuran solution,[4] and these anions, in turn, have been found to undergo rearrangement and fragmentation to the deoxybenzoins **3a–j** (eq 1). The results of the ketone preparations are summarized in Table I. This rearrangement is of interest, not only from a synthetic viewpoint but also from a mechanistic one, in that it bears striking similarities to the Stevens and related rearrangements.[5,6]

Since the participation of radical intermediates in the Stevens and related rearrangements is well documented,[6,8-19] it was decided to investigate the possible partici-

Table I. Rearrangement Reactions

Reissert analogue	Ar_1	Ar_2	Ar_3	% yield of **3**
1a	C_6H_5	C_6H_5	C_6H_5	57
b	*p*-ClC_6H_4	C_6H_5	C_6H_5	94
c	*p*-$CH_3OC_6H_4$	C_6H_5	C_6H_5	100
d	2-furyl	C_6H_5	C_6H_5	63
e	3,4-(methylenedioxy)phenyl	C_6H_5	C_6H_5	55
f	C_6H_5	C_6H_5	*p*-ClC_6H_4	50
g	*p*-ClC_6H_4	C_6H_5	*p*-ClC_6H_4	87
h	*p*-$CH_3OC_6H_4$	C_6H_5	*p*-ClC_6H_4	96
i	C_6H_5	*p*-$CH_3C_6H_4$	C_6H_5	62
j	*p*-$CH_3OC_6H_4$	*p*-$CH_3C_6H_4$	C_6H_5	64

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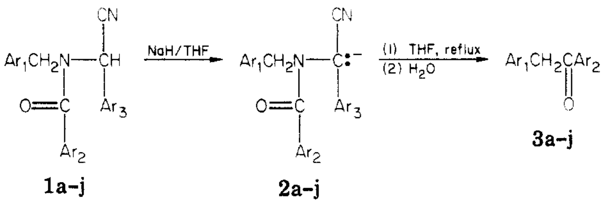
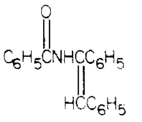

(1)

pation of radical intermediates in the rearrangement of **1** to **3**.

We have been able to show that seven products can be isolated directly from the rearrangement of Reissert analogue **1i**. These products have been identified as benzyl *p*-tolyl ketone (**3i**), benzonitrile (**4**), *p*-toluic acid (**5**), *p*-toluamide (**6**), α-*p*-toluamidostilbene (**7**), bibenzyl, and toluene. It should be noted that α-benzamidostilbene (**8**)

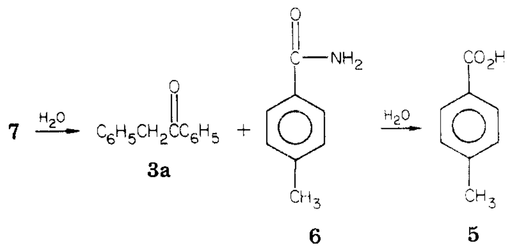

8

has been isolated in the rearrangement of analogue **1a** to **3a**. Compound **8** is identical in all respects with the same compound prepared by Huisgen[7] by a different method. The fact that α-benzamidostilbenes **7** and **8** are minor reaction products and not reaction intermediates is supported by control experiments which demonstrated the failure of **7** and **8** to fragment to the ketones **3a** and **3i** and benzonitrile in the presence of hydride or cyanide ion.

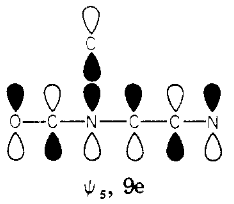
Although conclusive evidence for an exclusive radical pathway is not available as yet, there are several characteristics of the rearrangement which lend support to such a possibility. These are (a) the fact that the rearrangement occurs only with the *N*-benzyl (not the *N*-aryl) derivatives of open-chain analogues of Reissert compounds, reflecting the increased ease of formation of benzyl radicals as compared with that of aryl radicals, (b) the theoretical point that a concerted front-side nucleophilic displacement of the carbanionic center of **2** on the benzylic carbon is forbidden by orbital symmetry considerations,[6] (c) the detection of products (bibenzyl and toluene) resulting from radical intermediates, (d) the observation that the presence of electron-donating or electron-withdrawing groups in the para position of the benzyl group enhances the rearrangement rate and leads to higher yields of desoxybenzoins, and (e) CIDNP studies which, however, gave a positive result on one occasion only.

Possible mechanisms which account for all the observed results are illustrated in Schemes I and II.

p-Toluic acid (**5**) and *p*-toluamide (**6**) result from hydrolysis of **7** during the workup procedure (eq 2). Deoxybenzoin (3a) was also isolated when **7** was subjected to acid-catalyzed hydrolysis in a separate experiment. These results correspond to those previously reported by Huisgen[7] with respect to **8**.


(2)

Chantrapromma, Ollis, and Sutherland[20,21] have recently reported that certain ammonium ylides undergo thermal decomposition to give products derived from competing [1,2], [1,3], and [1,4] rearrangements. Their results are compatible with a radical-pair mechanism in which the initial homolysis of the ylide is followed by three possible modes of radical pair recombination. Ollis and his coworkers have subsequently reported in great detail on the complexities of these and related rearrangements.[22-28] Our results differ from those of Ollis in that anions of type **2** undergo thermal decomposition to give products resulting from two competing [1,2] rearrangements. Nevertheless, our results are also compatible with a radical-pair mechanism in which the initial homolysis of **2** is followed by more than one possible mode of radical-pair recombination. However, if the radical pair, **9** and **10** (Scheme I), were the transition state of a sigmatropic process and if **10** were a six-atom 9-π-electron moiety, the intriguing possibility


ψ_5, 9e

would arise that the minor product **7** could result from a symmetry allowed concerted process, even though a [1,2] rearrangement is involved. Obviously, such a conclusion must be regarded with considerable skepticism when applied to a charged molecule having several heteroatoms, but it is worthy of some consideration.

Experimental Section

The preparations of the open-chain Reissert analogues **1** were carried out as described previously, but the intermediate aminonitriles were not characterized. The properties of the Reissert analogues **1** are listed in Table II.

Rearrangement of 1i. A solution of 17.62 g (0.04 mol) of the open-chain Reissert analogue **1i** in 300 mL of anhydrous tetrahydrofuran was added to 2.0 g (0.04 mol) of sodium hydride as a 50% oil dispersion. The solution turned red, was stirred at room temperature for 10 min, and then was refluxed for 4 days. The reaction mixture was poured into about 700 g of ice and water and stirred until all of the ice had melted. A solid which had precipitated was collected by filtration. This consisted of 4.8 g (57%) of benzyl *p*-tolyl ketone (**3i**), mp 107–109 °C. The identity of the ketone was proved by comparison of its IR and NMR spectra with those of an authentic sample of the ketone and also by a mixture melting point test.

The filtrate was extracted with ether, and the ether solution, dried over anhydrous magnesium sulfate, was concentrated to give a yellow oil. When the oil was treated with a small amount of

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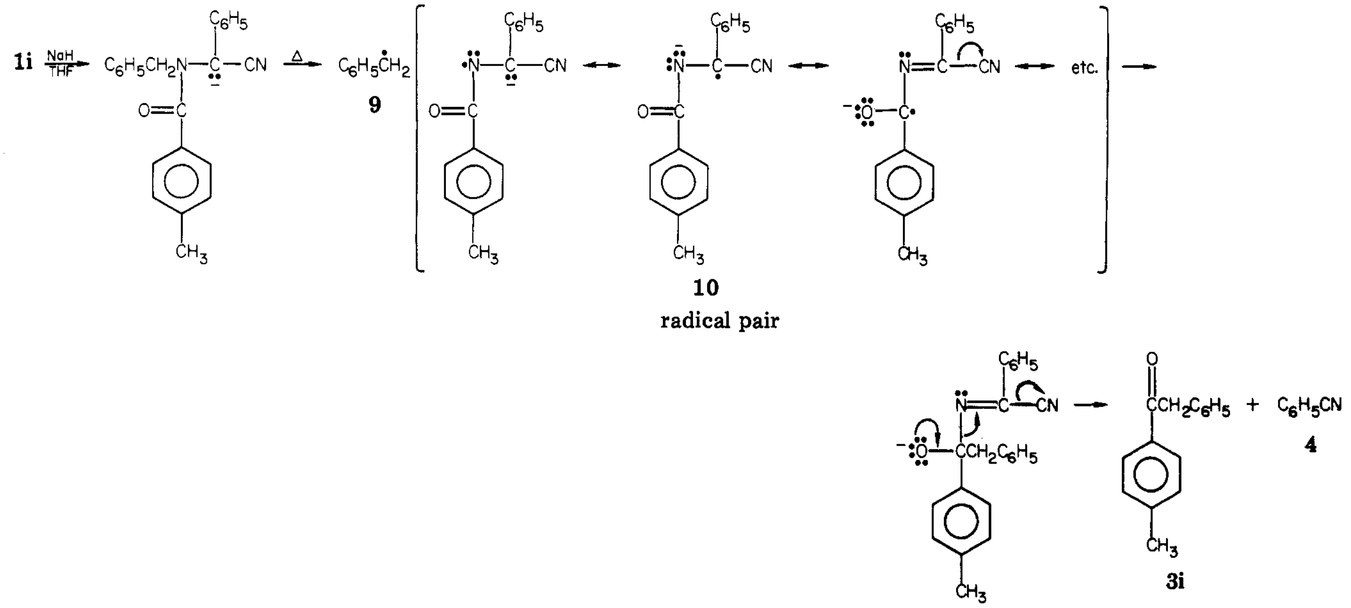
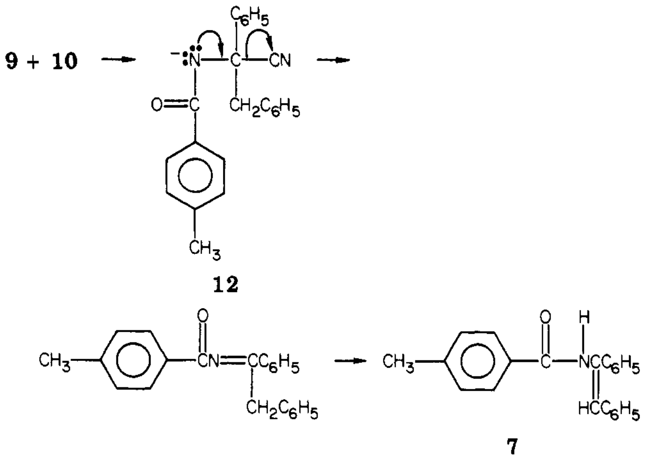
Scheme I. Major Reaction Pathway



Scheme II. Competing Radical Recombination



hot ethanol, a solid crystallized. There was obtained 1.0 g (8%) of α-*p*-toluamidostilbene (7): mp 173–174 °C; mass spectrum, *m/e* 313 (M^+); ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3 H), 6.50 (s, 1 H), 7.3 (m, 15 H, 14 H in presence of D_2O); IR ($CHCl_3$) 3200 (NH), 1640 (amide I), 1570 cm^{-1} (amide II). Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.46. Found: C, 84.06; H, 6.32; N, 4.45.

The filtrate was concentrated to dryness, and the residue was dissolved in 1:1 ether–hexane. A crystalline solid [0.2 g (4%), mp 158–160 °C] was obtained and was identified as *p*-toluamide (6) by comparisons of its NMR and IR spectra with those of an authentic sample and by a mixture melting point test with authentic material.

The filtrate was again concentrated to dryness, and the residue was distilled in vacuo. There was obtained 0.5 g (12%) of benzonitrile (4, bp 188–191 °C), identified by comparison of its IR and NMR spectra with those of an authentic sample.

The residue was subjected to VPC analysis (5% DC 550 on Chromosorb W, 5 × $^1/_8$ in. column, helium flow rate 30 mL/s, column temperature 120–250 °C) and, in addition to benzonitrile, toluene and bibenzyl were detected. Mixture VPC tests showed enhancement of the respective peaks when authentic samples of toluene and bibenzyl were added to the mixture.

The basic aqueous phase was acidified by addition of hydrochloric acid, and a solid which precipitated was collected. This consisted of 0.2 g (4%) of *p*-toluic acid (5), mp 181–182 °C (also in admixture with an authentic sample). Comparisons of IR and NMR spectra confirmed the identity of the acid.

Table II. Yields and Physical Properties of 1

Reissert analogue	mp, °C	yield, %	IR (KBr) (C=O), cm^{-1}	NMR ($CDCl_3$), δ (*J*, Hz)
1a	137–138[a]	87	1640	7.30 (m, 15 H), 6.60 (s, 1 H), 4.50 (d, 2 H, *J* = 15)
b	140–142[b]	73	1640	
c	125–127[c]	64	1640	7.20 (m, 14 H), 6.45 (s, 1 H), 4.55 (d, 2 H, *J* = 6), 3.75 (s, 3 H)
d	149–150[b]	76	1640	7.50 (m, 10 H), 6.7 (s, 1 H), 6.2 (m, 3 H), 4.4 (q, 2 H)[d]
e	135–136[b]	67		6.0–7.5 (m, 16 H), 4.5 (d, 2 H, *J* = 7)[e]
f	202–203[b]	48	1640	
g	190–192[b]	47	1630	
h	151–153[b]	38	1640	
i	120–122[b]	68	1640	
j	136–137[b]	68	1640	

[a] Lit.[3] mp 137–138 °C. [b] Satisfactory combustion analytical data for C, H, N, and Cl (where applicable), ±0.3%, were obtained. [c] Lit. mp 121–123 °C. [d] Diastereotropic splitting. [e] Taken in Me_2SO solution.

Other Rearrangements of 1. These were carried out as described in our previous paper.[3] The results are summarized in Table I.

Registry No. **1a**, 5367-12-4; **1b**, 72867-44-8; **1c**, 72867-49-3; **1d**, 76599-24-1; **1e**, 76599-25-2; **1f**, 76583-33-0; **1g**, 76583-34-1; **1h**, 76583-35-2; **1i**, 76583-36-3; **1j**, 76583-37-4; **3a**, 451-40-1; **3b**, 6332-83-8; **3c**, 24845-40-7; **3d**, 24954-15-2; **3e**, 40804-81-7; **3i**, 2001-28-7; **3j**, 60904-47-4; **4**, 100-47-0; **5**, 99-94-5; **6**, 619-55-6; **7**, 76583-38-5; toluene, 108-88-3; bibenzyl, 103-29-7.