Arylation of Several Carbanions by the SRN1 Mechanism[1]

ROBERTO A. ROSSI[2] AND J. F. BUNNETT*

University of California, Santa Cruz, California 95064

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The carbanions derived from 1,3-pentadiene, 1-(*p*-anisyl)propene, indene, fluorene, 2-butanone, and 3-methyl-2-butanone are phenylated by treating them with bromobenzene and sodium or potassium metal in liquid ammonia. The enolate ions of the two ketones are also phenylated by photostimulated reaction with bromo- or iodobenzene. By either method, 2-butanone is phenylated principally at the 3 position and 3-methyl-2-butanone mainly at the 1 position. In general, the carbanions derived from hydrocarbons give mixtures of mono-, di-, and triphenylated products. These reactions are believed to occur by the SRN1 mechanism.

Nucleophilic displacement of halogen in unactivated aryl halides by the familiar SNAr mechanism[3] tends to occur sluggishly, if at all. On the other hand, substitution reactions involving the very same halobenzenes and nucleophiles often take place with great facility if the novel SRN1 mechanism[4] can be brought into play.

An essential feature of the SRN1 mechanism for substitution at aromatic carbon is the high affinity of aryl radicals for certain strong nucleophiles such as amide ion,[4-6] the cyanomethyl anion,[5,7] and the acetone enolate ion.[8] The mechanism as a whole, depicted in eq 1–4, is initiated by electron transfer to substrate ArX from a suitable electron donor. The radical anion thus formed then splits (eq 2) to form an aryl radical, releasing the nucleofugic substituent as an anion (if initially neutral). The aryl radical combines (eq 3) with carbanion or other nucleophile to form an adduct, which then must dispose of an excess electron or otherwise react to form a stable product. If the excess electron is transferred to another substrate molecule, as in eq 4, a cycle is completed comprising eq 2, 3, and 4. A more complete description of the system would show termination steps as well as alternative reaction pathways available to some of the intermediates.

$$\text{electron donor} + \mathrm{ArX} \longrightarrow [\mathrm{ArX}]\cdot^- + \text{residue} \qquad (1)$$

$$[\mathrm{ArX}]\cdot^- \longrightarrow \mathrm{Ar}\cdot + \mathrm{X}^- \qquad (2)$$

$$\mathrm{Ar}\cdot + \mathrm{R}:^- \longrightarrow [\mathrm{ArR}]\cdot^- \qquad (3)$$

$$[\mathrm{ArR}]\cdot^- + \mathrm{ArX} \longrightarrow \mathrm{ArR} + [\mathrm{ArX}]\cdot^- \qquad (4)$$

The solvated electron in liquid ammonia is very effective for the purpose of getting the mechanism started (eq 1). In other studies, SRN1 reactions stimulated by solvated electrons have afforded high yields of substitution products.[5,6,8] Alternatively, an initiating electron transfer in the sense of eq 1 can be stimulated photochemically.[9]

We now report reactions of bromobenzene with some previously uninvestigated carbanions, induced by sodium or potassium metal in liquid ammonia, as well as photochemical and electron-stimulated reactions of bromo- and iodobenzenes with the enolate ions of 2-butanone and 3-methyl-2-butanone.

Results and Discussion

Phenylation of Carbanions from Hydrocarbons.— Reactions were conducted by (1) preparing KNH_2 in liquid ammonia, (2) adding the hydrocarbon and allowing the carbanion to be formed, (3) adding bromobenzene, (4) adding potassium (or sodium) metal in small pieces until electrons were in excess, and (5) acidifying with NH_4Cl. One set of experiments, summarized in Table I, involved the carbanions derived from 1,3-pentadiene, 1-(*p*-anisyl)propene (also known as anethole), indene, and fluorene.[10]

The carbanion from 1,3-pentadiene did not react with bromobenzene in ammonia at −78°. However, when potassium metal was also added, reaction occurred to form a complex mixture of products (eq 5).

$$\mathrm{CH_2{\cdots}CH{\cdots}CH{\cdots}CH{\cdots}CH_2^-} + \mathrm{C_6H_5Br} \xrightarrow[\mathrm{NH_3}]{\mathrm{K}} \mathrm{PhCH_2CH_2CH_2CH{=}CH_2} + \mathrm{PhCH_2CH{=}CHCH_2CH_3} + \mathrm{PhCH_2CH{=}CHCH{=}CH_2} + \mathrm{PhCH{=}CHCH{=}CHCH_3} + \text{other products} \qquad (5)$$

A small portion of the mixture was examined by glpc, and several components were isolated. These included 5-phenyl-1-pentene (20%), 1-phenyl-2-pentene (6%), 5-phenyl-1,3-pentadiene (18%), and 1-phenyl-1,3-pentadiene (13%), as well as products representing attachment of two or three phenyl groups to the five-carbon chain. The rest of the mixture was subjected to catalytic hydrogenation, and the resulting melange was found, by glpc, to contain 1-phenylpentane (57% yield), 1,1-diphenylpentane (9%), 1,5-diphenylpentane (7%), and a triphenylpentane fraction (9%). In another run, the yield of 1-phenylpentane after hydrogenation was 74%.

This reaction has both preparative and mechanistic interest. It provides a way of establishing a five-carbon straight chain on a benzene ring in place of a

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[1] Research supported in part by the National Science Foundation.

[2] Grateful recipient of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

[3] J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951); J. F. Bunnett, *Quart. Rev., Chem. Soc.*, **12**, 1 (1958).

[4] J. K. Kim and J. F. Bunnett, *J. Amer. Chem. Soc.*, **92**, 7463 (1970).

[5] J. K. Kim and J. F. Bunnett, *ibid.*, **92**, 7464 (1970).

[6] R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **37**, 3570 (1972).

[7] J. F. Bunnett and B. F. Gloor, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, ORGN 45.

[8] R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, **94**, 683 (1972).

[9] R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 1407 (1973).

[10] Inasmuch as the estimated pK_a of ammonia is 35 and those of indene and fluorene are respectively about 20 and 23, KNH_2 clearly will convert these hydrocarbons into their anions. The pK_a of allylic hydrogen in propene is estimated to be 35.5, and conjugation of a vinyl or *p*-anisyl group with the propenide system would cause 1,3-pentadiene or anethole, respectively, to have lower pK_a's. It is therefore expected that KNH_2 will also convert these compounds to their anions. This expectation is supported by our observation of a strong color change (colorless to red) on adding either compound to KNH_2 in ammonia. *Cf.* D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter I.

TABLE I

REACTIONS OF BROMOBENZENE WITH CARBANIONS AND ALKALI METALS IN LIQUID AMMONIA

Registry no.	Carbanion from	[Carbanion], *M*	[C_6H_5Br], *M*	[K],[a] *M*	Temp, °C	Products (yield, %)[b]	Registry no.
40719-28-6	1,3-Pentadiene	0.28	0.063	Nil	−78	None[c]	
		0.48	0.23	0.25	−78	1-Phenylpentane (57),[d,e] (40)[f]	538-68-1
						1,1-Diphenylpentane (9)[d]	1726-12-1
						1,5-Diphenylpentane (7)[d]	1718-50-9
						Triphenylpentanes (9)[d]	40719-26-4
		0.33	0.063	0.15	−78	1-Phenylpentane (74)[d]	
						Diphenylpentanes (7)[d]	
						Triphenylpentanes (3)[d]	
40719-29-7	Anethole	0.37	0.19	0.28	−78	1-Phenyl-1-(*p*-anisyl)propane (13)[d]	27238-93-3
						3-Phenyl-1-(*p*-anisyl)propane (31)[d]	40715-68-2
						Diphenyl-1-(*p*-anisyl)propanes (37)[d]	40715-69-3
						Triphenyl-1-(*p*-anisyl)propanes (9)[d]	40715-70-6
		0.27	0.14	0.57	−33	1-Phenyl-1-(*p*-anisyl)propane (13)[d]	
						3-Phenyl-1-(*p*-anisyl)propane (36)[d]	
						Diphenyl-1-(*p*-anisyl)propanes (33)[d]	
						Triphenyl-1-(*p*-anisyl)propanes (5)[d]	40715-71-7
40719-30-0	Indene	0.16	0.27	0.28	−78	1-Phenylindan (3)	26461-03-0
						3-Phenylindene (32)	1961-97-3
						Diphenylindenes[g] (11)	40719-27-5
						Triphenylindenes[h] (4)	
		0.31	0.20	0.45	−78	1-Phenylindan (9)	
						3-Phenylindene (32)	
						Diphenylindenes[g] (12)	
						Triphenylindenes[h] (6)	
35782-20-8	Fluorene	0.14	0.14	0.18[i]	−33	9-Phenylfluorene (44)	789-24-2
						9,9-Diphenylfluorene (5)	20302-14-1
		0.037	0.18	0.23	−78	9-Phenylfluorene (57) (40)[f]	
						9,9-Diphenylfluorene (23)	

[a] Concentration if no reaction had occurred. [b] Yields based on reactant in deficiency. [c] Recovered C_6H_5Br, 91%. [d] Product and yield after catalytic hydrogenation of crude product mixture. [e] For products before hydrogenation, see text. [f] Yield of isolated product. [g] Two isomers in approximately equal amounts. [h] Several isomers; composition tentative. [i] Sodium.

halogen atom or, we presume from experience with related reactions,[8] in place of a trimethylammonio, diethyl phosphate, or phenylthio group. The unsaturation in the immediate product would be useful in some syntheses for purposes of further elaboration, but in others hydrogenation to an *n*-pentyl group would be preferable. No doubt similar reactions could be carried out with carbanions from higher 1,3-alkadienes, but some complication would enter from the likelihood that arylation would occur at both the 1 and 5 positions, which in those cases would not be equivalent. It is anticipated that the carbanion from 1,3,5-heptatriene would be arylated at the ends of the seven-carbon chain.

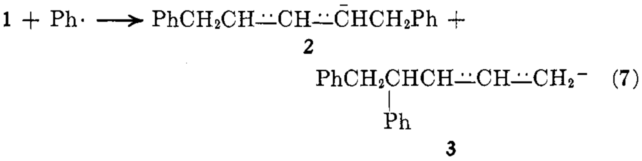
As to mechanism, the immediate consequence of the combination of phenyl radical with pentadienide ion is a radical anion **1** (eq 6). In part, this probably

$$\mathrm{Ph\cdot + CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} CH \overset{\cdots}{-} CH \overset{\cdots}{-} CH_2^- \longrightarrow \underset{\mathbf{1}}{[PhCH_2CH{=}CHCH{=}CH_2]^{\cdot -}}} \quad (6)$$

transfers an electron to a bromobenzene molecule in the sense of eq 4, and the resulting 5-phenyl-1,3-pentadiene is quickly converted to the 1-phenylpentadienide ion in the strongly basic environment. Upon ultimate acidification, protonation occurs at both the 1 and 5 positions, forming the two isomeric phenylpentadienes obtained. However, during the reaction proper the 1-phenylpentadienide ion may be further arylated, apparently to about equal extents at the positions α and ω to the aromatic ring. Similar events may lead to triphenyl and perhaps some more highly phenylated derivatives.

Radical anion **1** is evidently partially reduced in the reacting system, leading ultimately to the phenylpentenes detected as products.

The possibility that radical anion **1** may persist in the reaction mixture needs also to be considered. It ought to be able to couple with phenyl radical as shown in eq 7. The resulting allylic carbanions might



$$\mathrm{\mathbf{1} + Ph\cdot \longrightarrow \underset{\mathbf{2}}{PhCH_2CH \overset{\cdots}{-} CH \overset{\cdots}{-} \bar{C}HCH_2Ph}} + \underset{\mathbf{3}}{\mathrm{PhCH_2\underset{\displaystyle Ph}{\underset{|}{C}}HCH \overset{\cdots}{-} CH \overset{\cdots}{-} CH_2^-}} \quad (7)$$

then be further phenylated by phenyl radicals. No product with the carbon skeleton of **3** has been identified, however. If radical anion **1** persisted until quenching with NH_4Cl, disproportionation, protonation, and isomerization might occur during quenching to furnish some of the products that were obtained.

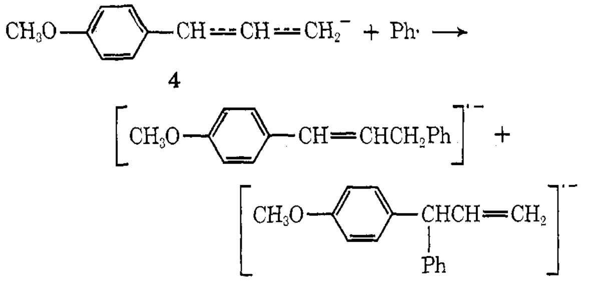
The crude products of phenylation of the carbanion **4** from 1-(*p*-anisyl)propene were catalytically hydrogenated. About three times as much 3-phenyl- as 1-phenyl-1-(*p*-anisyl)propane was obtained, indicating that phenyl radical combines with carbanion **4** preferentially at the allylic position remote from the *p*-anisyl group (eq 8). There were also products of further phenylation.

Table II

Reactions of Bromo- and Iodobenzenes with Ketone Enolate Ions in Liquid Ammonia at −33°

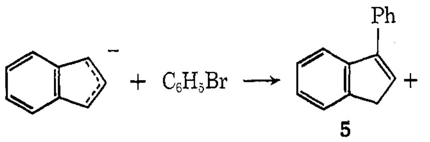
Ketone	Method of enolate ion prepn[a]	X of C_6H_5X	Stimulus	Yield, % C_6H_6	$PhCR(CH_3)$-$COCH_3$	$PhCH_2COCH$-$(R)CH_3$
2-Butanone	K	I	$h\nu$, 12 min	25	41	23
	K	I	K metal	30	31[b]	23[b]
	K	Br	$h\nu$, 20 min	20	43	26
	KNH_2	Br	$h\nu$, 50 min[c]	3	61	19
3-Methyl-2-butanone	K	Br	$h\nu$, 20 min	*d*	5	56
	KNH_2	Br	$h\nu$, 120 min	*d*	9	81
	KNH_2	Br	K metal	*d*	7[b]	55[b]

[a] Reaction of ketone with K metal or KNH_2. [b] After oxidation with $K_2Cr_2O_7$ and H_2SO_4. [c] Recovered C_6H_5Br, 7%. [d] Not measured.



(8)

The carbanion from indene afforded 3-phenylindene (5) in substantial amount. The fact that the yield of 1-phenylindan was much lower suggests that electron transfer in the sense of eq 4 occurred to a significant extent. It is noteworthy and surprising that the product distribution in the run with excess bromobenzene was nearly the same as in the run with excess carbanion. Some di- and triphenylindenes were also formed.



+ other products (9)

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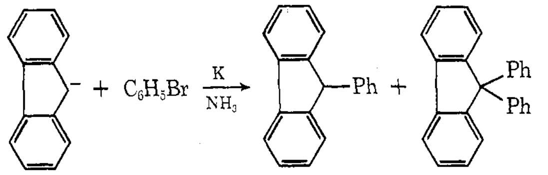
One run with the anion from fluorene was conducted with sodium metal and another with potassium metal. Both afforded mainly 9-phenylfluorene together with a lesser amount of 9,9-diphenylfluorene (eq 10). When bromobenzene was used in great excess over the carbanion, the yield of diphenylfluorene was somewhat higher than when those two reactants were employed in equal amounts.

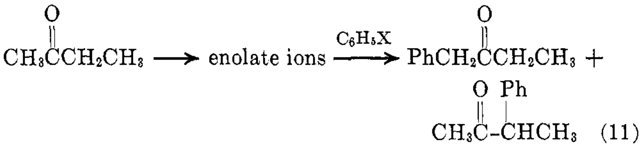


(10)

With respect to *application in synthesis,* these reactions require comparison especially with couplings between organocopper reagents and alkyl or aryl halides.[11] We are not aware that any of the products obtained by us have been made by organocopper coupling, but we expect that most could be. We believe also that carbanion arylation *via* aryne intermediates[12] could be performed in many of these cases. Which method is best for a particular synthetic objective depends on many factors, upon which we choose not to dwell.

Phenylation of Ketone Enolate Ions.—Two methods for converting ketones to their enolate ions in liquid ammonia were employed: reaction with KNH_2 and reaction with potassium metal. The latter method also reduces a considerable fraction of a ketone to the corresponding *sec*-alkoxide ion.[9] Most reactions were photochemically stimulated, but one run with each ketone was provoked by potassium metal. Results are summarized in Table II.

In reactions with the enolate ions from 2-butanone, arylation occurred preferentially at the more substituted α carbon, giving about twice as much 3-phenyl-2-butanone as 1-phenyl-2-butanone (eq 11). However, there was some variation in the product ratio between runs, for reasons unclear. A good deal of benzene (20–30%) was formed as a by-product when the enolate ions were generated by the potassium metal method, but the benzene yield was much lower when they were generated by reaction with KNH_2. The higher yields of benzene in the former case are attributed to hydrogen atom abstraction from *sec*-butoxide ions by phenyl radicals. A parallel dependence of benzene yields on the method of enolate ion generation has been observed in reactions with acetone enolate ion.[9]



$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3 \longrightarrow \text{enolate ions} \xrightarrow{C_6H_5X} PhCH_2\overset{\overset{O}{\|}}{C}CH_2CH_3 + CH_3\overset{\overset{O}{\|}}{C}\text{-}\underset{}{\overset{\overset{Ph}{|}}{C}}HCH_3 \quad (11)$$

Reactions stimulated by potassium metal afford some of the secondary alcohol corresponding to the phenylated ketone, as was previously observed in reactions with acetone enolate ion.[8] For purposes of quantification, the crude product mixtures were treated with $K_2Cr_2O_7$ in acidic medium to oxidize the seondary alcohols to ketones; however, some dehydration to olefins also occurred during chromic acid treatment.

The first and third runs with 2-butanone were substantially the same except that one used iodobenzene and the other bromobenzene as phenyl radical source. They gave similar results. The first and second runs both used iodobenzene, but one was stimulated by photons and the other by solvated electrons. The results were again fairly similar. These observations give assurance that essentially the same phenomena are involved regardless of the identity of the halogen in the halobenzene, the method of stimulation, or

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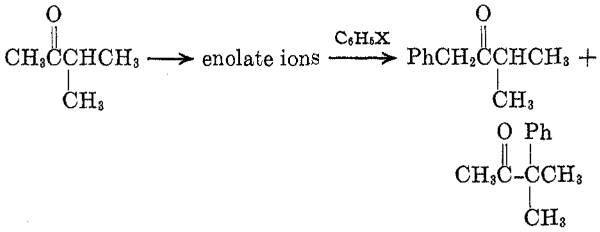
[11] C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **31**, 4071 (1966); E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967); **90**, 5615 (1968); G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *ibid.*, **91**, 4871 (1969).

[12] J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961).

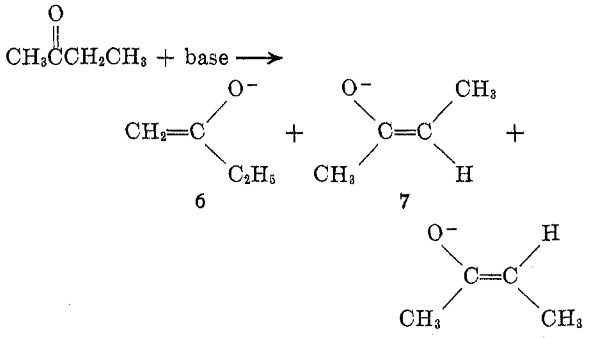
(except for the competing reaction of hydrogen atom abstraction) the method used to prepare the enolate ions.

Reactions with the enolate ions from 3-methyl-2-butanone occurred to give predominantly 1-phenyl-3-methyl-2-butanone and relatively little 3-phenyl-3-methyl-2-butanone (eq 12). Thus the less substituted α carbon is preferentially phenylated, in contrast to the situation with 2-butanone. The product ratio was much the same regardless of which method of stimulation or of enolate ion generation was employed.



$$CH_3C(=O)CH(CH_3)CH_3 \longrightarrow \text{enolate ions} \xrightarrow{C_6H_5X} PhCH_2C(=O)CH(CH_3)CH_3 + CH_3C(=O)C(Ph)(CH_3)CH_3 \quad (12)$$

Interpretation of the shift from predominant phenylation at the 3 position with 2-butanone to predominant phenylation at the 1 position with 3-methyl-2-butanone must take into account several factors. From 2-butanone, three enolate ions can be formed (eq 13) and from 3-methyl-2-butanone, two can be formed (eq 14). If the enolate ions from any ketone attain equilibrium with the ketone, and therefore with each other, before they are arylated, the relative rates of phenylation at the two α positions will depend on their equilibrium proportions and also on the reactivities of the enolate ions toward phenyl radical. On the other hand, if equilibrium is not established before arylation, the relative rates of formation of the enolate ions will determine their relative populations, but their relative reactivities will also be a factor when the enolate ion are in excess, as in our experiments.



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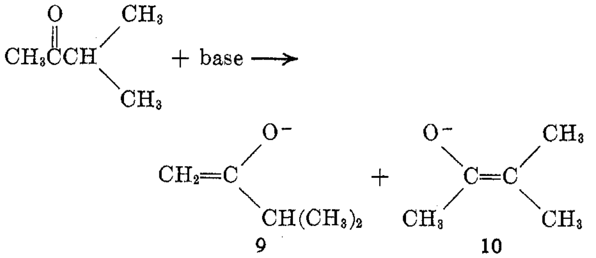

9 10 (14)

Inasmuch as relative rates of formation of enolate ions from several ketones roughly resemble the proportions of the enolate ions at equilibrium,[13] the outcome should be somewhat the same whether the populations of isomeric enolate ions are kinetically or thermodynamically determined. Moreover, rates of alkylation of enolate ions are not markedly dependent on the number of alkyl substituents on the α carbon,[14] and this is likely to be true also for rates of combination with phenyl radical. Therefore it is not surprising that the proportions of phenylation at the alternative α positions reported in Table II are approximately parallel to the proportions of enolate ion **9** *vs.* **10**, or of **6** *vs.* **7** plus **8**, that one would expect from the data of House and Kramar[13] concerning somewhat analogous ketones.

Photochemically stimulated reactions were slower when enolate ions were generated by the KNH_2 than by the potassium metal method. The analogous phenomenon has been observed for reactions with acetone enolate ion,[9] but the effect is not fully understood.

Comparison is now made with two other methods for the phenylation of ketones. One is reaction of ketone enolate ions with benzyne derived from reaction of bromo- or chlorobenzene with $NaNH_2$ or KNH_2 in liquid ammonia.[15] On the basis of evidence now available, that method and the method explored in the present work are roughly equivalent in yields and in preparative convenience. 2-Butanone was phenylated in 75% yield exclusively at the 3 position by the benzyne method, whereas we observed, in the fourth run of Table II, 61% of phenylation at that position and 19% at the 1 position. On the other hand, acetone afforded only 35% of phenylacetone by the benzyne method, far less than yields as high as 85% in photochemical SRN1 reactions with bromobenzene that we have described elsewhere.[9]

Ketones have also been phenylated through reaction of their enolate ions with diphenyliodonium chloride in *tert*-butyl or *tert*-pentyl alcohol.[16] α-Phenylation of isobutyrophenone in yields as high as 81% and of isovalerophenone in 23% yield were reported. In another study,[17] quite high yields were obtained in the γ-phenylation of dicarbanions from β diketones by diphenyliodonium chloride in liquid ammonia. For these reactions, an electron transfer, radical pair mechanism has been proposed;[18] it resembles the SRN1 mechanism in some respects, but is not a chain mechanism.

For general preparative application, the method investigated in the present work is superior to both of these alternatives. The aryne method is expected to give mixtures of aromatic positional isomers in many cases when substituted halobenzenes are used

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(13) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963); H. O. House and B. Trost, *ibid.*, **30**, 1341 (1965).

(14) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 193.

(15) W. W. Leake and R. Levine, *J. Amer. Chem. Soc.*, **81**, 1169 (1959). See also P. Caubere, N. Derozier, and B. Loubinoux, *Bull. Soc. Chim. Fr.*, 302 (1971); P. Caubere and G. Guillaumet, *C. R. Acad. Sci., Ser. C.*, **275**, 463 (1972).

(16) F. M. Beringer, W. J. Daniel, S. A. Galton, and G. Rubin, *J. Org. Chem.*, **31**, 4315 (1966).

(17) K. G. Hampton, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **29**, 3511 (1964).

(18) F. M. Beringer, S. A. Galton, and S. J. Huang, *J. Amer. Chem. Soc.*, **84**, 2819 (1962).

as aryne precursors, whereas the present method is not complicated by cine substitution.[8] Arylation by means of diaryliodonium salts suffers from the expense of these reagents or the extra work needed to prepare them.

Attempted Phenylation of Other Nucleophiles.—The potassium metal stimulated reaction of iodobenzene with anilide ion in ammonia affords diphenylamine and 2- and 4-aminobiphenyl, products which represent both N- and C-arylation.[5] Hoping to find analogous behavior, we studied the reaction of potassium metal with bromobenzene in the presence of thiophenoxide or phenoxide ion in ammonia solution. In the former case, we obtained in each of two runs about 0.5% of a product with the same glpc retention time as diphenyl sulfide, as well as benzene and some aniline. No diphenyl ether was obtained as a product from the phenoxide ion reaction, nor were any hydroxybiphenyls found, but benzene and a little aniline were detected.

The immediate product of the combination of phenyl radical with the sulfur atom of thiophenoxide ion would be the radical anion of diphenyl sulfide, a species indicated by other studies to have a propensity to dissociate into phenyl radical and thiophenoxide ion.[8] Our inability to get much diphenyl sulfide as a product is therefore understandable. The reasons for our failure to obtain well-defined products from reaction with phenoxide ion are unclear.

Experimental Section

Reactions Stimulated by Alkali Metals.—A procedure for phenylation of fluorene anion is representative. The reaction was performed in a three-neck, round-bottom flask fitted with a solid CO_2–isopropyl alcohol condenser, stirred by a magnetic stirrer and constantly swept by a slow stream of dry nitrogen. To liquid ammonia (350 ml) from a commercial cylinder, sodium metal (0.060 mol) was added and a little powdered ferric nitrate was added to catalyze formation of $NaNH_2$. After the blue color of the alkali metal had disappeared, 0.050 mol of solid fluorene was added, forming a deep red solution. After 10–15 min, bromobenzene (0.050 mol) was added and then sodium metal (0.065 mol), slowly and in small bits, until the color had changed to deep green. Excess sodium benzoate was added, causing the mixture to turn red. Ammonium chloride was then added in excess, followed by 250 ml of diethyl ether, and the ammonia was allowed to evaporate. An internal standard (anthracene) was added to a portion of the resulting ether solution, and it was analyzed by glpc on a column of 5% silicone rubber SE-30 on Chromosorb W. The ether was evaporated from the rest of the ether layer, and the residue was crystallized from a benzene–pentane mixture. 9-Phenylfluorene, mp 145–146°, was thereby isolated. 9,9-Diphenylfluorene, mp 220.5–221.5°, was isolated by preparative glpc. These products were further characterized by their nmr and mass spectra.

Phenylation of Indene Anion.—By a similar procedure, a product mixture was obtained whose glpc spectrum (on the same column, but with biphenyl as internal standard) showed major peaks for indene, 3-phenylindene, and two isomers of diphenylindene, as well as a minor peak for a phenylindan and a cluster of four small peaks at long retention times presumed to be for triphenylindenes. The compositions of the phenylindan, 3-phenylindene, and each of the two diphenylindenes were determined by the mass spectra of samples isolated by glpc, and the structure of 3-phenylindene was verified by its nmr spectrum.

Phenylation of 1,3-Pentadiene Anion.—By a similar procedure, a product mixture was obtained whose glpc spectrum (on the same column, with biphenyl as internal standard) showed a major phenylpentenes peak, substantial and well-separated peaks for two phenylpentadienes, a group of four small peaks for diphenylpentenes and/or diphenylpentadienes, and a few tiny peaks at long retention times presumed to be for triphenylation products. By distillation and then preparative glpc on a column of 10% silicone rubber SE-54 on Chromosorb P, three fractions were isolated. The nmr and mass spectra of the first were appropriate for a mixture of about 75% of 5-phenyl-1-pentene and 25% of 1-phenyl-2-pentene; attempts to separate these isomers on three different glpc columns were fruitless. The nmr and mass spectra of the second and third fractions indicated 5-phenyl-1,3-pentadiene and 1-phenyl-1,3-pentadiene, respectively.

The combined distillate fractions from distillation of the crude product mixture were hydrogenated (Pd/C, 1 atm) and the product was distilled. 1-Phenylpentane, bp 84–86° (15 Torr), characterized by n_D, nmr, and mass spectra and by the identity of its infrared spectrum with that of an authentic sample, was isolated. The residue from distillation of the crude product mixture was similarly hydrogenated; by preparative glpc on a column of 10% silicone rubber SE-54 on Chromosorb P, three fractions were isolated. The first two fractions had mass spectra appropriate to diphenylpentanes; the major fraction (55%) had an nmr spectrum indicative of 1,1-diphenylpentane and in agreement with that reported by Jung and Brini,[19] and the minor fraction (45%) had an nmr spectrum indicative of 1,5-diphenylpentane. The third fraction had a mass spectrum indicative of triphenylpentanes.

In glpc quantification of the products from fluorene, indene, and 1,3-pentadiene, it was assumed that the response of all hydrocarbons was proportional to molecular mass.

Phenylation of Anethole Anion.—By a similar procedure, with potassium metal being used in excess because of the dark red color of the reaction mixture throughout the reaction, was obtained a mixture of phenylation and/or reduction products. The mixture was hydrogenated (10% Pd/C, 1 atm, 5 hr), and the resulting material was separated into several fractions by distillation and then preparative glpc (column of 10% SE-30 silicone rubber on Chromosorb P). In order of increasing retention time, these were as follows: 1-phenyl-1-(*p*-anisyl)propane, identified by nmr and mass spectrum; 3-phenyl-1-(*p*-anisyl)propane, identified by nmr and mass spectrum; a mixture of 1,3-diphenyl-1-(*p*-anisyl)propane and 3,3-diphenyl-1-(*p*-anisyl)propane, inseparable by glpc and not separately recognizable by nmr, but recognized both to be present by the mass spectrum [m/e (rel intensity) 302 (molecular ion, 19), 198 (20), 197 (100), 182 (5), 181 (5), 168 (11), 167 (29), 166 (11), 165 (19), 154 (7), 153 (12), 152 (11), 136 (5), 135 (31), 134 (5), 122 (8), 121 (24), 105 (6), 104 (5), 103 (8), 91 (19) and 77 (12)], of which the peaks at m/e 197 (*p*-methoxybenzhydryl cation) and 91 (benzyl cation) are characteristic of the 1,3-diphenyl isomer, those at 167 (benzhydryl cation) and 121 (*p*-methoxybenzyl cation) are characteristic of the 3,3-diphenyl isomer, and the absence of a peak at 273 (*p*-anisyldiphenylmethyl cation) speaks against the possibility of 1,1-diphenyl-1-(*p*-anisyl)propane; and a triphenyl-1-(*p*-anisyl)propane, recognized by its mass spectrum, which indicated it probably to be the 1,3,3-triphenyl isomer.

Phenylation of Ketone Enolate Ions.—Solutions of the enolate ions in liquid ammonia were prepared by techniques described elsewhere.[9] The photochemically stimulated reactions were conducted, in a Rayonet photochemical reactor equipped with 350-nm lamps, as described elsewhere,[9] the progress of the reactions being monitored by withdrawing *ca.* 1-ml samples from time to time by means of a piece of 8-mm glass tubing J-shaped at the bottom, quenching them with water, extracting with ether, and analyzing the extracts by glpc. The potassium metal stimulated reactions were conducted much as described above for reaction with fluorene anion. The enolate ions were about 0.3 M and the halobenzene about 0.08 M in the reaction mixtures.

To the crude product mixtures, *p*-dichlorobenzene was added as internal standard, and analysis was conducted by glpc, using a column of 20% Carbowax M on Chromosorb P. Then, by preparative glpc on a similar column, phenyl derivatives of the starting ketones were isolated.

3-Phenyl-2-butanone was identified by its infrared, nmr, and mass spectra. 1-Phenyl-2-butanone was identified by its nmr and mass spectra, and by the identity of its infrared spectrum with that of an authentic sample.

3-Phenyl-3-methyl-2-butanone was identified by its infrared and nmr spectra; its mass spectrum did not display a molecular

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[19] M. Jung and M. Brini, *Bull. Soc. Chim. Fr.*, **55**, 587 (1965).

ion peak, but rather a prominent peak at m/e 119, attributed to the 2-phenyl-2-propyl cation. 1-Phenyl-3-methyl-2-butanone was characterized by its infrared, nmr, and mass spectra; the mass spectrum showed a molecular ion peak at m/e 162 but no peak at m/e 119.

Registry No.—Bromobenzene, 108-86-1; 5-phenyl-1-pentene, 1075-74-7; 1-phenyl-2-pentene, 27911-12-2; 5-phenyl-1,3-pentadiene, 1007-52-9; 1-phenyl-1,3-pentadiene, 1608-27-1; 3-phenyl-2-butanone, 769-59-5; 1-phenyl-2-butanone, 1007-32-5; 3-phenyl-3-methyl-2-butanone, 770-85-4.

The Preparation of Highly Fluorinated Ethers

RALPH J. DE PASQUALE

PCR, Inc., Gainesville, Florida 32601

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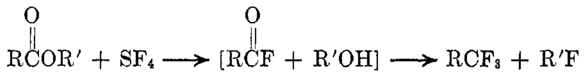
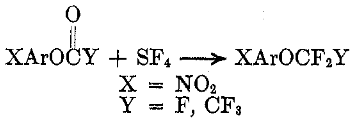
Highly fluorinated ethers are prepared by reducing their corresponding esters in HF at elevated temperature. Under the appropriate conditions the isolated yields of ethers exceed 80%; acyl–oxygen cleavage is negligible. The relative rates of reduction of a series of esters are reported and discussed.

Sulfur tetrafluoride[1] is a useful reagent for converting, among others, carbonyl to difluoromethylene and hydroxyl to fluoro groups. Our interest in this area stems from reports based on the attempted sulfur tetrafluoride reduction of esters to α,α-difluoro ethers. Pioneering investigations[2] dealing with reactions between sulfur tetrafluoride and various functional groups indicate that hydrocarbon aliphatic esters are reduced with predominant concomitance of acyl–oxygen cleavage. A subsequent study,[3] however,



$$R\overset{O}{\overset{\|}{C}}OR' + SF_4 \longrightarrow [R\overset{O}{\overset{\|}{C}}F + R'OH] \longrightarrow RCF_3 + R'F$$

demonstrates the conversion of aryl fluoroformates and trifluoroacetates to ethers by treatment with this reagent. Along these lines highly fluorinated aliphatic esters conceivably could be reduced to their corresponding ethers, a class of compound that would be difficult to prepare by alternate routes. The sulfur tetrafluoride reductions of this latter and related systems are described in this report.



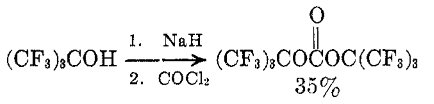
$$XArO\overset{O}{\overset{\|}{C}}Y + SF_4 \longrightarrow XArOCF_2Y$$
$$X = NO_2$$
$$Y = F,\ CF_3$$

Results and Discussion

Preparation of Esters and a Carbonate.—Esters of perfluoroalkyl acids were prepared by the reaction between acid chlorides and $C_2F_5CH_2OH$, $(CF_3)_2CHOH$, and $(CF_3)_3COH$. In the presence of DMF, the reaction between acid chlorides and $C_2F_5CH_2OH$ proceeds at 25°; however, higher reaction temperatures (50–60°) were required for esters derived from $(CF_3)_2CHOH$. The yields of the fluorinated propyl esters range from 70 to 90%. A side product, the corresponding acid, is suspected to have resulted from the presence of adventitious moisture which hydrolyzed the ester during distillation.

The reaction between perfluorooctanoyl chloride and perfluoro-*tert*-butyl alcohol afforded the corresponding ester languidly at 50° (17% conversion after 90 hr). However, the addition of a stoichiometric amount of Et_3N[4] effected complete alcohol to ester conversion under mild conditions. When reactions between acid fluorides and $C_2F_5CH_2OH$ or $(CF_3)_2CHOH$ were run in glass vessels, water was inevitably introduced into the reaction. A good yield of ester can be obtained by running acid fluoride esterifications in stainless steel vessels. The esters prepared by the reactions between acid chlorides or fluorides are presented in Table I; yields, reaction conditions, and by-products are included for convenience.

Perfluoro-*tert*-butyl carbonate was prepared by the reaction between sodium perfluoro-*tert*-butoxide (prepared *in situ*) and phosgene.



$$(CF_3)_3COH \xrightarrow[2.\ COCl_2]{1.\ NaH} \underset{35\%}{(CF_3)_3CO\overset{O}{\overset{\|}{C}}OC(CF_3)_3}$$

The yield obtained is not representative of the reaction. The reaction proceeded smoothly; however, the unexpected physical properties of the carbonate led to losses during work-up.

Reductions of Esters and Related Compounds with SF_4.—The literature[1] indicates that Lewis and Brønsted acids, BF_3 and HF being the most popular, catalyze the SF_4 reduction of carbonyl compounds. However, to the best of our knowledge, there has been no reported comparative study concerning the relative effectiveness of these catalysts on the reduction of carbonyl compounds by SF_4. To this end, preliminary experiments were run under similar conditions using several preselected catalysts. The results are summarized in Table II.

Apparently, HF is the most effective catalyst in this group, and the rate of reduction of the ester is faster when HF is used as solvent rather than in catalytic amounts.

For each ester small-scale experiments were run to determine the temperature and reaction time neces-

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[1] For recent reviews on this reagent, see W. C. Smith, *Angew Chem., Int. Ed. Engl.*, **1**, 467 (1962); D. G. Martin, *Ann. N. Y. Acad. Sci.*, **145**, 161 (1967); P. Boissin and M. Carles, *Commis. Energ. At.* [*Fr.*] *Serv. Doc., Ser. Bibliogr.*, **98**, 29 (1967); J. V. Urenovitch, "Sulfur Tetrafluoride," Technical Bulletin, Air Products and Chemicals, Inc.

[2] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960), and references stated therein.

[3] W. A. Sheppard, *J. Org. Chem.*, **29**, 1 (1964); J. A. Webster, Seventh Quarterly Progress Report, Contract NAS8-21401, "Thermally Resistant Polymers for Fuel Tank Sealants," Oct 1970.

[4] For an alternate preparation of a perfluoro-*tert*-butyl ester, see F. J. Pavlik and P. E. Toren, *J. Org. Chem.*, **35**, 2054 (1970).