steam bath. Ether extraction gave 0.200 g of a viscous oil which crystallized from acetonitrile. Repeated recrystallization gave colorless needles of dihydrotauranic acid epimeric mixture, mp 104–105° (lit.[12] mp 107°).

The nmr of this product was identical with that reported;[12] δ (CDCl$_3$) 0.79 (d, 1.5 H), 0.82 (s, 3 H), 0.86 (s, 6 H), 1.02 (s, 1.5 H), 1.0–2.6 (m, 15 H), 9.98 (s, 1 H).

Gas Chromatography of Methyl Dihydrotauranates.—The samples of dihydrotauranic acid obtained above, mp 104–105°, and an authentic sample,[16] mp 107°, were converted to their respective methyl esters *via* treatment with thionyl chloride and anhydrous methanol. Analysis of each ester mixture by gas chromatography on a 0.25 in. × 3 m 10% DC-11 silicon grease on Chromosorb W 60/80 column at 200° showed a 60:40 mixture of two epimeric esters. At this temperature their retention times were 25.7 and 28.6 min. Equal amounts of the esters from each source were combined and injected; identical results were obtained. A comparison was also completed on a 0.25 in. × 2 m 15% butanediol succinate on Chromosorb P 60/80 column at 215°. The esters had identical retention times of 8.8 and 10.0 min.

Cyclic Voltammetry of Zonarone (4).—The cyclic voltammetric measurements were done using a three-electrode system in a degassed electrochemical cell with dimethyl sulfoxide as solvent and tetraethylammonium perchlorate (0.1 F) as supported electrolyte. A Beckman platinum-inlay electrode was employed as the working electrode. An aqueous silver–silver chloride electrode in 0.4 F tetramethylammonium chloride was used as a reference with a potential of 0.00 V *vs.* the saturated calomel electrode. Potentials recorded for two-electron reduction of zonarone were: E_{pc} −0.525 V, E_{pa} −0.450 V and E_{pc} −1.350 V, E_{pa} −1.275 V.

Registry No.—2, 39707-54-5; 3, 39707-55-6; 4, 39707-56-7; 5 isomer A, 39707-57-8; 5 isomer B, 39707-58-9; 6, 39707-59-0.

The Pschorr Reaction by Electrochemical Generation of Free Radicals. II. Benzophenone Series. An Alternative Mechanism[1]

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Diazonium salts of 2-amino-R′-benzophenone (R′ = 4-CH$_3$, 4-OCH$_3$, 3-NO$_2$) were decomposed electrolytically, thermally, and by the iodide ion. Protic and aprotic solvents were employed, with a variety of catalysts and over a range of temperatures. Using our results and published data, a general inter- or intramolecular one-electron redox mechanism is proposed. Based on experimental results and theoretical calculations, this proposal alleviates many of the previously encountered difficulties in explaining the behavior of diazonium salts under varied conditions and specifically clarifies the Pschorr cyclization mechanism.

Phenyl radicals produced by the electrochemical reduction of benzenediazonium salts have been used for phenylation of aromatic substrates.[2] This technique was used in a new approach to the Pschorr reaction, in which intramolecular arylation occurred upon reduction of diazonium salts of 2-amino-α-(R′)-phenylcinnamic acids giving near quantitative yields of phenanthrene derivatives.[3] However, when this technique was applied to diazonium salts of 2-amino-R′-benzophenones to obtain fluorenone derivatives, some surprising results were obtained.

Various literature surveys[4–9] have revealed a long history of mechanistic studies on Pschorr-like systems. All agree that, depending on the reaction conditions, homolytic or heterolytic mechanisms, or a combination of the two, could explain the type and yield of products.

However, aryl diazonium cations have been shown to be strong oxidizing agents,[10] which upon reduction (electrolytically or thermally) release nitrogen and produce aryl radicals. This redox model has been used to explain the salient fact of diazonium salt chemistry.[11]

We now believe there are indeed two mechanisms operating in the Pschorr reaction: one is the conventional homolytic mechanism and the other is a substitute for the classical heterolytic mechanism. Both mechanisms involve a one-electron redox reaction: the homolytic one results from external reduction of the diazonium moiety, while the other invokes an *internal* or intramolecular reduction in which the system goes through an intramolecular charge-transfer or redox state.

Results

A. Electrolytic Reductions of Unsubstituted Diazonium Salts (Table I).—Protic and aprotic media were employed at different potentials. In aprotic media at 0.0 V cyclization was poor, while abstraction and attack on the electrode produced the major products. At higher potential attack on the cathode was reduced,

(1) Contribution No. 621 from the Research Council of Alberta, Edmonton, Canada. A part of this paper was presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

(2) (a) F. F. Gadallah and R. M. Elofson, *J. Org. Chem.,* **34,** 3335 (1969). (b) R. M. Elofson, F. F. Gadallah, and K. F. Schulz, *ibid.,* **36,** 1526 (1971).

(3) R. M. Elofson and F. F. Gadallah, *J. Org. Chem.,* **36,** 1769 (1971).

(4) D. F. De Tar, *Org. React.,* **9,** 409 (1957).

(5) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960, p 80.

(6) H. Zollinger in "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y., 1961.

(7) P. A. S. Smith in "Open Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, New York, N. Y., 1966.

(8) R. A. Abramovitch, *Advan. Free Radical Chem.,* **2,** 87 (1967).

(9) A. H. Lewin and T. Cohen, *J. Org. Chem.,* **32,** 3844 (1967).

(10) R. M. Elorson and F. F. Gadallah, *J. Org. Chem.,* **34,** 854 (1969).

(11) R. M. Elofson, F. F. Gadallah, and K. F. Schultz, meeting of the Chemical Institute of Canada, Halifax, Nova Scotia, June 2, 1971.
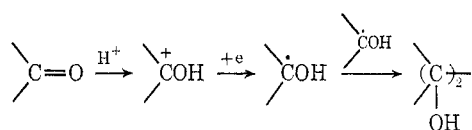
TABLE I

ELECTROLYTIC REDUCTION OF DIAZONIUM SALTS
OF 2-AMINOBENZOPHENONE

Expt[a]	Conditions	Temp in °C, V[b]	Fluorenone	Benzophenone	Mercury product	Other products
				Yields, %		
1	CH₃CN, Bu₄NClO₄	0–5, 0.0	5	38	55[c]	1 (2-F)
2	Sulfolane, Bu₄NClO₄	rt,[d] 0.0	2	46	42[c]	
3	CH₃CN, Bu₄NClO₄	0–5, 1.5	8	55	20[c]	
4	Sulfolane, Bu₄NClO₄	rt, 1.6	4	71	15[c]	
5	H₂SO₄ (0.6 N)	rt, 1.2	32	5	+	20[e]
6	H₂SO₄ (0.6 N)	rt, 1.6	42	7	+	23[e]
7	HF (anhyd)	0–5, 0.0	15	2		

[a] Note: in expt 1, 2, 3, 4, and 7, the counterion is BF_4^-; in expt 5 and 6, the counterion is HSO_4^-. [b] Cathodic potential *vs.* sce. [c] Bis(2,2)benzophenonemercury. [d] Room temperature. [e] Fluoropinacol.

hydrogen abstraction enhanced, and yield of cyclized product slightly improved. The slight difference between acetonitrile and sulfolane may be due to the reactivity of each solvent towards the phenyl radical.[12]

When protic media were employed, hydrogen abstraction yields dropped drastically and consequently cyclization increased. In expt 5 and 6, the last column gives fluoropinacol yields. The pinacol is formed by protonation and reduction followed by coupling, *i.e.*,

$$\underset{}{\diagdown}C=O \xrightarrow{H^+} \underset{}{\diagdown}\overset{+}{C}OH \xrightarrow{+e} \underset{}{\diagdown}\dot{C}OH \xrightarrow{\overset{\diagdown}{C}OH} \underset{\underset{OH}{|}}{\diagdown}(C)_2$$

The sum of the first and last columns, which is the total yield of cyclized products, was as high as 65% at 1.6 V. In anhydrous HF, while cyclization was substantial, the reaction was not carried to completion because of the slow course of electrolysis, due to absorption phenomena, occurring in this medium.[13] The high yields of organomercury compounds are due to the interaction between the intermediate radical and the mercury cathode.[14]

B. Thermal Decomposition of Unsubstituted Diazonium Salts (Table II).—Protic and aprotic media, with or without catalysts, were employed. In protic media, adding copper (groups a and b) reduced the yield of cyclized products slightly and phenols considerably. In group c (Lewin and Cohen experiments[9]), addition of copper did not make any appreciable change, but cuprous oxide gave mainly cyclization. These results were explained by Lewin and Cohen.

Decomposition in acetone or sulfolane alone (group d) gave cyclization as the major product. Phenol in 15% yield in expt 17 is due to the presence of water which was very difficult to eliminate.[15] The absence of deamination product is of vital importance since this product would be expected from a σ-radical mechanism (by hydrogen abstraction from the aliphatic solvents, as occurred in electrolytic reductions, Table I, or when copper was added, expt 18). The very small yield of fluorinated products, 5% in expt 16 and traces in

expt 17, decreases the chance of a conventional ionic mechanism.[16] A 65% yield of fluorenone, expt 17, strongly suggests some quite different mechanism.

Addition of copper (group e) reduced cyclization considerably and promoted abstraction. However, the high yield of benzophenone in the absence of copper, 90%, expt 20, strongly suggests that the cyclic ether tetrahydrofuran $[I_p(\text{THF}) = 9.45$ eV; see Discussion][17] might be playing an important role as a reducing agent. Group f results add support to the well-known fact of the absence of hydrogen abstraction from aromatic nuclei. The small effect of Cu illustrates the involvement of the two reaction mechanisms which will be discussed later.

Experiment 24 (Lewin and Cohen[9]) shows that Cu_2O is a strong reducing agent at moderate temperatures. This result, compared to expt 20 and 21, suggests that dioxane might also play a role as a reducing agent $[I_p(\text{dioxane}) = 9.52$ eV; see Discussion].[17]

Experiment 25 is significant. One would expect decomposition to occur *via* the cation since BF_4^- is conventionally thought to be a poor reducing agent. According to Schiemann,[16] we would then expect high yields of the fluoro compound. This was not the case. Thus there may be a redox mechanism and the discussion will deal with the nature of the reducing agent.

Experiments 26 and 27 emphasize the role of iodide ion as a strong reducing agent for diazonium salts.[3]

C. Substituent Effects (Table III).—Selected results of electrolysis and thermal decomposition of substituted benzophenonediazonium salts are collected in Table III.

As expected, the overall products and yields of 4-methoxy and 4-methyl compounds from electrolytic reduction were more or less the same as obtained from the unsubstituted salt. That is, activation by $-CH_3$ $-OCH_3$ groups in the *m* position is ~1.[2a]

Activation by the nitro group resulted in higher cyclized yields from 3-NO₂ substituted benzophenones.[2a] The results of thermal decomposition in protic media gave higher cyclized yields with copper than without (compare expt 35 and 40 and 36 and 39), for the reasons previously given.

The ratio of 4-nitrofluorenone to 2-nitrofluorenone followed two patterns: (i) higher than 2 in electrochemical reduction and acid and Cu; (ii) lower than 1 (0.4) in acid, sulfolane, sulfolane and acid, and dry salt.

For the diazonium salt of 2-amino-β-benzoylnaphthalene, electrolytic reduction gave a ratio of angular to linear benzofluorenones similar to that from reactions which are considered pure free radical (~9).[9,18] The results of Huisgen and Zahler[18] and Lewin and Cohen[9] are in agreement with our results in the case of free-radical mechanisms (A/L ≃ 9). Different conditions result in the same distribution ratio, a situation which will be explained in the following discussion.

Discussion

Two mechanisms have been invoked to explain Pschorr cyclization: (a) **ionic route** (Scheme I, 1-a)

(12) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 154.

(13) R. M. Elofson, *Can. J. Chem.*, **36**, 1207 (1958).

(14) F. Beck, *Angew. Chem., Int. Ed. Engl.*, **11** (a), 760 (1972).

(15) J. M. Simon, Ph.D. thesis, University of Pittsburgh, 1969.

(16) G. Balz and G. Schiemann, *Ber.*, **60**, 1186 (1927).

(17) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold (Publisher) Ltd., London, 1966.

(18) R. Huisgen and W. D. Zahler, *Ber.*, **96**, 736 (1963).

TABLE II

THERMAL DECOMPOSITION OF DIAZONIUM SALTS[a] OF 1-AMINOBENZOPHENONE WITH AND WITHOUT CATALYSTS

Group	Expt	Conditions	Temp, °C	Fluorenone	Phenol	Benzophenone	Other products	Ref
a	8	H_2O	75	60	40			
	9	H_2O, Cu	75	51	<1			
	10	H_2O, Pyridine	75	57	22	3.5	8 (2-Py)[b]	
b	11	HBF_4, 10%	75	72	20		9 (2-F)	
	12	HBF_4·Cu	75	58	6	2.4	2 (2-F)	
c	13	H_2SO_4 (0.1 N)	45	68	31			9
	14	H_2SO_4 (0.1 N), Cu	45	67	33			9
	15	H_2SO_4 (0.1 N), Cu_2O	45	93	1	6		9
d	16	Acetone	Reflux	54			5 (2-F) + polymers	
	17	Sulfolane	75	65	15		+ (2-F)	
	18	Acetone, Cu	Reflux	7		30	42 (dimer)[c]	
e	19	THF (0.05 M)[d]	Reflux	25		50	10 (2-F)	
	20	THF (0.0033 M)[d]	Reflux	8		90	Traces	
	21	THF, Cu (0.05 M)[d]	Reflux	1.5		97		
f	22	Benzene	Reflux	58			18 (2-F), 10 (2-Ph)	
	23	Benzene, Cu	Reflux	67			21 (2-F), 7 (2-Ph)	
	24	Dioxane, Cu_2O	25			100		9
	25	Dry salt		54			36 (2-F)	
	26	Acetonitrile, Pr_4NI	5	1.5		2	95 (2-I)	
	27	Acetone, NaI	5	1		8	90 (2-I)	

[a] Note: all are fluoroborate salts. [b] Three isomers, α-, β-, and γ-benzophenonepyridine. [c] Bis(2,2′)benzophenone. [d] Molarity of diazonium salt in THF.

where the C–N bond cleaves heterolytically to produce an aromatic cation; (b) **radical route** (Scheme I, 1-b) in which the diazonium cation accepts an electron and the diazo radical, then decomposes to molecular nitrogen and an aromatic radical. Combinations of these mechanisms have also been suggested.[8]

In route 1-b the electron is supplied by $X^{(-)}$ which could be a cathode, copper or appropriate metal, metal salts, suitable anion (OH⁻, Cl⁻, Br⁻, or I⁻), or a neutral molecule such as pyridine. The free radical VII can cyclize or couple with Z· which can be, for example, X·, H· abstracted from the solvent, another radical VII, or the electrode (*i.e.*, Hg). As can be seen, coupling and cyclization processes are in competition. The result of this competition is affected by the rate of each process, which in turn is controlled by the reaction conditions.

The electrochemical reactions listed in Table I have product distributions typical of sp² free radicals (route 1-b).[2a] They proceed primarily by hydrogen abstraction or attack on the electrode. Very little cyclized product is obtained, although it can be made the major product by running the reaction at high potential in protic media. In the electrochemical expt 34 and 42 (Table III) where both the 3-nitro group and 2,3-fused ring activate the B ring, the distribution of cyclized products formed follows free-radical arylation patterns.[8]

In electrolytic reduction of diazonium salts of 2-amino-α-phenylcinnamic acid, where (a) the gap between the reactive sites is small and (b) the molecule is rigid, cyclization was nearly quantitative.[3] Reduction with iodide ion resulted in 90% cyclization and 10% iodide product. On the other hand, benzophenone radicals produced by this technique, owing to the absence of a and b, prefer to abstract hydrogen from the aprotic solvent or couple with the iodine atom to give up to 95% of the iodo derivative (expt 26 and 27, Table II). Waters[19] suggested this mechanism in

1942, and recently an added evidence of the redox nature of similar reactions was demonstrated.[3,20,21]

It was argued that in the absence of an external reducing agent an SN1 reaction, as in route 1-a, can take place. Here, an aromatic cation (II) results after the release of N_2 and this cation either couples with $Z^{(-)}$ or attacks ring B and cyclizes. In Table II, clearly, the high yields of cyclized products cannot be obtained from the radical process (route 1-b), because of the hydrogen abstraction as mentioned before. However, a cationic mechanism with a discrete SN1 step (route 1-a) fails to explain the results, *viz.*, the low yields of hydroxy, fluoro compounds and the isomer ratios in the cyclized products of the nitro- or naphthoyl-substituted systems (Table III). The discrete sp² cation would not allow for a considerable amount of orbital overlap leading to cyclization and isomer ratio distributions observed (see below). Abramovitch, in his review,[8] argued against this heterolytic mechanism and attempted to improve this scheme by introducing the phenyl diradical cation model of Taft.[22] Very recent work has proposed redox mechanisms as alternatives for SN1 and SN2 reactions of diazonium salts.[23]

As route 1-a stands, the two ring moieties A and B in I are taken to be independently solvated; the reaction does not occur in a solvent cage. Invoking the solvent cage implies the existence of a stabilizing interaction between the two ring moieties. As will be shown later,

(19) W. A. Waters, *J. Chem. Soc.*, 266 (1942).

(20) R. Kumar and P. R. Singh, *Tetrahedron Lett.*, 613 (1972).

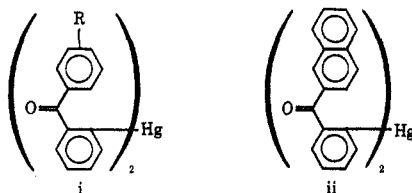(21) P. R. Singh and R. Kumar, *Aust. J. Chem.*, **25**, 2133 (1972).

(22) R. W. Taft, *J. Amer. Chem. Soc.*, **83**, 3350 (1961).

(23) Rieker, *et al.* [*Tetrahedron Lett.*, 2581 (1972)] observed diazo radicals in ¹³C-polarization experiments during reductive deamination of diazonium salts. Bubnov, *et al.*, published a series of papers and reviews on the one-electron transfer in organic reactions. The very recent one [N. N. Bubnov, *et al.*, *J. Chem. Soc., Chem. Commun.*, 1058 (1972)] which appeared during revision of this paper, showed that azo coupling proceeds *via* radical intermediates and previous work by this group [*Dokl. Akad. Nauk SSSR*, 583 (1970)] rules out the so-called SN1 nature of diazonium salt decomposition. The latter reference fully supports our suggested redox mechanism of diazonium salt reactions as proposed in our paper presented in Halifax (1971).[11] The work of the latter group was apparently stimulated by our polarographic measurements of the high oxidation potential (*sic*) of diazonium salts.[10]

TABLE III

EFFECT OF REACTION CONDITIONS ON DECOMPOSITION OF DIAZONIUM SALTS

Registry no.	Expt	R'	Reaction Conditions	Temp, °C	Cyclization	Isomer ratio	Phenol	Deamination	Mercury products	Other products	Ref
							Yield, %				
2-Amino-R'-benzophenonediazonium Salts											
39834-86-1	28	4-OCH₃	Elect. redn, CH₃CN, 0.0 V	0–5	1.5			23[f]	65[a]		
39834-87-2	29		H₂SO₄, Ag		80						4
342-63-2	30	4-CH₃	Elect. redn, CH₃CN, 0.0 V	0–5	2			32[g]	60		
39834-89-4	31		H₂SO₄ (1 N)	Reflux	61	35					b
	32		H₂SO₄ (1 N), Cu	rt	46	33		12			b
	33		H₂SO₄ (1 N), CuCl	rt	46	40		6			b
						4-/2-					
39834-90-7	34	3-NO₂	Elect. redn, CH₃CN, 0.0 V	0–5	18.5	2.4[c]		26.5[h]	50		
39834-91-8	35		H₂SO₄ (1 N), Cu	75	79	2.4	7	4			
	36		H₂SO₄ (1 N), only	75	57	0.4	41				
	37		Sulfolane	75	60	0.35	15			10 (2-F)	
	38		Dry salt		40	0.4				54 (2-F)	
	39		H₂SO₄ (1 N)	Heat	47		54				b
	40		H₂SO₄ (1 N), Cu	Heat	90		4	1			b
	41		H₂SO₄ (1 N), CuCl	Heat	74		2	19			b
2-Amino-β-benzoylnaphthalenediazonium Salts											
						A/L[d]					
2264-63-3	42		Elect. redn, CH₃CN, 0.0 V	0–5	17	9.5		38	35[e]		
39834-93-0	43		H₂SO₄ (3 N)	100	50	2.3	+				18
	44		H₂SO₄ (3 N), Cu	100	54	4.4	+			22 (dimer)	18
	45		Acetone, Cu	100	17	4.6					18
	46		Nitrosoacylamine, THF	20	4	10		7			18
	47		Nitrosoacylamine, PhH	20	15	9.4					18
	48		H₂SO₄ (0.1 N)	25	57.6	2.3	42.4				9
	49		H₂SO₄ (0.1 N), Cu	25	82	9.5		18.1			9
	50		H₂SO₄ (0.1 N), Cu₂O	25	68.2	8.9		31.8			9
	51		Dioxane, Cu₂O	25	25	9		75			9

[a] See structure i. [b] D. F. De Tar and T. E. Whiteley, J. Amer. Chem. Soc., 79, 2498 (1957). [c] 4-/2-, 4-nitrofluorenone/2-nitrofluor-

i

ii

enone. [d] A/L, angular/linear. [e] See structure ii. [f] Registry no., 39834-94-1. [g] Registry no., 39834-95-2. [h] Registry no., 39834-96-3.

such interactions destroy the pure cationic character of 1-a. Now, when diazonium fluoroborate salts of 2-aminobenzophenone are heated in aprotic solvents, the yield of cyclized material is close to that in the much more polar media (expt 17 and 11). This, contrary to the expectations of route 1-a, implies that solvent effects are small for these reactions, provided, of course, that there are no obvious reducing agents present; cf. Scheme I (1-b). More notably, the isomer ratio is similar whether the thermal decomposition of 3'-nitro-2-benzophenone salts is carried out in strong acid, in aprotic solvents, or as the dry salt (expt 36, 37, and 38, respectively), a rather unusual coincidence if the mechanism of 1-a is invoked.
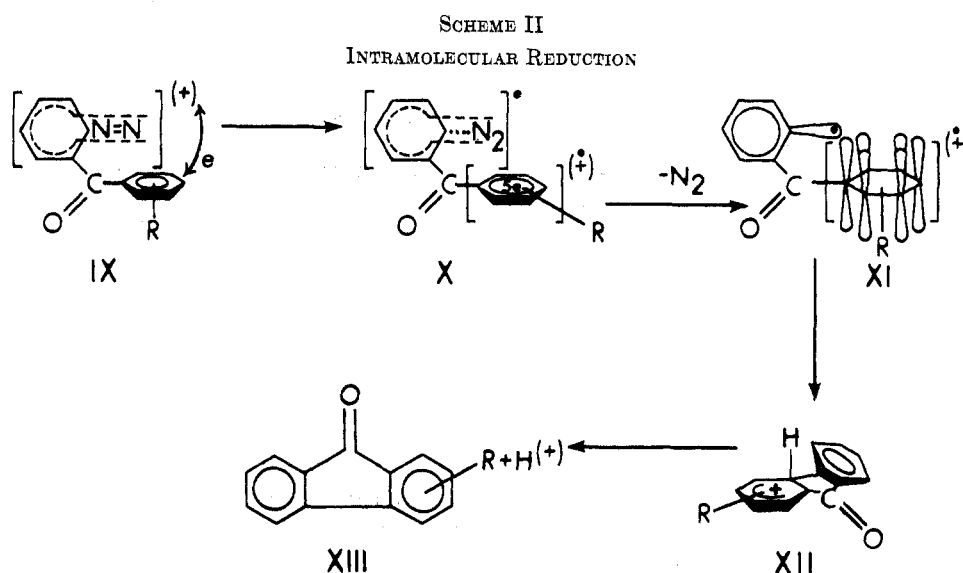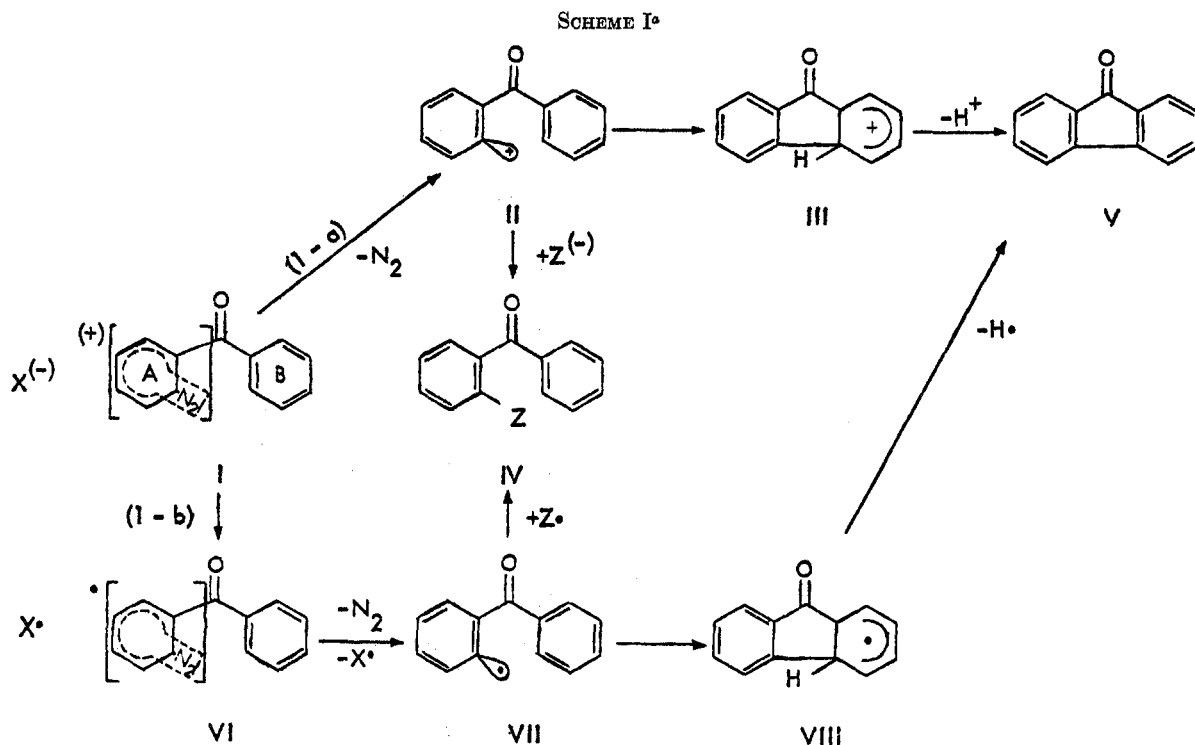
We wish to suggest an alternative mechanism to route 1-a based on studies of the redox behavior of diazotized aromatic amines conducted in this laboratory.[2,3,10] We believe that the reaction is taking place in a solvent cage and that reduction of the diazonium moiety is occurring with a simultaneous release of nitrogen. In the absence of external reducing agents, the only source of electrons for reducing

the diazonium moiety is the attached ring B. This mechanism of internal or intramolecular redox is initially described by Scheme II. The more real situation is delineated in Figure 1 which treats the decomposition of IX → XI. In effect, the change of IX to the Wheland complex (intermediate) occurs concertedly. The structures X and XI in Scheme II merely symbolize that N₂ release occurs simultaneously with the transfer of electrons; they are by no means necessarily intermediates or transition states. The transition state most likely occurs between the path of XI to XII. This proposal goes a long way to unify the theory of diazonium salts decomposition.

The general idea of a charge-transfer (CT) or redox mechanism in heterolytic aromatic substitution is not new. Nagakura and Tanaka,[24] and Brown[25] have long advocated such an approach. The internal redox state is more commonly known as an internal

(24) S. Nagakura and J. Tanaka, J. Chem. Phys., 22, 563 (1954).
(25) R. D. Brown, J. Chem. Soc., 2224, 2232 (1959).

SCHEME I[a]

[a] X·, Z·, and/or H· are atoms or radicals.

SCHEME II
INTRAMOLECULAR REDUCTION

charge-transfer state.[26] This would be X in Scheme II. Such a concept, where an external charge transfer may occur between the diazonium cation and X[(−)], is shown in route 1-b. Scheme II, which leads only to cyclization, is in the spirit of route 1-b, but is by no means a special case of it as the latter indicates external reduction. The two pathways, in fact, compete with each other, making the results complicated if one does not exercise careful control of experimental conditions. Let us now follow in detail the path for IX going to XI.

The stereochemistry of the diazonium salt of the 2-amino-3'-nitrobenzophenone cation is more precisely shown in Figure 2.[27] The geometry can be such that the N$_2$ moiety lies above the substituted benzene ring,

B. This is also shown in IX. The N$_2$ group is approximately at the van der Waals distance[27] from the ring B which provides the maximum opportunity for orbital overlap between the B-ring π orbitals and the N$_2$ π orbitals in the plane of the A ring. For this molecule, solvation occurs as a solvent shell or cage. In this geometry the carbonyl group has lost conjugation with ring B. Furthermore, the carbonyl group should not affect drastically the electron affinity of the aryl diazonium moiety. In fact, by the inductive effect, it would increase the electron affinity. Thus, for determining the position of the internal CT state in an energy diagram, it is reasonable to assume that the two ring moieties behave independently of the carbonyl group. Therefore, the interaction energy of the rings can be considered in three steps (Figure 1): (A) both rings are infinitely far apart; (B) they are brought together to their equilibrium geometry and are allowed

(26) R. S. Mulliken and W. B. Person, "Molecular Complexes: A Lecture and Reprint Volume," Wiley, New York, N. Y., 1969.
(27) Fisher-Hirschfelder-Taylor, Atom Model Kit, U. S. Patent 2,308,402 (1943).

$$\text{Ip}(C_6H_6) - \text{EA}(C_6H_5N_2^{\oplus})$$
$$= 9.25\,\text{ev} - 5.20\,\text{ev}$$
$$= 4.05\,\text{ev}$$

$$\text{EA}(C_6H_5^{\oplus}) - \text{Ip}(C_6H_6)$$
$$= 9.90\,\text{ev} - 9.25\,\text{ev}$$
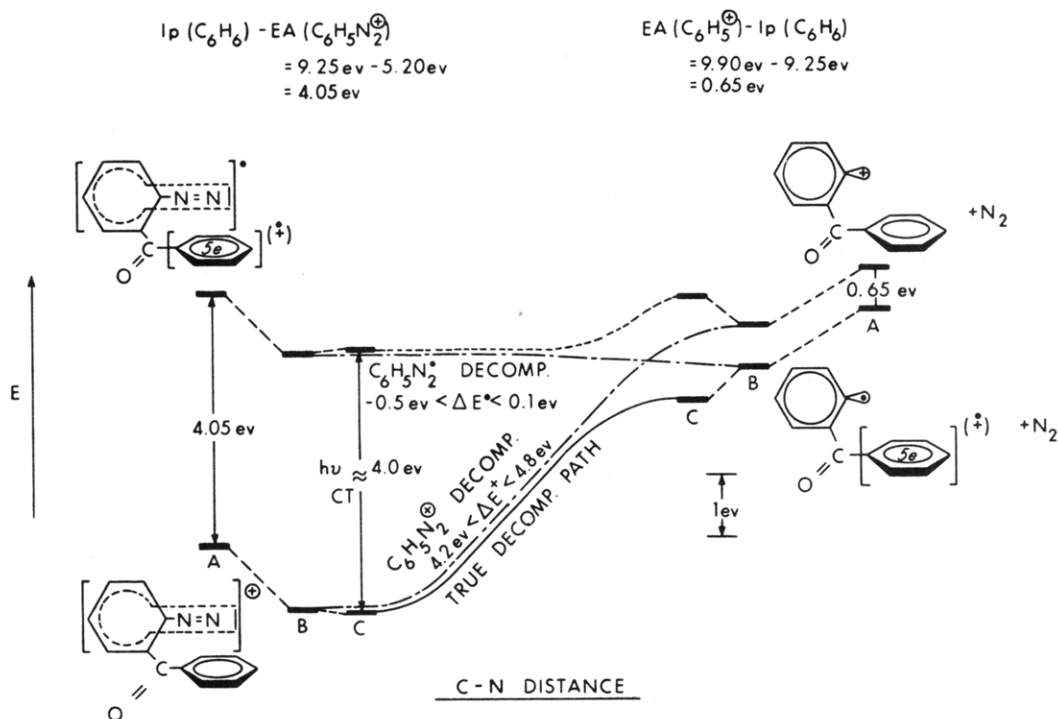$$= 0.65\,\text{ev}$$

Figure 1.—Decomposition behavior of IX to XI.

to interact *without* inclusion of CT interaction but including the solvation shell; and (C) a more complete interaction is formed by including the CT contribution. It is assumed throughout that step B leads to stabilization and this seems reasonable on the basis of known complexing[28] power of aryl diazonium cations. Stages A, B, and C for the ground state and CT state of the diazonium system are shown on the left of Figure 1. For simplicity, the B ring is taken as unsubstituted. In stage A the CT state is above the ground state by an energy of $I_p(C_6H_6) - \text{EA}(C_6H_5N_2^+)$ where I_p and EA mean, respectively, the ionization potential and electron affinity. An all-valence-electron SCF-CI calculation gave an electron affinity of 5.20 eV for $C_6H_5N_2^+$ and the accepted ionization potential of benzene[17,29] is 9.25 eV. This makes the CT state 4.05 eV above the ground state.[30] Even if the carbonyl group is introduced in the ortho position of $C_6H_5N_2^+$, or if the calculated electron affinity of $C_6H_5N_2^+$ is in error by 30%,[31] the electron affinity should be below 9.25 eV; hence the CT state lies *above* the ground state. The energy decrease from stage A to stage B may be assumed to be the same for both states since orbital overlap is the same in both states and there is a solvation shell around the entire molecule. Thus there remains approximately the same separation between the two states for step B as in stage A.[32] This holds as well for stage C, since there will be very small CT interaction due to the large separation between the two states. It is assumed here that there will not be a

(28) R. M. Elofson, A. A. Cantu, R. Ozubko, and F. F. Gadallah, to be published). See also Chr. Römming, *Acta Chem. Scand.*, **17**, 1444 (1963).

(29) Dr. S. Fraga, University of Alberta, Edmonton, Canada, private communication.

(30) Spectral and polarographic studies support the suggestion that the present compound exists largely as an internal CT complex. This will be reported in a subsequent paper.

(31) R. Carbo and S. Fraga, *An. Fis.*, LXVI, 270 (1970).

(32) It must be clearly understood that the CT complex contains none of the CT state but is merely a resonance hybrid of the CT and non-CT states.
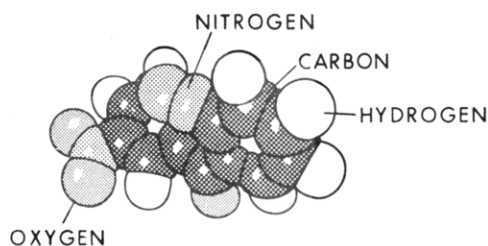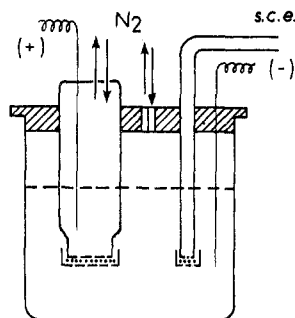

Figure 2.

significant change in solvation energy when state C is introduced. Thus for the left-hand side of Figure 1, the system IX is predominantly in the non-CT structure.

On the right-hand side of Figure 1, the dissociated species XI are considered. At stage A, the CT state lies below the non-CT state by an energy of $\text{EA}(C_6H_5^+) - I_p(C_6H_6) = 0.65$ eV. (The reported value for the electron affinity of $C_6H_5^+$ is 9.90 eV.[17]) In stage B it seems reasonable to assume that both states decrease the same amount as stage B at the left-hand side of Figure 1. In stage C, however, the small separation between the states makes the CT interaction very large.[26] Hence the lower energy state for XI is highly contaminated with CT structure. It should be noted that the two unpaired electrons depicted in Figure 1, or in X or XI, are only symbolic; the system must be in a singlet state (in order to have CT interaction) and thus these are really "paired" but in an excited state[26] (sometimes called singlet biradical).

Finally let us follow the decomposition by connecting the two sides of Figure 1. Decomposition without stage C is considered first. It has been shown[29] by an all-valence-electron calculation that the ground state of $C_6H_5N_2^+$ correlates with the ground state of the separated molecules $C_6H_5^+$ and N_2, and this correlation exists as well for the corresponding ground-state

Figure 3.

radicals. The photochemical work of Sukigara and Kikuchi[33] provides some limits on the ΔE^+ for the dissociation of $C_6H_5N_2^+$ in solution. They found that the $^1B_1$ state, which is 4.20 eV above the ground state, fluoresces, while the higher $^1A_1$ state, which lies 4.79 eV above the ground state, leads to dissociation. They contended that the photoproduced $C_6H_5^+$ was reduced by BF_4^- to give the phenyl radical, but did not exclude the possibility that BF_4^- reduced the excited $^1A_1$ $C_6H_5N_2^+$ with decomposition to nitrogen and a phenyl radical (route 1-b). In any case, ΔE^+ is between 4.20 and 4.79 eV.[34] This, in turn, provided limits on the ΔE. for the radical decomposition. Knowing the electron affinities of $C_6H_5N_2^+$ and $C_6H_5^+$, and assuming they both solvate to about the same extent, -0.5 eV $\leq \Delta E \cdot \leq 0.1$ eV. Thus, without considering CT contributions, in correlating the states there occurs *crossing*. Upon considering CT interaction (stage C), by the noncrossing rule, the crossing is avoided. Thus, in the decomposition, the system begins along a "heterolytic" path but ends up mainly along the internal-charge-transfer path. This, in turn, proceeds through a transition state to the Wheland complex and hence to the final cyclized product.

If the B ring is substituted and its ionization potential is still *less* than $EA(C_6H_5^+) = 9.90$ eV, then Scheme II is still valid. This is the situation with most cases considered here:[17] $I_p(C_6H_5-OCH_3) = 8.56$ eV, I_p-$(C_6H_5-CH_3) = 8.82$ eV, and $I_p(\text{naphthalene}) = 8.12$ eV. For nitrobenzene, a value of $I_p(C_6H_5-NO_2) = 10.18$ eV has been reported.[35] For this case, the stage B curves will not cross but will be very close (0.28 eV). Hence the reaction embarks along a pathway that becomes highly contaminated with the CT state. A pure cationic mechanism, route 1-a, does not occur. It should be stated that the value of I_p of nitrobenzene quoted was determined by mass spectrometry and that an analysis of a series of such I_p values reveals an overestimate in value from previous values determined by electron-impact methods. Thus, it may still be possible that $I_p(\text{nitrobenzene}) < 9.90$ eV. Furthermore, the introduction of the carbonyl group on the phenyl cation would make the electron affinity greater than 9.90 eV. It is thus conceivable that in all cases the substituted B ring will have an I_p less than the EA of the A ring.

(33) M. Sukigara and S. Kikuchi, *Bull. Chem. Soc. Jap.*, **40**, 461 (1967).

(34) Sukigara and Kikuchi[33] did not consider the possibility that the $C_6H_5N_2^+$ may be complexing with the solvent (water–ethanol) or BF_4^- in which case the "excited" states may not correspond to just $C_6H_5N_2^+$ but to the complex. Consequently, the bounds determined for ΔE^+ and thus for ΔE· may be wrong. This, however, does not affect the principal feature (avoided crossing) in Figure 1.

(35) G. F. Grable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).

The calculations represented in Figure 1 have an important consequence. Considering $C_6H_5N_2^+$ and a species X, if X is made to collide with $C_6H_5N_2^+$ forming a transient intimate pair, then the treatment of Figure 1 can be applied provided that $I_p(X) < 9.90$ eV. Such anions as BF_4^- or ClO_4^- [a value of $I_p(ClO_4^-) = 5.82$ has been reported[17]] are capable of reducing $C_6H_5N_2^+$ (the yields of 2-F products in Table II, along with expt 37 and 38 in Table III, strongly support this concept). The general conclusions of this redox model of aromatic diazonium chemistry must be (1) that reduction, by either an external or internal source, of the aromatic diazonium cation is necessary for the facile release of nitrogen; (2) that, unless completely isolated, an aryl cation does not exist, since there is generally a reducing species available and the combination prefers to undergo a redox reaction to reach a lower state; (3) that, for the Pschorr reaction, there always exists potential competition between route 1-b and Scheme II.

Regarding the third point, thermal decomposition of the dry salts of unsubstituted and substituted benzophenonediazonium tetrafluoroborate (expt 25 and 38) produces the fluoro compounds which could only occur through route 1-b (Bubnov, *et al.*[23]). The other product is the cyclized material and this occurs through route 1-b and Scheme II (competition between coupling with F· and cyclization). On the other hand, when these decompositions are carried out in acetone and sulfolane (expt 16, 17, and 37), it seems reasonable to say that the high yields of cyclized products are due to Scheme II. Benzene was used as a reaction medium in expt 22 and 23 to stop hydrogen abstraction and promote cyclization. This was achieved by comparison with the runs where aliphatic hydrocarbons were used.

The behavior of the isomer distribution of the nitrofluorenone and naphthoylfluorenone derivatives requires comment. For the external reduction mechanism, route 1-b, the isomer distributions of these compounds agree with the normal arylation patterns[5] predicted by the usual reactivity indices: free valences, F_r, or radical localization energies, L_r. In the case of internal reductions, Scheme II, the reaction occurs in a solvent cage and in a concerted manner (since the entire redox process is assumed to occur along a singlet state manifold). The orientation properties are believed determined by the electronic interactions (electrostatic repulsions) occurring before internal redox occurs (stage B). For example, since the diazo moiety in ring A is partially positive, as is the nitro group in ring B, Figure 2, then internal redox and eventual coupling occurs better at the position where these two groups are further apart. Thus the 2'-nitrofluorenone derivative predominates in the absence of an external reducing agent. This explains the reversal in going from route 1-b to Scheme II. Similarly, in the case of internal reduction of the 2-benzoylnaphthalenediazonium salts, the decrease, but not reversal, of the angular to linear ratio of the cyclized product follows the induced polarization effect of the diazonium moiety: it polarizes the naphthalene ring producing a partial positive charge on the outer ring (the one not attached to the carbonyl group). This partially positive charge then directs, in a manner weaker than the NO_2 group,

the diazonium moiety to the β-naphthalene position with the eventual result of a relative increase of linear cyclized product. These polar interaction arguments have been used previously by De Tar and Relyea,[36] but on the phenyl cation.

Experimental Section

Reagents.—All liquid reagents were purified by the methods described before.[2,3] Sulfolane was purified according to Jones,[37] by distilling under vacuum from NaOH, H_2SO_4, then solid NaOH, and twice from CaH_2. 2-Fluorobenzophenone was used as obtained commercially (98% pure)[38] for reference in glpc. Gatterman copper powder was prepared as mentioned before[3] and kept under vacuum. 2-Amino-4'-methoxy- and 2-amino-4'-methylbenzophenones were prepared according to Scheifele and De Tar.[39] 2-Amino-3'-nitro- and 2-hydroxy-3'-nitrobenzophenones were prepared according to De Tar and Whiteley.[40] 2-Nitrofluorenone was prepared by oxidizing 2-aminofluorenone.[41] 4-Nitrofluorenone was identified and estimated by mass spectrum and glpc. 2-o-Aminobenzoylnaphthalene and its products were prepared, identified and estimated according to Huisgen and Zahler.[18] 2-Phenylbenzophenone was prepared by Bradsher's method.[42] The three isomers of 2-pyridinobenzophenone were collected and were verified by mass spectrum. For quantitative work, 2-phenylbenzopheone was taken as their internal standard with an f value of 1. Boiling points, melting points, and mass spectra verified the purity of reagents, reference compounds, and products,

General Procedure for Electrolytic Reduction. A. In Aprotic Media.—Procedures and apparatus have been previously described.[2,3] Sulfolane or acetonitrile containing 0.1 M tetrabutylammonium perchlorate was used in both electrode compartments. The cathode compartment also contained 0.01 M diazonium tetrafluoroborate salt.

When the alkaline α-naphthol test was negative and output current dropped to less than 1 mA, the reaction was considered complete.

When acetonitrile was the solvent, the turbid reaction mixtures were separated from mercury, cooled, and filtered. The filtrates were concentrated, then chilled, and filtered again. The combined precipitates were washed with water, dried, and recrystallized from benzene yielding fine colorless needles, identified by mass spectrometry and elemental analysis as the organomercury compounds of bis(2,2')benzophenonemercury or its derivative i (R = H, CH_3, OCH_3, NO_2; see footnote *a*, Table III). Elemental analyses and melting points (uncorrected) are as follows. *Anal.* Calcd for $C_{26}H_{18}O_2Hg$ (R = H; mp 162–163°): C, 55.46; H, 3.22. Found: C, 55.36; H, 3.37. *Anal.* Calcd for $C_{28}H_{22}O_2Hg$ (R = CH_3; mp 173–174°): C, 56.89; H, 3.75. Found: C, 56.65; H, 3.92. *Anal.* Calcd for $C_{28}H_{22}O_4Hg$ (R = 4-OCH_3; mp 176.7°): C, 53.97; H, 3.56. Found: C, 53.97; H. 3.57. *Anal.* Calcd for $C_{26}H_{16}N_2O_6Hg$ (R = 3-NO_2; mp 222–224°): C, 47.82; H, 2.47. Found: C, 47.73; H, 2.49. Ether was added to the mother liquor to precipitate the perchlorate. The filtrate was evaporated to dryness and the residue taken up in benzene for glpc analysis for the other products.

When sulfolane was the solvent, the reaction mixture was pretreated by the addition of 3 vol. of water and extraction with

benzene. The benzene extract was evaporated to dryness, taken up in acetonitrile, and then subjected to the previous separation procedure.

B. In Protic Media.—(i) These reductions were carried out in dilute sulfuric acid. The amines were diazotized in dilute sulfuric acid and the solutions were used for electrolysis.

(ii) These reductions were carried out in anhydrous HF. The apparatus used consisted of two polyethylene jars with different diameters for cathode and anode compartments. The diaphragms between the two compartments and for the calomel bridge were Teflon (Millipore Cat. No. LSWPO). The calomel bridge was a polyethylene tube. The solutions were kept under N_2. A schematic diagram for the apparatus is shown in Figure 3.

General Procedure for Thermal Reactions. A. In Aprotic Media.—The diazonium salt was suspended or dissolved in the solvent and heated or refluxed until the test for diazonium cation was negative.

B. In Protic Media.—The diazonium salts were suspended with fast stirring at room temperature in the various media: fluoroboric acid (10%), acid and copper powder, water, water and copper powder, or water and pyridine. The temperature was increased to 75° in a short time ($\sim$5 min) and kept steady ($\pm2°$) until the test for diazonium cation was negative. The reaction mixtures were then cooled to room temperature and extracted with methylene chloride, extractions were washed with water, dried, and evaporated to dryness, and the residue was dissolved in benzene for analysis by glpc.

Reduction by Iodide Salts.—The diazonium salts were dissolved in acetonitrile or acetone at 5°. The solid iodide salt (10% excess) was added slowly with vigorous stirring under nitrogen. Fifteen minutes after the final addition, the diazonium cation test was negative and sodium thiosulfate solution (8% by weight) was added. Reaction mixtures were extracted with benzene, dried, and concentrated for the glpc analysis.

Thermal Decomposition of the Dry Salts.—Dry diazonium salts were placed in a flask fitted with a condenser guarded with a drying tube. Dry nitrogen stream was passed over it for 3 hr. Temperature was then increased gradually until decomposition commenced (maximum 150°) and kept constant for 15 min. The reaction mixtures were very dark. After the mixtures were cooled to room temperature, the condenser and flask were washed three times with benzene. The washings were concentrated and used for glpc analysis.

Identification and Estimation of Products.—All reaction mixtures were identified and estimated by glpc, using the internal standard method or the calibration curve method. Analyses were also performed with a directly coupled glpc–mass spectrometer combination, Bieman-Watson helium separator, and Nier-Johnson geometry. The reported yields are averages of duplicate or triplicate runs for each reaction.

Glpc Columns Used.—For compounds with R = H, 4'-CH_3, and 4'-OCH_3, a column of 6 ft $\times$ $^1/_8$ in. polyester of diethylene glycol and tetrachlorophthalic acid (10% w/w) on Chromosorb W (acid washed), 60–80 mesh, at 220° was used. For compounds with R = 3'-NO_2, a column of 6 ft $\times$ $^1/_8$ in. SE-30, 10% on Chromosorb W (acid washed), treated with hexamethyldisilazane, HMDS was used.

(36) D. F. De Tar and D. I. Relyea, *J. Amer. Chem. Soc.*, **76**, 1680 (1954).

(37) J. G. Jones, *Inorg. Chem.*, **5**, 1229 (1966).

(38) Aldrich Chemical Co., Inc.

(39) H. J. Scheifele and D. F. De Tar, *Org. Syn.*, **32**, 8 (1952).

(40) See footnote *b*, Table III.

(41) N. Ishikawa and M. Hayashi, *Yuki Gosei Kagaku Kyokai Shi*, **15**, 40 (1957); *Chem. Abstr.*, **51**, 16379a (1957).

(42) C. K. Bradsher, *J. Amer. Chem. Soc.*, **66**, 44 (1944).