Preparation of the Schiff Base of 9-Anthraldehyde and Racemic 2-Aminoöctane.—One gram (0.008 mole) of racemic 2-aminoöctane, 10 ml. of abs. ethanol and 1.65 g. (0.008 mole) of 9-anthraldehyde refluxed for ten minutes, allowed to come to room temperature and then placed in a refrigerator gave 2.3 g. of product, m.p. 60–62°. When recrystallized from 70% aqueous ethanol it yielded 2.1 g. (83% yield) of yellow crystals, m.p. 61–62°.

Anal. Calcd. for $C_{23}H_{27}N$: C, 87.0; H, 4.41; N, 8.51. Found: C, 87.0; H, 4.37; N, 8.51.

Catalytic Reduction of (+)α-Phenylnitroethane.—A solution of 6.0 g. (0.40 mole) of (+) α-phenylnitroethane (b.p. 92° (2 mm.), n^{20}D 1.5215, α^{27}D +2.80°) in 30 ml. of glacial acetic acid was reduced at 4 atm. (1.0 g. of Adams platinum oxide). The theoretical amount of hydrogen was absorbed in 18 minutes and there was obtained 2.8 g. (58% yield) of (+)α-phenylethylamine, b.p. 71–72° (10 mm.), n^{20}D 1.5269, α^{27}D +6.50°. This gave the benzamide; recrystallized from absolute ethanol (m.p. 124–125°) and then from petroleum ether (b.p. 60–70°); m.p. 124–125°; lit. values: (−)benzamide deriv., m.p. 124.5–125.5[15]; racemic benzamide of α-phenylethylamine has m.p. 120°.[16]

Anal. Calcd. for $C_{15}H_{15}NO$: C, 80.0; H, 6.67; N, 6.22. Found: C, 79.81, 79.82; H, 6.81, 6.89; N, 6.57, 6.48.

[15] W. Marckwald and R. Meth, *Ber.*, **38**, 808 (1905).

[16] M. Kann and J. Tafel, *ibid.*, **27**, 2308 (1894).

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Mechanism of the Reaction of Silver Nitrite with Alkyl Halides. The Contrasting Reactions of Silver and Alkali Metal Salts with Alkyl Halides. The Alkylation of Ambident Anions[1,2]

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The reaction of silver nitrite with alkyl halides proceeds *via* a transition state which has both SN1 and SN2 character in proportions that vary gradually with the structure of the halide. The products of the reaction reflect this variation in character: The greater the carbonium contribution to the transition state the greater is the yield of nitrite ester and the smaller is the yield of nitroparaffin. This preference of an anion (NO_2^-) for covalency formation at the atom of higher electronegativity (oxygen) is general and forms the basis of the contrasting reactions of silver salts and alkali metal salts (*e.g.*, AgCN and NaCN) with alkyl halides. Electrophilic attack by silver on the halogen of the alkyl halide greatly enhances the carbonium contribution to the transition state and this results in a preference for covalency formation to the most electronegative atom of the anion. Silver ions, while very effective for this purpose, are not unique. Changes in the reaction medium and in the structure of the alkylating agent also may have a profound effect on the nature of the transition state and, when this happens, the nature of the products changes. The following generalization about the alkylation of anions possessing two different reactive positions (*i.e.*, ambident anions), which is fully applicable even when silver is absent, provides a simple rationale for the hitherto unsolved problem of carbon *vs.* oxygen alkylation, oxygen *vs.* nitrogen alkylation, etc., in anions derived from acetoacetic ester, phenols, nitroparaffins, α-pyridone, acid amides, thioamides, etc.: The greater the SN1 character of the transition state the greater is the preference for covalency formation with the atom of higher electronegativity and, conversely, the greater the SN2 contribution to the transition state the greater the preference for bond formation to the atom of lower electronegativity. Specific examples of the application of this principle are given. The demonstration that the reaction of silver nitrite with alkyl halides has a transition state possessing SN1 and SN2 character rather than being the sum of two simultaneously occurring processes, the SN1 and the SN2, has an important bearing on the question of border-line mechanisms in substitution reactions at a saturated carbon atom.

The studies described in the present paper when taken in conjunction with the results of the preceding papers of this group[4] provide a secure basis for describing the mechanism of the reaction of silver nitrite with alkyl halides. This is a reaction which at one and the same time exhibits carbonium ion character and bimolecular nucleophilic displacement character. Precise allocation of the proportions of SN1 and of SN2 contribution to the transition state is, of course, not possible and, indeed, as will be seen, the relative importance of the pull exerted by silver and the push due to nitrite ion varies with the structure of the halide and with the solvent.

It will be recalled[4] that the yield of nitro compound falls progressively as silver nitrite is treated with primary, secondary and tertiary halides. In contrast, the yield of nitrite ester rises in going from primary, to secondary to tertiary halides.

Two explanations suggest themselves for this progressive change in the character of the reaction. The effect may be a steric one, for models reveal that NO_2^- has a greater steric requirement when it comes in to form a C–N bond than when it comes in to form a C–O bond. Consequently, it is conceivable that formation of nitro compounds is retarded more strongly than formation of nitrite esters when it becomes increasingly difficult to approach the carbon atom on the side rearward to the carbon–halogen bond.

A second possibility is that a carbonium ion would react more rapidly with the oxygen of a nitrite ion than with the nitrogen (perhaps because of simple electrostatic considerations inasmuch as the nitrogen is essentially neutral while the oxygen atoms share the negative charge between them). In any event, if we make this assumption, the increasing proportion of nitrite ester becomes intelligible since on going from primary to secondary to tertiary halides the ease of carbonium ion formation is increased.

Kinetic studies argue against the first and sup-

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[1] Paper IX in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

[2] This research was supported by the United States Air Force under Contract No. AF 18 (600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

[3] In part from the doctoral dissertation of Robert A. Smiley, Purdue University, June, 1954.

[4] (a) N. Kornblum, B. Taub and H. E. Ungnade, THIS JOURNAL, **76**, 3209 (1954); (b) N. Kornblum, R. A. Smiley, H. E. Ungnade, A. M. White, B. Taub and S. A. Herbert, *ibid.*, **77**, 5528 (1955); (c) N. Kornblum, L. Fishbein and R. A. Smiley, *ibid.*, **77**, 6261 (1955); (d) N. Kornblum and L. Fishbein, *ibid.*, **77**, 6266 (1955).

TABLE I

RELATIVE RATES OF SOLVOLYSIS OF BENZYL HALIDES

Halide	$Y{-}C_6H_4{-}C(C_6H_5)_2Cl$[a]	$Y{-}C_6H_4{-}CMe_2Cl$[b]	$Y{-}C_6H_4CH_2Br$[c]		$Y{-}C_6H_4CH_2Cl$[d]
Solvent	40% EtOH–60% Et_2O	10% H_2O–90% Me_2CO	10% H_2O–90% EtOH	+ $AgNO_3$	50% H_2O–50% EtOH
Temp., °C.	0	25	0	30	30
Y = *p*-NO_2	0.0065			0.019	0.044
Y = H	1	1	1	1	1
Y = *p*-Me	4.6	26	65		9.4
Y = *p*-OMe	>100				

[a] A. C. Nixon and G. E. K. Branch, THIS JOURNAL, **58**, 492 (1936). [b] H. C. Brown, private communication. [c] J. W. Baker, *J. Chem. Soc.*, 987 (1934). [d] S. C. J. Olivier, *et al.*, *Rec. trav. chim.*, **49**, 697 (1930).

port the second of these alternatives, for the reaction rate increases on going from primary to secondary to tertiary halides. From the half-lives for the reaction of silver nitrite with 1-bromobutane, 2-bromobutane and *t*-butyl bromide the relative rates are found to stand in the ratio 1:4:1500. An even greater difference is observed with iodides; 2-iodobutane reacts nine times faster than 1-iodobutane. And on comparing the half-lives of 1- and 2-iodoöctane it is found that the secondary iodide reacts ten times more rapidly than the primary. Finally, whereas primary and secondary chlorides are inert toward silver nitrite, tertiary chlorides react readily.[4] The reactivity sequence is, then, that of an SN1 process.

Of particular importance are the rates and products of the reaction of silver nitrite with the following set of bromides: *p*-nitrobenzyl bromide, benzyl bromide, *p*-methylbenzyl bromide, *p*-methoxybenzyl bromide. Here the reaction site has a constant steric requirement; hence it is possible to separate electrical from steric effects. Also, since dehydrohalogenation cannot occur, the reaction product is composed solely of the nitro compound and the nitrite ester—a very considerable advantage over the strictly aliphatic series.[4]

If replacement of the bromine by nitro and nitrite groups occurs as a process in which separation of the bromide ion has proceeded partly (or completely) before covalence with the NO_2^- is established, then the reaction has carbonium character in the transition state. The *p*-nitro group would resist such production of electron deficiency at the carbon holding the halogen and, so, of the four compounds listed *p*-nitrobenzyl bromide should react least rapidly. As the series is descended the rate of reaction should become progressively more rapid, being fastest for *p*-methoxybenzyl bromide. Such sensitivity of reactions whose transition states possess a large degree of carbonium character to *para* substituents is well established in solvolytic processes (*cf.* Table I).

On the other hand, if replacement of the bromine is an SN2 process then these four benzyl bromides should react with silver nitrite at rates which differ very little. The reaction of pyridine with benzyl bromides in acetone solution is an example of a typical bimolecular displacement process; here the relative second-order rate constants are benzyl bromide, 1; *p*-methylbenzyl bromide, 1.65; and *p*-nitrobenzyl bromide, 0.92. Nor is this the reactivity sequence routinely observed in SN2 processes; reactions are known, for example, in which the *p*-nitro group accelerates.[5]

Table II records the rates at which diethyl ether solutions of the four benzyl bromides react with silver nitrite at 0°. There is a large spread in the rates and, in addition, the four halides arrange themselves in the reactivity sequence to be expected for a carbonium ion process.

TABLE II

RATE OF REACTION OF SILVER NITRITE WITH BENZYL BROMIDES

Bromide	Half-life, min.
p-Nitrobenzyl	180
Benzyl	16
p-Methylbenzyl	1
p-Methoxybenzyl	Very small[a]

[a] Reaction is complete essentially as fast as the bromide is added to the silver nitrite.

This kinetic demonstration that the reaction of benzyl halides possesses carbonium character provides an opportunity to test the hypothesis that a carbonium ion reacts more rapidly at the oxygen of a nitrite ion than at the nitrogen. The theory predicts a distinct difference in the proportions of nitro compound and nitrite ester on descending the series of benzyl bromides. *p*-Nitrobenzyl bromide (which has the least carbonium character in the transition state) should give the smallest yield of nitrite ester and the highest yield of nitro compound while *p*-methoxybenzyl bromide (which has the most carbonium character) should give the largest yield of nitrite ester and the smallest one of nitro compound. Benzyl bromide and *p*-methylbenzyl bromide should prove to be intermediate cases. All these expectations are fully realized when the products of the reaction of silver nitrite with these benzyl halides are isolated.

TABLE III

PRODUCTS OF THE REACTION OF SILVER NITRITE WITH BENZYL BROMIDES

Bromide	Nitro compound,[a] %	Nitrite ester,[b] %
p-Nitrobenzyl	84 (75)	16 (5)
Benzyl	70 (61)	30 (28)
p-Methylbenzyl	52 (45)	48 (37)
p-Methoxybenzyl	39 (26)	61 (55)

[a] This yield of nitro compound by titration. The values given in parentheses are the yields of analytically pure nitro compounds actually isolated. [b] This yield by difference. The values given in parentheses are the yields of analytically pure nitrite esters actually isolated.

The SN1 character of the reaction of silver nitrite with alkyl halides reveals itself in yet a number of

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(5) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 519, 1840 (1935); also see C. G. Swain and W. P. Langsdorf, THIS JOURNAL, **73**, 2813 (1951); G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935); A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, **47**, 30 (1951).

other ways. Whereas primary bromides react completely with silver nitrite in 60 to 80 hours,[4] the reaction of the ethyl ester of bromoacetic acid is exceedingly slow being only 12% complete after 156 hours.[6] With an α-bromoester the pull exerted by silver on the halogen atom further polarizes the carbon–bromine bond and thereby enhances the electron deficiency of the carbon α to the carbonyl carbon. But the carbonyl carbon itself has an electron deficiency and, hence, the transition state for the reaction is of higher energy than it would be in the absence of the carbonyl group.[7] When silver nitrite reacts with a primary alkyl bromide no such violation of the adjacent charge rule obtains and the transition state is of correspondingly lower energy.

That the formation of a silver–halogen bond furnishes an important part of the driving force for the reaction of alkyl halides with silver nitrite is further shown by the failure of sulfonate esters to react with silver nitrite. Thus, the recoveries of *n*-butyl methanesulfonate, ethyl benzenesulfonate and ethyl *p*-toluenesulfonate are 98, 94 and 96%, respectively, when they are exposed to the action of silver nitrite for 96–116 hours. In contrast, the corresponding alkyl bromides and iodides react completely, and in but a fraction of the time.[4,8]

When a solution of silver nitrite in acetonitrile is treated with *t*-butyl chloride, N-*t*-butylacetamide is produced.[9] This can only mean that *t*-butylcarbonium ions, formed under the influence of silver ions, attack the acetonitrile in a manner completely analogous to that observed when carbonium ions, generated by the action of concentrated sulfuric acid on olefins and *t*-alcohols, react with acetonitrile.[10]

It is especially noteworthy that the reaction of silver nitrite with alkyl halides, while possessing all these SN1 attributes, simultaneously exhibits the characteristics of an SN2 process. Thus, when optically active 2-bromoöctane is treated with silver nitrite, 2-nitroöctane and 2-octyl nitrite are produced with clean inversion of configuration.[4] The same result is obtained with optically active 2-iodooctane. The importance of nucleophilic attack rearward to the carbon–halogen bond is also evident from the fact that neopentyl iodide is inert to silver nitrite under conditions which result in complete reaction with other primary iodides, *e.g.*, *n*-amyl iodide and *n*-octyl iodide.[4] And, finally, no examples of rearrangements are known in the reaction of silver nitrite with alkyl halides.[11]

The initial observations concerning the lack of reactivity of neopentyl iodide[4] have now been confirmed and extended by kinetic studies. At 0°, an ether solution of neopentyl iodide reacts with silver nitrite to the extent of only 10% in 29 days whereas the reaction of *n*-butyl iodide is half over in 1.5 hours. Even at 27° the reaction of an ether solution of neopentyl iodide and silver nitrite requires 260 hours to go half-way to completion.

Silver nitrite is very insoluble in diethyl ether[12] and this leads to the reasonable assumption that the reaction with alkyl halides, in this solvent at least, is a heterogeneous process. Consequently, in order to rule out the possibility that the inertness of neopentyl iodide derives from steric effects having to do with the crystal surface, experiments in acetonitrile, in which silver nitrite is soluble, were carried out. In this solvent, the reaction of neopentyl iodide at 26° has a half-life of 90 hours. A parallel experiment with *n*-butyl iodide is ***complete*** in six ***minutes***. At 0° the results in acetonitrile are again striking: neopentyl iodide has a half-life of 1600 hours whereas *n*-butyl iodide has a half-life of ten minutes.

Isobutyl bromide reacts with silver nitrite much more slowly than any other primary bromide studied,[4] an observation which again highlights the importance of the "push" exerted by NO_2^- in these reactions. The reaction with neopentyl bromide, which was not examined, would unquestionably be even slower since neopentyl iodide reacts very much less rapidly than isobutyl iodide.

All these facts, as well as a number to be discussed, become intelligible on the basis that in the reaction of silver nitrite with alkyl halides the pull of the silver on the halogen and the push of the NO_2^- are both important in the transition state, the proportions of SN1 and SN2 character varying as a function of the structure of the halide and of the reaction medium. With primary halides the silver ion, by exerting its electrophilic pull on halogen, further polarizes the carbon–halogen bond but the push of the nitrite ion is required to consummate the reaction. This gives the transition state a large amount of SN2 character which, as has been seen (Table III), promotes the formation of nitroparaffin. The clearest demonstration that the "SN2" reaction of NO_2^- with an alkyl halide produces nitroparaffin is the work of Mooberry. He has shown that the reaction of ***sodium*** nitrite with primary and with secondary alkyl bromides gives 55–65% yields of the pure nitro compounds and 30–33% yields of the nitrite esters. These reactions, which are conducted in dimethylformamide solution, are kinetically second order: first order in nitrite ion and first order in alkyl halide.[13]

With secondary halides the pull exerted by silver produces still further polarization of the carbon–halogen bond. Since the carbon undergoing substitution has a greater electronic deficiency in the transition state, the yield of nitrite ester rises while

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(6) Unpublished work by Mary E. Chalmers, Purdue University. The homologous α-bromoesters also react less rapidly than the corresponding alkyl bromide.

(7) For a discussion of the adjacent charge rule, see L. Pauling, "The Nature of the Chemical Bond," Ed. 2, Cornell University Press, Ithaca, N. Y., 1944, p. 199 *et seq.*

(8) In a personal communication Dr. Harold Shechter of Ohio State University informs us that silver nitrite fails to react with an ether solution of *n*-amyl methanesulfonate.

(9) B. Taub, Ph.D. Thesis, Purdue University, June, 1952.

(10) J. J. Ritter and P. Minieir, THIS JOURNAL, **70**, 4045 (1948). J. Cast and T. S. Stevens have recently reported the formation of N-benzhydrylacetamide by the reaction of acetonitrile with benzhydryl bromide under the influence of silver sulfate: *J. Chem. Soc.*, 4180 (1953). Still more recently it has been found that trityl chloride alkylates acetonitrile when silver nitrate is present, the product being N-tritylacetamide: G. W. H. Cheeseman, *Chemistry and Industry*, 281 (1954); S. J. Cristol and J. E. Leffler, THIS JOURNAL, **76**, 4468 (1954).

(11) N. Kornblum and C. Teitelbaum, THIS JOURNAL, **74**, 3076 (1952).

(12) We are indebted to Dr. H. E. Ungnade for this experiment; *cf.* Experimental.

(13) D. D. Mooberry, Ph.D. Thesis, Purdue University, June, 1954.

that of nitroparaffin falls. But the push of the nitrite ion is still an important feature of the reaction and this leads to clean inversion in the production of 2-nitroöctane and 2-octyl nitrite.[4] Simultaneous with this stereochemical manifestation of S_N2 character is a kinetic demonstration of S_N1 character: secondary halides react more rapidly than primary halides.

Since tertiary halides form carbonium ions most readily, polarization of the carbon–halogen bond under the influence of the silver ion is greatest with the consequence that the yield of nitrite ester rises to 65% while that of nitroparaffin becomes 0 to 5%.[14] Whether the reaction now goes *via* a free carbonium ion cannot be stated at present but the very large jump in rate (1°:2°:3° as 1:4:1500) is indicative, in itself, of considerable change in the character of the reaction. A knowledge of the stereochemistry of the reaction when an optically active tertiary halide is employed would reveal whether or not the push of the nitrite ion is a significant factor with tertiary halides: if the reaction is going *via* a carbonium ion, then active nitrite ester possessing the same configuration as the halide will be obtained (*cf.* the case of α-phenylethyl chloride below).

The puzzling fact[4] that, while the reaction of silver nitrite with optically active α-phenylethyl chloride gives α-phenylnitroethane of the opposite configuration as the halide, the α-phenylethyl nitrite has the *same* configuration as the chloride now finds a ready explanation. The nitro compound is formed in the same way as in strictly aliphatic systems, *i.e.*, by a process involving rearward attack by nitrite ion. Presumably some α-phenylethyl nitrite is also produced by this rearward displacement process; but in the α-phenylethyl series there is available a second path for the formation of nitrite ester—carbonium ion formation. The carbonium ion is produced by loss of chloride ion to the silver nitrite crystal and it reacts rapidly with a nitrite ion from the crystal surface. Since these nitrite ions are concentrated on the same side of the carbonium ion as the chlorine which has left, nitrite ester formation is attended by a strong preference for retention of configuration.[15,16]

A comparison of the reaction of α-iodoesters on the one hand and alkyl iodides on the other with silver nitrite is instructive. Whereas secondary iodides, *e.g.*, 2-iodopropane and 2-iodobutane, give about 15% yields of nitro compounds,[4] α-iodoesters such as ethyl α-iodopropionate and ethyl α-iodobutyrate give 80–85% yields of the α-nitroester.[6] From adjacent charge considerations[7] it is clear that in reactions involving α-iodoesters S_N1 character is minimized and, hence, the push of the NO_2^- is of greater importance than with iodoalkanes. This results in a preference for carbon–nitrogen bond formation in reactions involving α-iodoesters. This decrease in the development of carbonium character in the transition state also manifests itself in the matter of rate; at 0° the half-life of reaction for ethyl α-iodopropionate is 81 hours while the corresponding alkyl iodide, 2-iodopropane, has a half-life of 8 *minutes*.[6,17]

Thus use of the concept that the greater the carbonium character of the transition state the greater will be the yield of nitrite ester provides an explanation for the variation in yields of nitrite ester and nitroparaffin as a function of the structure of the alkyl halide. The same concept allows one to predict that solvent changes which favor ionization will bring about an increase in the yield of nitrite ester and a decrease in that of the nitro compound. In the one case thus far investigated this prediction has been fulfilled. When silver nitrite reacts with 1-iodoheptane in diethyl ether there is routinely isolated a 78–82% yield of 1-nitroheptane and a 7–12% yield of 1-heptyl nitrite. On conducting the reaction in acetonitrile (dielectric constant 38.8 as opposed to 4.31 for ether) reproducible 60–64% yields of 1-nitroheptane and 23–33% yields of 1-heptyl nitrite are obtained.[18] Much work remains to be done before this simple basis for predicting the result of solvent changes can be accepted,[19] but even at this juncture it does appear that in acetonitrile the transition state has more carbonium character than in diethyl ether. The concept that the product ratio varies as a function of the relative importance of bond breaking and bond making in the transition state should prove a valuable tool for studying the effect of solvents on the transition state, not only in the reaction of silver nitrite with alkyl halides but also in other substitution reactions at a saturated carbon atom.

The reaction of silver nitrite with alkyl halides is regarded as a pull–push process. The characterization "pull–push," as distinct from push–pull, is deliberate. Vona and Steigman,[20] who have investigated the kinetics of the reaction of silver nitrate with alkyl halides in pyridine solution, interpret their observations in terms of a push–pull mechanism. This is appropriate since they find, in contrast to the results of the present investigation, that primary halides react more rapidly than secondary halides.

Very recently Hammond and Hawthorne[21] reported that the reaction of methyl iodide with silver nitrate in acetonitrile solution shows third-order kinetics: first-order with respect to nitrate ion, methyl iodide and silver ion. The reaction of silver perchlorate with methyl iodide in acetone solu-

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[14] Dehydrohalogenation accounts for the remainder of the halide.

[15] It is a corollary of this explanation that the α-phenylethyl nitrite shall be more highly racemized than the α-phenylnitroethane; there are indications that this is so.[4]

[16] In this connection note the important researches of E. S. Lewis and C. E. Boozer on the reaction of α-phenylethanol, and other secondary alcohols, with thionyl chloride [THIS JOURNAL, **74**, 308 (1952); **75**, 3182 (1953)].

[17] α-Halonitro compounds, α-halonitriles, α-halocarbonyl compounds will all be expected to react distinctly less rapidly than the corresponding alkyl halides. A further expectation is that the yields of nitro compounds will be higher than for the simple alkyl halides. In contrast, α-halo ethers should react rapidly and give poor yields of α-nitroethers.

[18] Unpublished work by D. E. Hardies, Purdue University.

[19] Among other things this prediction ignores the fact that the reaction in ether is, almost certainly, a heterogeneous process whereas in acetonitrile the reactants are in solution. Then, too, solvents which are good ionizing media will, in many instances, complex with the silver ion and thereby attenuate its electrophilic power. This factor does not seem to be of overriding importance in acetonitrile.

[20] J. A. Vona and J. Steigman, Abstracts of New York Meeting of American Chemical Society, September 12–17, 1954, p. 42-O.

[21] G. S. Hammond and M. F. Hawthorne, Abstracts of New York Meeting of American Chemical Society, September 12–17, 1954, page 41-O.

tion was found to show similar third-order kinetics. These kinetic observations are fully consistent with the pull–push mechanism of the present paper. It is particularly striking that, at least for methyl iodide, the push exerted by such a very weak nucleophilic agent as perchlorate ion is kinetically significant. This furnishes additional support for the view that nitrite ion, a far more powerful nucleophilic agent, exerts a "push" in the reaction of silver nitrite with alkyl halides.

In addition to its intrinsic interest, the present study illuminates three very important problems of organic chemistry: 1. Border-line mechanisms in displacement reactions at a saturated carbon atom. 2. The basis for the different reactions which occur when an alkyl halide is treated with an alkali metal salt on the one hand or a silver salt on the other, *e.g.*, sodium cyanide *vs.* silver cyanide. 3. The factors which decide whether alkylation of an anion shall occur at one or the other of two available positions, *e.g.*, what decides whether acetoacetic ester will undergo carbon or oxygen alkylation?

Border-line Mechanisms in Displacement Reactions at a Saturated Carbon Atom

The recent paper by Gold, Hilton and Jefferson[22] shows that the question of border-line mechanisms in substitution reactions at a saturated carbon is still a controversial one despite the recent apparent acceptance by Hughes and Ingold[23] of the ideas advanced by Winstein,[24] by Swain[25] and by Hudson.[26] In the present paper numerous facts concerning the reaction of silver nitrite with alkyl halides have been shown to be readily intelligible on the basis that this is a reaction which at one and the same time exhibits carbonium ion character and bimolecular nucleophilic displacement character. The alternate view that this reaction is the sum of two simultaneously occurring processes, the SN1 and the SN2, will now be examined.

Case 1. Primary halides react by mechanism SN2, tertiary halides by mechanism SN1 and secondary halides by a mixture of these two mechanisms, the individual molecular act of substitution being either SN1 or SN2. Among the arguments which can be brought to bear against this possibility are the following: (a) If primary halides react by mechanism SN2 then the fact that the ethyl ester of bromoacetic acid reacts with silver nitrite much less rapidly than 1-bromobutane, the rate being only one-twentieth to one-fortieth as fast,[6] is incomprehensible since the second-order rate constant for the reaction of ethyl bromoacetate with sodium nitrite in dimethylformamide solution is 170 times *greater* than the second-order rate constant for 1-bromobutane.[27] The greater reactivity of an α-haloester in a nucleophilic process which exhibits clean second-order kinetics is, of course, not new. It has long been known, for example, that in the second-order reaction with sodium iodide in acetone, ethyl chloroacetate reacts 103 to 160 times as fast as 1-chlorobutane.[28]

(b) If the reaction of primary halides with silver nitrite in diethyl ether takes place by mechanism SN2 then no function is ascribed to the silver. This, coupled with the fact that in dimethylformamide *n*-butyl methanesulfonate and *n*-butyl *p*-toluenesulfonate react readily with sodium nitrite to give the nitroparaffin and nitrite ester,[27] just as do alkyl halides (*vide supra*), causes one to expect that sulfonate esters will react with silver nitrite. But, as has been seen, sulfonate esters are completely inert to silver nitrite in diethyl ether, a fact which cannot be accommodated by the view that primary halides react by mechanism SN2 whereas it is readily understandable on the basis of a "pull–push" mechanism.

(c) If some of the molecules of secondary halides react by mechanism SN1 then the clean inversion observed in reactions employing optically active 2-octyl iodide and 2-octyl bromide is not easy to understand.[29]

Case 2. In the reaction of a given halide with silver nitrite some of the molecules react by mechanism SN1 (giving thereby nitrite ester) while others go *via* mechanism SN2 (giving nitro compound). The gradation in yields of nitrite ester and nitro compound observed on going from primary to secondary to tertiary halides, and also with the benzyl bromides (*cf.* Table III) is then due to the change in the proportions of molecules reacting by one mechanism or the other. The following arguments militate against this interpretation: (a) If this were so then the 2-octyl nitrite and the 2-nitrooöctane obtained on treating optically active 2-bromooöctane and 2-iodooöctane, with silver nitrite would be of quite different optical purity. But this is not what happens. Instead, the 2-octyl nitrite and 2-nitrooöctane are both produced with inversion and with very little, if any, loss of optical activity.[4c]

(b) If nitrite esters result from the operation of mechanism SN1 then it is less than obvious why 2-octyl nitrite is formed with inversion of configuration while α-phenylethyl nitrite is produced with retention.[4c]

From the foregoing it is apparent that the reaction of silver nitrite with alkyl halides is a clear example of a process whose transition state has both SN1 and SN2 character in proportions which vary gradually with the structure of the halide. The alternate view that this reaction is the sum of two simultaneously occurring processes, the SN1 and the SN2, is seen to be completely indefensible.

For the purpose of providing an insight into the problem of borderline mechanisms this reaction is, then, of singular value—the more so since solvent changes are not necessary to bring out the graded proportions of SN1 and SN2 character of the transition state.

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[22] V. Gold, J. Hilton and E. G. Jefferson, *J. Chem. Soc.*, 2760 (1954).

[23] M. L. Bird, E. D. Hughes and C. K. Ingold, *ibid.*, 634 (1954).

[24] S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

[25] C. G. Swain and W. P. Langsdorf, *ibid.*, **73**, 2813 (1951).

[26] D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, 3352 (1953).

[27] R. K. Blackwood, unpublished work, Purdue University.

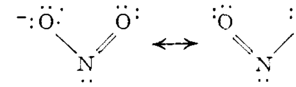
[28] J. B. Conant and R. E. Hussey, THIS JOURNAL, **47**, 476 (1925); J. B. Conant, W. R. Kirner and R. E. Hussey, *ibid.*, **47**, 488 (1925).

[29] For primary halides to be reacting by mechanism SN1, with tertiary halides going by mechanism SN2, and secondaries by SN1 and SN2 is palpably absurd. That this is so is underlined by the fact that neopentyl iodide is far and away the least reactive alkyl iodide studied.

The Basis for the Contrasting Reactions of Silver Salts and Alkali Metal Salts with Alkyl Halides

This paper provides a demonstration that the reaction of silver nitrite with alkyl halides involves a transition state simultaneously possessing SN1 and SN2 character. An increase in the carbonium character of the reaction results in an increased yield of nitrite ester while a decrease favors nitroparaffin production. This preference is taken to mean that in a reaction having a relatively large amount of SN1 character simple electrostatic forces govern the course of the reaction.

Clearly, in a nitrite ion the oxygens have a much higher electron density than nitrogen. The two resonance structures of lowest energy are



Then, too, oxygen has a higher electronegativity than nitrogen.[30] Thus, when the transition state has a large carbonium component the nitrite ion undergoes preferential covalency formation at the atom having the higher electron density.

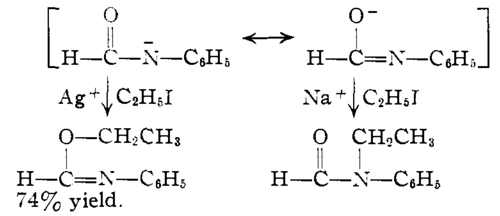
It is proposed that this is a general characteristic of the reactions of alkyl halides with anions capable of covalency formation at two different atoms; conditions conducive to establishing a comparatively large degree of carbonium character in the transition state produce a preference for bonding to the atom having the higher electron density. An effective way of enhancing the development of carbonium character is to have silver ions present and this is now seen to be the basis of the often recorded differences in the course of reaction of an alkyl halide with silver salts and with alkali metal salts. Where previously it has been assumed that the silver coördinated with one of the atoms of an anion and thereby affected the reactivity of that anion, it is now proposed that the silver salt differs from an alkali metal salt in bringing along a silver ion. This silver ion, to a greater or lesser degree, polarizes the carbon–halogen bond of the alkyl halides with results which are now predictable. Consider some specific examples:

1. Alkylation of the Salts of α-Hydroxypyridine (α-Pyridone).—The salt of this compound is capable of reacting at oxygen or at nitrogen (*cf.* footnote 30). Since the major fraction of the charge resides on the oxygen, treatment of the silver salt of α-hydroxypyridine with alkyl halides should favor oxygen alkylation. This is precisely what happens. When the silver salt is treated with ethyl iodide an 80% yield of the O-ethyl ether (with no detectable amount of N-ethyl-α-pyridone) is obtained. In contrast, the potassium salt gives only N-ethyl-α-pyridone (73% yield).[31] The homologs and benzologs of α-hydroxypyridine exhibit completely analogous behavior.[32]

The fact that the silver salt of α-hydroxypyridine gives a 50% yield of N-methyl-α-pyridone on reacting with methyl iodide,[31] while from the corresponding reaction employing ethyl iodide only the O-ether is isolated is easy to understand. With ethyl iodide the silver ion is able to generate a greater degree of carbonium character than with methyl iodide and this is reflected in the products obtained.

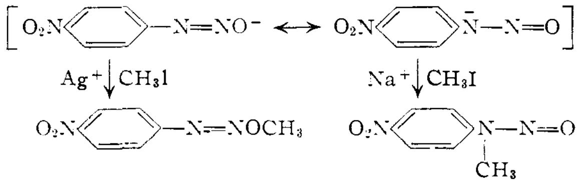
2. Alkylation of the Salts of Amides.—Silver salts strongly favor O-alkylation whereas alkali metal salts give N-alkylated products.[33] Here again, the facts are readily intelligible on the basis that (a) in the ion the oxygen has a distinctly higher electron density than nitrogen and (b) the silver ion enhances the degree of carbonium character in the transition state.

The following reactions are typical of this group of compounds.



Although no yield is given for the reaction of the sodium salt of N-phenylformamide with ethyl iodide, numerous other instances are known in which the sodium salts of amides give 62–96% yields of the N-alkylated amides.[33]

3. Alkylation of the Salts of Diazotates.—The silver salts and the alkali metal salts of aryl diazotates react differently with alkyl halides. Silver salts show a preference for O-alkylation while with alkali metal salts the preference is for N-alkylation.[34] The diazotate anion will have maximum electron density on oxygen[30] and, therefore, in the presence of silver ions alkylation at the oxygen will be favored.



4. Alkylation of Cyanides.—Alkali metal cyanides react with alkyl halides to give nitriles, only traces of the isocyanide being produced; with primary halides the yields are often 80–90%. In

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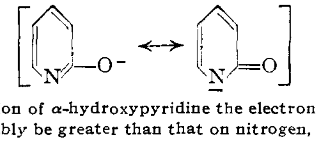
[30] With an ion such as the anion of α-hydroxypyridine it is less than obvious which atom has the higher electron density, but the decision reached by using Pauling's electronegativity scale: O > N > C = S (ref. 7, p. 64) provides the correct basis for predicting the products. In the anion of α-hydroxypyridine the electron density on oxygen will presumably be greater than that on nitrogen, not only in consequence of the greater electronegativity of oxygen, but also because this maximizes the aromatic character of the heterocyclic nucleus.



[31] H. von Pechmann and O. Baltzer, *Ber.*, **24**, 3148 (1891); C. Rath, *Ann.*, **489**, 107 (1931).

[32] M. T. Bogert and H. A. Sell, THIS JOURNAL, **29**, 517 (1907).

[33] L. I. Smith and J. Nichols, *J. Org. Chem.*, **6**, 502 (1941); W. J. Comstock and F. Kleeberg, *Am. Chem. J.*, **12**, 492 (1890); J. D. Lander, *J. Chem. Soc.*, **83**, 414 (1903); J. Tafel and O. Enoch, *Ber.*, **23**, 103, 1550 (1890); R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 572, 579.

[34] C. Schraube and C. Schmidt, *Ber.*, **27**, 514 (1894); H. von Pechmann and L. Frobenius, *ibid.*, **27**, 672 (1894); E. Bamberger, *ibid.*, **28**, 225 (1895).

contrast, silver cyanide produces isocyanides.[35] 2-Methyl-1-iodobutane, for example, is transformed into the isocyanide in 60% yield. Of special interest is the report that *t*-butyl iodide gives $(CH_3)_3$-C-NC on treatment with silver cyanide.[36] The fact that, under conditions favoring the development of carbonium character, reaction occurs at the nitrogen of the cyanide ion is taken to mean that this is the position of higher electron density.[37]

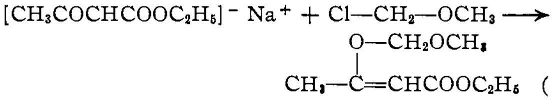
The ideas presented here do not require that alkylation of a silver salt will give a completely different product from the corresponding process employing a sodium salt and, of course, mixtures of the two possible alkylation products are often obtained. What is predicted is that the presence of silver ions will enhance the carbonium character of the transition state and this will favor covalence formation at that atom of the anion which has the highest electron density.

Throughout this discussion emphasis has been placed on the consequences of increasing the carbonium character of the reaction. With alkali metal salts, the S_N2 character of the transition state is dominant and here alkylation occurs preferentially at that atom of the anion which has the *lower* electron density. That this should be so is reasonable, for in anions composed of two or more atoms, a low electron density and a low value in the electronegativity scale[30] go hand in hand. Low electronegativity connotes a willingness to share electrons. Thus, when bond formation is the important feature of the transition state there is a preference for bonding to the atom of lower electronegativity.[38a,b]

The Basis for the Contrasting Alkylation Reactions of Ambident[39] Anions

The reactions of alkyl halides with silver salts and with alkali salts differ because silver ions, by interacting with the halogen of the alkyl halide, increase the amount of carbonium character in the transition state. Silver ions, while very effective for this purpose, are not unique. Changes in the reaction medium and in the structure of the alkylating agent are also able to affect the nature of the transition state profoundly; when this occurs the nature of the products is also changed. It will now be shown that the principles developed in the preceding section are fully applicable to ambident reactions in which silver is absent.

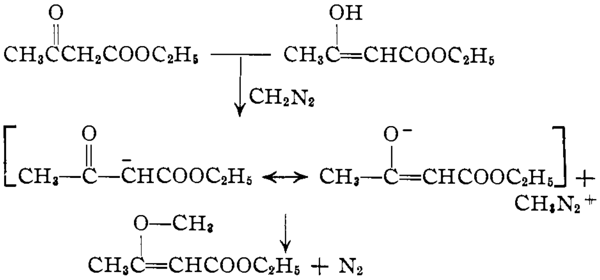
Carbon *vs.* Oxygen Alkylation.—1. Treatment of the sodio derivative of acetoacetic ester with primary halides gives only carbon alkylation. This is to be contrasted with reaction 1 in which the only alkylated product is the O-methoxymethylacetoacetic ester (*ca.* 74% yield).[40]



$$[CH_3COCHCOOC_2H_5]^- Na^+ + Cl{-}CH_2{-}OCH_3 \longrightarrow CH_3{-}\overset{\overset{\displaystyle O{-}CH_2OCH_3}{|}}{C}{=}CHCOOC_2H_5 \qquad (1)$$

Carbon alkylation of the ambident anion $[CH_3COCHCOOC_2H_5]^-$ by alkyl halides shows second-order kinetics.[41] It is an "S_N2" process and as such exhibits a strong preference for covalency formation to the atom of lower electronegativity. Alkylation with $Cl{-}CH_2OCH_3$, however, employs a reagent known to undergo very rapid hydrolysis and alcoholysis by the "S_N1" mechanism[42] and it, therefore, will take place with a relatively large amount of carbonium character in the transition state. This results in preference for that atom of the ambident anion having the highest electron density.[43]

2. The reaction of methyl iodide with sodioacetoacetic ester gives only the C-methyl derivative, as would be anticipated for an "S_N2" alkylation.[41] However, when diazomethane is allowed to stand with acetoacetic ester, methylation occurs exclusively at the oxygen.[44] This must occur as



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2COOC_2H_5 \;—\; CH_3\overset{\overset{\displaystyle OH}{|}}{C}{=}CHCOOC_2H_5 \xrightarrow{CH_2N_2} \left[CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{-}{C}HCOOC_2H_5 \longleftrightarrow CH_3{-}\overset{\overset{\displaystyle O^-}{|}}{C}{=}CHCOOC_2H_5\right] + CH_3N_2^+ \longrightarrow CH_3\overset{\overset{\displaystyle O{-}CH_3}{|}}{C}{=}CHCOOC_2H_5 + N_2$$

In the reaction of $CH_3N_2^+$ with the ambident anion, in consequence of the very great instability of the methyldiazonium ion, bond breaking is far more

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(35) H. Guillemard, *Ann. chim. phys.*, [8] **14**, 363 (1908); H. Rupe and K. Glenz, *Ann.*, **436**, 184 (1929); T. L. Davis and D. Yelland, THIS JOURNAL, **59**, 1998 (1937).

(36) J. U. Nef, *Ann.*, **309**, 154 (1899).

(37) The cyanide ion may be represented as a hybrid of the structures $:C{\equiv}\overline{N}:$ and $:C{=}\overline{N}:$. It would not be surprising if the second of these is the more important since in nitriles the corresponding structures, $R{-}C{\equiv}N:$ and $R{-}\overset{+}{C}{=}\underset{\cdot\cdot}{\overset{-}{N}}:$, are of about equal importance despite charge separation in the latter (*cf.* Pauling, ref. 7, pp. 198–199). The suggestion that the nitrogen has the higher electron density is consistent with the greater electronegativity of this element. It is striking that in every case one can predict from the electronegativity sequence O > N > C = S which atom of an anion with two different reactive positions will be the preferred point of bonding in alkylations having a large degree of carbonium character in the transition state.

(38) (a) This suggests that when the S_N2 character of the transition state is dominant the preferred alkylation product will be the thermodynamically stable isomer, a point which we plan to discuss subsequently. (b) Interactions between silver ion and the anion have been neglected throughout because it is felt that they are, in general, of secondary importance in comparison to the interactions between silver ions and the alkyl halides.

(39) It is desirable to have a simple name for anions which possess two different reactive positions. Among such ions are NO_2^-, CN^-, SCN^-, diazotate ions, enolate ions and the anions obtained from α-hydroxypyridine, nitroparaffins, acid amides, thio amides, etc. Since these anions undergo covalence formation at one or the other of two available positions the term ambident is proposed. The alkylation of ambident anions has been discussed in a completely different way by A. Brändström [*Arkiv För Kemi*, **6**, 155 (1953); *ibid.*, **7**, 81 (1954)].

(40) J. L. Simonsen and R. Storey, *J. Chem. Soc.*, **95**, 2106 (1909). The yield of *pure* O-alkylation product actually isolated was 37% (based on acetoacetic ester). This becomes about 74% when account is taken of the recovery of acetoacetic ester and also of the loss of ester by reaction with formaldehyde (derived from the chloromethyl ether).

(41) M. Conrad and C. Brückner, *Z. physik. Chem.*, **7**, 284 (1891).

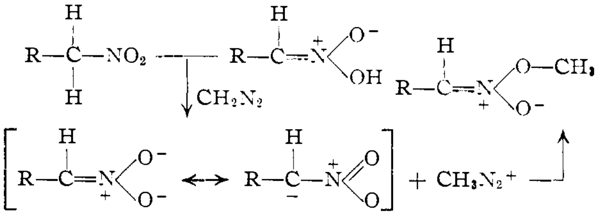
(42) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 332–333.

(43) Alkylations involving the anions of cyclic β-keto esters, cyclic β-cyano esters, etc., are subject to *endo–exo* double bond considerations [H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954)] and, also, to conformational effects. It is intended to discuss these more complicated cases at a later date.

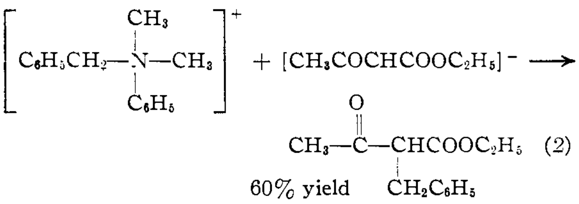
(44) Benzoylacetic ester, acetylacetone and benzoylacetonitrile also react with diazomethane giving only O-methylation: F. G. Arndt in "Organic Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, pp. 197–241. This chapter contains an excellent summary of the use of diazomethane in methylation.

important than bond making; indeed, it is conceivable that the acetoacetic ester anion actually is attacked by a free methylcarbonium ion. In any event, the reaction is one with a great deal of S_N1 character, the energy derived from bond formation is not needed to consummate the process and simple electrostatic forces decide the reaction course. Bonding, therefore, occurs at oxygen, since this has the highest electron density.

In precisely the same way nitroparaffins, and their *aci* forms, react with diazomethane to give nitronic esters, *i.e.*, oxygen alkylation. The *aci* forms being stronger acids react much more rapidly.



To obtain O-alkylation it is not sufficient that the ambident anion react with an alkylating agent of opposite sign. A more crucial requirement is that the bond of the alkyl group to the remainder of the alkylating agent should break easily. In contrast to the diazomethane reactions, this requirement is not fulfilled in the reaction of eq. 2. That this is so is apparent from the fact that the reaction requires refluxing of the ethanol solution for a matter of hours.[45] The presumption is clear



$$\left[C_6H_5CH_2-\overset{CH_3}{\underset{C_6H_5}{N}}-CH_3\right]^+ + [CH_3COCHCOOC_2H_5]^- \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_2C_6H_5}{CHCOOC_2H_5} \quad (2)$$

60% yield

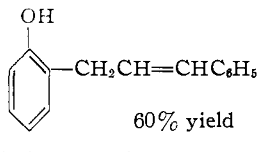
that this is an "S_N2" process; in order to obtain the requisite driving force, alkylation takes place at that atom of the anion which has the lower electronegativity.

3. The allylation of phenols can occur at oxygen or at carbon as the following examples show[46]

$$C_6H_5OH + CH_2{=}CHCH_2Br + K_2CO_3 \longrightarrow C_6H_5OCH_2CH{=}CH_2$$

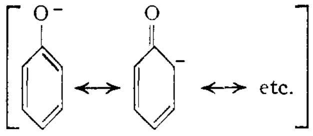
86% yield.

$$C_6H_5-O^-Na^+ + C_6H_5CH{=}CHCH_2Br \longrightarrow$$



60% yield

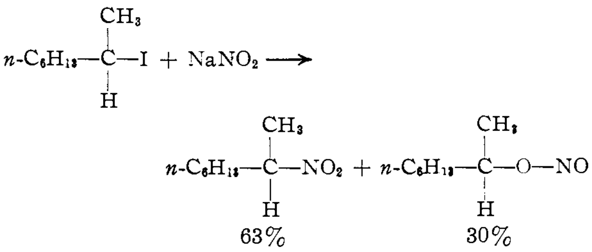
To form the ethers a weak base such as potassium carbonate is often employed. This leaves the phenol available to exert a strong electrophilic pull on the bromine of allyl bromide. Relatively polar solvents such as methanol, ethanol or acetone are taken and, frequently, water is present in appreciable amounts. These are conditions favoring the development of carbonium character in the transition state. Thus attack on the oxygen of the ambident anion I is observed.



I

C-Allylation, on the other hand, is facilitated by the use of benzene as the reaction medium, anhydrous conditions and complete conversion of the phenol to its salt prior to adding the allylic halide. These are, of course, devices for increasing the importance of the S_N2 contribution to the transition state and, as a result, a covalent linkage is formed to carbon, this being the less electronegative atom of the ambident anion I.

Nitrogen *vs.* Oxygen Alkylation.—The reaction of sodium nitrite with alkyl halides in dimethylformamide solution goes with clean second-order kinetics.[13] It is an "S_N2" process and as such one would anticipate a preference for bonding to nitrogen, this being less electronegative than oxygen.[30] The reaction of 2-iodoöctane is typical.



$$n\text{-}C_6H_{13}-\overset{CH_3}{\underset{H}{C}}-I + NaNO_2 \longrightarrow n\text{-}C_6H_{13}-\overset{CH_3}{\underset{H}{C}}-NO_2 + n\text{-}C_6H_{13}-\overset{CH_3}{\underset{H}{C}}-O-NO$$

63% 30%

The reaction of diazomethane with α-hydroxypyridine (α-pyridone) is reported to give exclusively the O-methyl ether.[47] This is completely analogous to the O-alkylation of acetoacetic ester and nitroparaffins by diazomethane (*vide supra*).

Manifestly these ideas are capable of very wide application. Both for reasons of space limitation and because experimental work is now in progress the extension of these ideas to other ambident systems will not be detailed here. It should be emphasized, however, that the same rules apply to anions in which alkylation can occur at more than two positions. Thus the anion II gives a 70% yield of the S-alkylated product.[48]

It is apparent that we have here a very useful principle which points the way to setting up conditions for controlling the course of the reactions of ambident anions. In its simplest form it can be stated: The greater the S_N1 character of the transition state the greater is the preference for covalency formation with the atom of higher electronegativity[30] and, conversely, the greater the S_N2 contribution to the transition state the greater the prefer-

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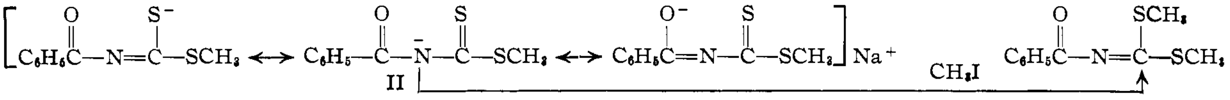
[45] H. R. Snyder, C. W. Smith and J. M. Stewart, THIS JOURNAL, **66**, 200 (1944).

[46] L. Claisen, *Ann.*, **442**, 210 (1925); D. S. Tarbell, "Organic Reactions," Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1944, pp. 26, 28; K. Schmid, W. Haegele and H. Schmid, *Helv. Chim. Acta*, **37**, 1087 (1954).

[47] H. von Pechmann, *Ber.*, **28**, 1625 (1895); H. Meyer, *Monatsh.*, **26**, 1311 (1906).

[48] H. L. Wheeler and H. F. Merriam, THIS JOURNAL, **23**, 292 (1901).



$$\left[C_6H_5\overset{O}{\overset{\|}{C}}-N=\overset{S^-}{\overset{|}{C}}-SCH_3 \longleftrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{-}{N}-\overset{S}{\overset{\|}{C}}-SCH_3 \longleftrightarrow C_6H_5\overset{O^-}{\overset{|}{C}}=N-\overset{S}{\overset{\|}{C}}-SCH_3\right]Na^+ \xrightarrow{CH_3I} C_6H_5\overset{O}{\overset{\|}{C}}-N=\overset{SCH_3}{\overset{|}{C}}-SCH_3$$

II

ence for bond formation to the atom of lower electronegativity.

The reactions of some ambident anions, of course, will be more susceptible to control than others. Which is to say, some anions will be more sensitive than others to changes in the proportions of SN1 and SN2 character of the transition state. One of our objectives is to arrive at a more detailed understanding of the variation in this sensitivity so that control of reactions involving ambident anions may be put on a somewhat more quantitative footing.

Acknowledgment.—We take much pleasure in acknowledging our indebtedness to Professors Herbert C. Brown and James H. Brewster for many stimulating discussions. Our best thanks are also due Professor Edward S. Lewis of The Rice Institute for an especially careful reading of this manuscript.

Experimental

The aliphatic halides employed were obtained as described earlier.[4] The benzyl bromides, except for *p*-methoxybenzyl bromide, were obtained from commercial sources. They were purified by rectification or recrystallization: benzyl bromide, n^{20}D 1.5762; *p*-methylbenzyl bromide, m.p. 35–35.5°; *p*-nitrobenzyl bromide, m.p. 98.5–99.5°. The silver nitrite was prepared as described previously.[4] Mallinckrodt anhydrous diethyl ether, analytical reagent was employed throughout. All experiments involving silver nitrite were conducted in total darkness. Illumination, when needed, was yellow light from a lamp covered with a Wratten Series OA Filter.

Benzyl nitrite was obtained by the method of Chretien and Longi; b.p. 67° (14 mm.), n^{20}D 1.5006; lit. b.p. 71° (18 mm.), $n^{24.7}$D 1.4989.[49]

Preparation of *p*-Methoxybenzyl Nitrite.—This was prepared from *p*-methoxybenzyl alcohol (m.p. 23–25°) by treatment with nitrosyl chloride in pyridine according to Kornblum and Oliveto[50]; b.p. 71.5° (1.5 mm.), n^{25}_{D} 1.5142.

Anal. Calcd. for $C_8H_9NO_3$: C, 57.48; H, 5.39; N, 8.38. Found: C, 57.75, 57.70; H, 5.64, 5.44; N, 8.55, 8.67.

Preparation of *p*-Nitrobenzyl Nitrite.—Several attempts were made to prepare this compound by the action of nitrosyl chloride on a solution of *p*-nitrobenzyl alcohol in pyridine; each time the alcohol was completely recovered. The following procedure was then used.

A mixture of 15.3 g. (0.1 mole) of *p*-nitrobenzyl alcohol (m.p. 92–93°) and 6 g. (0.25 mole) of sodium hydride in 100 ml. of dry benzene was placed in a 200-ml. three-necked flask fitted with a Hershberg stirrer, drying tube, and gas inlet tube. No gas was evolved. After cooling the flask in an ice-bath, nitrosyl chloride was bubbled through the mixture for two hours. The ice-bath was then removed and the reaction mixture allowed to come to room temperature. Although no heating up occurred there was a steady evolution of gas. When gas evolution had subsided (2 hr.) the inorganic material was separated by filtration, the benzene was removed at room temperature under reduced pressure and the residue was then distilled (*in vacuo*) through a small Claisen head. Four fractions were obtained, which on redistillation gave 6.15 g. of a yellow oil, b.p. 98° (2 mm.), n^{20}D 1.5498.

Anal. Calcd. for $C_7H_6N_2O_4$: N, 15.38. Found: N, 15.32.

This nitrite ester is very unstable. On exposure to the atmosphere overnight (in the dark at room temperature) complete decomposition occurs giving a very light yellow solid, m.p. 105–108°.

Reaction of Benzyl Bromide with Silver Nitrite.—A slurry of 100 g. of silver nitrite and 1 g. of calcium hydride in 250 ml. of anhydrous ether was cooled to 0° in a 500-ml. three-necked flask fitted with a dropping funnel, stirrer and drying tube and 85.5 g. (0.5 mole) of benzyl bromide (n^{20}D 1.5762) was added dropwise to the stirred mixture over a period of one hour. After stirring at 0° in the dark for a total of 25.5 hours, tests for unreacted halide using a saturated solution of silver nitrate in acetonitrile and the Beilstein test, were negative. The reaction mixture was filtered, the silver salts were washed with ether, and the washings were added to the original filtrate. About 1 gram of calcium hydride was added to the ether solution and the ether was distilled at atmospheric pressure through a 1 × 50 cm. glass helix packed column; the bath temperature was maintained between 48–50°. The last of the ether was removed under the vacuum of a water-pump and the residual liquid was distilled through a 6-in. Vigreux column. Nineteen grams (28% yield) of benzyl nitrite was obtained, b.p. 56–56.5° (8 mm.), n^{20}D 1.5006–1.5008; lit. b.p. 71° (18 mm.), $n^{24.7}$D 1.4989.[49] After a 3-g. interfraction there was obtained 41.4 g. (61% yield) of phenylnitromethane, b.p. 77–79° (1 mm.), n^{20}D 1.5315; lit. b.p. 141–142° (35 mm.), n^{20}D 1.5323.[51] The phenylnitromethane was completely soluble in 20% aqueous sodium hydroxide. After extracting the basic solution several times with benzene, the phenylnitromethane was regenerated with 40% aqueous hydroxylamine hydrochloride.[52] Distillation yielded a product with n^{20}D 1.5315.

Anal. Calcd. for $C_7H_7NO_2$: C, 61.31; H, 5.11; N, 10.22. Found: C, 61.20, 61.22; H, 5.13, 5.08; N, 10.17, 10.11.

Reaction of *p*-Methylbenzyl Bromide with Silver Nitrite.—A mixture of 60 g. (0.390 mole) of silver nitrite in 250 ml. of ethyl ether was cooled in an ice-bath and, while stirring, 55.5 g. (0.3 mole) of *p*-methylbenzyl bromide (m.p. 35–35.5°) dissolved in 250 ml. of ether was added over a period of an hour. The reaction was vigorously stirred at 0° for 12 hr. at which time a negative Beilstein test was obtained.

The silver salts were filtered, washed with more ether and the washings added to the filtrate. The ether was removed at room temperature under the vacuum of a water-pump and the yellow residue was distilled *in vacuo* through a 1 × 50 cm. glass helix packed column. The yield of *p*-methylbenzyl nitrite was 16.5 g. or 37%, b.p. 61° (6 mm.), n^{20}D 1.4994.

Anal. Calcd. for C_8H_9ONO: C, 63.57; H, 5.96. Found: C, 63.63, 63.58; H, 6.16, 6.20.

The *p*-tolylnitromethane isolated by continuation of the distillation was 20.1 g. or 45%, b.p. 99° (3 mm.), n^{20}D 1.5278; lit. b.p. 150–151° (35 mm.), n^{20}D 1.53106.[51] This was a light yellow liquid and all efforts to decolorize it, including passage through alumina, regeneration of the sodium salt, and redistillation failed to change the color; the refractive index remained constant through these operations.

Anal. Calcd. for $C_8H_9NO_2$: C, 63.57; H, 5.96; N, 9.27. Found: C, 63.59, 63.72; H, 6.05, 6.00; N, 9.39, 9.17.

Reaction of *p*-Nitrobenzyl Bromide with Silver Nitrite.—A mixture of 50 g. (0.325 mole) of silver nitrite and 500 ml. of ether was treated with a solution of 21.6 g. (0.1 mole) of *p*-nitrobenzyl bromide in 800 ml. of ether as described for benzyl bromide, except that the addition time was extended to 1 hr. and the reaction time to 24 hr. at 0°. When the ether solution of reaction products was concentrated, the nitro compound separated as a white crystalline solid. This was collected by filtration, washed with ether and dried in a vacuum desiccator; yield 13.6 g. (75%) of *p*-nitrophenylnitromethane, m.p. 89–90.5°; lit. m.p. 90–91°.[52]

Anal. Calcd. for $C_7H_6N_2O_4$: C, 46.15; H, 3.29; N, 15.38. Found: C, 46.04, 46.21; H, 3.41, 3.35; N, 15.38, 15.20.

The filtrate and ether washings were combined, dried over

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(49) A. Chretien and V. Longi, *Compt. rend.*, **220**, 746 (1945).

(50) N. Kornblum and E. P. Oliveto, THIS JOURNAL, **69**, 465 (1947).

(51) M. Konovalow, *Chem. Centr.*, **70**, I, 1238 (1899).

(52) A. Hantzsch and A. Veit, *Ber.*, **32**, 621 (1899).

Drierite, filtered and the ether was removed by distillation. After evacuating with an oil-pump to ensure complete removal of ether, the residue weighed 4.1 g. In a refrigerator this material solidified; on warming to room temperature it partially melted to a yellow oil. The oil (2.65 g.) was removed from the solid and distilled. Distillation was stopped when solid appeared in the condenser. The distillate, *p*-nitrobenzyl nitrite, weighed 1.10 g. (5% yield), $n^{20}\text{D}$ 1.5499 (*vide supra*). It decomposed on standing overnight to a light yellow powder, m.p. 104–108°.

Preparation of *p*-Methoxybenzyl Bromide.—A solution of 138 g. of *p*-methoxybenzyl alcohol (m.p. 23–25°) in twice its volume of dry benzene was cooled in an ice-bath and anhydrous hydrogen bromide was bubbled through until the solution was saturated (*ca.* 30 min.). The water layer which had formed was separated and the brown benzene solution was washed with saturated sodium carbonate and sodium bromide solutions. After drying over anhydrous magnesium sulfate and then calcium hydride, the benzene was completely removed under reduced pressure in 15-g. portions to avoid decomposition. An 82% yield (164 g.) of clear, colorless *p*-methoxybenzyl bromide, $n^{20}\text{D}$ 1.5818, was obtained. Molecular distillation, at 0.05 mm., of a small sample gave a colorless liquid having constant refractive index, $n^{20}\text{D}$ 1.5820.

Anal. Calcd. for C_8H_9BrO: Br, 38.09. Found: Br, 37.77, 37.83.

Reaction of *p*-Methoxybenzyl Bromide with Silver Nitrite.—Orienting experiments showed that when this halide is treated with silver nitrite in the usual way it fails to react completely. Much heat is evolved, the surface of the silver nitrite becomes white and reaction ceases. This phenomenon, which will require investigation to be understood, appears to involve surface decomposition of the silver nitrite or surface sintering because of the local overheating.

The reaction was finally made to proceed smoothly by operating with a more dilute solution of the halide and at −10° instead of 0°. A mixture of 20 g. of silver nitrite in 1.5 l. of anhydrous ether was prepared in a 2-l. flask fitted with a Hershberg stirrer and a drying tube. The flask was cooled to −10° in a salt–ice-bath. While stirring vigorously, 42 g. of *p*-methoxybenzyl bromide ($n^{20}\text{D}$ 1.5820) in 250 ml. of ether were added 5 ml. at a time. After each addition stirring was stopped, the salts were allowed to settle and a Beilstein test was made on the supernatant liquid. This test was negative every time, even after the final addition.

The silver salts were filtered off, washed with ether and the washings were added to the solution of products. The ether was removed from the light yellow solution by flash distillation under reduced pressure and the residue was distilled *in vacuo* from a few grams of calcium hydride through a small Claisen head. A yield of 19.4 g. (55%) of *p*-methoxybenzyl nitrite was obtained, b.p. 63–65° (0.5 mm.), $n^{20}\text{D}$ 1.5142. Continuation of the distillation gave 9.0 g. of orange liquid, b.p. 106–108° (0.6 mm.), $n^{20}\text{D}$ 1.5400. This corresponds to a 26% yield of *p*-methoxyphenylnitromethane. That it is indeed the nitro compound is shown by its complete solubility in cold 10% aqueous sodium hydroxide. After extraction of this alkaline solution with benzene, *p*-methoxyphenylnitromethane was recovered by acidification with hydroxylamine hydrochloride.[53] This yellow oil had $n^{20}\text{D}$ 1.5400, b.p. 102–103° (0.5 mm.), yield 5.8 g. (65% recovery).

Anal. Calcd. for $C_8H_9NO_3$: C, 57.48; H, 5.38; N, 8.38. Found: C, 57.44, 57.48; H, 5.48, 5.49; N, 8.42, 8.30.

Titrimetric Determination of the Yield of Nitro Compound from the Reaction of Benzyl Bromides.—A mixture of 5.0 g. (0.032 mole) of silver nitrite and 100 ml. of ether was prepared in a 300-ml. three-necked flask fitted with a Hershberg stirrer, dropping funnel and drying tube. The flask was cooled in an ice-bath and, while stirring, a solution of 0.01 mole of a benzyl bromide in 100 ml. of ether was run in over a 10-min. period. After a Beilstein test showed that the reaction was complete, the reaction mixture was filtered, the silver salts were washed several times with ether and the washings were added to the solution of products. The solution was then made up to 250 ml. with ether, 5-ml. samples were withdrawn, added to 50 ml. of 95% ethanol, and the nitro compound determined by titration with standard aq. sodium hydroxide. The results are summarized in Table III.

Rates of Reaction of Benzyl Bromides in Ether with Silver Nitrite at 0°.[54]—Exactly the same amounts of reactants and identical conditions were used as are described for the titrimetric determination of yields, except that the benzyl bromides were added in 1.5 min. After the addition was complete, aliquots were withdrawn periodically and added to 50 ml. of 95% ethanol. Except in the case of *p*-nitrobenzyl bromide, the nitro compound was determined by titration with standard aqueous sodium hydroxide to a phenolphthalein end-point. Since *p*-nitrophenylnitromethane produces a red color in sodium hydroxide solution, this compound was determined by potentiometric titration. Sampling was continued until the titer was constant. By plotting time *vs.* ml. of sodium hydroxide required to titrate the nitro compound, half-lives for the reactions of *p*-nitrobenzyl, benzyl and *p*-methylbenzyl were obtained (Table II). The results of a typical run are shown in Table IV.

TABLE IV

REACTION OF BENZYL BROMIDE WITH SILVER NITRITE

Min.	Titer,[a] ml.	Extent of reacn.
2	0.04	3.5%
5	.075	6.5
15	.505	43.9
25	.88	76.5
40	1.09	94.7
90	1.12	97.3
150	1.15	100[b]

[a] Ml. of 0.1033 *N* sodium hydroxide solution required to titrate the phenylnitromethane in a 5-ml. aliquot of the ether solution from the reaction mixture. [b] This is a 70% yield of phenylnitromethane.

Under these conditions, *p*-methoxybenzyl bromide reacts on contact with the silver nitrite. This is shown by the fact that a negative Beilstein test is obtained as soon as all of the halide has been added. Indeed, on stopping the stirrer, removing a sample of the supernatant liquid, adding it to water and titrating the resultant solution with standard silver nitrate no bromide is found. This demonstrates that *p*-methoxybenzyl bromide does not persist in the ether solution for any significant time.

Rate of Reaction of 1-Iodobutane in Ether with Silver Nitrite at 0°.—A 300-ml. three-neck flask was fitted with a True-bore stirrer having a Teflon blade, an addition funnel and drying tube packed with anhydrous calcium chloride. A solution of 6.44 g. (0.035 mole) of *n*-butyl iodide and 175 ml. of ether was prepared in the reaction flask and maintained at 0° in an ice-water-bath. A 1-ml. sample was withdrawn and the concentration of alkyl halide was determined by adapting the procedure of Schwenk, Papa and Ginsberg[55] as follows: After digestion for 30 min. with 0.35 g. of Raney nickel alloy and 10 ml. of 10% sodium hydroxide the alkaline solution was decanted and the nickel residue was washed three times with warm water. The combined alkaline solution and washings was acidified with 10% nitric acid and potentiometrically titrated with standard silver nitrate.

Having found the initial concentration of *n*-butyl iodide, 54 g. (0.35 mole) of silver nitrite was added rapidly to the ether solution and stirring was started. Periodically, 1-ml. samples were removed and treated in the above manner to determine the amount of unreacted alkyl halide. The re-

TABLE V

REACTION OF 1-IODOBUTANE IN ETHER WITH SILVER NITRITE

Min.	Mmole RI/ml. ether soln.
0	0.195
50	.142
85	.104
140	.035

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[53] N. Kornblum and G. E. Graham, THIS JOURNAL, **73**, 4041 (1951).

[54] We deeply appreciate the assistance of Mr. W. M. Weaver in some of these experiments.

[55] E. Schwenk, D. Papa and H. Ginsberg, *Anal. Chem.*, **15**, 576 (1943).

sults of a typical run are shown in Table V. It is estimated graphically from these data that the half-life for the reaction is 95 min.

Rates of Reaction of 2-Iodobutane, 1-Iodoöctane and 2-Iodoöctane in Ether with Silver Nitrite at 0°.[56]—Half-lives were obtained in precisely the same way as with 1-iodobutane (including identical concentrations), but here the organic iodide was converted to inorganic iodide by refluxing with saturated sodium methoxide in methanol for 1 to 1.5 hr. Results for a typical run are shown in Table VI. The half-lives as determined graphically were: 2-iodobutane, 11 min.; 1-iodoöctane, 109 min.; 2-iodoöctane, 11 min.

TABLE VI

REACTION OF 2-IODOÖCTANE IN ETHER WITH SILVER NITRITE

Min.	Mmoles RI/ml. ether soln.
0	2.00
3	1.76
6	1.58
9	1.18
12	0.74

Rates of Reaction of 1-Bromobutane, 2-Bromobutane and *t*-Butyl Bromide in Ether with Silver Nitrite at 0°.—The rates were followed exactly as described for 2-iodobutane, etc., except that a higher concentration of alkyl bromide (0.05 mole in 200 ml.) and less silver nitrite (0.13 mole) were used. Furthermore, the time of reflux with sodium methoxide was increased to 2–2.5 hr. Half-lives obtained for 1-butyl, 2-butyl and *t*-butyl bromides were 346, 96 and 0.25 hr., respectively.

The Rate of Reaction of Neopentyl Iodide in Ether with Silver Nitrite. (a) At 0°.—A solution of 6.93 g. (0.035 mole) of neopentyl iodide in 175 ml. of ether was stirred with 54 g. (0.35 mole) of silver nitrite. After 691 hours the silver salts were separated by filtration and washed thoroughly with ether. The unreacted silver nitrite was washed out with aqueous ammonia, the residue was washed with dilute nitric acid and then dried. There was obtained 0.79 g. of silver iodide; thus the reaction proceeded 10% toward completion. **(b) At 27°.**—A set of sealed tubes, each charged with 3.1 g. (0.02 mole) of silver nitrite and 10 ml. of an ether solution containing 0.396 g. (0.002 mole) of neopentyl iodide, was subjected to mechanical tumbling. Periodically, a tube was opened and the silver iodide isolated by centrifugation, following which it was washed successively with ether, water, 10% aq. ammonia, 10% aq. nitric acid and, finally, with water. Table VII records the results.

TABLE VII

REACTION OF NEOPENTYL IODIDE IN ETHER WITH SILVER NITRITE

Hours	Wt. AgI, g.	Reaction, %
11	0.0170	3.6
35	.0364	7.8
60	.0526	11.2
110	.0969	20.6
162	.1298	27.7
256	.2253	48.0

Rate of Reaction of 1-Iodobutane with Silver Nitrite in Acetonitrile at 0°.—A 25-ml. volumetric flask containing 0.73 g. (0.004 mole) of *n*-butyl iodide was cooled to 0°. A solution of silver nitrite in acetonitrile containing 0.1 g. of silver nitrite per ml. was cooled to 0° and quickly added to the *n*-butyl iodide to make a total volume of exactly 25 ml. The solution was maintained at 0° and, at intervals, 1-ml. portions were withdrawn using a pipet fitted with a cotton filter tip. The cotton filter was removed at once and the clear solution quickly transferred to a weighed 15-ml. centrifuge tube. The silver iodide which formed on standing overnight was washed twice with 1-ml. portions of acetonitrile and dried (Table VIII).

TABLE VIII

REACTION OF 1-IODOBUTANE WITH SILVER NITRITE IN ACETONITRILE AT 0°

Min.	Mg. of AgI	Reaction, %
0	(37.6)	0
2	34.4	8.5
4	29.6	21.3
6	23.3	38.0
8	21.2	43.6
10	18.5	50.8
12	14.5	61.5

Rate of Reaction of Neopentyl Iodide with Silver Nitrite in Acetonitrile at 0°.—A solution consisting of 2.5 g. (0.016 mole) of silver nitrite, 25 ml. of acetonitrile and 0.79 g. (0.004 mole) of neopentyl iodide was maintained at 0°. After 160 hours the acetonitrile solution was completely decanted from the precipitate, transferred to a new tared flask and continued at 0°. The precipitate was washed twice with acetonitrile and dried. The silver iodide was isolated after 732 and 1600 hours (Table IX).

TABLE IX

REACTION OF NEOPENTYL IODIDE WITH SILVER NITRITE IN ACETONITRILE AT 0°

Hours	Total wt. AgI, g.	Reaction, %
160	0.0545	5.8
732	.3115	32.2
1600	.4715	50.2

A second reaction prepared and conducted at 0° as above, but undisturbed for 1610 hours, produced 0.4787 g. of silver iodide (50.9% complete).

Rate of Reaction of 1-Iodobutane with Silver Nitrite in Acetonitrile at Room Temperature.—A reaction mixture was prepared at room temperature (25–28°) by rapidly delivering 5 ml. of a silver nitrite–acetonitrile solution which contained 0.10 g. of silver nitrite per ml. (0.0032 mole total), into a 25-ml. flask containing 0.15 g. (0.0008 mole) of *n*-butyl iodide. After 4 min., and continuing at 30-sec. intervals, approximately 0.5-ml. portions of the reacting solution were withdrawn and retained in pipets fitted with a cotton filter tip. Later the content of each pipet was examined for the presence of silver iodide in order to determine whether reaction continued after the sample was withdrawn. It was observed that the amount of silver iodide decreased rapidly as the sampling time increased and the samples collected after 6 minutes remained clear. Thus, the reaction was complete at this time.

Rate of Reaction of Neopentyl Iodide with Silver Nitrite in Acetonitrile at Room Temperature.—A solution of 2.5 g. (0.016 mole) of silver nitrite in acetonitrile was added to 0.79 g. (0.004 mole) of neopentyl iodide in a 25-ml. volumetric flask. After adjusting the volume to 25 ml., 5-ml. aliquots were transferred to weighed centrifuge tubes and allowed to remain at room temperature (25–28°). Periodically one of the tubes was centrifuged and the supernatant solution was separated using a small pipet. The silver iodide was washed twice with 1-ml. portions of fresh acetonitrile and dried at 140°. The results are shown in Table X.

TABLE X

RATE OF REACTION OF NEOPENTYL IODIDE WITH SILVER NITRITE IN ACETONITRILE AT ROOM TEMPERATURE

Hours	Mg. AgI	Reaction, %
21	28.3	14.5
52.5	69.6	37.0
74	85.7	45.5
92	95.9	51.0
117	107.9	57.3

Attempted Reaction of Alkyl Sulfonates with Silver Nitrite.—The procedure employed for the preparation of nitroalkanes from primary alkyl halides[48] was modified by substitution of an alkyl sulfonate for the alkyl halide. Thus, a mixture of 70 g. (0.45 mole) of silver nitrite, 45.6 g. (0.3 mole) of *n*-butyl methanesulfonate and 100 ml. of ether was stirred 20 hours at 0° and then 96 hours at room tem-

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[56] We are indebted to Dr. Alan M. White for these experiments.

perature. On working up in the usual way 44.7 g. (98%) of *n*-butyl methanesulfonate was recovered.

Repetition of this experiment using ethyl benzenesulfonate and stirring with silver nitrite for 20 hours at 0° and 72 hours at room temperature resulted in 95% recovery of the ester. Again, with ethyl *p*-toluenesulfonate in ether solution, after stirring with silver nitrite for 10 hours at 0° and 112 hours at room temperature, a 94% recovery of the ester was obtained.[57]

It should be noted that the above reaction times are much in excess of the time needed for complete reaction of primary alkyl halides.

The Solubility of Silver Nitrite in Ether.[12]—A preliminary experiment established that 50 g. of silver nitrite, shaken with 500 ml. of ether for 2 days, loses very little weight. The solvent contained no detectable solid material but gave an oil as main residue. Under identical conditions silver nitrite from another batch lost 0.14 g. The solvent left 0.13 g. of residue which was separated with ether into 0.04 g. of oil and 0.09 g. of colorless solid. The solid (0.0930 g.) was dissolved in water and made up to 50 ml. A portion of this solution failed to give any precipitate with 1:5 hydrochloric acid.

LAFAYETTE, INDIANA

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(57) Our thanks are due Miss Mary E. Chalmers for this experiment.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

Aromatic Substitution. II. The Acid Cleavage of Diphenylmercury[1]

BY FREDERICK KAUFMAN[2] AND ALSOPH H. CORWIN

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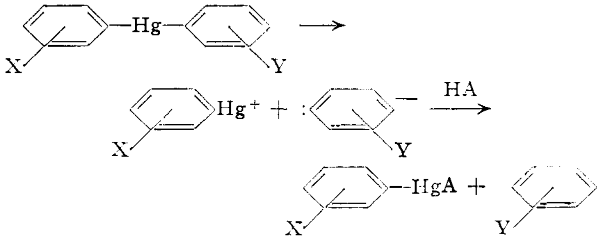
Independent and sensitive methods to determine rate constants of acid cleavage of diphenylmercury are described. The reaction with large excess of acetic and formic acid was found to be first order in diphenylmercury, the rate constant independent of initial mercurial concentration, and varying as the 3.37th power of acetic acid concentration. The reaction with dilute perchloric acid was found to be strictly second order in accordance with the proposed mechanism of acid attack on the ring carbon atom adjacent to the mercury. Protonated ethanol or dioxane give higher rates than hydronium ion. There is no salt effect for added perchlorate, but a definite rise in *k* for added chloride. Explanations for this behavior are discussed. The temperature dependence in three solvents shows large increases of the frequency factor overbalance the retarding effect of increased activation energy.

Introduction

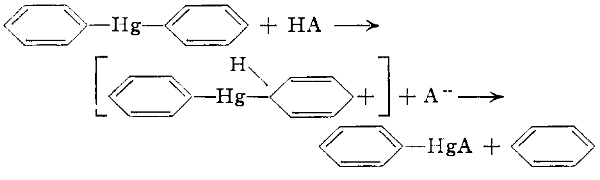
The acid cleavage of aromatic mercurials was recognized by Kharasch[3] as a valuable tool in the general problem of aromatic substitution. Unsymmetrically substituted diaryl mercury compounds were prepared, reacted with acid, and the resulting hydrocarbon and arylmercuric salt isolated. In most cases, only one of the two possible sets of products was formed, independent of the choice of acid or solvent, and this was attributed to the different electronegativities of the groups bonded to the mercury atom.

It was later shown by Corwin and Naylor[4] that Kharasch's proposed ionization mechanism



failed to account for the experimental results. The cleavage rate of diphenylmercury was found to be strongly dependent on the strength of the acid used, it was not strongly affected by increasing the dielectric constant of the solvent, and, above all, it led to an electronegativity series which was in inverted order to all findings of the English school, Hammett, and other investigators.

Corwin and Naylor studied the kinetics of the reaction of diphenylmercury with large excess of acetic and formic acid in dioxane using a tapless dilatometer. They concluded that a mechanism of acid attack leading to a protonated intermediate was in agreement with experiment. This can be formulated as



and explains the rate dependence on acid strength as well as the products obtained by Kharasch in the cleavage of unsymmetrical mercurials in terms of an electrophilic attack by acid on the ring carbon atom.

A free radical mechanism was ruled out by the absence of products such as diphenyl or phenol, and by the independence of the observed rate of peroxide concentration.

Before the general problem of aromatic substitution could be studied, as was the aim of the earlier paper, it was necessary to examine in greater detail the cleavage of diphenylmercury using more accurate methods. The alleged puzzling dependence of the rate constants on initial mercurial concentration had to be clarified, and the temperature dependence, the reaction with strong acids in dilute solution, solvent- and salt effects required further study.

Experimental

Apparatus.—Reactions were carried out in small round-bottom flasks immersed in a 15-gallon constant tempera-

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(1) From the doctoral dissertation of Frederick Kaufman at the Johns Hopkins University. Presented at the Symposium on Aromatic Substitution of the San Francisco Meeting of the American Chemical Society, March, 1949.

(2) Ballistic Research Laboratories, Aberdeen Proving Ground, Md.

(3) (a) M. S. Kharasch, H. Pines and J. H. Levine, *J. Org. Chem.*, **3**, 347 (1938); (b) M. S. Kharasch and S. Swartz, *ibid.*, **3**, 405 (1938); (c) M. S. Kharasch, R. R. Legault and W. R. Sprowl, *ibid.*, **3**, 409 (1938).

(4) A. H. Corwin and M. A. Naylor, Jr., THIS JOURNAL, **69**, 1004 (1947).