Stereochemistry and Mechanism in Reactions of Silver Salts with Alkyl Halides. The Reaction of Silver Nitrate with Alkyl Halides[1,2]

Nathan Kornblum and Donald E. Hardies

Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana 47907. *Received January 5, 1966*

Abstract: Optically active 2-bromooctane when treated with silver nitrate gives 2-octyl nitrate of the inverted configuration, regardless of the solvent. With α-phenylethyl chloride, however, the steric course of the reaction is solvent dependent; in ethyl ether, and in benzene, α-phenylethyl nitrate is produced with retention of configuration but in acetonitrile, or in petroleum ether, the nitrate ester is produced with inversion. The mechanism of silver salt reactions is discussed; it is shown that these seemingly whimsical results, and those of the preceding paper,[5] can be rationalized in a simple way by regarding the reactions of silver salts with alkyl halides as concerted SN1–SN2 processes in which the relative importance of the electrophilic pull of the silver and the nucleophilic push of the anion in the transition state varies as a function of the alkyl halide, the silver salt, and the solvent. At the extreme of this graded SN1–SN2 scale there are instances in which the reaction proceeds *via* a transition state which has so little SN2 character that it is usefully regarded as a carbonium ion process. A noteworthy by-product of these studies is the conclusion that the reaction of silver nitrate with α-phenylethyl chloride in benzene proceeds *via* an α-phenylethyl carbonium ion–benzene π complex which cleanly goes on to form α-phenylethyl nitrate rather than α-phenylethylbenzene.

Athough the reaction of silver nitrate with alkyl halides (eq 1) has been known for many years its

$$RX + AgNO_3 \longrightarrow RONO_2 + AgX \tag{1}$$

stereochemistry has not been established.[3] The present paper deals with the stereochemistry of this reaction and, then, the matter of the mechanism of silver salt reactions with alkyl halides is discussed.

Treatment of dextrorotatory 2-bromooctane with silver nitrate yields levorotatory 2-octyl nitrate, regardless of the solvent (Table I). Since in the 2-octyl series the bromide and nitrate have the same sign of rotation when they are of the same configuration,[4] it follows that the reaction routinely occurs with inversion, a result which duplicates that obtained with silver nitrite.[5]

Table I. The Reactions of Silver Nitrate with Optically Active 2-Bromooctane in Various Solvents[a]

Solvent	2-Bromo-octane, αD, deg	2-Octyl nitrate, αD, deg
Ethyl ether	+36.3	−13.5
Petroleum ether (bp 35–37°)	+10.4	−2.71
Acetonitrile	+36.3	−14.3

[a] All rotations are observed rotations of the pure liquid in a 1-dm tube at temperatures in the range 25–28°.

When, however, α-phenylethyl chloride is employed the steric course of the reaction with silver nitrate depends on the solvent (Table II). Since α-phenylethyl chloride and α-phenylethyl nitrate which have the same sign of rotation are of the same configuration,[4] it follows from the data of Table II that in ethyl ether, and in benzene, the reaction occurs with retention of configuration while in petroleum ether, and in acetonitrile, it goes with inversion. This is precisely the pattern which the reaction of silver nitrite with α-phenylethyl chloride exhibits.[5]

Table II. The Reactions of Silver Nitrate with Optically Active α-Phenylethyl Chloride in Various Solvents[a]

Solvent	α-Phenylethyl chloride, αD, deg	α-Phenylethyl nitrate, αD, deg
Ethyl ether	+37.04	+3.78
Acetonitrile	+37.04	−6.05
Benzene	−35.64	−1.80
Petroleum ether	−10.62	+1.63

[a] All rotations are observed rotations of the pure liquid in a 1-dm tube at temperatures in the range 25–27°.

It is apparent, especially from the data of Table II, that the reaction of silver nitrate with an alkyl halide does not occur with the same degree of stereospecificity in the various solvents; this is also true of reactions employing silver nitrite.[5] Indeed, not only does the extent of racemization vary from solvent to solvent but it may even vary from experiment to experiment in a given solvent (see, *e.g.*, Table II of ref 5). That this is so

---

(1) This research was supported by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under AFOSR Grant No. 122-65.

(2) Presented, in part, at the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1956, Abstracts, p 2-O, and, in part, at the 145th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, Abstracts, p 20M; from the Ph.D. dissertation of Donald E. Hardies, Purdue University, June 1957.

(3) E. D. Hughes, C. K. Ingold, and S. Masterman, *J. Chem. Soc.*, 1236 (1957), have reported that silver nitrate and levorotatory 2-bromooctane react in aqueous ethanol to give small amounts of dextrorotatory 2-octyl nitrate. But reference to the experimental portion of their paper raises questions and, in any event, the configuration of the nitrate was not known. On the other hand, the claim by W. A. Cowdrey, E. D. Hughes, and C. K. Ingold, *ibid.*, 1243 (1937), to have converted dextrorotatory methyl α-bromopropionate to levorotatory methyl α-nitratopropionate is solidly grounded for the nitrate ester was isolated and characterized. However, its configurational relationship to the methyl α-bromopropionate was not established.

(4) (a) S. J. Cristol, B. Franzus, and A. Shadan, *J. Am. Chem. Soc.*, 77, 2512 (1955); (b) N. Kornblum, L. Fishbein and R. A. Smiley, *ibid.*, 77, 6261 (1955); (c) N. Kornblum, W. J. Jones, and D. E. Hardies, *J. Org. Chem.*, 30, 1654 (1965).

(5) N. Kornblum, W. J. Jones, and D. E. Hardies, *J. Am. Chem. Soc.*, **88**, 1704 (1966).

is really not surprising for it is known that silver halides racemize optically active alkyl halides;[4b,6] α-phenylethyl chloride is particularly vulnerable to the racemizing action of silver chloride.[4b] Since the nature of the silver halide surface will vary with reaction conditions this provides a significant variable.[6b] Another variable which may be expected to influence the rate of racemization is the solvent.[7] Fortunately, the partial racemization which accompanies silver salt reactions does not impair the utility of our experiments; for, while no significance ought to be attached to the numerical value of the rotation, the rotations recorded in these two papers are *observed* rotations which, in all cases, are substantial. The *sign* of rotation is, thus, a reliable datum.

Silver nitrate dissolves readily in acetonitrile. It is, however, extremely insoluble in ethyl ether, petroleum ether, cyclohexane, and benzene. Nonetheless, it might be argued that more silver nitrate is able to dissolve once the very small amount in solution has been removed by reaction with an alkyl halide and, thereby, maintain something close to the equilibrium concentration in solution. Thus, despite the very low solubility of silver nitrate, the reaction could conceivably occur in solution rather than on the surface of the silver salt. But in this event it should be possible to dissolve appreciable amounts of silver nitrate by subjecting the salt to continuous extraction with fresh solvent in a Soxhlet apparatus. When such "dynamic" solubility tests are carried out for 5 days (a much longer period of time than the reactions of silver nitrate require) benzene leaches out only 24 mg of the salt while ethyl ether and cyclohexane do not dissolve any detectable amount.[8] Silver nitrite, subjected to this "dynamic" solubility test, also fails to dissolve to a detectable extent in ethyl ether, and in cyclohexane, while benzene dissolves but 16 mg.[5] Since the reactions of silver nitrate (and silver nitrite) consume from 17 to 63 g of these silver salts, usually in less than 1 day, it is very probable that in ethyl ether, cyclohexane, petroleum ether, and benzene the reactions occur on the surface of the silver salt.[9]

The Mechanism of Silver Salt Reactions

The steric course of the reactions of 2-octyl halides with silver nitrite, and with silver nitrate, is easily summarized: the nitrite ester, nitroparaffin, and nitrate ester are always produced with inversion regardless of the solvent. However, such a simple generalization is not possible with α-phenylethyl chloride; the steric results obtained in that system are tabulated in Table III.

Table III. Steric Course of the Reaction of α-Phenylethyl Chloride with Silver Nitrite and with Silver Nitrate

Solvent	α-Phenylethyl nitrite	α-Phenylnitroethane	α-Phenylethyl nitrate
Ethyl ether	Retention	Retention	Retention
Acetonitrile	Inversion	Inversion	Inversion
Benzene	Retention	Retention	Retention
Petroleum ether	Inversion	Inversion	Inversion
Cyclohexane	Inversion	Inversion	. . .

It is immediately apparent that the oft-repeated assertion that silver salt reactions are carbonium ion processes cannot explain these results,[10] nor, for that matter, can any other single type of mechanistic process. One can, however, explain them quite simply by the view that the reactions of silver salts with alkyl halides are ordinarily concerted processes in which the "pull" of the silver and the "push" of the anion play a role, the relative importance of the SN1 and SN2 contributions to the transition state varying with the structure of the halide.[11] As was pointed out earlier,[11] there will be cases, *e.g.*, with α-phenlyethyl chloride and *t*-butyl chloride, in which the graded SN1–SN2 mechanism gives way to the SN1 mechanism, the SN2 character of the transition state becoming so unimportant that the reaction is best considered as proceeding *via* a carbonium ion, *i.e.*, the "pull" completely outweighs the "push." And, as Vona and Steigman[12] have so clearly demonstrated, there are cases where reactions involving a silver salt proceed by a transition state in which the "push" is more important than the "pull."

It is useful to consider first the reactions conducted in ethyl ether, petroleum ether, cyclohexane, and benzene—all of which we regard as taking place on the surface of the silver salt. The alkyl halide, *e.g.*, 2-bromooctane, becomes adsorbed on the crystal surface as a result of the attractive forces which exist between silver ions and the bromine of the 2-bromooctane.[13] Despite the pull of the silver, a 2-octyl carbonium ion does not form readily and it is necessary for a nitrite (or nitrate) ion situated on the crystal surface rearward to the carbon–bromine bond to furnish the needed nucleophilic push. If, as must happen frequently, a nitrite (or nitrate) ion is not located at a suitable distance rearward to the carbon–bromine bond then the 2-bromooctane moves to another point on the surface (presumably by desorption–adsorption) until, eventually, it finds a site where a nitrite (or nitrate) ion is suitably positioned for providing the push needed to consumate the reaction. Such a concerted pull–push process would give rise to the observed stereochemical result—inversion of configuration.[14]

---

(6) (a) W. E. Doering and M. Farber, *J. Am. Chem. Soc.*, 71, 1514 (1949); (b) C. L. Arcus and G. V. Boyd, *J. Chem. Soc.*, 1582 (1951).

(7) With α-phenylethyl bromide it has been shown by Arcus and Boyd[6b] that heterogeneous catalysis of racemization is not confined to silver bromide.

(8) These determinations were carried out by Dr. Paul J. Berrigan to whom we wish to express our thanks.

(9) This is a view consistent with the fact that silver nitrite does not react with ethyl ether solutions of sulfonate esters: N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, 77, 6271 (1955).

(10) The assignment of a carbonium ion mechanism rests in large part on the claim that silver salt reactions involving 2-octyl and α-phenylethyl halides occur with inversion (accompanied by greater or lesser amounts of racemization): C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 358, 387–389.

(11) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, 77, 6269 (1955). By a graded SN1–SN2 mechanism we refer to a "three-body reaction" involving simultaneous electrophilic interaction between a silver ion and the halogen of RX and nucleophilic interaction between the entering anion and the carbon atom undergoing substitution. It should, perhaps, also be made explicit that this mechanistic description is predicated on a preequilibrium association, $RX + Ag^+ \rightleftarrows RX\cdots Ag^+$, in view of the generally recognized improbability of a termolecular reaction. For reactions occurring on the surface of the silver salt (*vide infra*) this preequilibrium association is, of course, the process of adsorption–desorption. In this connection, see D. W. Colcleugh and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 2542 (1964).

(12) J. A. Vona and J. Steigman, *J. Am. Chem. Soc.*, **81**, 1095 (1959).

(13) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 138. See also footnote 9 of this paper.

(14) Were it not for concomitant racemization of some of the 2-octyl

With α-phenylethyl chloride we deal with a halide which relatively readily could give a carbonium ion. However, if the silver salt reaction is conducted in a solvent incapable of providing significant solvation for the carbonium ion, *e.g.*, a paraffin hydrocarbon, then the system will fall back on the reaction pattern of the 2-octyl series: adsorption and desorption will be repeated until a site is found at which the anion is able to provide the necessary push. In consequence, when α-phenylethyl chloride reacts with a silver salt in cyclohexane, or in petroleum ether, the reaction proceeds *via* the concerted pull–push mechanism and the products have the inverted configuration (Table III).

In contrast, when α-phenylethyl chloride is treated with a silver salt in ethyl ether we not only have a halide which relatively easily gives a carbonium ion but, in addition, the reaction medium is able to provide solvation for the carbonium ion. No longer does the adsorbed α-phenylethyl chloride require a suitably positioned anion before giving up a chloride ion to the silver ion. Whether oxonium ion formation (eq 2) occurs,[15]

$$\mathrm{Et_2O + RCl + Ag^+ \longrightarrow Et\overset{+}{O}R + ClAg} \qquad (2)$$

or whether solvation takes the form of some less specific interaction, is not known. In either case the stereochemical result would be the same. Oxonium salt formation (eq 2) would proceed with inversion and this will be followed by a second inversion when the nitrite (or nitrate) ion dislodges the ethyl ether molecule to give α-phenylethyl nitrite and α-phenylnitroethane (or α-phenylethyl nitrate). Over-all retention of configuration also accrues from the process in which an α-phenylethyl carbonium ion is solvated by a rather less well-defined interaction between the carbonium ion and the lone pairs of electrons of ethyl ether. For, as the carbonium ion forms, the solvent molecules take up a position on the far side of the plane of the carbonium ion relative to the departing chloride ion; the carbonium ion is unsymmetrically solvated, the side facing the crystal surface being unsolvated or relatively poorly solvated. This α-phenylethyl carbonium ion must react rapidly with a nitrite (or nitrate) ion on the crystal surface and, since nitrite (or nitrate) ions are more numerous on the side of the carbonium ion from which the chlorine is leaving, this, too, favors the formation of products possessing the configuration of the α-phenylethyl chloride.

Thus, the fact that the reaction of α-phenylethyl chloride with silver nitrite (or nitrate) in ethyl ether, in contrast to the reaction in cyclohexane, proceeds with retention of configuration (Table III)[16] is readily intelligible. In ethyl ether most, perhaps all, of the α-phenylethyl chloride molecules react *via* the carbonium ion path rather than the concerted SN1–SN2 mechanism.[17,18]

The reaction of α-phenylethyl chloride with silver nitrite (or silver nitrate) in benzene is of exceptional interest. One wonders whether the π electrons of benzene can serve to stabilize the α-phenylethyl carbonium ion or whether lack of solvation leaves the system no alternative but to fall back on the concerted SN1–SN2 mechanism. And, if the carbonium ion path is followed, one wonders whether the π complex will pass over to the σ complex;[19] in other words, will alkylation of the solvent by the α-phenylethyl carbonium ion compete with the reaction of nitrite (or nitrate) ion with the carbonium ion? It turns out that silver nitrite (and silver nitrate), in benzene, react with retention of configuration (Table III).[16] Thus most, perhaps all,[17] of the α-phenylethyl chloride reacts by the carbonium ion mechanism; clearly, benzene is able to provide the solvation requisite for α-phenylethyl carbonium ion formation.

It is noteworthy that in benzene the reaction of α-phenylethyl chloride with silver nitrate gives a 94% yield of pure α-phenylethyl nitrate.[20] Manifestly, the α-phenylethyl carbonium ion–benzene π complex reacts with silver nitrate much more rapidly than it goes to α-phenylethylbenzene. That π solvation by benzene is important enough to decide the stereochemistry of the reaction and yet does not lead to detectable alkylation of the benzene is a result of considerable intrinsic interest, and it lends support to the postulate of Brown and Brady[19] that the conversion of a π complex to a σ complex is a relatively slow process.

Lastly, we consider the reactions of silver nitrite (and silver nitrate) in acetonitrile, a solvent which dissolves these salts readily. In the acetonitrile solution the nitrite (or nitrate) ions needed to consummate the concerted SN1–SN2 displacement, not being subject to the constraints of a crystal lattice, become readily available at the rear of the carbon–halogen bond. That the reactions of silver salts in acetonitrile make use of this availability, *i.e.*, they proceed by a mechanism which takes advantage of the possibility of the nucleophilic push of the anion, is clear from the fact that silver nitrate reacts more rapidly than silver perchlorate with alkyl halides;[21] the very low reactivity of neopentyl iodide toward acetonitrile solutions of silver nitrite,[9] and silver nitrate,[21] also accords with this view. Consequently, it comes as no great surprise to find that, in acetonitrile, reactions of silver salts with optically active 2-octyl and α-phenylethyl halides proceed with inversion. While, in principle, acetonitrile might have competed with nitrite (or nitrate) ions for the nucleophilic role, especially in the α-phenylethyl chloride case,

---

bromide by silver bromide it would be anticipated that the reaction would proceed stereospecifically. In the one case in which the extent of racemization of the 2-bromooctane has actually been established *for the particular experiment*, rather than being estimated from analogous experiments (the reaction with silver nitrite in ethyl ether), it has been found that the 2-nitrooctane and 2-octyl nitrite are indeed formed without loss of optical purity, or something very close to this.[4b]

(15) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1939); C. E. Boozer and E. S. Lewis, *J. Am. Chem. Soc.*, **75**, 3182 (1953); A. Streitwieser and S. Andreades, *ibid.*, **80**, 6553 (1958); W. B. Smith and P. S. Rao, *J. Org. Chem.*, **26**, 254 (1961).

(16) Here, as always, some racemization also occurs (*vide supra*).

(17) Whether the concerted SN1–SN2 process competes at all with the carbonium path is a question for which, at present, there is no answer.

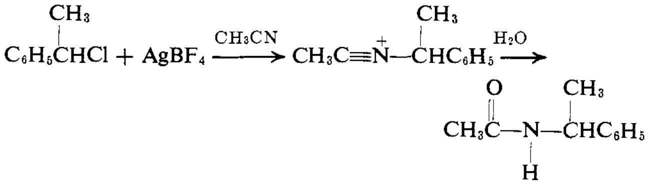
(18) It should be emphasized that retention of configuration due to neighboring group participation in silver salt reactions has been observed repeatedly, *e.g.*, W. A. Cowdrey, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1248 (1937); S. Winstein and R. E. Buckles, *J. Am. Chem. Soc.*, **64**, 2780 (1942); L. Fishbein, *ibid.*, **79**, 2959 (1957); W. T. Moreland, R. G. Berg, and D. P. Cameron, *ibid.*, **82**, 504 (1960); L. D. Hayward, M. Jackson, and I. G. Csizmadia, *Can. J. Chem.*, **43**, 1656 (1965).

(19) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3577 (1952).

(20) The yields of α-phenylethyl nitrate are excellent in all the solvents employed; 82 to 95% (*cf.* the Experimental Section). The silver nitrite reaction is, however, less clean for, in addition to giving two products, elimination of hydrogen chloride intrudes and this produces troublesome by-products: N. Kornblum, *Org. Reactions*, **12**, 101 (1962).

(21) G. S. Hammond, M. F. Hawthorne, J. H. Walters, and B. M. Graybill, *J. Am. Chem. Soc.*, **82**, 704 (1960).

to give nitrilium salts,[22] the isolation of pure α-phenylethyl nitrate in 82% yield shows that little, if any, competition from acetonitrile occurs.[23] In contrast, the reaction of α-phenylethyl chloride with a solution of silver fluoroborate in acetonitrile gives, at the very least, a 60% yield of N-α-phenylethylacetamide. This,



$$C_6H_5\overset{CH_3}{\overset{|}{C}}HCl + AgBF_4 \xrightarrow{CH_3CN} CH_3C{\equiv}\overset{+}{N}{-}\overset{CH_3}{\overset{|}{C}}HC_6H_5 \xrightarrow{H_2O} CH_3\overset{O}{\overset{\|}{C}}{-}\underset{H}{\underset{|}{N}}{-}\overset{CH_3}{\overset{|}{C}}HC_6H_5$$

if it is a concerted process, must involve more SN1 character than the reactions employing silver nitrite, or silver nitrate. Alternatively, the reaction may now be proceeding *via* the carbonium ion mechanism.

In reactions involving tertiary halides there can be little doubt that the graded SN1–SN2 mechanism gives way to carbonium ion formation. Thus, when a solution of silver nitrite in acetonitrile is treated with *t*-butyl chloride, N-*t*-butylacetamide is obtained.[9] Attempted alkylation, using *t*-butyl bromide, of silver nitroform dissolved in acetonitrile also leads to the formation of N-*t*-butylacetamide.[24] The reaction of silver dinitroacetonitrile with *t*-butyl bromide gives rise to the carbon and nitrogen alkylates, products which, again, are reasonably ascribed to the intermediacy of *t*-butyl carbonium ions.[24] And trityl chloride alkylates acetonitrile when silver nitrate is present, giving N-tritylacetamide.[25] With tertiary halides steric hindrance precludes operation of the concerted SN1–SN2 process and the system falls back on the carbonium ion mechanism.

Largely on the basis of kinetic studies in acetonitrile solution, it has been proposed that when a silver salt reacts with an alkyl iodide the first-formed product is an ion pair composed of an anion and a carbonium ion.[21] Very recently, the ion-pair description has been expanded to an ion quadruplet picture.[26] The specification of ion pairs, or ion quadruplets, as intermediates in silver salt reactions does not, however, seem warranted. The evidence for ion pairs or ion quadruplets is less than compelling and it is difficult to see how the data reported in this paper can be accounted for on the basis of such intermediates.

In summary, it is our view that the reactions of silver salts with alkyl halides are best described as concerted SN1–SN2 processes in which the relative importance of the electrophilic pull of the silver and the nucleophilic push of the anion in the transition state varies as a function of the alkyl halide, the silver salt, and the solvent. At the extreme of this graded SN1–SN2 scale situations exist, *e.g.*, with trityl chloride in acetonitrile and α-phenylethyl chloride in benzene, in which the reaction proceeds *via* a transition state which has so little SN2 character that it is usefully regarded as a carbonium ion process.[9,27,28]

Experimental Section[29]

Reagents and solvents were purified as before.[5] All the reactions employing silver nitrate were conducted in a dark room in flasks protected by a calcium chloride drying tube. Rotations are observed values taken on the pure liquid in a 1-dm tube.

Reactions of Optically Active 2-Bromooctane with Silver Nitrate. A. In Petroleum Ether. To a stirred mixture of 25.6 g (0.15 mole) of silver nitrate and 100 ml of petroleum ether (bp 35–37°) was added 19.3 g (0.1 mole) of dextrorotatory 2-bromooctane, $\alpha^{28}\mathrm{D}$ +10.4°, $n^{20}\mathrm{D}$ 1.4498, bp 52° (5 mm), over a period of 30 min. During this time, and for the remainder of the reaction, the system was maintained at room temperature. Stirring was continued for 70 hr at which time a negative halide test was obtained;[30] the silver salts were removed by filtration and washed with petroleum ether. The combined petroleum ether solutions were washed with saturated aqueous sodium bicarbonate and then with water. On drying (anhydrous magnesium sulfate) and rectification at 1 mm there was obtained 11.92 g (68% yield) of levorotatory 2-octyl nitrate, $\alpha^{28}\mathrm{D}$ −2.71°, $n^{20}\mathrm{D}$ 1.4249, bp 44–45°. *Anal.* Calcd for $C_8H_{17}NO_3$: C, 54.83; H, 9.78; N, 7.99. Found: C, 54.67; H, 9.68; N, 8.17. The material which had collected in the cold trap during the rectification was rerectified at 38 mm; this gave 1.25 g (11% yield) of a colorless liquid, bp 40–43°, $n^{20}\mathrm{D}$ 1.4123–1.4127. This liquid decolorized bromine in CCl_4 and had the composition of octene. *Anal.* Calcd for C_8H_{16}: C, 85.63; H, 14.37. Found: C, 85.53; H, 14.26.

B. In Acetonitrile. To a stirred solution of silver nitrate (33.6 g, 0.197 mole) in 200 ml of acetonitrile, 25.3 g (0.131 mole) of dextrorotatory 2-bromooctane, $\alpha^{25}\mathrm{D}$ +36.3°, $n^{20}\mathrm{D}$ 1.4503, bp 56° (4 mm), was added in 1hr. After 24 hr of stirring at room temperature the reaction was complete.[30] Work-up gave 18.52 g (81% yield) of 2-octyl nitrate, $\alpha^{26}\mathrm{D}$ −14.3°, $n^{20}\mathrm{D}$ 1.4254, bp 54–55° (2 mm). *Anal.* Calcd for $C_8H_{17}NO_3$: C, 54.83; H, 9.78; N, 7.99. Found: C, 54.85; H, 9.95; N, 8.09. In addition, 0.78 g (5% yield) of octenes, bp 53–54° (61 mm), $n^{20}\mathrm{D}$ 1.4124–1.4127, was isolated. *Anal.* Calcd for C_8H_{16}: C, 85.63; H, 14.37. Found: C, 84.36; H, 14.19.

C. In Ethyl Ether. To a stirred suspension of silver nitrate (25.6 g, 0.15 mole) in 150 ml of anhydrous ethyl ether, 19.3 g (0.1 mole) of dextrorotatory 2-bromooctane ($\alpha^{25}\mathrm{D}$ +36.3°, $n^{22}\mathrm{D}$ 1.4503) was added in 1 hr. After 26 hr of stirring at room temperature, reaction was complete.[30] Titration of an aliquot of the ethereal solution with aqueous NaOH showed that a 17% yield of acid (*i.e.*, olefin formation) had occurred. On working up, 11.5 g (66% yield) of levorotory 2-octyl nitrate, $\alpha^{26}\mathrm{D}$ −13.5°, $n^{20}\mathrm{D}$ 1.4255, bp 60–62 (3 mm), was obtained. *Anal.* Calcd for $C_8H_{17}NO_3$: C, 54.83; H, 9.78; N, 7.99. Found: C, 54.79; H, 9.83; N, 7.91.

Reactions of Optically Active α-Phenylethyl Chloride with Silver Nitrate. A. In Ethyl Ether. To a stirred suspension of 25.6 g

---

[22] H. Meerwein, P. Laasch, R. Mersch, and J. Neutwig, *Ber.*, **89**, 224 (1956).

[23] Other instances in which aliphatic nitriles exhibit relatively low nucleophilicity are known: *cf.* C. E. Boozer and E. S. Lewis, *J. Am. Chem. Soc.*, **75**, 3182 (1953); G. A. Russell, *ibid.*, **80**, 4987 (1958).

[24] G. S. Hammond, W. D. Emmons, C. O. Parker, B. M. Graybill, and J. H. Waters, *Tetrahedron Suppl.*, **1**, 177 (1963).

[25] S. J. Cristol and J. E. Leffler, *J. Am. Chem. Soc.*, **76**, 4468 (1954); G. W. H. Cheeseman, *Chem. Ind.* (London), 281 (1954).

[26] Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, **87**, 4760, 4771, 4778, 5060 (1965).

[27] A handsome illustration of the importance of the nucleophilic push is provided by the work of H. Peter, M. Brugger, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, **46**, 577 (1963). These investigators found that a γ-chloroamide, $R\ddot{N}HCOCH_2CH_2CH_2Cl$, rapidly reacts with $AgBF_4$ at 0° to give  $R{-}\underset{-}{\overset{H}{\overset{|}{N}}}{=}\underbrace{C{-}CH_2CH_2{-}CH_2}_{O}$ in 92% yield. This is all the more striking when it is realized that *n*-hexyl chloride is not attacked by $AgNO_2$ at room temperature; N. Kornblum, B. Taub, and H. E. Ungnade, *J. Am. Chem. Soc.*, **76**, 3209 (1954).

[28] In their reactions with silver salts, neopentyl, and substituted neopentyl, halides afford some clear examples of carbonium ion type rearrangements. From the reaction of neopentyl iodide with silver nitrite in acetonitrile solution, *t*-amylacetamide is the only pure product isolated (*ca.* 40–50% yield): D. C. Iffland and N. Kornblum unpublished work. M. L. Bender and H. Robbins, *J. Am. Chem. Soc.*, **78**, 1699 (1956), and J. D. Backhurst, *J. Chem. Soc.*, 3497 (1959), also report some interesting examples of such rearrangements.

[29] Analyses were performed by Dr. C. S. Yeh of Purdue University or Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[30] About 10 drops of the clear solution was placed in a small test tube, the solvent was expelled by heating for several seconds under a steam jet, and then 2 drops of a saturated solution of silver nitrate in acetonitrile was added. If no precipitate formed after warming for 1 min, the test was considered negative. When acetonitrile was the reaction medium it was not expelled before addition of the saturated silver solution.

(0.15 mole) of silver nitrate in 150 ml of anhydrous ethyl ether was added 14 g (0.1 mole) of dextrorotatory α-phenylethyl chloride (α^{25}D +37.04°, n^{20}D 1.5271) over a period of 1 hr. The reaction was conducted at room temperature for an additional 6 hr. The resulting mixture was filtered and the silver salts were washed with fresh ether. Distillation gave 13.6 g (82% yield) of dextrorotatory α-phenylethyl nitrate, α^{25}D +3.78°, n^{20}D 1.5089, bp 60–63° (1 mm). *Anal.* Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43. Found: C, 57.63; H, 5.41.

B. In Acetonitrile. Another 14-g sample of the dextrorotatory α-phenylethyl chloride (α^{25}D +37.04°) employed in A was added to a solution of 25.6 g of silver nitrate in 150 ml of acetonitrile in 1 hr After stirring for 20 hr at room temperature, on working up, there was obtained 13.72 g (82% yield) of levorotatory α-phenylethyl nitrate, α^{26}D −6.05°, n^{20}D 1.5088, bp 57–59° (1 mm). *Anal.* Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43. Found: C, 57.42; H, 5.22.

C. In Petroleum Ether. To a stirred suspension of 27.5 g of silver nitrate in 100 ml of petroleum ether (bp 35–37°) was added 15.11 g of levorotatory α-phenylethyl chloride, α^{25}D −10.62°, n^{20}D 1.5272, in 30 min. After 24 hr of stirring at room temperature, the reaction mixture was worked up. Distillation gave 16.92 g (95% yield) of dextrorotatory α-phenylethyl nitrate, α^{26}D +1.63°, n^{20}D 1.5089, bp 55–56° (1 mm). *Anal.* Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.27; H, 5.37; N, 8.36.

D. In Benzene. In 30 min, 14 g of levorotatory α-phenylethyl chloride (α^{27}D −35.64°, n^{20}D 1.5271) was added to a stirred suspension of 25.6 g of silver nitrate in 100 ml of benzene. After stirring for 6 hr at room temperature and working up there was obtained 15.67 g (94% yield) of levorotatory α-phenylethyl nitrate, α^{27}D −1.80°, n^{20}D 1.5088. *Anal.* Calcd for $C_8H_9NO_3$: N, 8.38. Found: N, 8.70.

Reaction of α-Phenylethyl Chloride with Silver Fluoroborate. Silver fluoroborate (1.66 g, 0.03 mole) was dissolved in 5 ml of acetonitrile and 2.8 g (0.02 mole) of α-phenylethyl chloride was added. The reaction mixture became somewhat warm and a precipitate formed. After 45 min at room temperature, ice was added and when it had melted the solution was ether extracted. The extracts were dried over anhydrous magnesium sulfate and concentrated, and the residue was distilled. Thirty per cent (0.83 g) of the α-phenylethyl chloride was recovered. Following this, 0.51 g (45% yield) of a liquid, bp 120–125° (1 mm), was obtained which, on seeding with N-α-phenylethylacetamide, crystallized, mp 76–77°. Authentic N-α-phenylethylacetamide, prepared according to Gotze,[31] had mp 75.6–76.5°.

Reaction of *t*-Butyl Chloride with Silver Nitrite.[32] To 79 g of silver nitrite in 200 ml of acetonitrile at 0°, 46.3 g of *t*-butyl chloride was added dropwise, with stirring, over a period of 2 hr. A precipitate formed at once; after 3 hr at 0° the system was allowed to come to room temperature. Finally, after 1 more day, the silver salts were isolated and the filtrate was distilled. This gave 10 g (17% yield) of N-*t*-butylacetamide, mp 99–100°.

The Solubility of Silver Nitrate in Organic Solvents.[8] Silver nitrate (20.0 g) was extracted[6] with cyclohexane for 5 days at 18–20° (*ca.* 40 ml of fresh solvent every 5 min). There was no loss in weight for the thimble and the sodium bromide test for silver[5] was negative. A duplicate experiment using anhydrous ethyl ether again showed that no silver nitrate had dissolved. However, when 23.0 g of silver nitrate was extracted with benzene (5 days, 18–20°, *ca.* 40 ml of fresh solvent every 5 min) it was found that 24 mg of silver nitrate had been extracted.

Acknowledgment. The senior author wishes to express his appreciation to the National Science Foundation for the award of a Senior Postdoctoral Fellowship for the academic year 1964–1965 during which time this paper was written. He is also indebted to the Eidgenössische Technische Hochschule, Zürich, where this year was spent in the Laboratorium für organische Chemie, for kind hospitality.

---

(31) J. Gotze, *Ber.*, 71, 2290 (1938).

(32) B. Taub, Ph.D. Thesis, Purdue University, June 1952, p 107.

Molecular Asymmetry. VI. The Resolution of Ethyl *p*-Tolyl Sulfoxide[1]

Arthur C. Cope and Edward A. Caress

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received November 22, 1965

Abstract: Resolution of ethyl *p*-tolyl sulfoxide has been accomplished *via* platinum complexes containing optically active α-methylbenzylamine. Fractional crystallization to constant rotation of the complex containing (+)-α-methylbenzylamine afforded (+)-*trans*-dichloro(ethyl *p*-tolyl sulfoxide)(α-methylbenzylamine)platinum(II) (**1a**), $[\alpha]^{25}$D +84.7°. In a similar manner, the complex containing (−)-α-methylbenzylamine afforded (−)-*trans*-dichloro(ethyl *p*-tolyl sulfoxide)(α-methylbenzylamine)platinum(II) (**2a**), $[\alpha]^{25}$D −84.6°. Decomposition of the enantiomeric complexes with aqueous sodium cyanide afforded optically active ethyl *p*-tolyl sulfoxide, $[\alpha]^{25}$D −203.6° and $[\alpha]^{25}$D +203.2°, respectively.

The resolution of *trans*-cycloalkenes[2,3] *via* platinum complexes containing optically active α-methylbenzylamine has been extended to include the use of platinum complexes as resolving agents for sulfoxides. The theoretical[4,5] and synthetic aspects[5,6] of optically active sulfoxides are well known. Until recently, the only methods available for the preparation of optically active sulfoxides have been the oxidation of the corresponding sulfide with an optically active peracid[7] and

---

(1) The first five papers in this series appeared under the title of Molecular Asymmetry of Olefins. For the previous paper in this series, see A. C. Cope, *et al.*, *J. Am. Chem. Soc.*, **88**, 761 (1966).

(2) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *ibid.*, **85**, 3276 (1963).

(3) A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. Whang, and H. J. S. Winkler, *ibid.*, **87**, 3644 (1965).

(4) R. L. Shriner, R. Adams, and C. S. Marvel, "Organic Chemistry," Vol. 1, H. Gilman, Ed., 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1943, p 421.

(5) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965).

(6) (a) K. K. Andersen, *J. Org. Chem.*, **29**, 1953 (1964); (b) K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Am. Chem. Soc.*, **86**, 5637 (1964); (c) K. K. Andersen, *Tetrahedron Letters*, 93 (1962).

(7) (a) A. Maccioni, F. Montanari, M. Secci, and M. Tramontini, *ibid.*, 607 (1961); (b) K. Balenovic, I. Bregovec, D. Francetic, I. Monkovic, and V. Tomasic, *Chem. Ind.* (London), 469 (1961); (c) A. Mayr, F. Montanari, and M. Tramontini, *Gazz. Chim. Ital.*, **90**, 739 (1960); (d) K. Balenovic, N. Bregant, and D. Francetic, *Tetrahedron Letters*, 20