(53) S. S. Joshi and D. N. Solanki, *J. Indian Chem. Soc.*, **14**, 323 (1937).

(54) M. Kilpatrick and R. D. Eanes, *J. Am. Chem. Soc.*, **65**, 589 (1943).

(55) H. D. Kirschman, B. Wingfield and H. J. Lucas, *J. Am. Chem. Soc.*, **52**, 23 (1930).

(56) H. Kloosterziel and H. J. Backer, *Rec. trav. chim.*, **71**, 295 (1952).

(57) I. M. Kolthoff and W. Bosch, *J. Phys. Chem.*, **36**, 1695 (1932).

(58) R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, **11**, 31 (1928).

(59) K. Lauer, *Ber.*, **70B**, 1288 (1937).

(60) N. N. Lichtin and H. P. Leftin, *J. Am. Chem. Soc.*, **74**, 4207 (1952).

(61) A. M. Liquori and A. Ripamonti, *Gazz. chim. ital.*, **85**, 578 (1955).

(62) B. N. Mattoo, *Trans. Faraday Soc.*, **52**, 1462 (1956).

(63) W. R. Maxwell and J. R. Partington, *Trans. Faraday Soc.*, **33**, 670 (1937).

(64) S. M. Neale, *Trans. Faraday Soc.*, **17**, 505 (1922).

(65) Y. Okamoto, and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(66) W. Ostwald, *Z. physik. Chem.*, **3**, 419 (1889).

(67) W. Ostwald, *Z. physik. Chem.*, **2**, 901 (1888).

(68) W. Pip, doctoral dissertation, quoted in reference 82.

(69) D. Pressman and D. H. Brown, *J. Am. Chem. Soc.*, **65**, 540 (1943).

(70) J. D. Roberts, R. A. Clement, and J. J. Drysdale, *J. Am. Chem. Soc.*, **73**, 2181 (1951).

(71) J. D. Roberts and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 628 (1950).

(72) J. D. Roberts, E. A. McElhill, and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 2923 (1949).

(73) J. D. Roberts and W. T. Moreland, Jr., *J. Am. Chem. Soc.*, **75**, 2267 (1953).

(74) J. D. Roberts and C. M. Reagan, *J. Am. Chem. Soc.*, **75**, 4102 (1953).

(75) J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

(76) C. K. Rule and V. K. LaMer, *J. Am. Chem. Soc.*, **60**, 1974 (1938).

(77) E. E. Sager, M. R. Schooley, A. S. Carr, and S. F. Acree, *J. Research Natl. Bur. Standards*, **35**, 521 (1945).

(78) B. Saxton and H. F. Meier, *J. Am. Chem. Soc.*, **56**, 1918 (1934).

(79) Schaller, quoted in reference 38.

(80) G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, **22**, 360 (1939).

(81) G. Schwarzenbach, A. Willi, and R. O. Buch, *Helv. Chim. Acta*, **30**, 1303 (1947).

(82) H. Scudder, *The Electrical Conductivity and Ionization Constants of Organic Compounds*, D. Van Nostrand Co., New York, 1914.

(83) J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 300 (1936).

(84) L. D. Smith and H. C. Jones, *Am. Chem. J.*, **50**, 39 (1913).

(85) F. Swarts, *Bull. acad. roy. Belg.*, **35**, 395 (1898).

(86) R. W. Taft, Jr., in M. S. Newman, ed., *Steric Effects in Organic Chemistry*, John Wiley and Sons, New York, 1956, Chap. 13.

(87) B. J. Thamer, *J. Phys. Chem.*, **59**, 450 (1955).

(88) B. J. Thamer and A. F. Voigt, *J. Phys. Chem.*, **56**, 225 (1952).

(89) E. P. Valby, and H. J. Lucas, *J. Am. Chem. Soc.*, **51**, 2718 (1929).

(90) J. M. Vandenbelt, C. Henrich, and S. G. Vandenberg, *Anal. Chem.*, **26**, 726 (1954).

(91) A. I. Vogel and G. H. Jeffery, *Chem. & Ind.* (*London*), **53**, 779 (1934).

(92) G. F. White and H. C. Jones, *Am. Chem. J.*, **44**, 197 (1910).

(93) S. Widequist, *Arkiv. Kemi*, **2**, 383 (1950).

(94) A. V. Willi and W. Meier, *Helv. Chim. Acta*, **39**, 318 (1956).

(95) A. V. Willi and J. F. Stocker, *Helv. Chim. Acta*, **38**, 1279 (1955).

(96) H. Zollinger, W. Büchler, and C. Wittwer, *Helv. Chim. Acta*, **36**, 1711 (1953).

(97) H. Zollinger and C. Wittwer, *Helv. Chim. Acta*, **39**, 347 (1956).

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[CONTRIBUTION FROM THE CARR LABORATORY, MOUNT HOLYOKE COLLEGE]

Kinetics of the Reaction between a Vinyl Fluoride and Sodium Ethoxide

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Received August 22, 1957

The synthesis of 1,1-diphenyl-2-fluoroethylene is reported. This vinyl fluoride is converted to 1,1-diphenyl-2-ethoxyethylene by sodium ethoxide in ethanol. At 99.75° the kinetics are second-order, first-order with respect to each reactant, and the rate is 270 times faster than that of 1,1-diphenyl-2-chloroethylene. The results are consistent with an addition-elimination mechanism.

The unexpectedly high reactivity of fluorine attached to unsaturated carbon atoms toward nucleophilic substitution has been observed by a number of workers.[1-6] For example, piperidine reacts with 2,4-dinitrofluorobenzene more rapidly than with the other 2,4-dinitrohalobenzenes.[1] Also, the vinylic fluorine atoms of perfluorocyclobutene can be replaced by ethoxide more readily than the allylic ones.[2] These observations probably rule out an S_N2 displacement mechanism that

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(1) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *J. Am. Chem. Soc.*, **79**, 385 (1957).

(2) J. D. Park, M. L. Sharrah, and J. R. Lacher, *J. Am. Chem. Soc.*, **71**, 2337 (1949).

(3) K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3642 (1950).

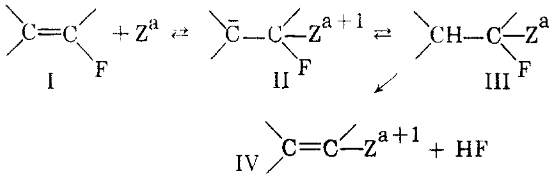
(4) R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3646 (1950).

(5) N. B. Chapman and R. E. Parker, *J. Chem. Soc.*, 3301 (1951).

(6) N. B. Chapman, R. E. Parker, and P. W. Soanes, *Chem. & Ind.* (*London*), 148 (1951).

involves some carbon-fluorine bond fission in the transition state on two grounds. First, the carbon-fluorine bond is less readily cleaved than the other carbon-halogen bonds.[1,7–10] Second, substituents attached to unsaturated carbon atoms ordinarily undergo nucleophilic substitution less readily than those attached to saturated carbon.[11–14]

It has been pointed out that "C—F bond-breaking cannot have made significant progress in the transition state of any substitution in which fluorine is the most rapidly replaced of the halogens."[1] Furthermore, additions to the double bond of vinyl fluorides are common.[3,4,15–23] Therefore, an addition-elimination mechanism, summarized in Equation 1, has been suggested for the nucleophilic displacement of vinyl fluorine.[3,21] In Equation 1, the addition is written in two steps as previously suggested,[20] and Z^a represents a nucleophilic agent with charge a. It is also possible that the anion II is directly converted to product (IV) by loss of a fluoride ion.



(1)

In order to test this mechanism, a study was made of the kinetics of the reaction between 1,1-diphenyl-2-fluoroethylene and sodium ethoxide in ethanol. The progress of the reaction was followed by periodic determinations of the sodium ethoxide concentration. Three runs, in which the ratio of the initial concentration of olefin to that of ethoxide ranged from 0.69 to 2.5, were carried out. Second-order rate constants were calculated in the usual way,[24] and the results are tabulated in Table I. A typical run is summarized in Table II. If an excess of olefin is used (run 3, Table I), the ethoxide concentration reaches zero after 1.1 × 10^6 seconds, showing that the reaction is essentially irreversible. The data indicate that the kinetics are second-order, first-order with respect to olefin and with respect to ethoxide. In a separate experiment, the product of the reaction was isolated and identified as 1,1-diphenyl-2-ethoxyethylene.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF 1,1-DIPHENYL-2-FLUOROETHYLENE WITH SODIUM ETHOXIDE IN ETHANOL AT 99.75 ± 0.05°

Run	Initial Concn. of $NaOC_2H_5$ (M)	Initial Concn. of Olefin (M)	10^5 k (l. Mole^{-1} Sec.$^{-1}$)
1	0.0952	0.1036	4.62 ± 0.09[a]
2	0.1617	0.1112	4.38 ± 0.18
3	0.0740	0.1860	4.31 ± 0.16

[a] Mean deviation.

TABLE II

RATE OF THE REACTION BETWEEN 0.1860M 1,1-DIPHENYL-2-FLUOROETHYLENE AND 0.0740M SODIUM ETHOXIDE IN ETHANOL AT 99.75 ± 0.05°

Time (10^4 Sec.)	Titer[a]	10^5 k (l. Mole^{-1} Sec.$^{-1}$)
0	6.15	
2.16	5.13	4.58
4.32	4.38	4.39
6.48	3.69	4.53
8.64	3.30	4.22
10.80	2.87	4.22
15.48	2.15	4.17
23.67	1.39	4.08
		4.31 ± 0.16[b]

[a] Milliliters of 0.0602M hydrochloric acid needed to titrate a 5-ml. sample. [b] Mean deviation.

A similar run was carried out with 1,1-diphenyl-2-chloroethylene, but the reaction rate was too low to make measurement convenient at the temperature (99.75°) used for the fluorine analog. After 1.19 × 10^6 seconds, the ethoxide concentration had decreased from 0.1370 M to 0.1324M (the initial olefin concentration was 0.1826M.) This yields a second-order rate constant of 1.66 ×

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(7) J. Hine, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 167.

(8) D. N. Glew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc. (London)*, **211A**, 254 (1952).

(9) B. V. Tronov and E. A. Krüger, *Zhur. Russ. Fiz.-Khim. Obshchestva*, 58, 1270 (1926); *Chem. Abstr.*, **21**, 3887^9 (1927).

(10) N. B. Chapman and J. L. Levy, *J. Chem. Soc.*, 1673 (1952).

(11) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 141–142.

(12) L. F. Fieser and M. Fieser, *Organic Chemistry*, 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1956, p. 152.

(13) J. B. Conant, W. R. Kirner, and R. E. Hussey, *J. Am. Chem. Soc.*, **47**, 488 (1925).

(14) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(15) J. D. Park, W. R. Lycan, and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 711 (1951).

(16) J. D. Park, M. L. Sharrah, W. H. Breen, and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 1329 (1951).

(17) J. D. Park, D. K. Vail, K. R. Lea, and J. R. Lacher, *J. Am. Chem. Soc.*, **70**, 1550 (1948).

(18) W. E. Hanford and G. W. Rigby, U. S. Patent **2,409,274** (1946).

(19) P. Tarrant and J. A. Young, *J. Am. Chem. Soc.*, **75**, 932 (1953).

(20) W. T. Miller, Jr., E. W. Fager, and P. H. Griswold, *J. Am. Chem. Soc.*, **70**, 431 (1948).

(21) J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 4480 (1950).

(22) P. Tarrant and H. C. Brown, *J. Am. Chem. Soc.*, **73**, 1781 (1951).

(23) E. T. McBee and R. O. Bolt, *Ind. Eng. Chem.*, **39**, 412 (1947).

(24) A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 17.

10^{-7} l. mole^{-1} sec.$^{-1}$, which is smaller than the rate constant for the reaction of the fluoroolefin by a factor of about 270. This observation demonstrates that the S_N2 mechanism does not play an important role in the reaction of the fluoroolefin.[1]

All of the present results support the mechanism given in Equation 1 for the reaction of the fluoroolefin. This mechanism is applied to the present system in Equations 2–5.

$$(C_6H_5)_2C{=}CHF + OC_2H_5^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (C_6H_5)_2C^-{-}CH(OC_2H_5)F \quad (2)$$

$$(C_6H_5)_2C^-{-}CH(OC_2H_5)F + C_2H_5OH \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} (C_6H_5)_2CH{-}CH(OC_2H_5)F + OC_2H_5^- \quad (3)$$

$$(C_6H_5)_2C^-{-}CH(OC_2H_5)F \xrightarrow{k_3} (C_6H_5)_2C{=}CHOC_2H_5 + F^- \quad (4)$$

$$(C_6H_5)_2CH{-}CH(OC_2H_5)F + OC_2H_5^- \xrightarrow{k_4} (C_6H_5)_2C{=}CHOC_2H_5 + C_2H_5OH + F^- \quad (5)$$

We feel that the process corresponding to k_{-2} (Equation 3) is probably not important in the present case. The anion resulting from such a reaction could become involved in reactions corresponding to k_{-1}, k_2, and k_3. The combination of processes k_{-2} and k_{-1} is an ethoxide-catalyzed removal of the elements of ethanol, which lacks precedent.[25] Processes k_{-2} and k_3 constitute a two-step dehydrohalogenation, and it has been clearly demonstrated that one-step dehydrohalogenations (Equation 5) are favored[26] unless (a) the fragments to be eliminated can not assume a *trans* configuration,[27] (b) the hydrogen is strongly activated,[28] or (c) a base stronger than ethoxide ion is used.[29] Thus, the process corresponding to k_{-2} can probably be followed only by its reverse process (k_2), and since k_2 is undoubtedly much larger than k_{-2} (*i.e.*, the equilibrium of Equation 3 lies far to the right), process k_{-2} is not important in the overall reaction.

The observed second-order kinetics are consistent with a mechanism consisting only of equations 2 and 4; *i.e.*, it is not necessary that 1,1-diphenyl-2-fluoro-2-ethoxyethane be involved at all. The kinetics are also in agreement with a mechanism that involves the α-fluoroether (Equations 2, 3, and 5) provided that the rate of formation of the α-fluoro ether is considerably faster than or considerably slower than the conversion of α-fluoroether to 1,1-diphenyl-2-ethoxyethylene [*i.e.*, provided that $k_1k_2/(k_{-1} + k_2) \gg k_4$ or $k_1k_2/(k_{-1} + k_2) \ll k_4$].

The 1,1-diphenyl-2-haloethylenes used for the kinetic studies were prepared by dehydration of the corresponding 1,1-diphenyl-2-haloethanols, which in turn were synthesized by the reaction of ethyl haloacetate with phenylmagnesium bromide. To our knowledge, this method represents a new approach to the synthesis of the rather inaccessible[30] simple (*i.e.*, containing no halogen atoms except one vinylic fluorine) vinyl fluorides.[31]

EXPERIMENTAL[32]

Ethyl fluoroacetate. Ethyl fluoroacetate was prepared by the method of Bacon *et al.*[33] Our yield was improved by mechanically stirring the mixture during the reaction. Even with stirring, only 15.0 g. (21%, lit.[33] 45%) of product, b.p. 114–117° (lit.[33] 117.5°), was obtained from 110 g. of ethyl bromoacetate and 129 g. of anhydrous potassium fluoride.

1,1-Diphenyl-2-fluoroethanol. An ethereal solution of phenylmagnesium bromide was prepared from 10.0 g. of magnesium, 30.0 g. of bromobenzene, and 200 ml. of ether. The solution was freed from solid impurities by decantation, and a solution of 6.1 g. of ethyl fluoroacetate in 200 ml. of ether was added to it over a period of one hour. During the addition, which was done in an atmosphere of dry nitrogen, the mixture was stirred and maintained at −65 ± 10° by cooling with a Dry Ice–acetone bath. After the addition, the mixture was allowed to warm to −11°, and a solution of 15 g. of ammonium chloride in 200 ml. of water was added slowly with stirring. The ether layer was separated and dried with sodium sulfate. The solvent was removed and the residue was fractionated at reduced pressure. The fraction boiling at 130° (2 mm.) soon solidified, and recrystallization from hexane yielded 4.8 g. (41%) of white crystals, m.p. 71.8–72.6°.

Anal. Calcd. for $C_{14}H_{13}OF$: C, 77.76; H, 6.06. Found: C, 77.86; H, 6.35.

1,1-Diphenyl-2-fluoroethylene. A solution of 1.55 g. of 1,1-diphenyl-2-fluoroethanol in 50 ml. of dry benzene was heated at reflux with 1.59 g. of phosphorus pentoxide for 2.75 hr. The solution was decanted and the solvent removed; distillation of the residue yielded 0.83 g. (55%) of a colorless liquid, b.p. 102–103° (2 mm.).

Anal. Calcd. for $C_{14}H_{11}F$: C, 84.82; H, 5.59. Found: C, 84.74; H, 5.98.

The product decolorized solutions of bromine and potassium permanganate. Oxidation with alkaline permanganate[34] gave a product which yielded a 2,4-dinitrophenylhydrazone melting at 240° (lit.[35] for benzophenone 2,4-dinitrophenylhydrazone, 239°) and did not depress the melting point of an authentic sample of benzophenone 2,4-dinitrophenylhydrazone.

1,1-Diphenyl-2-chloroethanol. An ethereal solution of phenylmagnesium bromide, prepared from 17 g. of magnesium,

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(25) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, pp. 420–472.

(26) Ref. 7, pp. 168–173.

(27) S. J. Cristol and D. D. Fix, *J. Am. Chem. Soc.*, **75**, 2647 (1953).

(28) H. L. Goering, D. I. Relyea, and K. L. Howe, *J. Am. Chem. Soc.*, **79**, 2502 (1957).

(29) C. R. Hauser, *J. Am. Chem. Soc.*, **62**, 933 (1940).

(30) A. L. Henne in R. Adams, *Organic Reactions*, John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, pp. 53 and 66–67.

(31) For other methods of synthesizing simple vinyl fluorides, see ref. 30 and E. T. McBee and W. R. Hausch, *Ind. Eng. Chem.*, **39**, 418 (1947); O. W. Cass, U. S. Patent **2,442,993** (1948); D. D. Coffman and R. D. Cramer, U. S. Patent **2,461,523** (1949); F. B. Downing, A. F. Benning, and R. C. McHarness, U. S. Patent **2,480,560** (1949); P. R. Austin, U. S. Patent **2,585,529** (1952).

(32) Temperatures are uncorrected. Analyses were carried out by Drs. G. Weiler and F. B. Strauss, Oxford, England.

(33) J. C. Bacon, C. W. Bradley, E. I. Hoegberg, P. Tarrant, and J. T. Cassaday, *J. Am. Chem. Soc.*, **70**, 2653 (1948).

(34) Ref. 11, p. 250.

(35) Ref. 11, p. 318.

85 g. of bromobenzene, and 150 ml. of ether, was added, dropwise, and with stirring, to a solution of 20 g. of ethyl chloroacetate in 200 ml. of ether which was cooled by an ice bath. Ice water (200 ml.) was added. The ether layer was separated, washed with water, dried with magnesium sulfate, and fractionated. The fraction distilling at 140° (2 mm.) solidified in the receiver, and yielded 9.0 g. (24%) of white crystals, m.p. 63.4–65.0° (lit.[36] 64–65°), on recrystallization from hexane.

1,1-Diphenyl-2-chloroethylene. A mixture of 6.4 g. of 1,1-diphenyl-2-chloroethanol, 6.0 g. of phosphorus pentoxide, and 50 ml. of dry benzene was heated at reflux for 1 hr. Distillation yielded 4.3 g. (70%) of a colorless liquid, b.p. 138–139° (5 mm.) [(lit.[37] 189° (39 mm.)].

Anal. Calcd. for $C_{14}H_{11}Cl$: C, 78.32; H, 5.16. Found: C, 78.23; H, 5.25.

The product was unsaturated and yielded benzophenone (identified as the 2,4-dinitrophenylhydrazone) on cleavage with alkaline permanganate.[34]

Rate determinations. Solutions of sodium ethoxide in ethanol were prepared by adding sodium to absolute ethanol. The reaction solutions were prepared by diluting weighed samples of 1,1-diphenyl-2-haloethylene with ethanol containing sodium ethoxide in volumetric flasks at 25°. These solutions were heated at 99.75 ± 0.05° in ampoules, and the sodium ethoxide concentrations were determined periodically by titrating 5-ml. aliquots with standard hydrochloric acid, using phenolphthalein as the indicator.

1,1-Diphenyl-2-ethoxyethylene. A solution of 3.0 g. of 1,1-diphenyl-2-fluoroethylene in 70 ml. of absolute ethanol which was 0.64*M* in sodium ethoxide was heated at 99.75° for 118 hr. Water (500 ml.) was added, and the mixture was extracted with four 100-ml. portions of ether. The ether was removed, and distillation of the residue yielded a colorless liquid, b.p. 136–138° (2 mm.) [lit.[47] 178–182° (18 mm.)].

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 86.02; H, 7.09.

The product decolorized bromine and potassium permanganate solutions, and permanganate oxidation[34] gave benzophenone, identified as the 2,4-dinitrophenylhydrazone.

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(36) H. Gilman and C. C. Wanser, *J. Am. Chem. Soc.*, **73**, 4030 (1951).

(37) W. T. Buttenberg, *Ann.*, **279**, 324 (1884).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Aromatic Cyclodehydration. XXXVII[1,2] Quinolizinium Derivatives Related to the Protoberberine Alkaloids

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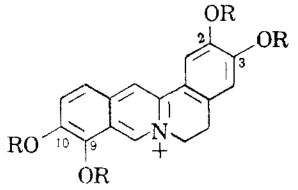
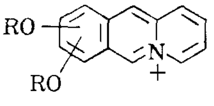
Received August 16, 1957

It has been found that isoquinoline-1-carboxaldehyde may be substituted for picolinic aldehyde in the acridizinium ion synthesis, affording a new method for the synthesis of the benz[*a*]acridizinium system (V). Salts of three new alkoxybenz[*a*]acridizinium ions have been synthesized.

In earlier model experiments[3] directed toward the synthesis of the protoberberine alkaloids (I), it was shown that salts produced by the reaction of alkoxybenzyl halides with picolinic aldehyde can be cyclized in the presence of hydrochloric acid to yield alkoxyacridizinium salts (II). It seemed likely that if 1-isoquinoline aldehyde (IV) were used instead of picolinic aldehyde a route to benzo[*a*]acridizinium salts (V) would be afforded.



I



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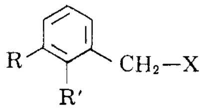

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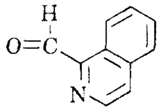
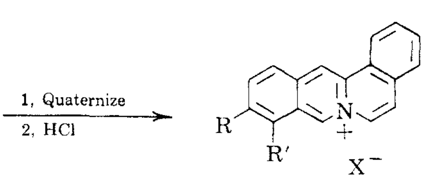


IV



V

The aldehyde (IV), available by the selenium dioxide oxidation of 1-methylisoquinoline,[4] was found to quaternize with benzyl bromide satisfactorily. Cyclization of the crude salt gave the expected benzo[*a*]acridizinium bromide (V, R = R′ = H; X = Br) in 52% yield. This new salt (V) might be regarded as the parent substance of all of the protoberberine alkaloids and could be referred to as a "dehydroprotoberberinium" salt. By the use of alkoxybenzyl halides several alkoxybenzo[*a*]acridizinium salts were produced (Table I).

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(1) For the previous communication of this series see *J. Am. Chem. Soc.*, **80**, 930 (1958).

(2) This investigation was supported by a research grant (H-2170) from the National Heart Institute of the National Institutes of Health. Abstracted in part from a dissertation to be submitted by James H. Jones in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Duke University.

(3) C. K. Bradsher and James H. Jones, *J. Am. Chem. Soc.*, **79**, 6033 (1957).

(4) R. S. Barrows and H. G. Lindwall, *J. Am. Chem. Soc.*, **64**, 2430 (1942).