yielded 3.1 g. (64%) of IIa melting with decomposition at 225°, ν_{CO} 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{12}ClN_3O_2$: C, 59.71; H, 4.01; N, 13.93. Found: C, 59.93; H, 4.34; N, 13.65.

This compound (1 g.) was refluxed for 18 hr. in a mixture of equal volumes of methanol and concentrated hydrochloric acid to give 5-chloro-3-phenylindazole (IVa), which was identical with an authentic specimen.[5]

1-Amino-1,3-dihydro-7-nitro-5-phenyl-2H-1,4-benzodiazepin-2-one 4-Oxide (IIb).—To a solution of 9 g. (0.03 mole) of Ib[12] in 100 ml. of dimethylformamide was added 1.5 g. (0.031 mole) of a 50% suspension of sodium hydride in mineral oil. The solution was stirred for 30 min. at 25° after which time 365 ml. of a 0.11 *N* solution (0.04 mole) of chloramine in ether was added. After stirring the solution for 20 hr. at 25° it was poured into dilute sodium hydroxide and the ether layer was separated. The aqueous phase was extracted with methylene chloride. The organic layers were combined, washed free of alkali, and concentrated. The solid residue on recrystallization from benzene gave 1.9 g. (20%) of tan prisms melting at 200–203° dec., ν_{CO} 1700 cm.$^{-1}$ (IIb).

Anal. Calcd. for $C_{15}H_{12}N_4O_4$: C, 57.69; H, 3.87; N, 17.94. Found: C, 58.03; H, 4.00; N, 18.14.

Evaporation of the mother liquor of this product left a crystalline residue which, after recrystallization from benzene gave white prisms melting at 190–191°. The yield was 1.8 g. (25% of theory). This compound was identical with an authentic sample of 5-nitro-3-phenylindazole[7] (IVb).

1-Amino-7-chloro-5-(2-chlorophenyl)-1,3-dihydro-2H-1,4-benzodiazepin-2-one (VIa).—A solution of 25 g. (0.082 mole) of Va[13] in 250 ml. of tetrahydrofuran was treated with 5.0 g. (0.104 mole) of a 50% suspension of sodium hydride in mineral oil and heated on a steam bath for 15 min. The mixture was allowed to cool to 25° before adding 500 ml. of a 0.18 *N* solution (0.09 mole) of chloramine in ether. The mixture was then stirred for 16 hr. at room temperature.

The reaction mixture was poured into water and extracted with ether. The organic layers were washed with water, dried over sodium sulfate, and concentrated. The residue crystallized on addition of methanol to give white prisms which after recrystallization from methanol melted at 202–204°. The yield was 20.4 g. (78%), ν_{CO} 1690 cm.$^{-1}$ (VIa).

Anal. Calcd. for $C_{15}H_{11}Cl_2N_3O$: C, 56.27; H, 3.46; N, 13.12. Found: C, 55.94; H, 3.42; N, 13.07.

Addition of a molar amount of sodium nitrite in aqueous solution to an acetic acid solution of compound VIa gave a precipitate which, after recrystallization, was identified as Va.

Acetyl Derivative of VIa.—A solution of 5 g. of compound VIa in a mixture of 50 ml. of acetic anhydride and 50 ml. of pyridine was heated on a steam bath for 20 min. The solution was poured onto ice and the solid precipitate which formed was collected on a filter. Recrystallization from ether gave 3.7 g. (65%) of prisms melting at 221–223°.

Anal. Calcd. for $C_{17}H_{13}Cl_2N_3O_2$: C, 56.37; H, 3.62; N, 11.60. Found: C, 56.31; H, 3.81; N, 11.45.

Benzylidene Derivative of VIa.—A solution of 6 g. of compound VIa in 25 ml. of methanol, 25 ml. of pyridine and 10 ml. of benzaldehyde was heated under reflux for 18 hr. The reaction mixture was concentrated to a small volume, poured into water, and extracted with ether. The ether layer on concentration gave crystals which after recrystallization from ether yielded white prisms melting at 169–171°. The yield was 5.2 g. (68%).

Anal. Calcd. for $C_{22}H_{15}Cl_2N_3O$: C, 64.72; H, 3.70; N, 10.29. Found: C, 64.92; H, 4.00; N, 10.63.

1-Amino-1,3-dihydro-7-nitro-5-phenyl-2H-1,4-benzodiazepin-2-one (VIb).—To a solution of 10 g. (0.036 mole) of Vb in 250 ml. of tetrahydrofuran was added 2.0 g. (0.042 mole) of a 50% suspension of sodium hydride in mineral oil. The mixture was stirred for 1 hr. at 25°, after which time 150 ml. of a 0.28 *N* solution (0.042 mole) of chloramine in ether was added. After stirring the solution for 19 hr. at 25° it was poured into ice-water. The ether layer was washed with 1 *N* aqueous sodium hydroxide and water and then it was dried with sodium sulfate. Evaporation of the ether gave a residue which crystallized on addition of ethanol. Recrystallization from benzene gave 4.6 g. (44%) of yellow prisms melting at 155–157°, ν_{CO} 1700 cm.$^{-1}$ (VIb).

Anal. Calcd. for $C_{15}H_{12}N_4O_3$: C, 60.80; H, 4.08; N, 18.91. Found: C, 60.53; H, 4.20; N, 19.00.

This compound (0.5 g.) was refluxed for 6 hr. in a mixture of methanol (10 ml.) and concentrated hydrochloric acid (10 ml.) to give 0.3 g. (74%) of 5-nitro-3-phenylindazole.[7]

Acknowledgment.—We are indebted to Dr. Al Steyermark and his staff for the microanalyses and Dr. V. Toome and Mr. S. Traiman for spectroscopic determinations.

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[12] L. H. Sternbach, R. I. Fryer, O. Keller, W. Metlesics, G. Sach, and N. Steiger, *J. Med. Chem.*, **6**, 261 (1963).

[13] L. H. Sternbach, R. I. Fryer, W. Metlesics, E. Reeder, G. Sach, G. Saucy, and A. Stempel, *J. Org. Chem.*, **27**, 3788 (1962).

Quinazolines. I. The Structure of the Polychlorinated Products Obtained by the Phosphorus Pentachloride–Phosphorus Trichloride Chlorination of 2-Methyl-4-quinazolone and 2-Ethyl-4-quinazolone

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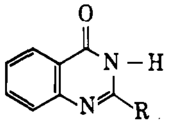
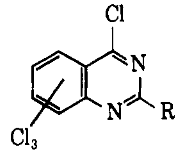
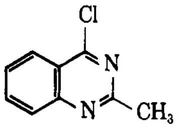
In 1890 Dehoff[2] reported that the chlorination of 2-methyl-4-quinazolone (I) with PCl_5–PCl_3 at 160° yielded a trichlorobenzo-2-methyl-4-chloroquinazoline (II) instead of the desired 2-methyl-4-chloroquinazoline (III). In 1909 Bogert and May[3] confirmed Dehoff's work and reported several unsuccessful attempts to obtain III by the chlorination of I under milder conditions.[4] Bogert and May also reported that a trichlorobenzo-2-ethyl-4-chloroquinazoline (V) is obtained by the chlorination of 2-ethyl-4-quinazolone (IV) with "a mixture of $POCl_3$–PCl_5." [5]



I, R=CH_3
IV, R=C_2H_5



II, R=CH_3
V, R=C_2H_5



III

To us it seemed quite improbable that an alkyl group in the 2-position of 4-quinazolone should have such a profound influence in activating the benzo ring toward nuclear chlorination. A more likely site for the introduction of the "extra" chlorines seemed to be the 2-alkyl substituents, and the n.m.r. spectra of the polychlorinated products clearly substantiate this contention.

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[1] National Science Foundation Undergraduate Research Participant, 1963–1964.

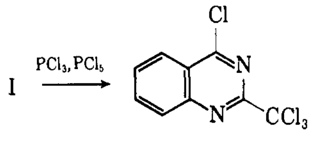
[2] L. H. Dehoff, *J. prakt. Chem.*, [2] **42**, 354 (1890).

[3] M. T. Bogert and C. E. May, *J. Am. Chem. Soc.*, **31**, 507 (1909).

[4] H. C. Scarborough, B. C. Lawes, J. L. Minielli, and J. L. Compton [*J. Org. Chem.*, **27**, 957 (1962)] have accomplished the synthesis of III by the chlorination of I with $POCl_3$ in the presence of N,N-dimethylaniline.

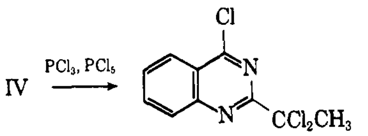
[5] Some confusion exists concerning the actual composition of the chlorinating agent employed by Bogert and May. Although they claim to have followed Dehoff's procedure, their experimental procedure reports the use of $POCl_3$ in place of the PCl_3 employed by Dehoff. In our hands, the use of $POCl_3$–PCl_5 in place of PCl_3–PCl_5 in the chlorination of both I and IV led to extensive decomposition under conditions ranging from reflux temperature to 170° and no pure products could be isolated.

The n.m.r. spectrum of Dehoff's tetrachlorinated methyl compound clearly showed that *only aromatic protons* were present (τ 1.64–2.42). Accordingly, structure II has been revised to 2-(trichloromethyl)-4-chloroquinazoline (VI).



VI

In our hands, the chlorination of 2-ethyl-4-quinazolone did not proceed as reported by Bogert and May. Utilizing a variety of reaction conditions, we have been unable to isolate any of the tetrachlorinated material reported by Bogert and May. Chlorination of IV by the same procedure that was employed for the conversion of I to VI resulted in the formation of a low yield of a *trichloro compound* (VII). The n.m.r. spectrum of this compound showed the presence of a singlet at τ 7.29 (3 H) and an aromatic multiplet at τ 1.50–2.42 (4 H). On the basis of the n.m.r. spectrum, nuclear chlorination is ruled out and the structure of the trichloro compound is most likely 2-(1,1-dichloroethyl)-4-chloroquinazoline (VII).



VII

Experimental

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Analyses are by Mr. Kenneth Fleisher and his staff of the Sterling–Winthrop Research Institute. N.m.r. spectra were run in deuteriochloroform on a Varian A-60 spectrometer using tetramethylsilane as the internal standard.

2-Trichloromethyl-4-chloroquinazoline (VI).—The procedure of Dehoff[2] was followed with a few modifications. A sealed tube containing 2.0 g. (0.0125 mole) of 2-methyl-4-quinazolone,[6] 6.25 g. of PCl_5, and 5.00 g. of PCl_3 was heated behind a safety screen at 170° for 4 hr. The tube was cooled to Dry Ice–acetone temperature and cautiously opened. The volatile phosphorus halides were removed at steam-bath temperature *in vacuo*. The residue was stirred with 50 ml. of warm 6 *N* NaOH and filtered. The insoluble material was dissolved in ethanol, decolorized with charcoal, and reprecipitated with water to give 1.31 g. (37%) of VI, m.p. 114–116°. Recrystallization from dilute ethanol gave white crystals, m.p. 121–123°, lit.[2] m.p. 125°.

Anal. Calcd. for $C_9H_4Cl_4N_2$: C, 38.33; H, 1.43; N, 9.94. Found: C, 38.43; H, 1.78; N, 10.07.

2-(1,1-Dichloroethyl)-4-chloroquinazoline (VII).—By employing the same procedure described above, the chlorination of 2-ethyl-4-quinazolone yielded 26% of crude VII, m.p. 86–89°. Recrystallization from dilute ethanol gave white needles, m.p. 96–96.5°.

Anal. Calcd. for $C_{10}H_7Cl_3N_2$: C, 45.92; H, 2.70; Cl, 40.67; N, 10.71. Found: C, 46.01; H, 3.03; Cl, 40.89; N, 10.57.

Acknowledgment.—We thank the National Science Foundation for an Undergraduate Research Participation Grant and the Research Foundation of the State University of New York for a Grant-in-Aid. We also wish to thank Mr. Kenneth Fleisher and his staff of the Sterling–Winthrop Research Institute for the analytical results and Miss Katherine Martini of Sterling–Winthrop for the n.m.r. determinations.

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(6) A. Buzas and C. Hoffmann, *Bull. soc. chim. France*, 1889 (1959).

Convenient Preparations of α-Halo Sulfones and Their Use in the Synthesis of Deuterated Olefins, the Desulfurization of Alkyl Sulfones, and the Homologization of Olefins

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During a study of the mechanism of the alkaline degradation of α-haloalkyl sulfones (Ramberg–Bäcklund reaction)[1] convenient synthetic methods were developed for a variety of α-halo sulfones. The reactions used in the syntheses and the halo sulfones themselves have a chemical utility which would seem worthy of further attention. Procedures are given in this brief paper for the preparation of several α-chloro, α-bromo, and α-iodo sulfones and for the use of these sulfones as part of three broader chemical schemes: (1) the synthesis of olefins deuterated at the double bond, (2) the desulfurization of alkyl sulfones, and (3) the homologization of olefins.

Synthesis of α-Halo Sulfones.—A simplified procedure has been developed for the oxidation of α-halo sulfides to sulfones by using a dried solution of 40% commercial peracetic acid in methylene chloride.[2,2a] Very high yields were obtained when the starting sulfides were pure. Details are given in the Experimental section.

A different technique was employed for α-bromo and α-iodo sulfones. Dialkyl sulfones in benzene solution were treated with 1 mole of commercial butyllithium. The resulting slurry of the α-lithium salt was then halogenolyzed in the cold with either bromine or iodine. While yields were not extremely good and while the products were contaminated with some impurities, the simplicity of the reaction and the ready availability of the starting materials justify its use. Details are given in the Experimental section.

Synthesis of Deuterated Olefins.—The Ramberg–Bäcklund reaction of α-halo sulfones is shown schematically (see p. 1314, top of col. 1).

In the course of our mechanistic studies of this reaction,[1] it was found that the hydrogens α to the sulfonyl group exchange with the basic medium much more rapidly than the olefinic product is formed. In

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(1) Reported in communication form: N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963).

(2) Previously reported methods employed perbenzoic acid, monoperphthalic acid, or peracetic acid alone: see (a) H. Böhme, *Ber.*, **70**, 379 (1937); (b) L. Ramberg and B. Bäcklund, *Arkiv Kemi, Mineral. Geol.*, **13A**, No. 27 (1940); (c) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5184 (1951).

(2a) Note Added in Proof.—Since this work was completed, *m*-chloroperbenzoic acid has become commercially available. This material in chloroform solution is a particularly convenient reagent for anhydrous oxidation of sulfides to sulfones. Its use has been reported by L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4085, 4089, 4383 (1964), in transformations analogous to several in the present report.