not react with selenium tetrachloride even on extended refluxing in benzene.

Selenoxide Preparations.—All selenoxides were prepared by the same procedure. A slurry made from several grams of the selenium dichloride and 100 ml. of water was stirred for 2 hr. at room temperature. The resulting material was recrystallized from acetone yielding a white solid. The results are shown in Table I. Stirring for longer periods (up to 2 days) did not result in hydrolysis of the chlorine-chlorine linkages as is reported by Smedsland[11] for bis-2-chloroethylselenium dichloride.

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(11) T. Smedsland, *Finska Kemistamfundets Medd.*, **41**, 13 (1932); *Chem. Abstr.*, **26**, 5905 (1932).

(12) Too low a combustion temperature was used resulting in the low carbon results observed.

Potassium *p*-Phenylazophenoxide as a Reagent for the Identification of Organic Halogen Compounds

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The literature records many reagents which have been suggested for the identification of alkyl halides.[2,3] No one of these is entirely satisfactory, either because of difficulty in preparation or because their application is not general. It has been suggested[4] that thiourea and *p*-bromobenzenesulfon-*p*-anisidide appear to be the most generally useful reagents. However, the *S*-alkyl isothioureas have to be isolated as picrates or styphnates and the *n*-alkyl-*p*-bromobenzenesulfon-*p*-anisidides have low melting points. More recently it has been stated[3] that the best method for making derivatives of alkyl halides was their conversion into the corresponding Grignard reagents and the reaction of these with phenyl-, *p*-tolyl-, or α-naphthyl isocyanate to give the anilides, toluides, or α-naphthalides. However, this is a rather lengthy experimental procedure for preparing derivatives, and its application is limited only to organic halogen compounds which form Grignard reagents.

Among the many other derivatives suggested for the identification of alkyl halides are the *p*-alkoxybenzoic acids,[5] alkyl triiodophenyl ethers,[6] alkyl β-naphthyl ethers,[7] *p*-alkoxydiphenylamines,[8] alkyl 2,4-dinitrophenyl sulfides,[9] alkyl 6-nitro-2-mercaptobenzothiazolyl sulfides,[10] and *S*-alkylmercaptosuccinic acids.[11] In terms of suitability, each of these derivatives has certain limitations, except the alkyl 2,4-dinitrophenyl sulfides, which appear to have general applicability. The preparation of the *p*-alkoxybenzoic acids involves a lengthy experimental procedure, and the alkyl triiodophenyl ethers, *p*-alkoxydiphenylamines, and alkyl 6-nitrobenzothiazolyl sulfides are low melting derivatives. The alkyl β-naphthyl ethers usually were separated as oils and had to be isolated as picrates. The usefulness of *S*-alkylmercaptosuccinic acids has been demonstrated only for alkyl bromides which require long reaction times (four to twenty-four hours) for preparing derivatives.

We wish to report the use of *p*-phenylazophenol as a reagent for the identification and chromatographic separation of organic halogen compounds. Similarly, Hurd and coworkers[12,13] have reported the use of *p*-phenylazophenol as a reagent for the preparation and chromatographic separation of *p*-phenylazophenyl polyacetylglycosides. In several instances,[14-16] the reaction of an alkyl halide with *p*-phenylazophenol under alkaline conditions to form an ether has been reported.

The potassium salt of *p*-phenylazophenol (m.p. 155–156°) reacted readily with organic halogen compounds in dimethylformamide or dimethoxyethane to form crystalline *p*-phenylazophenyl ethers in good yields. In a few cases of these derivatives similar melting points were obtained; however, a mixture melting point showed a marked depression in all such cases.

Of fifty halides investigated, all the primary and secondary halides reacted, in many instances with only mixing and no heating. The reagent also reacted with straight- and branched-chain halogen esters, halohydrins, halo ketones, halo ethers, and chloroformates. Good yields of the derivatives of the chloroformates were obtained only by allowing their reaction mixtures to stand for sixteen hours at room temperature. The vicinal halide, 1,2-dibromoethane, gave constant melting point material (196.0–198.0°); however, analytical results indicated that this material was a mixture of the mono- and diderivatives. A well defined

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(1) This paper is based on work presented by Elwood Donaldson and Muerl Payne in partial fulfillment of requirements for an undergraduate research course offered in the Department of Chemistry of Central State College.

(2) A comprehensive review of the reagents, which have been suggested for the identification of alkyl halides, has been published by Hopkins and Williams Research Staff, "Organic Reagents for Organic Analysis," 2nd ed., Chemical Publishing Co., Inc., Brooklyn, New York, 1950, pp. 32–33.

(3) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1956, p. 242.

(4) L. L. Merritt, Jr., S. Levey, and H. B. Cutter, *J. Am. Chem. Soc.*, **61**, 15 (1939).

(5) W. M. Lauer, P. A. Sanders, R. M. Leekley, and H. E. Unguade, *ibid.*, **61**, 3050 (1939).

(6) R. D. Drew and J. M. Sturtevant, *ibid.*, **61**, 2666 (1939).

(7) V. H. Dermer and O. C. Dermer, *J. Org. Chem.*, **3**, 289 (1938).

(8) D. F. Houston, *J. Am. Chem. Soc.*, **71**, 395 (1949).

(9) R. W. Bost, P. K. Starnes, and E. L. Wood, *ibid.*, **73**, 1968 (1951).

(10) H. B. Cutter and H. R. Golden, *ibid.*, **69**, 831 (1947).

(11) J. G. Hendrickson and L. F. Hatch, *J. Org. Chem.*, **25**, 1747 (1960).

(12) C. D. Hurd and W. A. Bonner, *ibid.*, **11**, 50 (1946).

(13) C. D. Hurd and R. P. Zelinski, *J. Am. Chem. Soc.*, **69**, 243 (1947).

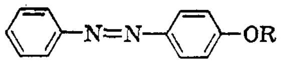
(14) S. Scichilone, *Gazz. chim. ital.*, **12**, 110 (1882).

(15) P. Jacobsen and W. Fischer, *Ber.*, **25**, 994 (1892).

(16) L. Claisen and O. Eisleb, *Ann.*, **401**, [See *Chem. Abstr.*, **8**, 64 (1914)].

TABLE I

DATA ON *p*-PHENYLAZOPHENYL ETHERS



	Halide used		Yield,[a]	
	R	X	%	M.p.. °C.[b]
C_1	Methyl[c]	I	93	51.5–52.0
	Methylene[d]	I	81	183.0–184.5
C_2	Ethyl[e]	I	86	71.0–72.0
	Hydroxyethyl[f]	Cl	80	99.0–100.0
C_3	1-Propyl[g]	Br	68	59.5–60.0
	3-Chloropropyl	Br	76	77.0–87.0*
	2-Propenyl[h]	Br	77	50.5–51.5
	Carbomethoxymethyl	Br	77	115.5–116.5
	Carboethoxy	Cl	95(s)	84.0–84.5
C_4	1-Butyl[i]	Br	90	60.0–61.5
	1-Butyl[i]	Cl	30	60.0–61.5
	1-Butyl[i]	I	90	60.0–61.5
	2-Butyl	Br	72	62.0–63.0
	2-Butyl	Cl	58	62.0–63.0
	2-Butyl	I	49	62.0–63.0
	Carboethoxymethyl[j]	Br	95	75.5–76.0
	Carbo-γ-chloropropoxy	Cl	95(s)	57.0–59.0
C_5	3-Methylbutyl	Br	81	36.5–37.0
C_6	1-Hexyl	Br	90	57.4–57.7
	1-Hexyl	Cl	70	57.4–57.7
	1-Hexyl	I	91	57.4–57.7
	2,4-Dinitrophenyl	Br	73	137.0–138.0
	4-Nitrophenyl	Br	93	138.0–140.0
C_7	1-Heptyl	Br	95	68.05–69.0
	1-Heptyl	Cl	91	68.05–69.0
	1-Heptyl	I	92	68.05–69.0
	1-Carboethoxy-2-methylpropyl	Br	64	58.0–59.0
C_8	1-Octyl	Br	93	72.0–73.0
	1-Phenylethyl	Br	87	108.0–109.0
	2-Phenylethyl	Br	40	84.5–85.0
	Benzoylmethyl	Br	90	128.0–128.5
	Benzoylmethyl	Cl	71	128.0–128.5
C_9	3-Phenoxypropyl	Br	94	92.5–93.0
C_{10}	1-Decyl	Br	94	63.0–64.0
	1-Decyl	Cl	94	63.0–64.0
	1-Decyl	I	97	63.0–64.0
C_{16}	1-Hexadecyl	Br	96	79.0–80.0
C_{18}	1-Octadecyl	Br	96	83.0–84.0

[a] Yields are reported on crude products from reactions run in dimethylformamide. Reactions were carried out under reflux unless indicated by (s) = shaking and standing. [b] Melting points are on derivatives purified by chromatography then recrystallized. The found analyses agreed with the calculated values to within ±0.2% nitrogen except in six cases and the difference was not greater than ±0.5% except in one case. Microanalyses were performed by the Du Good Chemical Laboratory, St. Louis, Missouri. *Nitrogen and chlorine analyses were performed on this compound and both agreed with the calculated value within ±0.2%. [c] Melting points which have been reported for the methyl ether prepared by various synthetic methods were: 56° [A. Colombano, *Gazz. chim. ital.*, **37**, 11, 474 (1907)]; 54° [H. Gorke, E. Köppe, and F. Staiger, *Ber.*, **41**, 1157 (1908)]; 55.5° [P. Pfeiffer and O. Angern, *Z. angew. Chem.*, **39**, 258 (1926)]; 64° [J. Burns, H. McCombie, and H. A. Scarborough, *J. Chem. Soc.*, 2934 (1928)]; 54° [E. Bergmann and A. Weizmann, *Trans. Faraday Soc.*, **32**, 1321 (1936)]; 56° [A. Burawoy and I. Markowitsch-Burawoy, *J. Chem. Soc.*, 39 (1936)]; 53.5° [R. P. Zelinski and W. A. Bonner, *J. Am. Chem. Soc.*, **71**, 1792 (1949)]; 52–53° [J. N. Ospenson, *Acta Chem. Scand.*, **5**, 491 (1951)]. [d] Bis-ether structure in which R group is connected to two *p*-phenylazophenoxy radicals. [e] Melting points which have been reported for the ethyl ether prepared by various synthetic methods were: 77–78° [see ref. 15]; 78° [G. Charrier and G. Ferreri, *Gazz. chim. ital.*, **44**, 175 (1914)]; 85° [E. Naegeli, *Bull. soc. chim.* [3], **11**, 897 (1894)]; 85° [H. Gorke, E. Köppe, and F. Staiger, *Ber.*, **41**, 1157 (1908)]. [f] Melting point reported for the hydroxyethyl ether obtained by reaction of *p*-phenylazophenol with ethylene oxide was 100° [D. R. Boyd and E. R. Marle, *J. Chem. Soc.*, **105**, 2123, 2137 (1914)]. [g] The melting point of *n*-propyl ether has been reported to be 61° [H. Gorke, E. Köppe, and F. Staiger, *Ber.*, **41**, 1157 (1908)]. [h] The 2-propenyl ether has been reported to melt at 52° [see ref. 16]. [i] The *n*-butyl ether has been reported to melt at 67° [H. Gorke, E. Köppe, and F. Staiger, *Ber.*, **41**, 1157 (1908)]. [j] The carboethoxymethyl ether has been reported to melt at 70° [J. Mai and F. Schwabacher, *Ber.*, **34**, 3937 (1901)].

product also was not obtained with 1-bromo-2-chloropropane. The disjunctive halide, 1-bromo-3-chloropropane, gave a well defined product in which the bromo group had been displaced as shown by analysis for nitrogen and chlorine. The reagent also reacted with the aryl halides, 1-bromo-4-nitrobenzene and 1-bromo-2,4-dinitrobenzene. The reagent did not react with cyclohexyl bromide, tertiary alkyl halides, bromo or iodo aromatics, and 1,2- and 1,3-bromonitrobenzene.

The various *p*-phenylazophenyl ethers prepared during this investigation and their physical properties are given in Table I.

The brilliantly colored ethers can be eluted from columns of alumina, silicic acid, and mixtures of each of these adsorbents with Celite. Our chromatographic studies indicated that there is not a large enough difference in the adsorption affinities of homologous ethers differing by less than four carbon atoms to permit separation of mixtures of them.

Experimental

Reagents.—The organic halogen compounds were commercially available grades, and were used without further purification. *p*-Phenylazophenol is manufactured by Distillation Product Industries.

The solvent Skellysolve B (b.p. 60–71°) was redistilled and ethyl alcohol, dimethylformamide, and dimethoxyethane were used as purchased.

The adsorbents used in preparing the chromatographic columns were silicic acid (Mallinckrodt, prepared by the method of Ramsey and Patterson), alumina (Aluminum Company of America, Grade F-20) and Celite-535 (Johns-Manville).

Potassium *p*-Phenylazophenoxide.—Potassium hydroxide pellets (1.5 g.) were added to a solution of 5 g. of *p*-phenylazophenol in 20 ml. of absolute alcohol. The mixture was refluxed until complete dissolution of the potassium hydroxide occurred. The solution was concentrated and the last traces of solvent were removed *in vacuo* under a stream of nitrogen. The salt obtained as a deep red powder was dried in a vacuum desiccator.

Preparation of *p*-Phenylazophenyl Ethers.—A mixture of approximately 0.5 g. (0.002 mole) of potassium *p*-phenylazophenoxide and an equal molar quantity of the halide was dissolved in 10 ml. of dimethylformamide. In many cases there was an immediate reaction as indicated by the formation of salt. The mixture was then heated under reflux for 1-hr. Better results were obtained with the chloroformates if the reaction was allowed to stand at room temperature for about 16 hr. When the refluxing was completed, the mixture was cooled to room temperature and poured into a mixture of ice and water. The inorganic salt dissolved. The crude reaction product was filtered, washed with water, and dried. The crude product was dissolved in Skellysolve B or dimethoxyethane or a mixture of these two solvents and chromatographed on silicic acid on which a small amount of gummy material was strongly adsorbed. The derivative was then recrystallized from alcohol or alcohol–water mixtures. The crude products could be recrystallized to give substantially constant melting points over a range of two degrees. However, for good analysis it was necessary to remove a small amount of impurity by chromatography.

Acknowledgment.—We are indebted to the National Science Foundation for financial aid in the pursuance of this work.

Reaction of 1-Naphthyl Isocyanate with 3-Hydroxymethyl-3-methoxymethyl-2-butanone. A Reinvestigation

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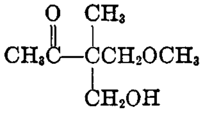
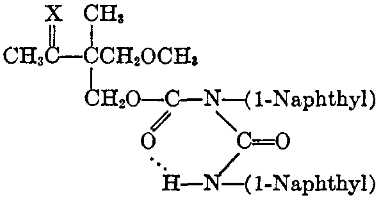
Upon reaction of 1-naphthyl isocyanate with 3-hydroxymethyl-3-methoxymethyl-2-butanone (I) in the presence of pyridine, Tieman and Gold[2] obtained a compound (no experimental details or yield given), m.p. 162–163°, the analysis of which indicated the empirical formula $C_{29}H_{28}N_2O_5$.[3] They suggested reaction of the second equivalent of isocyanate with the hydroxyl group formed by enolization of the acetyl group, although they noted that the acetate of I did not form a urethane with the isocyanate. The present report identifies by spectral and chemical data the reaction product obtained by Tieman and Gold as (2-methoxymethyl-2-methyl-3-oxo)butyl 2,4-bis(1-naphthyl)allophanate (II).

Several unsuccessful attempts were made to prepare II using the usual methods for the preparation of urethanes. The method of Kogon[4] for the preparation of allophanates was successfully used to prepare II in good yield. The melting point of II was dependent on the rate of heating; melting was accompanied by decomposition and resolidification took place upon further heating. Pyrolysis of II at 170° (below 1 mm.) yielded 1-naphthyl isocyanate. No other product of the pyrolysis (which might include the 1-naphthylurethane of I) was isolated.



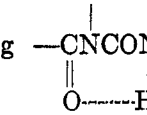
$CH_3\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2OCH_3$

I



II. X = O
III. X = NOH

Single attempts to reduce the keto group of II with either sodium borohydride or lithium tri-*tert*-butoxyaluminohydride and attempted reaction of II with 2,4-dinitrophenylhydrazine or semicarbazide failed to give isolable products. Sodium hypoiodite did not yield a positive iodoform test with II, although a reaction did occur. In contrast, a color test for methyl or methylene ketones[5] was positive for II and reaction between II and hydroxylamine yielded the oxime III.

Substituted allophanates are distinguishable from urethanes in that the latter, but not the former, possess an absorption band in the region of 6750 cm.$^{-1}$, attributable to the first overtone of the NH stretching vibration at 3500 cm.$^{-1}$.[6] In substituted allophanates the band at 6750 cm.$^{-1}$ is replaced by one at 4831–4877 cm.$^{-1}$ which is characteristic of the hydrogen-bonded grouping  $-\underset{\underset{\textstyle O\cdots\cdots}{\|}}{C}\overset{|}{N}CO\underset{\underset{\textstyle H}{|}}{N}-$ in these compounds.[6] The near infrared spectrum of II in benzene shows a strong band at 4819 cm.$^{-1}$ but absorption in the 6667–7042-cm.$^{-1}$ region is lacking.

The infrared spectrum of II obtained at high resolution possesses twin absorptions at 1725 and 1734 cm.$^{-1}$, which may be assigned to the two allophanate C=O groups.[4] A third band at 1701 cm.$^{-1}$ is probably due to the keto C=O absorption.[7] In the oxime III the characteristic allophanate C=O bands are well resolved peaks at 1727 and 1733 cm.$^{-1}$. A band at 1690 cm.$^{-1}$ may be assigned to the C=N vibration of the oxime.[8]

All the above evidence is in good agreement with the structures postulated for II and III.

Experimental[9]

3-Hydroxymethyl-3-methoxymethyl-2-butanone (I) was prepared according to the procedure of Tieman and Gold.[2]

(2-Methoxymethyl-2-methyl-3-oxo)butyl 2,4-bis(1-naphthyl)allophanate (II) was prepared essentially according to the procedure of Kogon.[4] A mixture of 8.7 g. (0.06 mole) of the alcohol I and 60.8 g. (0.36 mole) of 1-naphthyl isocyanate (protected by a calcium chloride tube) was heated in an oil bath at 130° for 24 hr. Distillation of the reaction mix-

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture. Mention of trade names and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

[2] C. H. Tieman and M. H. Gold, *J. Org. Chem.*, **23**, 1856 (1958).

[3] Tieman and Gold erroneously reported the formula $C_{28}H_{26}N_2O_5$; their actual analysis is correct for $C_{29}H_{28}N_2O_5$.

[4] I. C. Kogon, *J. Am. Chem. Soc.*, **78**, 4911 (1956).

[5] F. Feigl, "Spot Tests in Organic Analysis," 6th English ed., Elsevier Publishing Co., New York, 1960, p. 236.

[6] I. C. Kogon, *J. Am. Chem. Soc.*, **79**, 2253 (1957).

[7] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, 1958, p. 132.

[8] Ref. 7, p. 268.

[9] Melting points and boiling points are uncorrected. Infrared spectra were obtained from potassium bromide disks with the Perkin-Elmer spectrophotometers, Models 21 and 221. Near infrared spectra were obtained in benzene solution with the Cary Model 14 spectrophotometer.