material was stored at −20° for periods not longer than one month before use.

Hexachlorocyclopentadiene was received as a sample from Hooker Electrochemical Company (C-56) and was used as such.

5-Methylenebicyclo[2.2.1]-2-heptene (I). A 2960 ml. stainless steel autoclave was cooled to −78° while purging with dry nitrogen and was then charged with 330 g. (5.0 mol.) cyclopentadiene and 200 g. (5.0 mol.) allene (determined by passage through a calibrated flow meter). The autoclave was capped, placed in a rocker, and heated to 200° over a 1.25-hr. period. At 200° the autogeneous pressure reached 620 p.s.i. and began dropping. During the next 5 hr. the temperature was maintained between 200 and 230° with a subsequent drop in pressure to 280 p.s.i. (210°). When the autoclave had cooled to room temperature, it was vented (while warming) through a trap at −78° to collect 55.4 g. of unreacted allene. The straw yellow liquid (479.2 g.) in the autoclave was distilled rapidly through a 3-inch tube containing a side arm at a total take off yielding 200.9 g. liquid, b.p. 26–100°/160 mm. This crude product was redistilled through a 10-inch glass spiral column at atmospheric pressure yielding 186 g. (48.6% yield based on allene) I, b.p. 115–120°, n_D^{25} 1.4834–1.4840. A heart cut, b.p. 73.0°/172 mm., n_D^{25} 1.4838, n_D^{20} 1.4860, d_4^{20} 0.889, from the redistillation of combined I from several runs was used for analyses. The infrared spectrum showed principal bands at 5.72, 6.03, 6.38, 11.44, 13.8, and 14.6 μ. Mass spectroscopy analyses support the structure of I.

Anal. Calcd. for C_8H_{10}: C, 90.6; H, 9.4. Found: C, 90.5; H, 9.5.

Mol. refr. calcd.: 33.8. Found 34.1. Mol. wt. calcd.: 106.2. Found (ebulioscopic): 114.

A sample of I, b.p. 73.0/160 mm., absorbed 4 equivalents of hydrogen in 4 hr. at 175–185° and 1500 p.s.i. over Harshaw 0104 Ni/Kieselguhr catalyst. Distillation gave a 95% yield of 2-methylbicyclo[2.2.1]heptane,[7] b.p. 124.5–125.0°, n_D^{25} 1.4516, n_D^{20} 1.4541.

1,2,3,4,4a,5,8,8a-Octahydro-2-methylene-1,4,5,8-dimethanonaphthalene (II). The residues from the rapid distillation and from the redistillation above were combined and distilled through a 10-inch glass spiral column yielding 74.8 g. (12.1% yield based on allene) II, b.p. 92–98°/7.0 mm., n_D^{25} 1.5312–1.5330, d_4^{20} 1.020. A heart cut, b.p. 92.0°/6 mm., n_D^{25} 1.5319, n_D^{20} 1.5338, d_4^{20} 1.012, from redistillation of combined II from several runs was used for analyses. The infrared spectrum showed principal bands at 5.72, 6.03, 6.38, 11.44, 13.2, and 13.6 μ.

Anal. Calcd. for $C_{13}H_{16}$: C, 90.6; H, 9.3. Found: C, 90.10; H, 9.88.

Mol. refr. calcd.: 52.5. Found: 52.8. Mol. wt. calcd.: 172. Found: 170.

1,2,3,4,4a,5,5a,6,9,9a,10,10a-Dodecahydro-2-methylene-1,4,5,10,6,9-trimethanoanthracene (III). Continued distillation of the above residues at reduced pressure yielded 10.9 g. (9.3% yield based on allene) III, b.p. 71–76°/0.07 mm., n_D^{25} 1.5444. A heart cut, b.p. 74.5°/0.07 mm., n_D^{25} 1.5442, n_D^{20} 1.5463, d_4^{20} 1.048, was used for analyses. The infrared spectrum of III showed principal bands at 5.72, 6.03, 6.38, 11.44, 13.29, and 13.4 μ.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.71; H, 9.33. Found: C, 90.0; H, 8.6. Mol. ref. calcd.: 71.6. Found: 71.9. Mol. wt. calcd.: 238.0. Found: 218.

Polymer. The 31.5 g. of residue from the above distillation cooled to a hard glass which was dissolved in 100 ml. boiling benzene. The cooled solution was slowly poured into 3 l. of methanol and the resulting brown precipitate was filtered, mixed with 300 ml. methanol, beaten 1 min. in a Waring blendor, filtered, and air dried 3 days yielding 30 g. (15.0% yield based on allene) of cream colored powder. This polymer softened at 81° and melted at 162–165°.

Anal. Calcd. for $(C_6H_8)_n$: C, 90.0; H, 10.0. Found: C, 86.5; H, 9.2. Mol. wt. calcd. for n = 11.5: 920. Found: 903 ± 1%. % Unsatn. calcd. for $(C_6H_8)_{11.5}$: 30. Found (Bromination): 29.

The infrared spectrum of a Nujol mull of this polymer has bands at 6.04, 11.45, and 12.57 μ.

1,2,3,4,7,7-Hexachloro-5-methylenebicyclo[2.2.1]-2-heptene (VI). A 2960 ml. stainless steel autoclave was charged as above with 1173.8 g. (4.3 mol.) hexachlorocyclopentadiene (V) and 208.7 g. (5.2 mol.) allene. After capping and placing in a rocker, the autoclave was heated to 150° while rocking. At 150° the autogeneous pressure reached 245 p.s.i. and remained constant during the next 6 min. while the temperature continued to rise to 176° without external heating. The heat of reaction produced a maximum rise in temperature to 200° while the pressure dropped to 190 p.s.i. over the next 23 min. The temperature then began dropping. Over a 2.25-hr. period the temperature had risen from 150° to a maximum 200° and dropped to 170° while the pressure dropped from 245 p.s.i. to a constant 150 p.s.i. After the autoclave had cooled to room temperature it was vented through a trap (−78°) yielding 7.8 g. allene. Gaseous hydrogen chloride was also liberated during venting. The black liquid (1347.1 g.) remaining in the autoclave was subjected to reduced pressure for 1 hr. to remove absorbed hydrogen chloride. Rapid distillation of the residual liquid through a 4-inch Vigreaux column yielded 1098.7 g. yellow liquid, b.p. 74 (0.5 mm.) −80° (0.08 mm.), and 185 g. black charred residue. Redistillation of the 1098.7 g. of distillate through a 24-inch glass helices packed column yielded 1021.9 g. (76% yield based on hexachlorocyclopentadiene charged) VI, b.p. 72° (0.08 mm.) −85° (0.25 mm.), n_D^{25} 1.5590. A heart cut, b.p. 90°/0.3 mm., n_D^{25} 1.5592, n_D^{20} 1.5611, d_4^{20} 1.605, was used for analyses. Infrared spectrum showed principal bands at 6.02, 6.23, 10.95, 13.5, 13.8, and 15.38 μ.

Anal. Calcd. for $C_7H_4Cl_6$: C, 30.73; H, 1.29; Cl, 68.0. Found: C, 30.44; H, 1.66; Cl, 67.97. Mol. refr. calcd.: 63.0. Found: 63.0. Mol. wt. calcd.: 312.9. Found: 326.

Acknowledgment. We wish to acknowledge the able assistance of Mr. W. D. Beck in carrying out several of the autoclave reactions and Mr. D. H. Wolfe for his help in hydrogenating one of the products.

ORGANIC PROCESS DEVELOPMENT LABORATORY
THE DOW CHEMICAL COMPANY
FREEPORT, TEXAS

(7) These properties agree with the values, b.p. 126.9–127.3° and n_D^{20} 1.4540, reported by G. Calingaert, H. Soross, and H. Shapiro, *Ind. Eng. Chem.*, **36**, 1055 (1944).

The Chemistry of β-Bromopropionyl Isocyanate. II. Use in Identification of Alcohols[1]

HARRY W. JOHNSON, JR., HENRY A. KREYSSLER, AND HOWARD L. NEEDLES

Received August 24, 1959

The reaction of β-bromopropionyl isocyanate (I) with alcohols has been examined to determine the utility of I in making solid urethanes for the

(1) Supported in part by grant G 7850 from the National Science Foundation under the Undergraduate Research Participation Program.

identification of alcohols. It has been found useful for this purpose.

Solid β-bromopropionylcarbamates ($BrCH_2CH_2CONHCO_2R$) were obtained from the reaction of compound I with most common alcohols: *e.g.*, methyl, *i*-propyl, *t*-butyl, propargyl, and allyl alcohols; benzohydrol and triphenylcarbinol; and several glycols. Long chain alcohols (cetyl and stearyl) and cholesterol formed solid urethanes without difficulty; the β-bromopropionylcarbamates appear to be among the most easily obtained derivatives of the long chain alcohols. The most important difficulty with compound I was the tendency of some secondary alcohols to form oils (in Table I, those alcohols which formed oils instead of solid urethanes are noted). Glycerol did not appear to react with compound I, apparently because of immiscibility with the chloroform solvent.

Compound I offers two advantages over the more conventional aryl isocyanates. First, it may be prepared as needed from the stable, easily stored *N*-bromosuccinimide.[2] Compound I is not isolated from the rearrangement; the alcohol is added to the solution in which the rearrangement was conducted. Secondly, the reaction product of compound I with water is β-bromopropionamide,[2,3] which can be removed in most instances by crystallization.[4] Thus terpin hydrate and pinacol hydrate gave normal diurethanes without removel of the water of hydration. 95% Ethanol also gave a satisfactory derivative. With the more soluble derivatives, particularly those of secondary alcohols, better results were obtained with dry alcohols. Compound I is more reactive than the aryl isocyanates, and forms carbamates with even the longer chain alcohols very rapidly. A study of quantitative differences in reactivity will be undertaken shortly.

The usual range of melting points is encountered with the β-bromopropionylcarbamates. Some have melting points too near to be of value in differentiation; the long chain urethanes are particularly poor in this respect.[5]

Reasonable care should be exercised in the use of compound I. Although it did not appear to be more toxic than phenyl or α-naphthyl isocyanates, 10% solutions of compound I in chloroform did produce rashes when allowed to come into contact with skin. No investigation of the toxicity of compound I or its derivatives was undertaken.

TABLE I. TABLE OF DERIVATIVES

Alcohol[a]	M.P. of β-Bromo-[b] propionylcarbamate, °C.	Nitrogen, %[c] Calcd.	Found
Methyl	137–139	[d]	
Ethyl	111–113	6.25	6.49[e]
n-Propyl	95–97	5.89	6.37
iso-Propyl	103–104	5.89	5.92
n-Butyl	90–92[f]	5.57	5.38[e]
iso-Butyl	80–82	5.57	5.61[e]
sec-Butyl	Oil		
tert-Butyl	97–99	5.57	5.18[e]
n-Amyl	81–83[f]	5.27	5.18[e]
2-Pentanol	85–87	5.27	4.96[e]
3-Pentanol	Oil		
iso-Amyl	87–88	5.27	5.03[e]
tert-Amyl	101–103	5.27	5.44[e]
n-Hexyl	72–74	5.01	4.60
n-Heptyl	75–77	4.77	4.37[e]
2-Octanol	Oil		
n-Decyl	86–88	4.17	4.46
n-Dodecyl	87–89	3.85	3.95
n-Tetradecyl	92–93	3.57	3.23
Cetyl	92–94[f]	3.34	3.53
Stearyl	97–98	3.12	2.76
Allyl	99–100	5.94	5.77
Propargyl	117–118	5.99	6.36
Cyclohexyl	82–84	5.04	5.44
Benzyl	125–127	4.91	5.24
p-Methoxybenzyl	113–115	4.44	4.24[e]
α-Phenylethyl	Oil		
β-Phenylethyl	86–88	4.67	4.71
γ-Phenylpropyl	76–77	4.47	4.33
β-Chloroethyl	125–127	5.45	5.49
β-Hydroxypropionitrile	152–154	11.37	11.62
Cinnamyl	132–133	4.49	4.19[e]
Cholesterol	238–240 (sl. dec.)[g]	2.49	2.76[e]
Terpin hydrate	162–163[g]	5.14	4.78
Furfuryl[h]	123–127 (dec.)		
Tetrahydrofurfuryl	96–98	5.08	4.68
2-Ethoxyethyl	90–92[f]	5.23	4.88[e]
Ethylene glycol	162–163	6.72	6.65
Diethylene glycol	162–164[g]	6.07	5.77
Isoborneol	122–124	4.19	3.82[e]
Benzohydrol	137–139	3.89	3.85
Triphenyl carbinol	82–84	2.94	3.20
Diacetone alcohol	109–110[f]	4.86	4.99[e]
Pinacol hydrate	200–201	5.98	5.62
meso-2,3-Butanediol	128–130	6.28	6.31[e]
1,1,1-Trichloro-2-2-methyl-2-propanol	137–138	3.94	4.29
1-Methoxy-2-propanol	102–104	5.23	5.33
2-Methoxyethanol	95–97	5.52	5.58
3-Hydroxy-2-butanone	105–107	5.26	5.49[e]
Geraniol	65–67	4.22	3.90[e]
Benzoin	135–137	3.59	3.25
2,2-Dimethylpropanediol	170–172	6.09	5.72[e]

[a] Alcohols were obtained from commercial sources and were used as obtained. [b] Melting points were measured on a Fischer-Johns block and were not corrected. [c] Dumas nitrogen by C. F. Geiger, 312 Yale St., Ontario, Calif. [d] Calcd. for $C_5H_8O_3NBr$: C, 28.60; H, 3.84; N, 6.67; Br, 38.05. Found: C, 28.7; H, 3.8; N, 6.5; Br, 38.0. Analyses by Analytical Laboratories, The Dow Chemical Co., Midland, Mich. [e] Determined by authors using Kjeldahl method. [f] Crystallized from benzene. [g] Crystallized from tetrahydrofuran. [h] Decomposed on standing at room temperature. No analysis performed.

(2) H. W. Johnson, Jr., and D. E. Bublitz, *J. Am. Chem. Soc.*, **80**, 3150 (1958).

(3) J. C. Martin and P. D. Bartlett, *J. Am. Chem. Soc.*, **79**, 2533 (1957).

(4) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Identification of Organic Compounds*, 4th ed., John Wiley & Sons, New York, N. Y., 1956, p. 207.

(5) See the melting points of the phenylurethanes and α-naphthylurethanes of lauryl, myristyl, and cetyl alcohols in ref. 4, p. 282, for other examples of similar behavior in this series.

EXPERIMENTAL

β-Bromopropionyl isocyanate. The rearrangement of *N*-bromosuccinimide was carried out as indicated previously.[2] The *N*-bromosuccinimide should be crushed to break up lumps of material for maximum rate. We have carried out the rearrangement on scales which ranged from 0.2 to 50 g. *N*-bromosuccinimide without difficulty.

Reaction of compound I *with alcohols.* In preparative scale reactions a solution of chloroform containing 5 g. of rearranged *N*-bromosuccinimide was allowed to react with 0.7 mol. equivalent of the alcohol. The solution was cooled in an ice bath. If a precipitate appeared, the solution was filtered, and the precipitate was recrystallized from methanol. If the derivative did not precipitate, the solution was evaporated on a steam bath using an air jet. The residue was induced to crystallize with Dry Ice, and the material was recrystallized.

On a smaller scale, 0.5 g. *N*-bromosuccinimide was rearranged in 5 ml. chloroform (dried over calcium chloride), *ca.* 0.5 ml. allyl chloride, and a trace of benzoyl peroxide. The solution was refluxed 30 min. beyond the time required for the *N*-bromosuccinimide to dissolve, and cooled to room temperature. Then 0.2–0.4 ml. of the alcohol was added, and the solution was cooled or evaporated as required. A slight excess of the isocyanate appears desirable to give the most easily crystallized urethanes. With secondary alcohols less trouble was encountered with oils if the reaction mixture were worked up reasonably quickly (less than 2 hr.) rather than allowing the mixture to stand overnight.

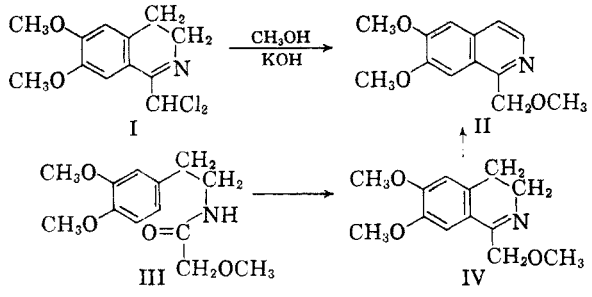
DIVISION OF PHYSICAL SCIENCES
UNIVERSITY OF CALIFORNIA
RIVERSIDE, CALIF.

A New Base-Catalyzed Aromatization Reaction[1]

DIETER PAWELLEK AND C. K. BRADSHER

Received August 18, 1959

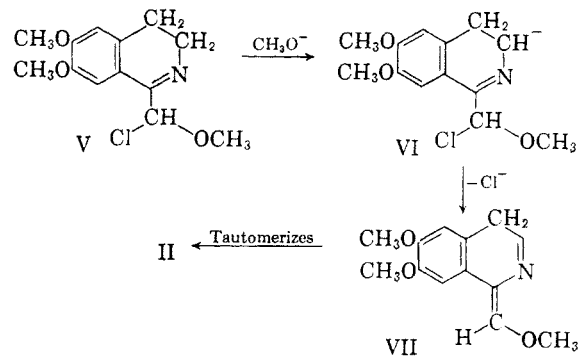
We have had occasion to study the effect of 5% methanolic potassium hydroxide solution on 1-dichloromethyl-6, 7-dimethoxy-3, 4-dihydroisoquinoline (I). The crystalline product, obtained in excellent yield, was shown to be halogen-free, and the infrared absorption spectrum was without significant absorption in the 5.83–5.90 region (aromatic aldehyde). The composition of the new compound did not correspond with that of a simple



acetal, but gave best agreement with the empirical formula $C_{13}H_{15}NO_3$.

Of the compounds which could have the observed composition the previously unknown 1-methoxymethyl-6,7-dimethoxyisoquinoline (II) appeared most likely, and an unequivocal synthesis was undertaken *via* the Bischler-Napieralski cyclization of *N*-homoveratrylmethoxyacetamide (III). Dehydrogenation of the cyclization product (IV) yielded 1 - methoxymethyl - 6,7 - dimethoxyisoquinoline identical in every respect with the product obtained by the action of methanolic potassium hydroxide on 1-dichloromethyl-6,7-dimethoxy-3,4-dihydroisoquinoline (I).

Since this type of aromatization reaction does not appear to have been reported before, speculation concerning a possible mechanism is in order. A logical sequence of events would involve a simple



nucleophilic displacement of chlorine by methoxide ion to yield V. This would be followed by the abstraction of a proton to yield some of the anion (VI). The loss of a chloride ion from anion VI would, through the sequential shift of electrons lead to structure VII, which would be expected to tautomerize to 1-methoxymethyl-6,7-dimethoxyisoquinoline (II).

The new aromatization reaction occurs in 80–94% yield and is thus of preparative as well as theoretical interest.

EXPERIMENTAL[2]

1-Dichloromethyl-6,7-dimethoxy-3,4-dihydroisoquinoline (I). A mixture containing 12 g. of *N*-homoveratryl-1,1-dichloroacetamide,[3] 100 ml. of dry toluene and 30 ml. of phosphorus oxychloride was refluxed for about 2 hr. when the majority of the solvent was removed under vacuum and the residue carefully decomposed with water and dilute hydrochloride acid. After the acidic solution had been extracted with ether to remove any neutral material, the aqueous solution was made basic and the dihydroquinoline derivative extracted with ether or benzene. The product afforded 7.0 g. (64%) of colorless plates from ligroin, m.p. 90–90.5°. A dilute hydrochloric acid solution of the product was not fluorescent.

Anal. Calcd. for $C_{12}H_{13}Cl_2NO_2$: N, 5.13; Cl, 25.65. Found: N, 5.22; Cl, 25.80.

(1) This research was supported by a research grant (H-2170) from The National Heart Institute of The National Institutes of Health.

(2) Except as noted all melting points were determined on the Fisher-Johns block and are uncorrected. The analyses were carried out by Drs. Weiler and Strauss, Oxford, England.

(3) A. P. Phillips, *J. Am. Chem. Soc.*, **74**, 6125 (1952).