and melted at 199–201°. One recrystallization from methanol raised the melting point to 207–208°.

Anal. Calcd. for $C_{12}H_{15}Cl_5INS$: C, 28.28; H, 2.96; N, 2.75. Found: C, 28.58; H, 2.97; N, 2.55.

(o-Bromobenzyl)dimethyl[3-(pentachlorophenylthio)propyl]-ammonium bromide. To 0.05 mole of 3-dimethylaminopropyl pentachlorophenyl sulfide in 100 ml. of acetone was added 12.5 g. (0.05 mole) of *o*-bromobenzyl bromide.[2] On standing 4 hr. at room temperature, an oil precipitated and solidified. The product was cream-colored and weighed 20 g. (65%), m.p. 181–182°. Two recrystallizations from a mixture of ethanol and 2-propanol did not raise the melting point.

Anal. Calcd. for $C_{18}H_{18}Br_2Cl_5NS$: C, 35.01; H, 2.94; N, 2.27. Found: C, 35.31; H, 3.19; N, 2.23.

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[2] D. F. DeTar and L. A. Carpino, *J. Am. Chem. Soc.*, **78**, 477 (1956).

Synthesis of Benzyl Vinylcarbamate and 3-*O*-Vinylcarbamoyl-D-mannitol Pentanitrate[1]

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After completion of the investigation concerned with the preparation of poly(vinylamine),[2] further amounts of this polymer were desired for study. In the interim, Hart had described a new synthetic route for this material.[3,4] This report is concerned with the preparation of a monomer having potential use in this synthesis and certain anomalous reactions encountered.

In essence, the synthesis involves the application of the Curtius reaction to acryloyl chloride followed by conversion of the vinyl isocyanate (II) obtained to benzyl vinylcarbamate (III). Hart[3,4] has described a three-step process which involves the

$$CH_2{=}CHCOCl \xrightarrow{NaN_3} \underset{I}{CH_2{=}CHCON_3} \qquad (1)$$

$$CH_2{=}CHCON_3 \xrightarrow{Heat} \underset{II}{CH_2{=}CHNCO} \qquad (2)$$

$$CH_2{=}CHNCO \xrightarrow{C_6H_5CH_2OH} \underset{III}{CH_2{=}CHNHCO_2CH_2C_6H_5} \qquad (3)$$

isolation of the intermediate materials. It has been found that this process can be considerably simplified and the isolation of the intermediates eliminated. Thus, acryloyl chloride[5] was converted to the azide by treatment in toluene solution with aqueous sodium azide solution.[3] The acryloyl azide (I) was then heated in the presence of benzyl alcohol to produce the benzyl vinylcarbamate (m.p. 43–44°) in 60% over-all yield from the acryloyl chloride. Lower yields were experienced if attempts were made to isolate the intermediate vinyl isocyanate. Furthermore, if the acryloyl azide solution in toluene was not carefully purified to remove all traces of acid contamination, the expected product was not obtained. In the best method, pyridine was added to the azide decomposition mixture to ensure the absence of acid conditions.

The product obtained in the above process, if the system was contaminated with acid, was dibenzyl ethylidenedicarbamate (IV).

$$RCH(NHCO_2CH_2C_6H_5)_2$$
$$IV.\ R = CH_3$$
$$V.\ R = CH_3CH_2$$

The structure of this new compound was established by direct synthesis from acetaldehyde and benzyl carbamate and by hydrolysis and isolation of derivatives in addition to elemental analysis and molecular weight determination. Dibenzyl ethylidenedicarbamate (IV) also resulted from the acid-catalyzed reaction of benzyl alcohol and vinyl isocyanate (II), from the treatment of benzyl vinylcarbamate (III) with various acids, and from the acid-catalyzed reaction of benzyl carbamate and benzyl vinylcarbamate (III). In this last instance, the yield was higher than could have been due to the benzyl vinylcarbamate alone.

The acid-catalyzed conversion of benzyl vinylcarbamate (III) to dibenzyl ethylidenedicarbamate (IV) probably proceeds by initial cleavage of the reactant to benzyl carbamate and an unidentified fragment. The benzyl carbamate subsequently condenses with the unchanged benzyl vinylcarbamate to afford the product. Martell and Herbst[6] have made similar suggestions about the course of the reaction between benzyl carbamate and aldehydes.

Martell and co-workers,[6,7] in their studies of the condensation of benzyl carbamate with aldehydes, investigated only a single aliphatic aldehyde, isovaleraldehyde. Thus, an attempt was made to explore the generality of the reaction; following the method developed for acetaldehyde, propanal afforded dibenzyl propylidenedicarbamate (V). However, the corresponding derivatives could not be obtained with methanal, butanal, 2-propanone,

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[1] This work was carried out under contract between the Ordnance Corps (DA-33-019-ORD-2025) and The Ohio State University Research Foundation (Project 675). The support of the supervising agency, the Ballistic Research Laboratories of Aberdeen Proving Ground, Md., is gratefully acknowledged.

[2] M. L. Wolfrom and A. Chaney, *J. Org. Chem.*, **26**, 1319 (1961).

[3] R. Hart, *Ind. chim. belge*, **20**, Numéro Special, Vol. 3, 403 (1955).

[4] R. Hart, *Ind. chim. belge*, **23**, 251 (1958).

[5] G. H. Stemple, Jr., R. P. Cross, and P. P. Mariella, *J. Am. Chem. Soc.*, **72**, 2299 (1950).

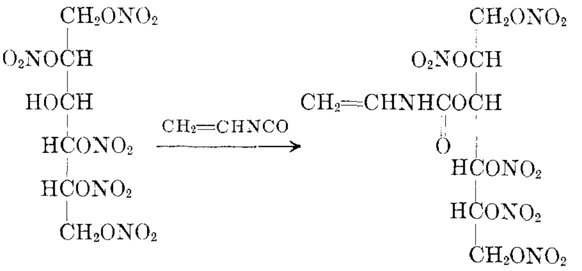
[6] A. E. Martell and R. M. Herbst, *J. Org. Chem.*, **6**, 879 (1941).

[7] T. R. Lewis, Jr., F. R. Butler, and A. E. Martell, *J. Org. Chem.*, **10**, 145 (1945).

or 3-pentanone. No reason for the apparent selectivity of the reaction can be offered.

In part of this study, vinyl isocyanate was isolated by distillation from the decomposing acryloyl azide. The walls of the apparatus became coated with a white solid which was subjected to elemental analysis. Excellent concordance with the expected values for poly(vinyl isocyanate) was obtained. However, the polymer was undoubtedly highly cross-linked and its insolubility prevented further study.

D-Mannitol 1,2,3,5,6-pentanitrate[8] (VI) was found to react with vinyl isocyanate to give crystalline 3-*O*-vinylcarbamoyl-D-mannitol pentanitrate (VII).



VI VII

EXPERIMENTAL

Acryloyl chloride. Following the method of Stemple, Cross, and Mariella,[5] acrylic acid (216 g.) benzoyl chloride (844 g.) and 2 g. of hydroquinone were mixed and distilled (hood) at atmospheric pressure. All the distillate collected below 85° was redistilled through a Snyder column; yield 206 g. (75%), b.p. 71.5–72.0°.

Anal. Calcd. for C_3H_3ClO: C, 39.81; H, 3.34; Cl, 39.17. Found: C, 39.89; H, 3.53; Cl, 39.01.

Acryloyl azide (I). This material was prepared according to the directions of Hart[9] and was not isolated from the resulting toluene solution. Although Hart indicated that the toluene solution should be washed until neutral, the importance of the neutrality cannot be overemphasized. In the current study, the solution was washed with water until the washings failed to give a precipitate on the addition of silver nitrate.

Benzyl vinylcarbamate (III). Acryloyl chloride (55. g.) was converted[9] to the azide (see above) and the toluene solution (150 ml.) was added dropwise to a stirred (under nitrogen) and heated (110°) mixture of benzyl alcohol (76 g.), 3 g. of hydroquinone and 3 g. of pyridine. The solution was stirred at 100° for 30 min. and distilled under reduced pressure; yield 64 g. (60%), b.p. 116–120° (0.1 mm.), m.p. 43–44°.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 68.04; H, 6.31; N, 8.03.

The melting point of this substance was unchanged after crystallization from either ethanol-water or petroleum ether-benzene at low temperatures; purification by distillation appeared preferable.

Dibenzyl ethylidenedicarbamate (IV). Benzyl carbamate (5.0 g.) was dissolved in 50 ml. of paraldehyde; no reaction was noted until 2 drops of 95% sulfuric acid (hydrogen chloride gas or *p*-toluenesulfonic acid will also serve) were added. A white precipitate formed immediately and was recovered after 1 hr. by filtration and washed with ether; yield 4.3 g. (78%), m.p. 207–208° after crystallization from hot ethyl acetate.

Anal. Calcd. for $C_{18}H_{20}N_2O_4$: C, 65.83; H, 6.14; N, 8.53; mol. wt., 328. Found: C, 65.78; H, 6.19; N, 8.52; mol wt., 311 (Rast) and 344 (ebullioscopic, chloroform).

If the acryloyl azide toluene solution employed for the synthesis of benzyl vinylcarbamate was not completely free of acid or if the neutral solution was treated with trace amounts of either hydrochloric acid or acryloyl chloride, dibenzyl ethylidenedicarbamate was the only isolable product.

Benzyl vinylcarbamate (III, 10 g.), dissolved in ethanol, diethyl ether, or benzyl alcohol, afforded dibenzyl ethylidenedicarbamate (IV) on treatment of the solution with either gaseous hydrogen chloride, *p*-toluenesulfonic or sulfuric acids; yield 5–6 g. in some ten trials under the varying conditions. If half the benzyl vinylcarbamate was replaced by benzyl carbamate, yields of 6.5–7.0 g. were obtained. Efforts to recover two-carbon fragments from these reactions were not fruitful.

Dibenzyl ethylidenedicarbamate (1.94 g.) was stirred with 250 ml. of 0.1999*N* sulfuric acid at 100°. The ammonia formed by the hydrolysis was determined by subsequent titration of the mixture with standard alkali; yield 0.17 g. (85%). The acetaldehyde generated was swept into a solution of 2,4-dinitrophenylhydrazine in 95% ethanol with a stream of nitrogen. The solid formed was collected by filtration; yield 0.85 g. (65%), m.p. 163–165° after crystallization from ethanol; melting point undepressed on admixture with authentic acetaldehyde 2,4-dinitrophenylhydrazone. The carbon dioxide formed in the hydrolysis was swept into a trap containing standard alkali which was titrated with acid; yield 0.42 g. (81%). The only alternate possible structure is the known[10] dibenzyl ethylenedicarbamate and this is eliminated by its melting point of 165°.

Dibenzyl propylidenedicarbamate (V). A solution of 5.8 g. of propanal and 5.0 g. of benzyl carbamate in 100 ml. of ether was treated with 0.5 ml. of concd. hydrochloric acid and stirred at room temperature. After 20 hr., the crystals were filtered, washed with ether and crystallized from absolute ethanol; yield 5.1 g. (90%), m.p. 174–175° after two additional crystallizations.

Anal. Calcd. for $C_{19}H_{22}N_2O_4$: C, 66.65; H, 6.48; N, 8.18. Found: C, 66.79; H, 6.42; N, 8.21.

In the above procedure, the propanol was replaced by formaldehyde, butanal, acetone, and 3-pentanone; none of these reactants afforded solid products.

Reactions of vinyl isocyanate (II). Vinyl isocyanate was prepared in 72% yield (basis acryloyl chloride) from acryloyl azide (above) following the procedure of Hart.[9]

During the distillation (b.p. 41.5–42.0°) of this material (n_D^{20} 1.4223), the walls of the apparatus in contact with the distilling vapor became coated with a white, solid, polymeric material; the only solvent found was concd. sulfuric acid.

Anal. Calcd. for $(C_3H_3NO)_n$: C, 52.16; H, 4.35; N, 20.28. Found: C, 51.99; H, 4.15; N, 20.03.

Benzyl alcohol (65 g.) containing 2 g. of pyridine was stirred at room temperature while adding 42 g. of vinyl isocyanate dropwise. On cooling overnight at 5°, crystals of benzyl vinylcarbamate (III) formed; yield 105 g. (99%) after washing with petroleum ether. Repetition of this experiment, except that the pyridine was replaced by an equal weight of concd. sulfuric acid, resulted in the formation of dibenzyl ethylidenedicarbamate (IV) as the sole product.

3-O-Vinylcarbamoyl-D-mannitol pentanitrate (VII). A solution of D-mannitol 1,2,3,5,6-pentanitrate[8] (VI, 9.0 g., 22 mmoles) in 100 ml. of acetonitrile containing 2 ml. of

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[8] M. L. Wolfrom, E. P. Swan, K. S. Ennor, and A. Chaney, *J. Am. Chem. Soc.*, **81**, 5701 (1959); L. Hayward, *J. Am. Chem. Soc.*, **73**, 1974 (1951); J. H. Wigner, *Ber.*, **36**, 794 (1903).

[9] R. Hart, *Bull. soc. chim. Belg.*, **65**, 291 (1956).

[10] R. P. Linstead, B. R. Shephard, and B. C. L. Weedon, *J. Chem. Soc.*, 2854 (1951).

pyridine was treated at 0° with 9 g. (130 mmoles) of vinyl isocyanate dissolved in 100 ml. of acetonitrile. The mixture was stirred and allowed to warm to room temperature slowly. After 18 hr., the mixture was concentrated under reduced pressure and the residue was dissolved in warm ethanol. Activated carbon was added and the mixture was filtered. Addition of water to the filtrate afforded an oil which slowly crystallized. After two further crystallizations from ethanol-water, using carbon for decolorization, pure material was obtained; yield 6.4 g. (61%), m.p. 136–137°, $[\alpha]_D^{28}$ +61.6° (*c*, 4.44, acetonitrile).

Anal. Calcd. for $C_9H_{12}N_6O_{17}$: C, 22.70; H, 2.54; N, 17.65. Found: C, 22.71; H, 2.61; N, 17.73.

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1-(β-Hydroxyethyl)-6-methoxy-1,2,3,4-tetrahydroisoquinoline[1]

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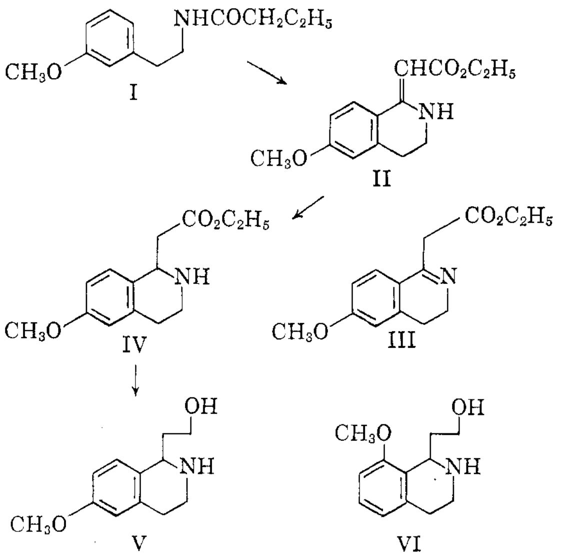
In work directed at the total synthesis of azasteroids, we had occasion to prepare 1-(β-hydroxyethyl)-6-methoxy-1,2,3,4-tetrahydroisoquinoline (V), a substance possessing the A and B rings of an azasteroid nucleus. This note gives the details for the preparation of V and describes spectroscopic data which were used to distinguish alternative structures for the compounds produced.



Treatment of ethyl *N*-*m*-methoxyphenethylmalonamate (I) with phosphorus pentoxide in refluxing toluene[3] gave a noncrystalline red-colored product which resisted purification.[4] The infrared spectrum of the product is not consistent with structure III, which is the usual structure written for the product of a Bischler-Napieralski reaction.[3–6] For example, the spectrum exhibits an absorption band at 3320 cm.$^{-1}$ (presumably N—H stretching)[7] and no appreciable absorption in the range 1660–1800 cm.$^{-1}$ (indicating the absence of a normal ester carbonyl group). Structure II fits the spectral data and is also consistent with the known tendency of a β-imino-carbonyl compound (such as III) to exist in the tautomeric β-amino-α,β-unsaturated carbonyl system.[8]

Hydrogenation of the crude 1-carbethoxymethylene-6-methoxy-1,2,3,4-tetrahydroisoquinoline (II)[3] in acetic acid using Adams catalyst resulted in the absorption of one molecular equivalent of hydrogen and gave ethyl 6-methoxy-1,2,3,4-tetrahydro-1-isoquinolylacetate (IV). This material could be purified by distillation under highly reduced pressure, but ordinarily it was sufficiently pure to be used directly in the next step. Reduction of IV with lithium aluminum hydride yielded the crystalline 1-(β-hydroxyethyl)-6-methoxy-1,2,3,4-tetrahydroisoquinoline (V). The ultraviolet spectrum of V is very similar to that of 6-methoxy-1,2,3,4-tetrahydroisoquinoline,[9] thus demonstrating the point of ring closure in the cyclization of the malonamate I. This result is in accord with the generally accepted fact that the Bischler-Napieralski reaction of *N*-*m*-methoxyphenethylamides results in cyclization at the position *para* to the methoxyl group.[6]

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(1) This investigation was supported in part by research grants, CY-2999 (C1-C3), from the National Cancer Institute, Public Health Service.

(2) Research Laboratories of the Upjohn Company, Kalamazoo, Mich.

(3) Using the procedure of A. R. Battersby, H. T. Openshaw, and H. C. S. Wood, *J. Chem. Soc.*, 2463 (1953).

(4) *Cf.* A. Brossi, H. Lindlar, M. Walter, and O. Schnider, *Helv. Chim. Acta*, **41**, 119 (1958).

(5) J. M. Osbond, *J. Chem. Soc.*, 3464 (1951).

(6) W. M. Whaley and T. R. Govindachari, *Org. Reactions*, **VI**, 74 (1951). These authors also list some examples of products in which the newly created double bond is exocyclic.

(7) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank, and D. J. Wallace [*J. Am. Chem. Soc.*, **71**, 3337 (1949)], have described several *N*-alkyl-β-amino-α,β-unsaturated ketones in which no N—H stretching band was observed in the region of 3300 cm.$^{-1}$ They concluded that this absorption band was probably broadened and shifted to lower frequencies due to strong chelation and was thereby obscured by the C—H absorption bands. In our case this absorption band may be due to a weaker chelated N—H stretching, or the N—H stretching of the *trans* isomer of II. Since the position of absorption does not shift appreciably in going to very dilute solutions (0.01*M*), the former assignment is preferred. Finally, since the product is not crystalline, the possibility that this absorption band is caused by an impurity cannot be excluded.

(8) S. A. Glickman and A. C. Cope, *J. Am. Chem. Soc.*, **67**, 1017 (1945).

(9) Prepared as described by W. M. Whaley and T. R. Govindachari, *Org. Reactions*, **VI**, 172 (1951). The sample had the following physical constants: b.p. 144° (9 mm.); $\lambda_{max}^{C_2H_5OH}$ 221.5 (ϵ 7200), 278.5 (ϵ 2010), and 287 mμ (ϵ 1800) with minima at 246 and 285 mμ.