the Cope[6] procedure or under much more vigorous conditions[7]; the I was usually recovered. This is in sharp contrast to the behavior of the closely related aldehyde IV[5] which quickly gives the normal condensation product with methyl cyanoacetate. Moreover, the 3-piperidone derivative II and the phenylcyclohexanone VI[8] failed to participate in this reaction, giving results similar to those obtained with I. Again in contrast, the bicyclic compound V[8] (somewhat resembling both VI and II in structure) and malononitrile give an excellent yield of the expected product. Concerning the failure of I, II (and the open nitrogen analog of V[8]) to yield Knoevenagel products, it may be pointed out that they contain enolizable carbonyl groups, whereas IV and V, the reactive compounds, cannot enolize. The aldehyde IV would be expected to be markedly more reactive than its methyl ketone counterpart I, although so vast a difference was not foreseen. The bicyclic ketone V, in addition to being nonenolizable (Bredt's rule), also has potentially less hyperconjugative stabilization of the carbonyl than its open nitrogen analog VI and II.

Compound I, structurally similar to methadone, was about 30 times less effective and 5 to 10 times less toxic than methadone when tested in mice. The α-*dl*-IIIa and α-*dl*-IIIb were 30 times less effective than *alpha*-prodine. The β-*dl*-IIIb was twice as active as the α-isomer.[2,9]

EXPERIMENTAL[10]

5-Dimethylamino-3-methyl-3-phenyl-2-pentanone (I)[3] *hydrochloride.* γ-Dimethylamino-α-methyl-α-phenylbutyronitrile (20.5 g., from 26.5 g. of nitrate[5]) in 80 ml. of dry xylene was added rapidly to a stirred solution prepared from 5 g. of magnesium, 50 ml. of ether, and 33.1 g. of methyl iodide. The mixture was distilled (stirring) until the vapor temperature reached 60° (*ca.* 15 min.) then refluxed for an additional 10–15 min. When the magma could no longer be stirred 80 ml. of 20% HCl was added at such a rate as to cause gentle refluxing. Stirring was resumed when possible, and after 30 min. the aqueous phase was basified with concentrated NH_4OH; the liberated base was dried in ether. Evaporation of the ether left 17.5 g. of I[3] (λ_{max}^{smear} 5.85μ)[11] which was redissolved in ether and acidified with 18 ml. of 33% HBr-acetic acid to give 24.3 g. (87%) of I hydrobromide,[3] m.p. 156–159°. Treatment of the I above with ethereal hydrogen chloride gave the hydrochloride, m.p. 159–161°, λ_{max}^{nujol} 5.86μ; needles from acetone.

Anal. Calcd. for $C_{14}H_{22}ClNO$: C, 65.7; H, 8.7. Found: C, 65.6; H, 8.6.

The *picrate* crystallized from alcohol in yellow prisms, m.p. 109–110.5°.

Anal. Calcd. for $C_{20}H_{24}N_4O_8$: C, 53.6; H, 5.4. Found: C, 53.9; H, 5.6.

α-dl-1,4-Dimethyl-4-phenyl-3-piperidinol (IIIa).[4] Platinum oxide (0.1 g.), 2.0 g. of II,[3] and 10 ml. of methanol absorbed one molecular equivalent of hydrogen during 15 min. The filtered solution was evaporated to dryness *in vacuo* to give a syrup which crystallized from acetone in a yield of 1.8 g.; m.p. 198–203°. This mixture of diastereoisomers[12] was dissolved in water and basified with concentrated NH_4OH to give 1.4 g. of the α-IIIa,[13] m.p. 143–145°; needles from acetone, m.p. 145–146.5°.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.1; H, 9.3. Found: C, 75.8; H, 9.1.

The *hydrochloride*, plates from acetone, melted at 211–213.5°.

Anal. Calcd. for $C_{13}H_{20}ClNO$: C, 64.4; H, 8.3. Found: C, 64.4; H, 8.3.

α-dl-1,4-Dimethyl-4-phenyl-3-propionoxypiperidine (IIIb) *hydrochloride.* Propionic anhydride (1.5 ml.), 1.0 g. of the mixture (m.p. 198–203°) of IIIa hydrochlorides, and 2.0 ml. of dry pyridine were kept on the steam bath until solution was complete. Dilution with ether and cooling to 0° gave 1.2 g. of hydrochloride mixture, m.p. 235–245°. It was dissolved in *ca.* 150 ml. of boiling acetone. Concentrating the solution to 40–50 ml. gave, after cooling to 0°, 0.8 g. (65%) of the α-IIIb hydrochloride, m.p. 253–256°; fine needles from 2-propanol, m.p. 257–258.5°.

Anal. Calcd. for $C_{16}H_{24}ClNO_2$: C, 64.5; H, 8.1. Found: C, 64.5; H, 8.0.

Propionylation of 0.2 g. of pure α-*dl*-IIIa hydrochloride gave 80% of α-*dl*-IIIb hydrochloride, m.p. 250–253°.

β-dl-1,4-Dimethyl-4-phenyl-3-propionoxypiperidine (IIIb) *hydrochloride.* The filtrate from the 0.8 g. of α-*dl*-IIIb hydrochloride above was concentrated and diluted with an equal volume of ether to give 0.2 g. of principally plates, m.p. 216–220°. Two recrystallizations from acetone gave 0.1 g. (8%) of pure β-*dl*-IIIb hydrochloride, m.p. 247–250°; oblong plates.

Anal. Calcd. for $C_{16}H_{24}ClNO_2$: C, 64.5; H, 8.1. Found: C, 64.4; H, 7.8.

The *picrate*, yellow prisms from acetone, melted at 215–216.5° (dec.).

Anal. Calcd. for $C_{22}H_{26}N_4O_9$: C, 53.9; H, 5.4. Found: C, 54.1; H, 5.2.

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(6) A. C. Cope and E. M. Hancock, *Org. Syntheses*, **25**, 46 (1945).

(7) For example boiling xylene as the medium. Sodamide in boiling xylene was also used.

(8) E. L. May and J. G. Murphy, *J. Org. Chem.*, **19**, 618 (1954).

(9) N. B. Eddy, personal communication.

(10) Melting points are corrected (Hershberg apparatus); microanalyses are from the Institutes' service analytical laboratory, under Dr. William C. Alford's direction.

(11) There was also very slight absorption at 2.98 μ perhaps indicating the presence of a small amount of enol tautomer.

(12) By recrystallizing this mixture from 2-propanol-acetone a low yield of fairly pure α-hydrochloride could be obtained, but separation at this stage did not appear practicable.

(13) No attempt was made to recover the apparently water soluble β base.

Carbamates and Ureas Derived from 4-Methyl-*m*-phenylene Diisocyanate

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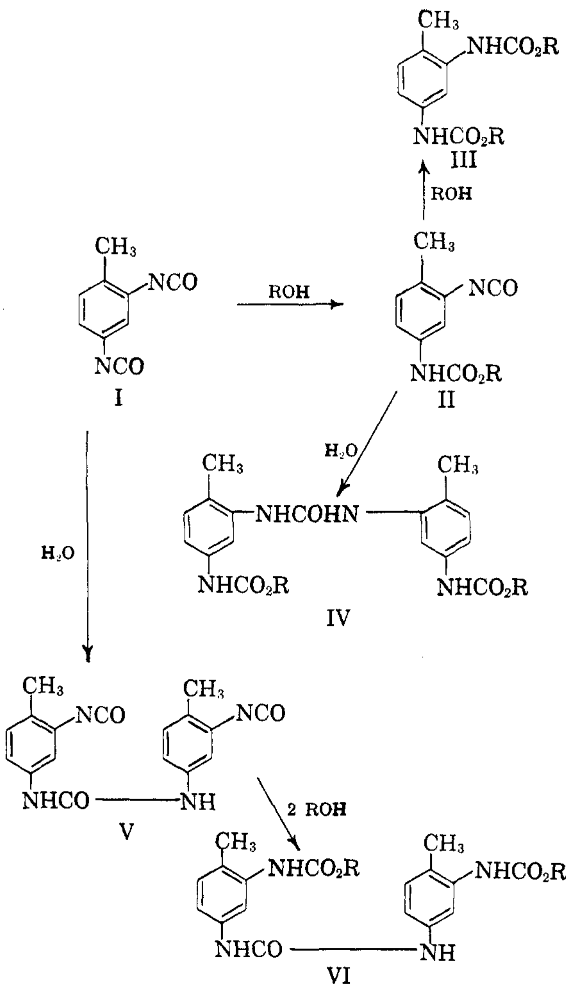
The current interest in polyisocyanates, particularly 4-methyl-*m*-phenylene diisocyanate (I), for use in the preparation of useful high molecular weight polymers has presented a need for model compounds with which to study the reactions of this particular diisocyanate. In this laboratory, model compounds which represent a wide range of polymer end groups have been prepared. The preparation of these compounds is part of a program designed to study systematically the polymerization and cross-linking mechanism of polyisocyanates.

It has been postulated[1,2] and later proven[3,4] that alkyl or alkoxy groups *ortho*- to an isocyanate exert a rate-retarding effect. This effect was proved[3] by the reaction of equimolar amounts of 4-methyl-*m*-phenylene diisocyanate and aniline followed by hydrolysis of the remaining isocyanate group. This reaction yielded 68% of theory of 3-amino-4-methyl carbanilide, proving the greater reactivity of the *p*-isocyanate group. Infrared spectroscopic studies[4] have also shown the difference in reactivity of the two isocyanate groups. We have taken advantage of this difference in reactivity to prepare carbanilates (II) having free isocyanate groups in the *o*-position.

Dicarbamates (III) of 4-methyl-*m*-phenylene diisocyanate have already been reported[5] with yields that are practically quantitative, some of these were repeated and some new ones are presented here.

The 3-isocyanato-4-methyl carbanilates have been prepared by adding equimolar amounts of the alcohol to the diisocyanate slowly, using the utmost care to exclude moisture. Purification is made difficult by a small amount of dicarbamate formed by these reactions accounting for the discrepancies in some of the carbon, hydrogen analysis; however, the proof of structure lies in the formation of the corresponding ureas by the reaction of water with the carbanilates. Further proof is given by reversing the procedure, reacting water first with the isocyanate followed by the alcohol which yields an entirely different set of ureas as shown in the diagram.



EXPERIMENTAL

Materials. The 4-methyl-*m*-phenylene diisocyanate was obtained from National Aniline and used without further purification. Commercial alcohols were dried by conventional techniques and distilled, except the hexadecyl alcohol which was purified by recrystallization from petroleum ether. The petroleum ether was ACS grade (b.p. range 36.5°-38°C.) stored over sodium and used without further purification.

Preparation of 3-isocyanato-4-methyl carbanilates. Methyl-3-isocyanato-4-methyl carbanilate represents a typical case and will be used to illustrate the method. A mixture of two drops of pyridine[6] and 0.20 mole of anhydrous methanol was added dropwise with stirring to a solution of 0.2 mole of I in 50 ml. of anhydrous petroleum ether at a rate sufficient to cause gentle refluxing of the solvent. The reaction was allowed to stand for an additional 4 hr. with moderate stirring.

The flask was then cooled to room temperature and the methyl-3-isocyanato-4-methyl carbanilate filtered, washed with anhydrous petroleum ether, dried in a vacuum desiccator, and purified by recrystallization from hot 1:1 hexane-cyclohexane. The product was converted to the urea by dissolving 0.05 mole of I in 50 ml. of acetone and 0.1 mole of water. Two drops of pyridine were added to catalyze the reaction which was allowed to reflux slowly with stirring for 8 hr. The urea which precipitated from the reaction was filtered, washed with additional acetone, and dried under vacuum.

The butyl-3-isocyanato-4-methyl carbanilate, a liquid at room temperature, was purified by molecular distillation in a Hickman pot still with a bath temperature of 90 ± 5°C. and at a pressure of 0.002 mm. The product boils at 144°C./0.2 mm. with decomposition and could not be distilled by simple techniques. Recrystallization at lower temperatures (about 0°C.) invariably led to contamination with moisture and the resultant production of urea.

Preparation of 3,3'-diisocyanato-4,4'-dimethylcarbanilide. (V). To a solution of 0.050 mole of I in 200 ml. of stirred anhydrous diethyl ether a mixture of 0.024 mole of water, 50 ml. of anhydrous ether and 0.5 ml. of pyridine was added slowly with no external heating. The urea precipitated as a fine powder. After the addition of the water, the reaction was allowed to stand with stirring for an additional 0.5 hr. The product was filtered, washed several times with 1:1

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(1) O. Bayer, *Angew. Chem.*, **59**, 257 (1947).

(2) W. Siefken, *Ann.*, **562**, 75 (1949).

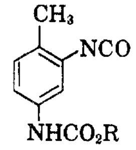
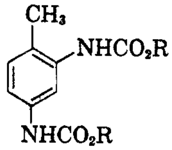
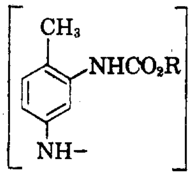
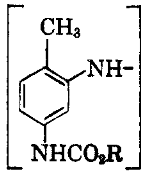
(3) D. M. Simons and R. G. Arnold, *J. Am. Chem. Soc.*, **78**, 1658 (1956).

(4) M. E. Bailey, V. Kirss, R. G. Spaunburgh, *Ind. Eng. Chem.*, **48**, 796 (1956).

(5) N. G. Gaylord and J. J. O'Brien, *Rec. trav. chim.*, **74** 218 (1955).

(6) Pyridine is used as a catalyst to prevent the induction period normally experienced with an autocatalyzed reaction. If a catalyst is not used, there is an induction period followed by a vigorous exothermic reaction which increases the temperature, causing side reactions to occur.

TABLE I

Compound		R	Carbon		Hydrogen		Nitrogen			
			Calcd.	Found	Calcd.	Found	Calcd.	Found	M.P., °C.	Yield, %
II		Methyl	58.23	57.82	4.88	5.18	13.58	13.65	94–96	79
		Ethyl	60.05	60.28	5.49	5.71	12.75	12.91	51–59	85
		Butyl	62.88	63.78	6.49	6.55	11.28	11.35	144/0.2 mm.	70
		Octyl	67.06	67.38	7.94	7.67	9.20	9.47	40–42	69
		Hexadecyl	72.08	72.87	9.67	9.78	6.72	6.60	70.5–73.5	87
III		Methyl[5]							170–171	99
		Ethyl[5]							136	97
		Butyl	63.33	63.57	8.12	7.99	8.68	8.81	80	96
		Octyl	69.09	69.13	9.74	8.93	6.44	6.40	69	96
		Hexadecyl	74.72	73.60	11.32	10.60	4.25	4.47	95–96	97
VI		Methyl	61.46	59.71	5.74	5.91	14.50	14.00	201–204	89
		Ethyl	60.85	61.30	6.32	6.35	13.52	13.60	197–198	68
		Butyl	63.80	63.94	7.28	7.05	11.91	12.16	152–154	82
		Octyl	68.01	67.68	8.65	7.77	9.61	9.26	131–132	75
		Hexadecyl	72.91	71.05	10.24	9.27	6.94	7.24	124–125	62
IV		Methyl	61.46	61.52	5.74	5.23	14.50	14.81	239–240	91
		Ethyl	60.85	60.87	6.32	6.33	13.52	13.63	206–207	82
		Butyl	63.80	62.74	7.28	7.15	11.91	12.05	186	90
		Octyl	68.01	68.24	8.65	8.50	9.61	10.03	180	85
		Hexadecyl	72.91	72.80	10.24	10.40	6.94	6.77	173.5–174	41

anhydrous petroleum ether–diethyl ether, and dried in a vacuum desiccator.

The product, after drying, was pulverized in a mortar and washed again with diethyl ether, petroleum ether, and dried in a vacuum oven at 50°C. The infrared spectrum was identical with that of a commercial sample prepared by du Pont under the trade name Hylene T. U., melting range[7] 172–178°C. Melting point of the product, 172–175°C.

The reaction of methanol with V to yield the corresponding urea-carbamate was carried out by weighing 0.05 moles Compound V into a 100 ml. three-neck flask followed by the addition of 0.10 mole methanol, 0.5 ml. of pyridine, and 50 ml. of chloroform. The reaction was allowed to reflux for 16 hr. with stirring. The unreacted V was removed by filtration and the desired product obtained by evaporating the filtrate under vacuum. The product was pulverized in a mortar and washed several times with acetone.

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Halogen-Containing Silane Monomers

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The work reported herein covers the synthesis of several new halogen-containing silane monomers. These compounds were prepared in connection with a study of silicon elastomers with potential resistance to hydrocarbon solvents. Three approaches were utilized: additions of silicon halides to Grignard reagents, Diels-Alder additions of halogenated dienes to vinyl and allyl silanes, and additions of perhalogenated methanes to vinyl silanes. Table I summarizes the pertinent information for the five new compounds prepared.

The Diels-Alder reaction of vinyltrichlorosilane and of vinyltriethoxysilane with hexachlorocyclopentadiene has been described by Kleiman.[1] Tarrant[2] has reported the peroxide-catalyzed addition of $CBrCl_3$ to vinyltrichlorosilane and to vinyltrimethylsilane. Lovelace and Rausch[3] have reported

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(7) Hylene, T. U., Pamphlet HR-9, E. I. du Pont de Nemours & Co., Inc., December 1955.

(1) Morton Kleiman, U. S. Patent 2,697,089 (Dec. 14, 1954).

(2) P. Tarrant, WADC Progress Report No. 2 (Aug. 12, 1954), and WADC Progress Report 3 (Oct. 15, 1954). Contract AF 33(600)-26593.

(3) A. M. Lovelace and D. A. Rausch, *Abstracts of 128th Meeting of the American Chemical Society*, Minneapolis, September 1955, p. 40.