cause one of the C–O bonds to break. The resultant radical is in a favorable position to form Thiodan ether with expulsion of another radical which decomposes to sulfur dioxide and the original radical.

A similar mechanism could result if the radical attacked an oxygen atom.

Except upon the rare occasions when two radicals combine, other collisions of a radical with a Thiodan molecule can result in a chlorine radical, a hydrogen radical, or a radical in which the odd electron is attached to a carbon in the Thiodan molecule. The radicals should, therefore, have high efficiency in the production of Thiodan ether, for other types of radical decompositions would not readily occur, although radical transfers may be frequent, and radical rearrangements can occur.

The $G(-M)$ values were calculated for each sample, when this was possible, and are shown in Table I. Although most of the values are not far apart, the values for sample 8A are considerably larger than the others. This result may be due to the fact that β-rays and volatile free radicals can escape less easily from a large compact mass of matter than from smaller pieces. Samples 6A, 7, and 8A were solid lumps of 2.3, 14, and 31 g., respectively; samples 6B and 8B were loose crystals, 0.6 and 0.13 g., respectively.

Experimental

Recrystallization of Radio-Thiodan.—A 30-g. sample of radio-Thiodan, 0.95 μc./mg., 119 weeks after preparation, consisted of 23% Thiodan ether, 53% lower melting Thiodan isomer, 21% higher melting Thiodan isomer, and 3% Thiodan alcohol. The sample was recrystallized from 150 ml. of hexane. Infrared spectra showed that the first fraction was mostly higher melting Thiodan isomer with some Thiodan ether present and the three subsequent fractions were largely lower melting Thiodan isomer with diminishing amounts of Thiodan ether. Recrystallization of the third fraction from hexane gave as the first crop 1.7 g. with 11% Thiodan ether, 86% lower melting Thiodan isomer, and 3% higher melting Thiodan isomer as shown by gas phase chromatography.

Column Chromatography of Radio-Thiodan.—A 140-g. portion of Florisil[6] activated for 2 hr. at 300° was packed in a chromatographic column, 75 × 2.5 cm. After 500 ml. of hexane had been allowed to pass through the column, 2.0 g. of a fraction of radio-Thiodan from the preceding fractional crystallizations was applied in ethyl ether solution. The chromatogram was developed with hexane containing increasing per cents of ethyl ether.

The second radioactive fraction from the column chromatogram of the higher melting Thiodan isomer showed one peak in the gas phase chromatogram; but the infrared spectrum showed an extraneous weak band at 810 cm.$^{-1}$.

Similar column chromatography of samples of lower melting radio-Thiodan isomer gave, at best, a greater concentration of Thiodan ether in the earlier fractions than in the later ones.

Infrared Spectra.—Infrared spectra were determined with a Baird Model 4-55 apparatus. Samples for qualitative examination were best determined in a potassium bromide pellet, but frequently a film on a sodium chloride flat was used. Quantitative determinations were run in carbon disulfide solution in a 0.5-mm. cell.

The following characteristic bands were used: higher melting Thiodan isomer, 1245 and 840; lower melting Thiodan isomer, 1266 and 862; Thiodan ether, 649 (other bands at 1212, 1053, and 810); Thiodan alcohol, 3280 cm.$^{-1}$. Other bands were used to confirm the presence of the various compounds.

Gas Chromatography.—F & M Model 202 instrument was used with 10 ft. of 0.2-in. o.d. stainless steel tubing packed with 60–80-mesh Chromasorb W containing 20% Dow 11 silicone. The column temperature was 250° with a helium flow of 100 ml. per minute. Samples were injected in chloroform solution. Elution times were as follows: Thiodan ether, 9; lower melting Thiodan isomer, 21; higher melting Thiodan isomer, 32 min. Thiodan alcohol gave two or three unresolved peaks at *ca.* 15.5, 18–20, and 26 min. Peak areas were corrected for thermal response by multiplying with the following factors: Thiodan ether, 1.48; lower melting Thiodan isomer, 1.72; higher melting Thiodan isomer, 1.77.

Acknowledgment.—The authors wish to thank Mr. Arthur Weed and Mr. John Zarembo for doing the gas phase chromatographic work and Mr. Herman Adelman for the determination and interpretation of the infrared spectra. The mechanism for the formation of Thiodan ether evolved as a result of discussions with Professor R. H. Herber of Rutgers University.

Formation and Benzylation of the Dianion of *sym*-Diphenylurea by Potassium Amide in Liquid Ammonia. Results with Related Compounds

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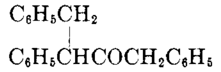
Dibenzyl ketone previously has been converted by two molecular equivalents of potassium amide in liquid ammonia to its dipotassio salt I, which was alkylated in this medium with a molecular equivalent of benzyl chloride to form the monobenzyl derivative (II) in 82% yield.[2] The monopotassio salt of dibenzyl ketone not only underwent benzylation much more slowly under similar conditions, but the dibenzyl derivative as well as II was obtained.[2]

$$C_6H_5\overset{K}{C}HCO\overset{K}{C}HC_6H_5$$

I

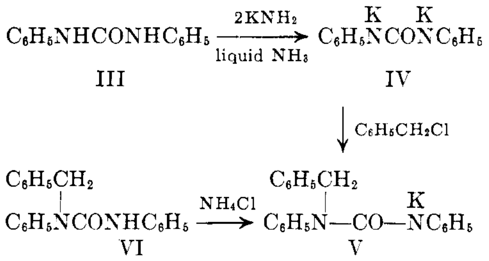


$$C_6H_5\overset{C_6H_5CH_2}{C}HCOCH_2C_6H_5$$

II

In the present investigation *sym*-diphenylurea (III), which may be regarded as a dinitrogen analog of dibenzyl ketone, likewise was converted to its dipotassio salt IV, which was benzylated to give the monobenzyl derivative (VI) in 75% yield (Scheme I). Benzylation of the monopotassio salt of III under similar conditions afforded VI in only 2% yield.

SCHEME I



$$\underset{\text{III}}{C_6H_5NHCONHC_6H_5} \xrightarrow[\text{liquid NH}_3]{2KNH_2} \underset{\text{IV}}{C_6H_5\overset{K}{N}CO\overset{K}{N}C_6H_5} \xrightarrow{C_6H_5CH_2Cl} \underset{\text{V}}{C_6H_5\overset{C_6H_5CH_2}{N}—CO—\overset{K}{N}C_6H_5} \xrightarrow{NH_4Cl} \underset{\text{VI}}{C_6H_5\overset{C_6H_5CH_2}{N}CONHC_6H_5}$$

Structure VI was supported by analysis and by its infrared spectrum which exhibited a band at 2.96 μ, in-

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[1] (a) National Science Foundation Predoctoral Fellow, 1958–1961; (b) National Science Foundation Cooperative Graduate Fellow, 1959–1962.

[2] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **81**, 1154 (1959).

dicating the presence of an N–H group.[3] This band would be absent in the possible dibenzylation product.

Structure VI was confirmed by an independent synthesis from phenyl isocyanate and benzylaniline (eq. 1).[4]

$$C_6H_5N{=}C{=}O \xrightarrow{C_6H_5NHCH_2C_6H_5} VI \qquad (1)$$

It may be concluded that dipotassio salt IV is not only much more nucleophilic than the monopotassio salt of *sym*-diphenylurea, but also much more nucleophilic than monopotassio salt V, since further alkylation of V was not observed under the conditions employed. The greater nucleophilicity of dipotassio salts such as IV and I may be ascribed to a reinforcing effect of each of the negative charges of the dianion on the other in the 1,3-resonance system.[5]

Attempted Benzylation of Other Urea Compounds.—As in the experiment with *sym*-diphenylurea (III), urea, phenylurea, benzoylurea, and acetylurea were each added to two molecular equivalents of potassium amide in liquid ammonia, followed by one equivalent of benzyl chloride. However, in contrast to III, none of these compounds afforded an isolable amount of the benzyl derivative. In the experiment with urea a purple color appeared and stilbene was obtained, but in the other experiments no purple color was observed and no stilbene was isolated. In the experiments with phenylurea, benzoylurea, and acetylurea the starting compounds were recovered. Results are summarized in Table I.

TABLE I

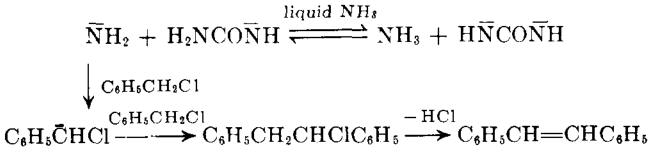
ATTEMPTED BENZYLATION OF CERTAIN UREA COMPOUNDS THROUGH DIANIONS IN LIQUID AMMONIA

Urea compound	Purple color	Stilbene yield, %	Starting compounds recovered: Urea compound, %	Starting compounds recovered: Halide, %
NH_2CONH_2	Yes	40	*a*	30
$C_6H_5NHCONH_2$	No	None	73	50
$C_6H_5CONHCONH_2$	No	None	97	73
$CH_3CONHCONH_2$	No	None	45	*a*

[a] No attempt was made to recover compound.

These results may be rationalized on the basis that the conversions of phenyl-, benzoyl-, and acetylureas to their dianions were essentially complete, whereas the conversion of urea to its dianion was not, and that amide ion in the latter equilibrium effected self-condensation of benzyl chloride to form stilbene (Scheme II).

SCHEME II



$$\bar{N}H_2 + H_2NCO\bar{N}H \overset{\text{liquid }NH_3}{\rightleftharpoons} NH_3 + H\bar{N}CO\bar{N}H$$

$$\downarrow C_6H_5CH_2Cl$$

$$C_6H_5\bar{C}HCl \xrightarrow{C_6H_5CH_2Cl} C_6H_5CH_2CHClC_6H_5 \xrightarrow{-HCl} C_6H_5CH{=}CHC_6H_5$$

It has been shown previously[6] that amide ion in liquid ammonia readily converts benzyl chloride to stilbene and that this reaction is accompanied by the appearance of a purple color like that observed in the experiment with urea (see Table I). However, the possibility that the dianion of urea effects this reaction is not excluded, since this dianion is more strongly basic than those of the other urea compounds listed in Table I. Incidentally, the isolation of dipotassio urea, prepared from urea and potassium amide in liquid ammonia, has been reported, but few details were given.[7]

The failure of the dianion of phenylurea to undergo benzylation (see Table I) may be ascribed to the extreme insolubility of its dipotassio salt in liquid ammonia, since the nucleophilicity of this dianion should be greater than that of diphenylurea which readily undergoes benzylation under similar conditions. However, the failure of the dianions of benzoyl- and acetylureas to undergo benzylation might be due either to insolubility or to lack of sufficient nucleophilicity. The benzylations of the dianion of phenylurea and even the dianions of the acylureas might be accomplished in another solvent.

Experimental[8]

Benzylation of *sym*-Diphenylurea (III) through Dipotassio Salt IV.—To a stirred suspension of 0.1 mole of potassium amide in 500 ml. of commercial anhydrous liquid ammonia[9] was added 10.61 g. (0.05 mole) of finely powdered *sym*-diphenylurea (III) from an erlenmeyer flask through Gooch tubing fitted with a standard taper joint. After stirring for 0.25 hr., the resulting white suspension was assumed to contain 0.05 mole of dipotassio salt IV. Benzyl chloride (6.33 g., 0.05 mole) in 25 ml. of anhydrous ether was added during 5 min. to the stirred suspension of IV; no change in the appearance of the reaction mixture was observed. After stirring for 1 hr., 5.35 g. (0.1 mole) of powdered ammonium chloride was added, and the ammonia evaporated as an equal volume of ether was added. Water (150 ml.) was added to the ethereal suspension to dissolve inorganic salts. The remaining precipitate was collected to give 1.79 g. (17%) of recovered *sym*-diphenylurea (III), m.p. 238–240°.

The aqueous and ethereal layers of the filtrate were shaken and separated. The ethereal phase was washed with 50 ml. of saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The solvent was removed to leave 14.8 g. of a clear, lightly colored oil, which crystallized on addition of 50 ml. of *n*-hexane. The mixture was filtered to give 10.73 g. (71%) of N-benzyl-N,N′-diphenylurea (VI), m.p. 83–85°, and 0.67 g. (4%) of a second crop, m.p. 79–81°. Recrystallization from absolute ethanol–hexane raised the melting point to 84–85.5°, lit.[10] m.p. 85°.

Anal. Calcd. for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.27. Found: C, 79.79; H, 5.99; N, 9.11.

The infrared spectrum of VI exhibited a band at 2.96 μ, indicating the presence of an N–H group.[3]

Independent synthesis of VI[4] was accomplished by addition, during 5 min., of 5.95 g. (0.05 mole) of phenyl isocyanate to a stirred solution of 9.16 g. (0.05 mole) of N-benzylaniline in 25 ml. of anhydrous ether. Most of the ether was removed on the steam bath and 2 drops of 3 *N* hydrochloric acid were added. After heating for 0.5 hr., the viscous oil was dissolved in 75 ml. of 95% ethanol and cooled overnight. The resulting precipitate was collected to give 10.3 g. (68%) of N-benzyl-N,N′-diphenylurea (VI), m.p. 83–85° and 84–86°, after one recrystallization from 95% ethanol. This compound was shown to be identical with VI prepared by the benzylation of dipotassio salt IV by comparison of infrared spectra and by the mixture melting point method.

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[3] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, New York, N. Y., 1958, p. 206.

[4] A. Mailhe, *Bull. soc. chim. France*, [4] 25, 321 (1919).

[5] The resonance forms shown may not make the most important contributions to the structures of the dianons, but they are the most convenient to use for the present purpose.

[6] C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

[7] J. S. Blair, *ibid.*, **48**, 96 (1926); E. C. Franklin and O. F. Stafford, *Am. Chem. J.*, **28**, 83 (1902).

[8] Melting points were taken on a Mel-Temp capillary melting point apparatus. Infrared spectra were determined with a Perkin-Elmer Infracord by the potassium bromide pellet method. Elemental analysis was by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[9] See C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

[10] R. Stolle, *J. prakt. Chem.*, **117**, 185 (1927).

Benzylation of III through Its Monopotassio Salt.—To a stirred suspension of 0.05 mole of potassium amide in 500 ml. of liquid ammonia was added 10.61 g. (0.05 mole) of finely powdered III, followed, after 0.25 hr., by 6.33 g. (0.05 mole) of benzyl chloride in 25 ml. of anhydrous ether. After stirring for 1 hr., the reaction mixture was worked up essentially as described previously to give 0.25 g. (2%) of N-benzyl-N,N'-diphenylurea (VI), m.p. 84–85°, and 9.65 g. (91%) of recovered III, m.p. 243–243.5°.

Attempted Benzylation of Certain Urea Compounds.—In Table I are summarized the results obtained on adding other urea compounds to two molecular equivalents of potassium amide in liquid ammonia, followed by one molecular equivalent of benzyl chloride. These experiments were performed essentially as described previously for that with the dipotassio salt of *sym*-diphenylurea (IV).

The urea compounds remained as precipitates after the water was added to the ethereal suspension of the reaction products, and were collected by suction filtration. Additional quantities of the urea compounds were precipitated and recovered by evaporation of the ethereal layers of the filtrates. The remaining oils were fractionally distilled *in vacuo* to give recovered benzyl chloride.

The urea compounds were identified by their melting points and by mixture melting points with authentic samples. The benzyl chloride was identified by comparison of its boiling point and refractive index with known values.

In the experiment with urea a purple color was observed during the addition of the benzyl chloride and no precipitate remained after the addition of water. The layers of the reaction mixture were shaken and separated. The ethereal layer was washed with saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and the solvent removed. The oily residue was triturated with cold methanol, and the mixture filtered. The solvent was removed from the filtrate, and the residue was distilled *in vacuo* to give benzyl chloride. The remaining pot residue was recrystallized from methanol to give stilbene, which was identified by melting point and mixture melting point with an authentic sample.

The Preparation of (2,2-Dicarbethoxypropyl)ethoxydimethylsilane

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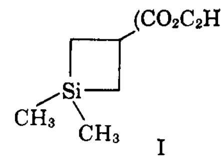
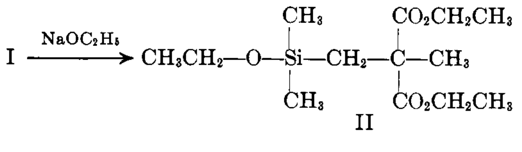
In connection with a program concerned with the preparation, properties, and reactions of small-ring organosilicon compounds, it became desirable to repeat the preparation of a compound previously designated as 3,3-dicarbethoxy-1,1-dimethyl-1-silacyclobutane (I). The preparation of this compound has been reported by several workers.[1,2] The general method utilized was a ring closure reaction of bis(halomethyl)dimethylsilane and diethyl malonate effected with sodium alkoxide. In our work we employed the published procedure reporting the highest yield of this material.[2]

In our preparation a compound was obtained the properties of which were in excellent agreement with those previously reported.[1,2] The infrared spectrum of this material was shown to be superimposable with that of a known sample.[3] However, an examination of the n.m.r. spectrum of this material showed that it was not the previously reported silacyclobutane I, but rather a ring opened product, namely, (2,2-dicarbethoxypropyl)ethoxydimethylsilane (II). The formation of II can be explained in terms of a cleavage of I by sodium ethoxide.

$$(CH_3)_2{-}Si{-}(CH_2X)_2 + H_2C(CO_2C_2H_5)_2 \xrightarrow{NaOR}$$

$X = I$[1] or Cl[2]
$R = CH_3$[1] or C_2H_5[2]

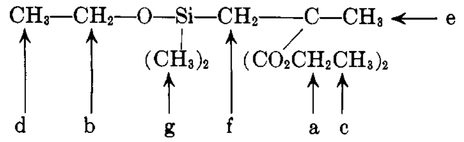

I



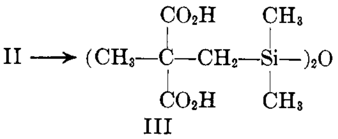
$$I \xrightarrow{NaOC_2H_5} CH_3CH_2{-}O{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}{-}CH_2{-}\overset{\displaystyle CO_2CH_2CH_3}{\underset{\displaystyle CO_2CH_2CH_3}{C}}{-}CH_3$$

II

The n.m.r. spectrum of II contained a pair of quartets centered at 5.92 (J = 7.2 c.p.s.) and 6.42 τ (J = 7.2 c.p.s.) assigned to the protons a and b, respectively. The c and d protons appeared as a pair of triplets[4] centered at 8.78 (J = 7.2 c.p.s.) and 8.89 τ (J = 7.2 c.p.s.), respectively. The remainder of the spectrum consisted of singlets centered at 8.62, 8.81, and 9.92 τ assigned to the e, f, and g protons, respectively. The relative areas of all peaks were in agreement with the proposed structure.



It was previously reported[1] that the basic hydrolysis of I proceeded with ring opening to yield *sym*-bis(2,2-dicarboxypropyl)tetramethyldisiloxane (III). Although the reactivity of other known silacyclobutanes[5–7] would predict such behavior for I, the above observation also can be explained in terms of our proposal. Thus, we have found that hydrolysis of II under similar conditions yields III. On the basis of the physical, chemical, and spectral evidence presented in this report it appears that the compound previously designated as 3,3-dicarbethoxy-1-silacyclobutane (I) is (2,2-dicarbethoxypropyl)ethoxydimethylsilane (II).



$$II \longrightarrow (CH_3{-}\overset{\displaystyle CO_2H}{\underset{\displaystyle CO_2H}{C}}{-}CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}{-})_2O$$

III

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(1) R. West, *J. Am. Chem. Soc.*, **77**, 2339 (1955).

(2) Incidental to the preparation of 4,4-dimethylsilacyclohexanone, R. A. Benkeser and W. E. Bennett [*ibid.*, **80**, 5414 (1958)] isolated a compound identical with that reported by Dr. West (ref. 1). Their identification was based on a comparison of physical constants with those reported in ref. 1.

(3) We wish to thank Dr. R. A. Benkeser for providing us with an infrared spectrum of this material. Dr. R. West informed us that unfortunately, due to a change in academic location, neither an authentic sample nor an infrared spectrum of his original material was available for comparison purposes.

(4) The pair of triplets overlapped giving rise to four peaks of unequal intensity.

(5) L. H. Sommer and G. A. Baum, *J. Am. Chem. Soc.*, **76**, 5002 (1954).

(6) L. H. Sommer, U. R. Bennett, P. G. Campbell, and D. R. Weyenberg, *ibid.*, **79**, 3295 (1957).

(7) W. H. Knoth, Jr., and R. V. Lindsey, Jr., *J. Org. Chem.*, **23**, 1392 (1958).