lised from ethanol and sublimed *in vacuo*. Yield of dibenzofuran 65 mg, 14 %, m.p. 76–78° (lit.[19] m.p. 82.8–83°). A mixed melting point with an authentic sample of dibenzofuran (m.p. 81–83°) showed no depression (m.p. 78–82°).

Dehydration of 2,3,2'-trihydroxybiphenyl. Paper chromatography indicated that a little 2,3,2'-trihydroxybiphenyl[2] (R_F 0.43, brown) was present after 24 h, but the main spot was ascribable to 4-hydroxydibenzofuran (R_F 0.90, brown). Much ether-insoluble material was formed during the reaction. The ether-soluble residue was recrystallised from water and sublimed *in vacuo*. Yield of 4-hydroxydibenzofuran 31 mg, 7 %, m.p. 99–101° (lit.[20] 102°).

Attempted dehydration of 2,3,2',3'-tetrahydroxybiphenyl. Only a small amount of ether-soluble material (12 mg) was present in the reaction mixture after 24 h. Paper chromatography of this material gave one spot (R_F 0.0, brown). The material could not be sublimed *in vacuo*.

Dehydration experiments with zinc chloride. General procedure. The polyhydroxybiphenyl (30 mg) and anhydrous zinc chloride (300 mg) were thoroughly mixed and heated at 300° for 5 min in an argon atmosphere. After cooling, the mixture was treated with dilute hydrochloric acid and extracted with ether. The ether solution was dried over magnesium sulphate and investigated by means of paper chromatography.

Zinc chloride fusion of 2,3,2'-trihydroxybiphenyl. The only phenol detected after the reaction was 4-hydroxydibenzofuran (R_F 0.90, brown). After removal of the ether, the residue was recrystallised from water and sublimed *in vacuo*. Yield of 4-hydroxydibenzofuran 10 mg, 37 %, m.p. 99–100° (lit.[20] 102°).

Zinc chloride fusion of 2,3,2',3'-tetrahydroxybiphenyl. Only ether-insoluble material was formed in the reaction.

1. Stjernström, N. E. *Svensk Kem. Tidskr.* **75** (1963) 184.
2. Pettersson, E. and Stjernström, N. E. *Arkiv Kemi* **21** (1963) 49.
3. Forsén, S. and Stjernström, N. E. *Arkiv Kemi* **21** (1963) 65.
4. Kraemer, G. and Weissgerber, R. *Ber.* **34** (1901) 1662.
5. Oae, S., Fukumoto, T. and Kiritani, R. *Bull. Chem. Soc. Japan* **36** (1963) 346.
6. Oae, S. and Kiritani, R. *Bull. Chem. Soc. Japan* **37** (1964) 770.
7. Oae, S. and Kiritani, R. *Bull. Chem. Soc. Japan* **38** (1965) 1381.
8. Pring, B. G. and Stjernström, N. E. *Acta Chem. Scand.* **22** (1968) 538.
9. Koizumi, M. *Bull. Chem. Soc. Japan* **14** (1939) 353.
10. Ingraham, L. L., Corse, J., Bailey, G. F. and Stitt, F. *J. Am. Chem. Soc.* **74** (1952) 2297.
11. Musso, H. and von Grunelius, S. *Chem. Ber.* **92** (1959) 3101.
12. Aulin-Erdtman, G. and Sandén, R. *Acta Chem. Scand.* **17** (1963) 1991.
13. Ullmann, F. and Loewenthal, O. *Ann.* **332** (1904) 62.
14. Horner, L. and Weber, K. H. *Chem. Ber.* **96** (1963) 1568.
15. Li-Chin Chiang and Giswold, O. *J. Am. Pharm. Ass. (Sci. Ed.)* **41** (1952) 348.
16. Van Arendonk, A. M., Cupery, M. E. and Adams, R. *J. Am. Chem. Soc.* **55** (1933) 4225.
17. Simada, T. and Hata, K. *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)* **35** (1939) 365.
18. Wachtmeister, C. A. *Personal communication, unpublished results.*
19. Williams, A. F. *Nature* **162** (1948) 925.
20. Gilman, H. and Young, R. V. *J. Am. Chem. Soc.* **57** (1935) 1121.

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A Stable Carbamic Acid Anhydride

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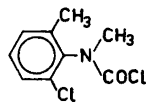
When *N*-(2-chloro-6-methylphenyl)-*N*-methylcarbamoyl chloride (I) was reacted with the sodium salt of *N*-ethyl-3-hydroxypiperidine in refluxing toluene, a crystalline compound was obtained as a byproduct. Spectral and chemical data characterize the compound as *N*-(2-chloro-6-methylphenyl)-*N*-methylcarbamic acid anhydride (II) which appears to the first reported stable anhydride of a carbamic acid.



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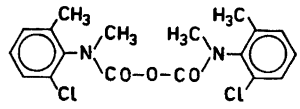

II

Carbamic acid anhydrides have been suggested as possible intermediates in the formation of 1,3-disubstituted ureas from the reaction of water with arylisocyanates.[1,2] These anhydrides are unstable and form the urea under loss of CO_2 at or below room temperature. Mixed anhydrides between carbamic and carboxylic acids are readily formed from equimolar mixtures of isocyanate and carboxylic acid.[3-5] Stronger acids like cyanoacetic or trichloroacetic acid form mixed anhydrides which spontaneously decompose into amides and carbon dioxide, while mixed anhydrides with weaker aliphatic or aromatic acids decompose at elevated temperatures into disubstituted ureas, carboxylic acid anhydrides and CO_2.[4,5]

Compound II is a white solid which melts at 163—164°C without decomposition. The infrared spectrum is very similar to that of the starting material I except for two bands in the carbonyl region at 1760 and 1710 cm^{-1} and one band at 960 cm^{-1}, all of which indicate an anhydride. The carbamoyl chloride I exhibits one band at 1735 cm^{-1} and has no significant absorption between 900 and 1000 cm^{-1}. The IR-, UV-, and NMR-spectra and the elementary analysis of the by-product are all consistent with the formulation of the compound as *N*-(2-chloro-6-methylphenyl)-*N*-methylcarbamic acid anhydride (II). Further supporting evidence was obtained by alkaline hydrolysis, which yielded 2-chloro-6-methyl-*N*-methylaniline. Steric factors are most probably responsible for the stability of II. Experiments designed to elucidate the mode of formation of the compound are in progress.

*Experimental. 2-Chloro-6-methyl-*N*-methylaniline.* Ethyl 2-chloro-6-methylphenylcarbamate (140 g, 0.66 mole), prepared from 2-chloro-6-methylaniline and ethyl chloroformate as described by Dahlbom and Misiorny,[6] was reduced with lithium aluminium hydride (19 g, 0.5 mole) in dry tetrahydrofuran. After the appropriate work-up a colourless oil was obtained (52 g, 51 %), b.p. 94°/13 mm; n_D^{20} 1.5555. (Found: C 61.5; H 6.47; N 9.17. Calc. for $C_8H_{10}ClN$: C 61.5; H 6.48; N 9.00).

N-(2-Chloro-6-methylphenyl)-N-methylcarbamoyl chloride (I). A mixture of 2-chloro-6-methyl-*N*-methylaniline (8.0 g, 0.051 mole) and triethylamine (10 g) was slowly added to a stirred solution of 50 % phosgene in toluene (60 ml) cooled with a bath of dry ice in ethanol. The reaction mixture was allowed to reach room temperature overnight and was then filtered. The filtrate was concentrated to a small volume to give white crystals (7.5 g, 69 %) of m.p. 64—65° after recrystallization from ligroin. (Found: C 49.77; H 4.53; N 6.37. Calc. for $C_9H_9Cl_2NO$: C 49.56; H 4.16; N 6.42). The ultraviolet spectrum (chloroform) showed maxima at 267 mμ (ε 708) and 274 mμ (ε 582). The infrared spectrum (KBr) had a strong band at 1735 cm^{-1} (C=O). The NMR spectrum (carbon tetrachloride) showed signals at τ 2.80 (multiplet, Ar*H*), 6.78 (singlet, NCH_3), and 7.70 (singlet, $ArCH_3$).

Formation of N-(2-chloro-6-methylphenyl)-N-methylcarbamic acid anhydride (II). *N*-Ethyl-3-hydroxypiperidine (2.1 g, 0.016 mole) and sodium (0.37 g, 0.016 mole) was stirred and refluxed in toluene (60 ml) until all the sodium had reacted (3 h). The carbamoyl chloride I (3.5 g, 0.016 mole) in dry toluene (10 ml) was added and the mixture stirred and refluxed for 0.5 h. After filtration, the solvent was removed *in vacuo* affording an oily residue from which crystals separated after two days. Recrystallization from hexane-benzene gave white needles (0.5 g), m.p. 163—164°. (Found: C 57.1; H 4.82; N 7.35. Calc. for $C_{18}H_{18}Cl_2N_2O_3$: C 56.9; H 4.76; N 7.35). The ultraviolet spectrum (chloroform) showed maxima at 267 mμ (ε 645) and 275 mμ (ε 542). The infrared spectrum (KBr) showed strong bands at 1760, 1710, and 960 cm^{-1}. The NMR spectrum (carbon tetrachloride) showed signals at τ 3.00 (multiplet, Ar*H*), 6.95 (singlet, NCH_3), and 8.03 (singlet, $ArCH_3$).

Hydrolysis of the anhydride II. The anhydride II (75 mg) was dissolved in methanol (1 ml) and a few drops of 5 M sodium hydroxide were added. The solution was heated in a sealed ampoule on a steam bath for 2 h. Water (5 ml) was then added and the mixture extracted with chloroform. After drying over sodium sulphate the solvent was evaporated, the residue dissolved in ether and the solution treated with ethereal hydrogen chloride. The

infrared spectrum of the hydrochloride thus obtained was superimposable on that of 2-chloro-6-methyl-*N*-methylaniline hydrochloride, and a mixed m.p. was undepressed (210°).

1. Naegeli, C., Tyabji, A., Conrad, L. and Litwan, F. *Helv. Chim. Acta* **21** (1938) 1100.
2. Shkapenko, G., Gmitter, G. T. and Gruber, E. E. *Ind. Eng. Chem.* **52** (1960) 605.
3. Dieckmann, W. and Breest, F. *Ber.* **39** (1906) 3052.
4. Naegeli, C. and Tyabji, A. *Helv. Chim. Acta* **17** (1934) 931.
5. Naegeli, C. and Tyabji, A. *Helv. Chim. Acta* **18** (1935) 142.
6. Dahlbom, R. and Misiorny, A. *Acta Chem. Scand.* **11** (1957) 1350.

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Chlorobutatriene — Identification and Spectrochemical Characterization

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Dehydrochlorination of 1,4-dichloro-2-butyne by alkali gives diacetylene [1] as an end product. Several intermediates appear in which one of the chlorine atoms is retained. We have noticed that under certain conditions a considerable amount of chlorobutatriene is formed, according to the formula

$$ClCH_2-C\equiv C-CH_2Cl =$$
$$ClHC=C=C=CH_2 + HCl$$

The substance can readily be purified by gas chromatography. On a di-ethyl-hexyl-sebacate column at 50°C the three substances 1,4-dichlorobutyne, chlorobutatriene, and carbon tetrachloride have the relative delays of 21.6, 2.21, and 1.00, respectively.

The identification is primarily based on the mass spectrum obtained by using a combined gas chromatograph-mass spectrometer.[2] After correction for background the largest peaks are: *m/e* — rel. int.; 49—2.1; 50—30.9; 51—100.0; 52—4.4; 60—2.5; 62—1.3; 84—0.8; 85—2.7; 86—87.2; 87—6.5; 88—29.2; 89—1.7.

The occurrence of chlorine is demonstrated by the intensity relation 3:1 of the mass bumbers 86:88 corresponding to the molecular ions with ^{35}Cl and ^{37}Cl. The molecular weight is consequently 86.5. The relation ^{13}C:^{12}C in the substance appears most evident from the intensity relation 4.4:100.0 between the mass numbers 52:51 (corresponding to the ions $^{12}C_3{}^{13}CH_3{}^+$ and $^{12}C_4H_3{}^+$, respectively). Hence, the assumption of four carbon atoms is confirmed. IR- and NMR spectra provide other necessary data for the identification.

Of simple butatriene compounds only the hydrocarbon itself has been described so far, 1952 by Schubert.[3] The preparation by treatment of 1,4-dibromo-2-butyne with alkali and zinc is closely related to the one described here; and there is reason to assume that bromobutatriene is formed as an intermediate.

In UV an absorption with maximum at 278—279 mμ is observed. The chlorine atom has caused a considerable bathochromic displacement — the absorption maximum [3] of unsubstituted butatriene

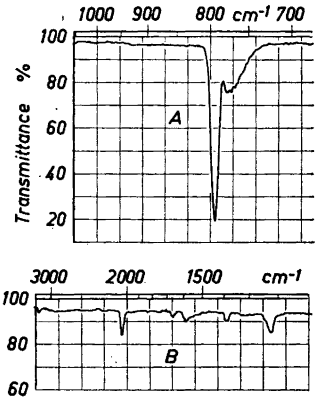

Fig. 1. IR spectrum of chlorobutatriene. Vapour mixed with He, 10 cm cell, NaCl optics, 25°C. A: *Ca.* 1.9×10^{-4} mole · l^{-1}; B: *Ca.* 1.5×10^{-3} mole · l^{-1}.