crystallized from EtOAc, m.p. >300°C, m/z (EIMS) 502; ^{1}H-NMR (CDCl$_3$): δ = 1.81 (m, 4 H), 2.33 (m, 4 H), 2.61 (m, 4 H), 4.92 (s, 4 H), 4.97 (bs, 4 H), 4.99 (s, 4 H), 5.09 (s, 4 H), 6.99 (s, 2 H); ^{13}C-NMR (CDCl$_3$): δ = 25.7, 43.2, 85.0, 85.3, 100.9, 110.2, 143.1, 144.2, 144.6].

6a: 6 (156 mg, 0.88 mmol) was heated under reflux (48 h, N$_2$) with anthracene (50 mg, 0.28 mmol) in xylene (5 mL); yield of the crude product: after chromatography (SiO$_2$/CHCl$_3$-Et$_2$O) 17 mg, 11%. Colorless crystals [m.p. >300°C), m/z (positive ion FABMS) 535 for (M + H)$^\circ$] suitable for X-ray crystallography, were grown by the vapor diffusion method (CHCl$_3$-ClCH$_2$CH$_2$Cl-light petroleum).

8: Reaction (CH$_2$Cl$_2$, 9-10 kbar, 55-60°C, 200 h) of 7 (373 mg, 0.74 mmol) with 5 (156 mg, 0.74 mmol) yielded, after chromatography (SiO$_2$/CHCl$_3$-MeOH), 8 [105 mg, 20%, recrystallized from CHCl$_3$, m.p. >300°C, m/z (positive ion FABMS) 713 for (M + H)$^\circ$; ^{1}H-NMR (CDCl$_3$): δ = 1.62 (m, 4 H), 2.32 (m, 8 H), 2.63 (m, 8 H), 4.89 (s, 8 H), 5.08 (s, 4 H), 6.98 (s, 4 H); ^{13}C-NMR (CDCl$_3$): δ = 27.1, 44.2, 84.8, 86.6, 110.1, 144.6, 152.5], which was also obtained in very low yield (3.5%) by heating 6 under reflux (48 h, N$_2$) in xylene. Single crystals, suitable for X-ray analysis, were obtained by slow evaporation of a chloroform solution of 8 at room temperature.

[1] Champions of highly speculative projects are few and far between; here, they were Dr. R. D. Handscombe (University of Sheffield) and Prof. G. Stagno d'Alcontres (University of Messina). We thank them for their moral support—and for their enthusiastic efforts, all the many postgraduate students, who over the years, have received their introduction to the research laboratory in Sheffield making starting materials for "the crazy molecule". One of the authors (J. F. S.) also thanks the Leverhulme Trust for the award of a Research Fellowship.

[2] Recently, some force-field calculations have been carried out (R. W. Alder, R. B. Sessions, J. Chem. Soc. Perkin Trans. 2 1985, 1849) on molecular belts built from cyclohexa-1,4-diene rings. Compounds of the type 1 were referred to in the above paper as [n]beltenes; the strain energy per 2-butene-1,2,3,4-tetrayl unit was found to decrease monotonically from [3]beltene to [12]beltene. Calculations on encapsulated complexes of small molecules led to the prediction that, in the case of acetylene, for example, [9]beltene will be the optimum molecular receptor.

[3] In looking to the future in cyclophane chemistry, F. Vögtle (Top. Curr. Chem. ("Cyclophanes II") 115 (1983) 157) has highlighted the challenge posed by the synthesis of the [n]cyclacenes 2, which are also of considerable theoretical interest (S. Kivelson, O. L. Chapman, Phys. Rev. B 28 (1983) 7236) as a class of new materials with possibly novel one-dimensional conducting properties.

[4] In the beginning, we prepared 4 in a six-step synthesis (P. Vogel, A. Florey, Helv. Chim. Acta 57 (1974) 200) starting from dimethyl 3,4-furandicarboxylate and dimethyl acetylenedicarboxylate. More recently, the highly efficient four-step synthesis (C. Mahaim, P.-A. Carrupt, J.-P. Hagenbuch, A. Florey, P. Vogel, Helv. Chim. Acta 63 (1980) 1149) of 4 from the Diels-Alder adduct of furan and maleic anhydride has been employed. An X-ray crystal structure analysis (F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, unpublished results) on single crystals of the intermediate tetramethyl 7-oxabicyclo[2:2:1]heptane-2,3,5,6-tetracarboxylate has indeed confirmed that it has the all-exo configuration.

[5] The preparation of 1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene from 1,2,4,5-tetrabromobenzene and furan, and the chromatographic isolation of the syn-isomer 5 were achieved after the kind provision (Prof. H. Hart, personal communication, 1986) of a detailed experimental procedure which provided some essential additional information to that already published (H. Hart, N. Raja, M. A. Meador, D. L. Ward, J. Org. Chem. 48 (1983) 4357). Identification of the syn-isomer 5 in our hands followed from X-ray crystallography on single crystals of a compound isomeric with 5. Although the crystal data we have obtained (F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, unpublished results) are totally different to those reported in the above paper by Hart et al. for the anti-isomer of 5, determination of the X-ray structure showed that the crystals only contain molecules of anti geometry. These two crystal structures must clearly represent alternative polymorphs.

[6] These principles have been capitalized upon by others (see, for example, D. J. Cram, Science 219 (1983) 1177; H. C. Kang, A. W. Hanson, B. Eaton, V. Boekelheide, J. Am. Chem. Soc. 107 (1985) 1979; D. J. Cram, K. D. Stewart, I. Goldberg, K. N. Trueblood, J. Am. Chem. Soc. 107 (1985) 2574) in the synthesis of molecules with enforced cavities.—An example of a molecule similar to 8 with a rigid collar-like structure is cucurbituril which can be readily assembled (W. A. Freeman, W. L. Mock, N.-Y. Shih, J. Am. Chem. Soc. 106 (1984) 1416) from urea, glyoxal, and formaldehyde. It forms (W. L. Mock, N.-Y. Shih, J. Org. Chem. 48 (1983) 3618; 51 (1986) 4440) host-guest solution complexes and catalyzes (W. L. Mock, T. A. Mirra, J. P. Wepsiec, T. L. Manimaran, J. Org. Chem. 48 (1983) 3619) 1,3-dipolar cycloadditions between appropriate substrates in a highly regioselective manner.

[7] The X-ray crystal structure analysis of 6a (Fig. 1) not only established the stereochemistry in 6 but also demonstrated that the cycloaddition of anthracene occurs preferentially to the exo-face of the dienophilic C=C double bond of 6. This strongly suggests that the 1:2 adduct formed (H. Hart, N. Raju, M. A. Meador, D. L. Ward, J. Org. Chem. 48 (1983) 4357) between 5 and anthracene has the exo-exo configuration.

[8] As a result of their negative volumes of activation, Diels–Alder reactions are accelerated at high pressures (for a recent review, see N. S. Isaacs and A. V. George, Chem. Br. 23 (1987) 47). We thank Prof. S. V. Ley (Imperial College) for removing any hesitation we had about employing this technique and Dr. N. S. Isaacs (SERC High Pressure Service Facility, University of Reading) for the superb service and help he has given us in preparing 8.

[9] Although intramolecular Diels–Alder reactions with flexible trienes have been much studied (for a recent review, see E. Ciganek, Org. React. 32 (1984) 1) during the last decade, their occurrence in highly rigid molecules containing diene and dienophilic units has, surprisingly, not been investigated.

[10] P.-A. Carrupt, P. Vogel, Tetrahedron Lett. 1979, 4533; Y. Bessiére, P. Vogel, Helv. Chim. Acta 63 (1980) 232.

[11] A. A. Pinkerton, D. Schwarzenbach, J. H. A. Stibbard, P.-A. Carrupt, P. Vogel, J. Am. Chem. Soc. 103 (1983) 2095; J.-M. Tornare, P. Vogel, A. A. Pinkerton, D. Schwarzenbach, Helv. Chim. Acta 68 (1985) 2195.

[12] Nicolet R3m diffractometer, ω-scans, Cu$_{Kα}$ radiation (graphite monochromator). A crystal of 8 was sealed in a Lindemann capillary tube under chloroform, which was drawn away to opposite ends of the tube thus leaving the crystal in a vapor pressure of solvent: a numerical absorption correction was carried out. Both structures were solved by direct methods and refined anisotropically: the R-factors are high as a result of severe disorder involving included chlorinated solvents, which is particularly pronounced in the case of 8. Further details of these structural investigations can be obtained from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (England). Any request should be accompanied by the full literature citation for this communication.

[13] The monoadduct 6 is unstable and undergoes polymerization. It is for this reason that we prefer to approach the synthesis of 8 via the bisadduct 7, which can be stored for several months at −20°C in the dark without detectable decomposition.

[14] All new compounds gave satisfactory elemental analyses and spectroscopic data. We are extremely grateful to Mr. P. R. Ashton for obtaining EIMS and FABMS on a Kratos MS80RF spectrometer and to Dr. C. M. Spencer for recording high field NMR spectra on a Bruker WH400 spectrometer. We also thank Dr. A. D. McNaught (The Royal Society of Chemistry, London) for his freely given advice on trivial—as well as systematic—nomenclature for these new compounds.

[15] See, for example, R. O. Angus, Jr., R. P. Johnson, J. Org. Chem. 48 (1983) 373; L. L. Miller, A. D. Thomas, C. L. Wilkins, D. A. Weil, J. Chem. Soc. Chem. Commun. 1986, 661.

[16] See, for example, G. A. Russell, N. K. Suleman, H. Iwamura, O. W. Webster, J. Am. Chem. Soc. 103 (1981) 1560; E. Lipczynska-Kochany, H. Iwamura, Chem. Lett. 1982, 1075; C. S. Wilcox, L. M. Greer, V. Lynch, J. Am. Chem. Soc. 109 (1987) 1865.

[17] This clathration phenomenon explains the instantaneous loss of chloroform with concomitant collapse of the crystals on removal from their mother liquor.

[18] For some excellent reviews on this topic see, W. H. Watson (Ed.): Stereochemistry and Reactivity of Systems containing π-Electrons, Verlag Chemie International, Deerfield Beach, FL (USA) 1983.
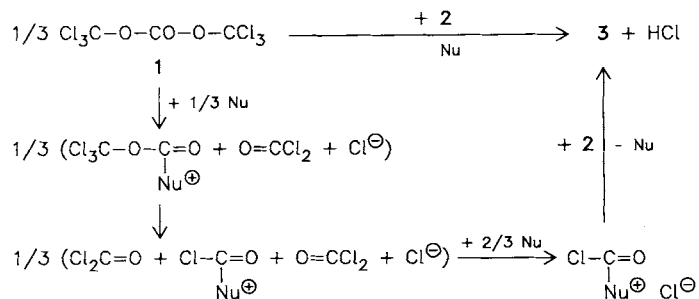
Triphosgene, a Crystalline Phosgene Substitute**

By Heiner Eckert* and Barbara Forster

The "defusing" of dangerous and risky chemicals is exemplified here by the avoidance of the highly toxic, gaseous basic chemical phosgene (COCl$_2$) as a reagent. Liquid trichloromethyl chloroformate (ClCO$_2$CCl$_3$, "diphosgene"),[1] which has already been used as a phosgene substitute, has proved useful in all common phosgene reactions,[2] but, as a liquid, its transport and storage still pose considerable dangers. Bis(trichloromethyl) carbonate 1 ("triphosgene"),[3] on the other hand, is a crystalline, stable

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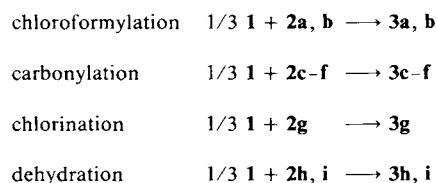Lichtenbergstrasse 4, D-8046 Garching (FRG)

$$1/3 \; Cl_3C-O-CO-O-CCl_3 \xrightarrow[Nu]{+2} 3 + HCl$$

1

$$\downarrow + 1/3 \; Nu$$

$$1/3 \; (Cl_3C-O-\underset{\underset{Nu^{\oplus}}{|}}{C}=O + O=CCl_2 + Cl^{\ominus}) \qquad +2 \uparrow \downarrow -Nu$$

$$1/3 \; (Cl_2C=O + Cl-\underset{\underset{Nu^{\oplus}}{|}}{C}=O + O=CCl_2 + Cl^{\ominus}) \xrightarrow{+2/3 \; Nu} Cl-\underset{\underset{Nu^{\oplus}}{|}}{C}=O \; Cl^{\ominus}$$
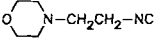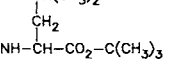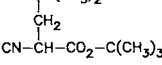
Scheme 1. Triphosgene as a phosgene substitute.
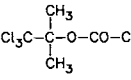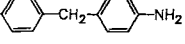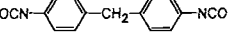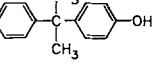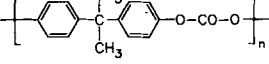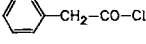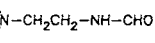
solid (m.p. = 80°C, b.p. = 206°C; at the boiling point, only slight decomposition to phosgene occurs[3c]), which is easy to transport and to store. Compound 1 was first prepared in 1880 by Councler[3a] by chlorination of dimethyl carbonate and has so far been used in reactions with primary alcohols to give esters,[3c, d] with ammonia and aniline to give ureas,[3c, d] and with aldehydes.[3b]

1/3 mol of 1 reacts under the influence of a nucleophile Nu similarly to 1 mol of phosgene, which can also arise as an intermediate (Scheme 1). Table 1 lists a selection of the reactants 2 and the products 3 thereby obtained. The auxiliary nucleophile Nu can also be identical with 2. The functions of phosgene, e.g.,

chloroformylation	1/3 1 + 2a, b ⟶ 3a, b
carbonylation	1/3 1 + 2c-f ⟶ 3c-f
chlorination	1/3 1 + 2g ⟶ 3g
dehydration	1/3 1 + 2h, i ⟶ 3h, i

can also be performed by 1. Good to very good yields of 3 are thereby obtained by the use of 2 in equivalent amounts in the usual solvents (dichloromethane, o-dichlorobenzene) or without solvent. Phosgene, on the other hand, has to be used in severalfold excess and, even in this case, the yields are often only moderate. A further advantage of 1 is that, as a solid, it can be exactly weighed out in milligram amounts. Furthermore, owing to the relatively low volatility of 1, only the usual safety precautions are necessary.

Experimental Procedure

[1] a) W. Hentschel, J. Prakt. Chem. NF 36 (1887) 99, 305; b) H. C. Ramsperger, G. Waddington, J. Am. Chem. Soc. 55 (1933) 214; c) K. Kurita, T. Matsuma, Y. Iwakura, J. Org. Chem. 41 (1976) 2070; d) G. Skorna, I. Ugi, Angew. Chem. 89 (1977) 267; Angew. Chem. Int. Ed. Engl. 16 (1977) 259; e) K. Kurita, Y. Iwakura, Org. Synth. 59 (1979) 195.
[2] a) H. Babad, A. G. Zeiler, Chem. Rev. 73 (1973) 75; b) R. Gottschlich, Kontakte 1981, No. 1, p. 14.
[3] a) C. Councler, Ber. Dtsch. Chem. Ges. 13 (1880) 1697; b) Bayer & Co., DRP 121223 (1901); Chem. Zentralbl. 72 II (1901) 69; c) D. Marotta, Gazz. Chim. Ital. 59 (1929) 955; d) W. Nekrassow, N. Melnikow, J. Prakt. Chem. NF 126 (1930) 81.

Table 1. Reaction conditions and yields for the reaction 1/3 1 + 2 → 3.

2	3	Nu	1:2	t [h]	T [°C]	Yield [%]
a Cl₃C–C(CH₃)₂–OH	Cl₃C–C(CH₃)₂–O–CO–Cl	C₅H₅N	1:3	96	20	91
b (ClCH₂CH₂)₂NH	(ClCH₂CH₂)₂N–CO–Cl	C₅H₅N	1:3	72	20	85
c (2-aminotoluene, NH₂, CH₃)	(2-isocyanatotoluene, NCO, CH₃)	Et₃N	1:3	2	70	82
d (Cl, NH₂, CH₃ benzene)	(Cl, NCO, CH₃ benzene)	2d	1:3	1 / 2	70 / 130	68
e H₂N–C₆H₄–CH₂–C₆H₄–NH₂	OCN–C₆H₄–CH₂–C₆H₄–NCO	2e	2:3	2 / 1	130 / 180	92
f HO–C₆H₄–C(CH₃)₂–C₆H₄–OH	[–C₆H₄–C(CH₃)₂–C₆H₄–O–CO–O–]ₙ	Et₃N	1:3	8	20	75
g C₆H₅–CH₂–CO₂H	C₆H₅–CH₂–CO–Cl	trace DMF [a]	1:3	24	60	71
h O(morpholine)N–CH₂CH₂–NH–CHO	O(morpholine)N–CH₂CH₂–NC	Et₃N	1:3	8	20	74
i OHC–NH–CH(CH₂–CH(CH₃)₂)–CO₂–C(CH₃)₃	CN–CH(CH₂–CH(CH₃)₂)–CO₂–C(CH₃)₃	Et₃N	1:3	2	20	94

[a] Dimethylformamide.