

We recently found the usefulness of the Wittig-Horner reaction of 2-dimethylphosphono-1,3-benzodithiole **3a** with conjugated 1,4-diketones for the preparation of 2,2'-bis(1,3-dithiole) donors.^[4] We have now used the Wittig-Horner reaction of **3b**, which was synthesized by a similar method as that for **3a**,^[5] to prepare **1**. In this case, a cyclopentadiene adduct of *p*-benzoquinone **4** was used as a diketone and after introduction of the 1,3-dithiole rings the cyclopentadiene was removed by a retro-Diels-Alder reaction, since the direct reaction of *p*-benzoquinone with **3b** gave a complex mixture of products without formation of **1**.

Thus, a solution of **3b** in dry THF was treated with 1.1 equivalents of *n*-butyllithium at -78°C under nitrogen, and after stirring for 5 min, 0.43 equivalent of **4** was added. The solution was then stirred at -78°C for a further 10 min and allowed to warm to room temperature, whereupon the bis(1,3-dithiole) derivative **5** was obtained in 27% yield. Thermolysis of **5** at 200°C under reduced pressure furnished, via a retro-Diels-Alder reaction, dark red crystals of **1** in 54% yield.^[6] The benzo derivatives **6a, b** were prepared analogously by reaction of the Diels-Alder adducts of 1,4-naphthoquinone and the corresponding methyl compound, respectively with cyclopentadiene. The dibenzo derivative **7** could be synthesized in 74% yield by direct Wittig-Horner reaction of **3b** with 9,10-anthraquinone. The dibenzotetrathiafulvalene (TTF) analogue **2a** could be prepared by a retro-Diels-Alder reaction of **8**, which was obtained in 73% yield by reaction of **3a** and **4**. **9a, b** and **10** were prepared similarly. The decomposition temperatures of the new donors are listed in Table 1. The TTF analogues **1** and **6a, b** are air sensitive, whereas the benzo analogues **2a, 7, 9a, b**, and **10** are stable towards air.

The oxidation potentials of the donors (Table 1) were measured by cyclic voltammetry. The values for the donors with quinoid structures are lower than those of TTF mea-

Table 1. Decomposition temperatures and oxidation potentials [a] of the donors.

Donor	$T_{\text{dec.}} [^{\circ}\text{C}]$	$E_{1/2} [\text{V}]$
1	230–245	– 0.11, – 0.04
6a	160–170	0.00
6b	190–194	– 0.04
7	320–325	+ 0.25 [b]
9a	260–270	+ 0.18
9b	243–248	+ 0.15
10	314–317	+ 0.24
5	168–170	+ 0.17
8	260–265	+ 0.37

[a] 0.1 M Et_4NClO_4 in MeCN, Pt electrode, scan rate: 100 mV s^{-1} ; E vs. standard calomel electrode (SCE). [b] Irreversible. Calculated as E_{pa} (anodic peak potential) – 0.03 V.

sured under the same conditions (0.28, 0.64 V vs. SCE); the parent compound **1**, in particular, is an extremely strong electron donor. This may be due to the fact that the quinoid structures form a new aromatic sextet upon oxidation.

Other characteristic features are that the difference between the first and second oxidation potentials of **1** is very small and that two-electron oxidation waves are observed in the other new donors. Accordingly, the donors with quinoid structures form dications more readily upon oxidation, due to the decreased Coulombic repulsion. With tetracyanoquinodimethane (TCNQ), the donors **1, 6a, b, 2a**, and **9a, b** gave charge-transfer complexes which exhibit good conductivities (Table 2).

Table 2. Properties of charge-transfer complexes with TCNQ.

Donor (D)	$T_{\text{dec}} [^{\circ}\text{C}]$	Molar ratio [a] D:A	$\sigma [\text{S cm}^{-1}]$ [b]
1	> 400	3:4	5.3×10^{-4}
6a	> 360	2:3	2.9×10^{-2}
6b	> 400	2:3	1.9×10^{-2}
2a	250–253	1:1	4.1×10^{-3}
9a	245–249	3:5:3 H_2O	1.9×10^{-2}
9b	220–225	1:1.8: H_2O	2.2×10^{-2}

[a] Based on elemental analyses. [b] Electrical conductivities measured on compressed pellets by two-probe technique at room temperature.

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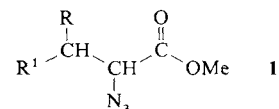
- [1] P. J. L. Galigné, B. Liautard, S. Peytavin, G. Brun, M. Maurin, J. M. Fabre, E. Torrelles, L. Giral, *Acta Cryst.*, B36 (1980) 1109; M. R. Bryce, *J. Chem. Soc. Perkin Trans. 1*, 1985, 1675.
- [2] Y. Ueno, A. Nakayama, M. Okawara, *J. Chem. Soc. Chem. Commun.* 1978, 74; M. Sato, M. V. Lakshminathan, M. P. Cava, A. F. Garito, *J. Org. Chem.* 43 (1978) 2084.
- [3] Y. Ueno, M. Bahry, M. Okawara, *Tetrahedron Lett.* 1977, 4607; J.-M. Fabre, E. Torrelles, L. Giral, *ibid.* 1978, 3703; M. R. Bryce, *Mol. Cryst. Liq. Cryst.* 120 (1985) 305; M. R. Bryce, A. J. Moore, *Tetrahedron Lett.* 29 (1988) 1075.
- [4] Y. Yamashita, T. Miyashi, *Chem. Lett.* 1988, 661.
- [5] K. Akiba, K. Ishikawa, N. Inamoto, *Bull. Chem. Soc. Jpn.* 51 (1978) 2674.
- [6] **1** absorbs at longer wavelengths than **5**. UV (CH_2Cl_2): **1**: $\lambda(\lg \epsilon) = 495(4.78)$, 469 (sh, 4.50), 257(4.07); **5**: $\lambda(\lg \epsilon) = 440(4.65)$, 416(4.58), 395 (sh, 4.31).

2-Isocyanato-2-alkenoates – Synthesis and Reactions**

By Franz Effenberger,* Christan Baumgartner,
and Jürgen Kühlwein

Dedicated to Professor Christoph Rüchardt on the occasion of his 60th birthday

Very few data have been quoted in the literature about 2-isocyanato-2-alkenoates; they have been detected spectroscopically as reaction intermediates,^[1a, b] and in two cases have even been isolated.^[1c] α -Isocyanatoacrylic acid esters have on one occasion been presumed as intermediates in the thermolysis of ethyl 1-isocyanatocyclobutane-2-carboxylate,^[2a] and on another their formation and their spectroscopic detection – likewise in thermolysis reactions – have been reported in a patent.^[2b]



In the perhenate-catalyzed decomposition of α -azido-carboxylic acid derivatives such as **1**^[3] we could successfully replace acetic anhydride by other acylating reagents, thereby providing easy access to a series of interesting *N*-substituted α, β -didehydroamino acid esters.^[4a]

[*] Prof. Dr. F. Effenberger, Dr. C. Baumgartner, Dr. J. Kühlwein
Institut für Organische Chemie der Universität
Pfaffenwaldring 55, D-7000 Stuttgart 80 (FRG)

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The results which we have now found with phosgene and diphosgene as "acylating reagent" in this decomposition reaction, although hoped for, are still surprising: as reaction products, the 2-isocyanato-2-alkenoates **2** were obtained in very good yields (Table 1).^[4]

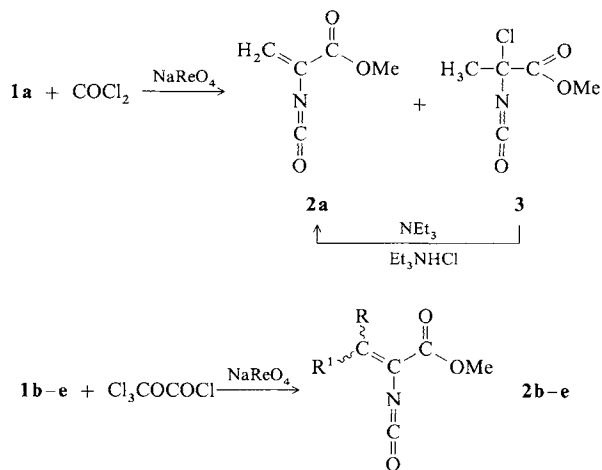
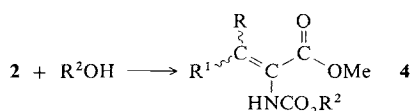


Table 1. R and R¹ in **1** and **2** and yields of **2**.

	R	R ¹	Yield of 2 [%]
a	H	H	69
b	H	Me	88
c	Me	Me	82
d	H	<i>n</i> Pr	80
e	H	Ph	53

Whereas the substituted esters **2b-e** could be isolated and worked-up by distillation without any problem, the synthesis of pure α -isocyanatoacrylate **2a** at first presented great difficulties, because it was always formed in a mixture with its—distillatively—inseparable HCl-adduct **3**, and because it is exceptionally reactive, and easily polymerizes. However, the addition product **3** could be completely converted into the acrylate **2a** by careful extrusion of HCl with triethylamine in diethyl ether, so that **2a** was obtained in 69% yield—referred to **1a**—in this way.

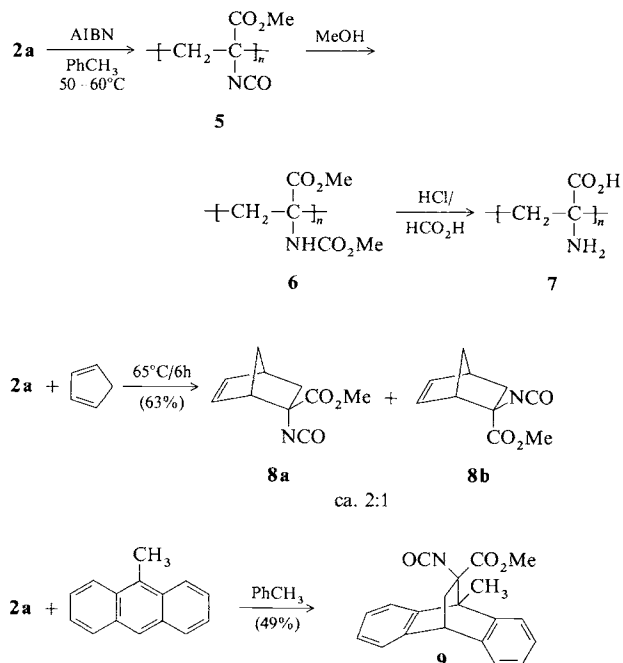
As expected, all usual addition reactions to the isocyanato group of the compounds **2** could be carried out, which, e.g., upon using appropriate alcohols (*tert*-butyl alcohol, benzyl alcohol) yield directly the urethane-protected dehydroamino acids **4**, which are of special interest in peptide chemistry.



R² = *t*Bu, PhCH₂

The acrylic ester **2a**, which, besides the isocyanato group, has an activated and sterically unhindered C—C double bond, provides access to further, versatile reactions. In the presence of azoisobutyronitrile (AIBN) radical polymerization leads to the polymers **5**; with methanol these yield the polymeric urethanes **6**, which can be hydrolyzed to the poly(α -aminoacrylic acid) **7**. We have no explanation for the astonishingly low degree of polymerization of **5** ($n = 14-15$).^[5] The properties of **7** are almost identical with the prop-

erties of the poly(α -aminoacrylic acid) obtained by hydrolysis of the *N*-acetyldehydroalanine polymers.^[6]



That the acrylic ester **2a** is also suitable as dienophile for Diels-Alder reactions is demonstrated by the reactions with cyclopentadiene to give **8** and with 9-methylanthracene to give **9**, whereby **2a** proves to be distinctly more reactive than *N*-acetyldehydroalanine.^[7] The cycloadducts **8a, b** can be further converted by alcohol addition into urethane-protected cyclic α -amino acids and by acid hydrolysis into the corresponding free cyclic α -amino acids.^[8]

The previously reported reactivity sequence for Diels-Alder reactions with anthracenes is confirmed in the reactions of **2a** with anthracenes: no cycloadducts were obtained at temperatures up to 115 °C, neither with anthracene nor with 9-methoxyanthracenes. Higher reaction temperatures are not possible because of the thermolability of **2a**.

Experimental

2a: Phosgene was passed into a cold mixture of sodium perchlorate (1.0 g, 3.66 mmol) and methanesulfonic acid (0.2 g) in ethyl acetate (500 mL). After addition of 64.5 g (0.5 mmol) of **1a** and of 300 mg of hydroquinone, phosgene was condensed into the mixture such that it was always present in excess. The mixture was then heated at 70–80 °C until completion of evolution of gas, cooled down, and the whole liquid distilled rapidly under high vacuum into a cooled receiver. After evaporation of the ethyl acetate, distillation at 50 °C/12 torr furnished 69 g of a mixture of **2a** and **3** in the ratio 1:2. At 0 °C, 125 mL of diethyl ether were added, then a solution of triethylamine (in equimolar amount to **3**; 31.0 g, 310 mmol) in 125 mL of diethyl ether was added dropwise at 0 °C. After removal of precipitated triethylamine hydrochloride by filtration, the filtrate was evaporated and distilled at 44.5 °C/12 torr. Yield: 43.6 (69%) of **2a** as a colorless, viscous liquid. ¹H NMR (CDCl₃): $\delta = 3.93$ (s, 3H, CH₃), 5.82, 5.50 (each s, each 1H, =CH). Correct elemental analysis (C, H, N).

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- [1] a) B. W. Metcalf, P. Casara, *J. Chem. Soc. Chem. Commun.* 1979, 119; b) T. J. Nitz, E. M. Holt, B. Rubin, C. H. Stammer, *J. Org. Chem.* 46 (1981) 2667; c) C. Herdeis, U. Nagel, *Arch. Pharm. (Weinheim, FRG)* 317 (1984) 86.
[2] a) R. D. Miller, W. Theis, *Tetrahedron Lett.* 27 (1986) 2447; b) J. F. Engel, T. J. Byerley, H. W. Christie, US Pat. 4704466 (1987), Midwest Research Institute; *Chem. Abstr.* 108 (1988) 56770s.
[3] a) F. Effenberger, T. Beisswenger, *Chem. Ber.* 117 (1984) 1497; b) T. Beisswenger, F. Effenberger, *ibid.* 117 (1984) 1513.

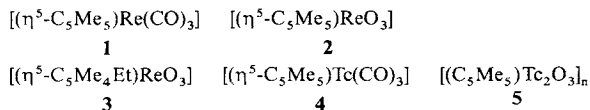
- [4] a) J. Kühlwein, *Dissertation*, Universität Stuttgart 1986; b) F. Effenberger, J. Kühlwein, K. Drauz, DOS 3 508 564 (1986), Degussa AG; *Chem. Abstr.* 107 (1987) 354 750j.
- [5] Determined in collaboration with Prof. Dr. L. Dulog and Dr. R. Seidemann, 2. Institut für Technische Chemie der Universität Stuttgart.
- [6] G. Nelson, C. Chang, I. St. Pierre, *Makromol. Synth.* 9 (1985) 89.
- [7] H. Horikawa, T. Nishitani, T. Iwasaki, Y. Mushika, I. Inoue, M. Miyoshi, *Tetrahedron Lett.* 21 (1980) 4101.
- [8] A. Mielert, C. Braig, J. Sauer, J. Martelli, R. Sustmann, *Liebigs Ann. Chem.* 1980, 954.

A Polymeric Technetium Compound of the Composition $[\text{Tc}_2\text{O}_3(\text{C}_5\text{Me}_5)_n]$

By Basil Kanellakopoulos,* Bernd Nuber, Konstantinos Raptis, and Manfred L. Ziegler*

Dedicated to Professor Margot Becke on the occasion of her 75th birthday

The tricarbonylrhenium complex **1**^[1] reacts with H_2O_2 to give the trioxo-complex **2**, which has proved to be an interesting and versatile starting compound for exploring the remarkable chemistry of rhenium in high oxidation states.^[1] So far it has not been possible to carry out an X-ray structure analysis of **2** itself; however, the structure of one of its derivatives is already known, namely that of **3**, which forms discrete molecules. This might also be assumed in the case of **2**.



In the reaction of the tricarbonyltechnetium complex **4** with perhydrol it has now been shown that the technetium species **4** behaves differently than its rhenium homologue **1**. Elemental analysis, mass spectra, and, above all, an X-ray structure analysis yielded the empirical formula $\text{C}_{10}\text{H}_{15}\text{Tc}_2\text{O}_3$ for the product **5** in a polymeric structure. It is clear from Figure 1 that, in **5**, two Tc atoms are bridged by three μ -oxo ligands and the coordination of the Tc atoms is in each case completed by a C_5Me_5 ring (= Cp*). These Cp*

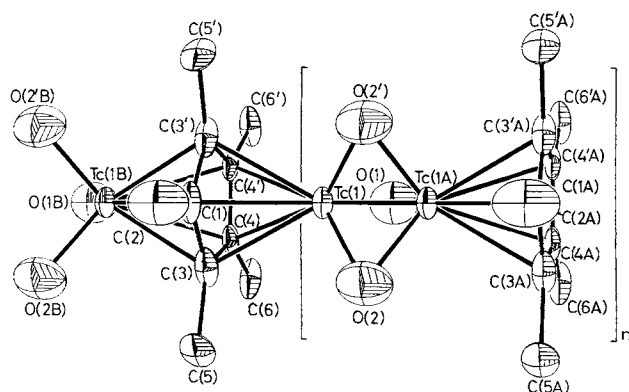


Fig. 1. Section of the polymer **5** in the crystal. The vibration ellipsoids are drawn at the 50% probability level. **5** is viewed along one of the mirror planes. Important bond lengths [pm] and angles [°]: Tc1–O1 190(2), Tc1–O2 185(2), Tc–C_{Ring} 238(2); Tc1–O1–Tc1A 58.8(8), Tc1–O2–Tc1A 60.7(6), O1–Tc1–O2 97.5(5), O2–Tc1–O2' 96.3(9).

*] Prof. Dr. B. Kanellakopoulos, Dipl.-Chem. K. Raptis Kernforschungszentrum Karlsruhe, Institut für Heisse Chemie Postfach 3640, D-7500 Karlsruhe (FRG)

Prof. Dr. M. L. Ziegler, Dr. B. Nuber Anorganisch-chemisches Institut der Universität Im Neuenheimer Feld 270, D-6900 Heidelberg (FRG)

rings are, however, concomitantly a component of the neighboring units, so that the above mentioned empirical formula results. The planes of the Cp* rings and of the oxo-bridge ligands are, crystallographically exactly parallel to one another, i.e. a kind of polydecker structure is formed (distances: Cp*–O₃ planes 297.3(3), Tc–O₃ plane 93.4(3), Tc–Cp* plane 204.0(4) pm). A striking feature is the unusually short distance (186.7(4) pm) between the two Tc atoms coupled by the three μ -oxo ligands (distance between the Cp*-bridged Tc atoms 407.7(4) pm); the shortest Tc–Tc distance recorded so far is 213(1) pm. Shorter metal–metal distances are found only in binuclear chromium complexes^[5] with a minimum of 182.8(2) pm in $[\text{Cr}_2(2\text{-MeO-5-MeC}_6\text{H}_3)_4]$.^[6]

Formally, the two technetium centers must be assigned on oxidation number of +3.5. This would mean that the ground state has the relatively rare $\sigma^2 \pi^4 \delta^1$ configuration and thus a bond order of 3.5.^[7] This bond order together with the three μ -oxo ligands makes the extremely short Tc–Tc distance understandable.

The spectroscopic data are fully consistent with the results of the X-ray structure analysis. Thus, in the EI mass spectrum the molecular peak is clearly visible at m/z 381.6 (18%), and the Tc–O stretching vibrations appear in the IR spectrum at 909 (symmetric) and 880 cm^{-1} (antisymmetric). In the ¹H NMR spectrum the methyl protons are observed at $\delta = 1.606$.

Experimental

A solution of **4** (180 mg, 0.57 mmol) in C_6H_6 (15 mL) was treated with 5 mL of 30% H_2O_2 and the mixture stirred at room temperature. The initial concentration of **4** first started to decrease after 24 h. After 3 days, **4** could no longer be detected. After separation of the phases the organic phase was dried with Na_2SO_4 and freed of oily reaction products by chromatography (silica gel 60, 30 × 20 cm, C_6H_6). Subsequent elution with C_6H_6 /diethyl ether (1/1) gave a yellow zone. After slow evaporation of solvent from the eluate (ca. 12 h), **5** was recovered in the form of needle-shaped yellow crystals. Yield: 25.0 mg (16.0%). ⁹⁹Tc 51.6% (calcd. 51.94%). EI-MS fragmentation (relative intensity [%] in parenthesis): Cp*⁺ (100); Cp*⁺Tc⁺ (36); Cp*⁺TcO⁺ (0.0); Cp*⁺TcO₃⁺ (18). The corresponding relative intensities for **2** under similar conditions are 100, 35, 100, and 0.0%.

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[1] W. A. Herrmann, *Angew. Chem.* 100 (1988) 1269; *Angew. Chem. Int. Ed. Engl.* 27 (1988) 1297, zit. Lit.; A. H. Klahn-Oliva, D. Sutton, *Organometallics* 3 (1984) 1313.

[2] J. Okuda, E. Herdtweck, W. A. Herrmann, *Inorg. Chem.* 27 (1988) 1254.

[3] Yellow column-shaped crystals (0.23 × 0.26 × 0.31 mm³); $a = 594.6(5)$, $b = 869.7(4)$, $c = 1063.0(7)$ pm; $V = 549.70 \times 10^6$ pm³; $Z = 4$; space group $D_{2h}^{13}\text{-Pmmn}$ (No. 59). Data collection with a Siemens-Stoe diffractometer (AED II), θ/ω scan ($3^\circ < 2\theta < 60^\circ$); $h(\text{min}/\text{max})$ 0/8, k 0/12, l 0/15, MoK_α radiation ($\lambda = 0.71069$ Å); 969 possible reflections in the measuring range, 381 ($I > 2.0 \sigma(I)$), 348 independent ($I > 2.25 \sigma(I)$); empirical absorption correction (χ scans, 4 reflections $13^\circ < 2\theta < 42^\circ$, transmission factors (min/max) 0.74/1.00, $\mu = 24.41 \text{ cm}^{-1}$, $\rho_{\text{calcd}} = 2.3 \text{ g cm}^{-3}$); solution of structure by Patterson, Fourier and Difference Fourier syntheses, refinement by method of least squares (all non-hydrogen atoms anisotropic, H atoms fixed at ideal positions), $R = 0.059$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.044$, $\text{Goof} = [\sum w(|F_o| - |F_c|)^2 / (\text{NO-NV})]^{1/2} = 2.19$, residual electron density 1.47/−3.13 e/Å³, shift/esd (mean/max) 0.18/1.8. All calculations based on the program system SHELXTL. Further details of the crystal investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53780, the names of the authors, and the journal citation.

[4] F. A. Cotton, L. D. Gage, *Nouv. J. Chim.* 1 (1977) 441; F. A. Cotton, W. K. Bratton, *J. Am. Chem. Soc.* 87 (1965) 921.

[5] P. O'Brien in G. Wilkinson, R. D. Gillard, J. A. McCleverty (Eds.): *Comprehensive Coordination Chemistry*, Vol. 3, Pergamon Press, Oxford 1987, p. 741 ff.

[6] F. A. Cotton, S. A. Koch, M. Miller, *Inorg. Chem.* 17 (1978) 2084.

[7] M. H. Chisholm in F. A. Cotton (Ed.): *Reactivity of Metal-Metal Bonds*, ACS Symp. Ser. 155 (1981).