tron-rich double bond.[3] It is difficult to predict which bond in phenylallene should be attacked more rapidly because the rates of reaction of styrene and 1-alkenes with 2,4-dinitrobenzenesulfenyl chloride are not greatly different[5,6] ($k_2 \times 10^3$ l. mol^{-1} sec^{-1}; styrene, 0.737; 4-methyl-1-pentene, 0.82; 1-hexene, 1.18). A possible explanation for exclusive formation of 1 is reaction through a charge transfer complex between the phenyl group of the allene and the aromatic ring of the sulfenyl chloride. A molecular model shows that the –SCl in such a complex would be in position to react easily with the π-electrons of the terminal double bond from the phenyl side if the phenyl group is oriented for maximum conjugation with the π-electrons of the internal double bond of the allene. This would give an adduct in which the phenyl and sulfenyl groups are on the same side of the double bonds, as observed.

Type B structures are assigned to the major adducts RCHClC(SAr)=CH$_2$ because the chemical shifts of the nmr signals for the vinyl protons are close to those for ClCH$_2$C(SAr)=CH$_2$[1]: R = CH$_3$, δ 6.05, 6.45; C$_2$H$_5$, 6.15, 6.45; n-C$_3$H$_7$, 6.10, 6.45. Signals for the –CHClR protons are also as expected: 4.60 (q), J = 7 Hz; 4.35 (m); and 4.45 (t), J = 6.5 Hz, respectively.

1,3-Disubstituted allenes give mixtures of adducts of types A and B. Type B structures are assigned to the major products on the basis of the chemical shifts of the nmr signals for olefinic and allylic protons as described earlier.[1] Relative amounts of these types as determined by integration of the nmr spectra of the crude reaction mixtures are given in Table II. The

Table II. Relative Amounts of Adducts from RCH=C=CHR'

Adduct	%	Nmr[a]			
		H	J	H	J
CH$_3$C=C(SAr)CClCH$_3$[b] H$_A$ H$_B$	60	6.55 (q)	7	5.25 (q)	6.5
CH$_3$C=CClC(SAr)CH$_3$[c] H$_A$ H$_B$	40	6.95 (q)	7	4.80 (q)	6.5
C$_2$H$_5$C=C(SAr)CClCH$_3$[c] H$_A$ H$_B$	56	6.40 (t)	7	5.20 (q)	6.5
CH$_3$C=C(SAr)CClC$_2$H$_5$[b] H$_A$ H$_B$	29	6.55 (q)	7	4.90 (t)	6.5
C$_2$H$_5$C=CClC(SAr)CH$_3$[c] H$_A$ H$_B$	15	6.80 (t)	7	4.75 (q)	6.5
C$_2$H$_5$C=C(SAr)CClC$_2$H$_5$[c] H$_A$ H$_B$	80	6.45 (t)	7	4.95 (t)	7
C$_2$H$_5$C=CClC(SAr)C$_2$H$_5$[c] H$_A$ H$_B$	20	6.80 (t)	7	4.45 (t)	7
(CH$_2$)$_6$C=C(SAr)CCl[b] H$_A$ H$_B$	83	6.65 (t)	8.5	$\simeq$5.30[d]	

[a] Chemical shifts in δ, J in Hz. [b] Crystalline. [c] Oil. [d] Probably overlapping triplets.

relative chemical shifts of isomeric type A and type B adducts are in accord with the earlier discussion.[1] It was shown that type B adducts did not rearrange to type A even on long exposure to the reaction conditions.

Experiments with 1,2-cyclotridecadiene and 1,3-di(1-adamantyl)allene were preliminary only; no type A adducts could be detected by nmr on the crude reaction mixtures. The chemical shifts in the nmr spectra indicated that type B adducts were obtained from 1,2-cyclotridecadiene, =CH, δ 6.40 (t), J = 8.5 Hz, CHClR,

(5) W. L. Orr and N. Kharasch, J. Amer. Chem. Soc., 75, 6030 (1953).
(6) D. R. Hogg and G. M. Beverly, J. Chem. Soc. B, 175 (1971).

5.05, and from diadamantylallene, =CH, δ 5.95 (s), CHClR, 5.20 (s).

Addition of an equimolar amount of tetramethylallene to 2,4-dinitrobenzenesulfenyl chloride in methylene chloride gave an exothermic reaction. After stirring for 6 days at room temperature, solvent was removed to give an oil. Chromatography on silica gel gave a 55% yield of H$_2^a$C=C(CH$_3^b$)C(SAr^d)=C-(CH$_3^c$)$_2$, red needles, mp 88–89.5°, the expected product[7]: nmr H$_a$ 5.95 (m, 2), H$_b$ 2.15 (s, 3), H$_c$ 1.70 (s, 3) and 1.80 (s, 3), H$_d$ 7.65 (d, 1), 8.35 (dd, 1), 9.10 (d, 1); uv (95% alcohol) λ_{max} 255 (ϵ 11,400), 362 nm (ϵ 10,200). A red oil was also obtained (30% yield); it was a mixture but did not appear to contain any monoadduct.

(7) W. H. Mueller and P. E. Butler, J. Org. Chem., 33, 1533 (1968).

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Tris(dimethylaminato)tris(N,N-dimethylcarbamato)-tungsten(VI). The Product of the Remarkable Reaction between Hexakis(dimethylaminato)tungsten and Carbon Dioxide

Sir:

We have synthesized a new series of compounds of the early transition elements according to the general reaction A.[1] Although these N,N-dimethylcarbamato

$$N(NMe_2)_n + nCO_2 \longrightarrow M(O_2CNMe_2)_n \qquad (A)$$

where M = Ti, Zr, V, or Mo for n = 4; M = Nb or Ta for n = 5;

M = Mo or W for n = 3

complexes bear a formal similarity to N,N-dialkyldithiocarbamato complexes[2] of the early transition elements, significant differences in their chemistry are apparent.[1] We wish at this time to report on the reaction between W(NMe$_2$)$_6$ and CO$_2$ which does *not* conform to eq A but rather leads to the novel compound W(NMe$_2$)$_3$(O$_2$CNMe$_2$)$_3$.

A hydrocarbon solution of W(NMe$_2$)$_6$ reacts rapidly with CO$_2$ (6 or more equiv) in a sealed tube at room temperature to give W(NMe$_2$)$_3$(O$_2$CNMe$_2$)$_3$ (1). When the reaction is carried out in an nmr tube the formation of 1 is seen to be quantitative, although the transient species W(NMe$_2$)$_5$(O$_2$CNMe$_2$) and W(NMe$_2$)$_4$(O$_2$-CNMe$_2$)$_2$ have been detected spectroscopically. 1 is an air-sensitive, light orange crystalline solid, sparingly soluble in pentane and hexane and appreciably soluble in benzene and toluene. A cryoscopic molecular weight determination shows that 1 is monomeric in benzene. The mass spectra of W(NMe$_2$)$_3$(O$_2$-^{12}CNMe$_2$)$_3$ and of the ^{13}C labeled W(NMe$_2$)$_3$(O$_2$-^{13}CNMe$_2$)$_3$ show parent ions at 536 and 539, respectively (^{184}W), corresponding to loss of Me$_2$N·

(1) M. H. Chisholm and M. Extine, results to be submitted for publication.
(2) E.g., in their method of preparation, see D. C. Bradley and M. H. Gitlitz, Chem. Commun., 289 (1965).

from the molecular ion. At 30° the ^1H nmr spectrum of **1** in toluene-d_8 shows two singlets of equal intensity at δ 4.85 and 2.87 ppm from HMDS (hexamethyl-disiloxane). Below −5° the high field singlet splits into a doublet (splitting 2.0 Hz at 60 MHz). No further change is observed on cooling to −90°. We assign the low field resonance (δ 4.85 ppm) to the W–NMe₂ protons and the high field resonance to the carbamato-methyl protons. This assignment is substantiated by the observation of $^3J_{^{13}C-H}$ = 3.0 Hz for the high field resonance in the ^{13}C labeled compound W(NMe₂)₃-(O₂^{13}CNMe₂)₃. The infrared spectra of N,N-dimethyl-carbamato complexes of the early transition elements show strong bands in the region 1550–1690 cm⁻¹ characteristic of the NCO₂ moiety.[1] For **1** a *single* band is found at 1632 cm⁻¹. Thus all the spectroscopic data may be rationalized in terms of either six-coordinated tungsten, *fac*-WN₃O₃, or nine-coordinate tungsten, *fac*-WN₃O₃O₃′. We decided to resolve this interesting and important structural question unequivocally[3] by taking advantage of rapid and cheap commercial crystallographic services.[4]

Crystal data: W(NMe₂)₃(O₂CNMe₂)₃; M = 580.34; trigonal; $a = b$ = 12.899 (4) Å, c = 9.509 (2) Å; $\alpha = \beta$ = 90°, γ = = 120°; Z = 2; D_{calcd} = 1.407 g/cm³; space group $P\bar{3}$. Intensity data were collected on a Syntex P $\bar{1}$ computer-controlled diffractomer using Mo Kα radiation. In the refinement of the structure, 2658 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used. The tungsten was refined anisotropically, and the other nine non-hydrogen atoms were refined isotropically to give the final agreement factors R_1 = 0.054 and R_2 = 0.076. An ORTEP view of the molecular structure of **1** is shown in Figure 1 and pertinent bond distances and bond angles are given in Table I. See paragraph at
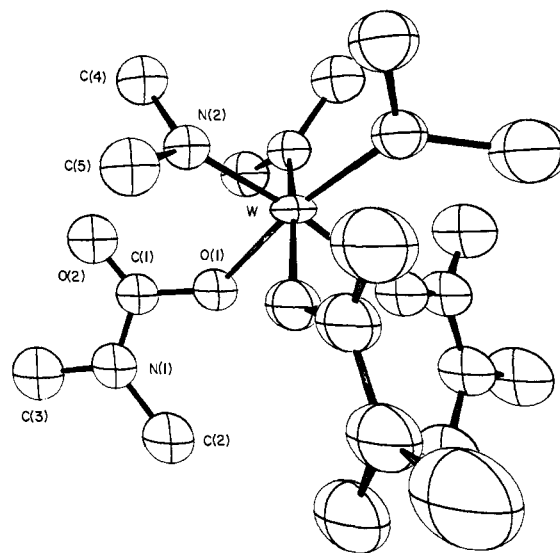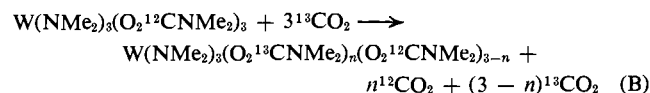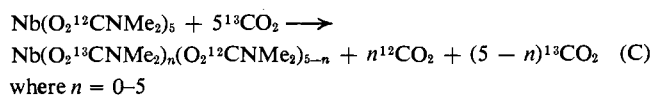

Figure 1. A view of the molecular structure of W[N(CH₃)₂]₃-[O₂CN(CH₃)₂]₃ showing the atomic numbering scheme. The sizes and shapes of the atoms are determined by their final thermal parameters and by their perspective view.

Table I. Bond Distances (Å) and Bond Angles (deg)

W–O(1)	2.041 (6)	N(1)–C(2)	1.44 (1)
W–N(2)	1.922 (7)	N(1)–C(3)	1.47 (1)
O(1)–C(1)	1.30 (1)	N(2)–C(4)	1.48 (1)
C(1)–O(2)	1.24 (1)	N(2)–C(5)	1.50 (1)
C(1)–N(1)	1.35 (1)		
O(1)–W–O(1)′	82.1 (2)	O(1)–C(1)–O(2)	122.8 (9)
O(1)–W–N(2)	93.2 (3)	O(1)–C(1)–N(1)	114.9 (9)
O(1)–W–N(2)′	89.3 (3)	O(2)–C(1)–N(1)	122.3 (9)
O(1)–W–N(2)″	170.7 (3)	C(1)–N(1)–C(2)	123.3 (8)
N(2)–W–N(2)′	94.8 (3)	C(1)–N(1)–C(3)	119.9 (9)
W–O–(1)–C(1)	133.7 (6)	C(2)–N(1)–C(3)	116.6 (9)
W–N(2)–C(4)	125.7 (6)	C(4)–N(2)–C(5)	107.6 (7)
W–N(2)–C(5)	126.5 (6)		

Weighted Least-Squares Planes (Å)

| Plane I		Plane II	
O(1)	0.012	N(2)	0.0
C(1)	−0.015	C(4)	0.0
O(2)	−0.003	C(5)	0.0
N(1)	−0.026		
C(2)	0.003		
C(3)	0.061		

W distance from plane I = 0.79 Å

W distance from plane II = 0.10 Å

(3) A plausible distinction between mono- and bidentate Me₂NCO₂ ligands based on ¹²C¹⁶O₂, ¹³C¹⁸O₂, and ¹²C¹⁸O₂ labeling studies will be presented subsequently, ref 1.

(4) Molecular Structure Corporation, College Station, Texas 77840. Total time, including postal deliveries, from sending crystals to receiving full details was 2 weeks; total cost, including crystal mounting and drawing of structure was $1328.00.

end of paper regarding supplementary material. The molecular structure belongs to the symmetry point group C_3. Tungsten is six-coordinate and the local geometry about the metal, WN₃O₃, is suitably described as a distorted fac-octahedron. Of particular note are the following observations: (i) the N(2)–W–N(2)′ angles (94.8 (3)°) are greater than the O(1)–W–O(1)′ angles (82.1 (2)°), (ii) the W–N(2) bond distances (1.922 (7) Å) are considerably shorter than the W–O(1) bond distances (2.041 (6) Å), and (iii) the O₂CNMe₂ and W–NMe₂ moieties are planar.

The reaction between W(NMe₂)₆ and CO₂ is remarkable in several ways. For example, (1) W(NMe₂)₆ is an extremely sterically congested molecule[5] yet it reacts with CO₂ very rapidly, much more rapidly that it reacts with alcohols, ROH, which yield W(OR)₆.[1] (2) The reaction is unique in not conforming to the general reactions of eq A. (3) Although W(NMe₂)₆ consumes only 3 mol equiv of CO₂, **1** reacts with CO₂ according to eq B where n = 0–3. However, this type of ex-

$$W(NMe_2)_3(O_2^{12}CNMe_2)_3 + 3^{13}CO_2 \longrightarrow$$
$$W(NMe_2)_3(O_2^{13}CNMe_2)_n(O_2^{12}CNMe_2)_{3-n} +$$
$$n^{12}CO_2 + (3-n)^{13}CO_2 \quad (B)$$

change reaction is not unique to **1**; Nb(O₂CNMe₂)₅ readily exchanges CO₂ according to eq C.[1] At 25° an equilibrium mixture of products is reached for eq B after *ca.* 48 hr and for eq C after *ca.* 15 min.

$$Nb(O_2^{12}CNMe_2)_5 + 5^{13}CO_2 \longrightarrow$$
$$Nb(O_2^{13}CNMe_2)_n(O_2^{12}CNMe_2)_{5-n} + n^{12}CO_2 + (5-n)^{13}CO_2 \quad (C)$$

where n = 0–5

The mechanism of the insertion of CO₂ and related molecules (*e.g.*, COS, CS₂, XYC=O) into M–N covalent bonds is not known and has received little attention.[6] It seems likely that it should involve a transi-

(5) D. C. Bradley, M. H. Chisholm, C. E. Heath, and M. B. Hurst-house, *Chem. Commun.*, 1261 (1969).

(6) M. F. Lappert and B. Prokai, *Advan. Organometal. Chem.*, **5**, 225 (1967).

tion state of the type shown below for which electronic and steric factors will be important. A consideration

$$O=C=O$$
$$M-N \overset{Me}{\underset{Me}{}}$$
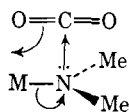
of the structures of $W(NMe_2)_6$[5] and **1** leads us to believe that steric factors are not the sole controlling factors in the formation of **1**. We suggest that insertion is limited by the nucleophilicity of the NMe_2 ligands. Six dimethylaminato ligands, Me_2N^-, offer tungsten a total of 24 electrons although the available metal valence orbitals can accommodate only 18 electrons. Thus for $W(NMe_2)_6$ ligand to metal π-bonding may lead to a maximum W–N bond order of 1.5. However, in $W(NMe_2)_3(O_2CNMe_2)_3$ replacement of three NMe_2 ligands by weaker π-donating oxygen ligands leads to greater N to W π bonding as evidenced by the very short W–N bond length of 1.922 (7) Å; cf. W–N 2.032 (25) Å in $W(NMe_2)_6$.[5] The fac-WN_3O_3 geometry of **1** allows for maximum W–N π bonding. The nucleophilic character of the dimethylamido lone pairs is thus diminished and further insertion of CO_2 is not favored. Insertion of CO_2 into metal–nitrogen covalent bonds may thus parallel the insertion of CO_2 into metal–alkyl bonds for which the importance of the carbanionic character of the alkyl group has recently been emphasized.[7]

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(7) T. Tsuda, K. Veda, and T. Saegusa, J. Chem. Soc., Chem. Commun., 380 (1974).

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## Photochemistry of Aromatic Compounds. Photorearrangement of 3,5-Dimethoxybenzyl Acetate

Sir:

The photochemical reaction pathway of a carboxylic acid ester is dependent on structure and on reaction conditions.[1] Reactions involving either stepwise or concerted homolytic processes usually predominate,

(1) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 434–441.

including, for example, photodecarboxylation,[2] photodecarbonylation,[2c,3] Norrish type II analogs,[4] and the photo-Fries rearrangement.[5] Several reactions involving heterolytic processes have also been observed, for example, photosolvolysis of substituted benzyl acetates[6] and photohydrolysis of aryl benzoates.[7] We wish to report the novel photochemical rearrangement of a substituted benzyl acetate to a relatively stable nonaromatic isomer.[8]

Irradiation[9] of a 0.006 M hexane solution of acetate **1a**[6] gave a mixture of **1a** (3.6%),[10] 1,3-dimethoxy-5-methylene-6-acetoxycyclohexa-1,3-diene (**2a**, 17.2%),
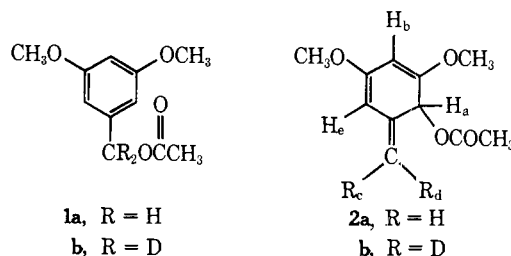
3^{11} (5.6%), 4^{12} (46.8%), **5** (9.5%), mp 106–107° (lit.[13] 102°), and 6^{14} (17.2%) obtained as a mixture.[15] Column

3, R = H
4, R = CH₃
5, R = 3,5-(CH₃O)₂C₆H₃CH₂
6, R = C₆H₁₃

7a, R = H
b, R = D
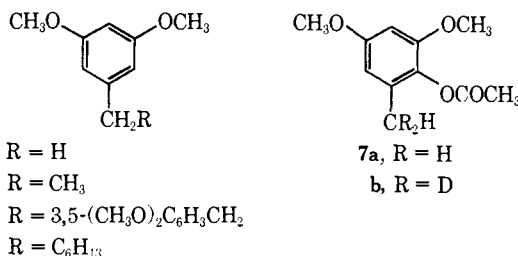
chromatography on silica gel with ether–hexane allowed

(2) (a) B. Matuszewski, R. S. Givens, and C. Neywick, J. Amer. Chem. Soc., **95**, 595 (1973); (b) T. O. Meiggs, L. I. Grossweiner, and S. I. Miller, ibid., **94**, 7986 (1972); (c) T. O. Meiggs and S. I. Miller, ibid., **94**, 1989 (1972); (d) R. S. Givens and W. F. Oettle, J. Org. Chem., **37**, 4325 (1972); (e) L. J. Mittal, J. P. Mittal, and E. Hayon, J. Phys. Chem., **77**, 2267 (1973), and references therein.

(3) (a) P. Ausloos, J. Amer. Chem. Soc., **80**, 1310 (1958); (b) M. H. J. Wijnen, ibid., **82**, 3034 (1960), and references therein.

(4) (a) M. L. Yarchak, J. C. Dalton, and W. H. Saunders, Jr., J. Amer. Chem. Soc., **95**, 5224, 5228 (1973); (b) Y. Ogata, K. Takagi, and Y. Takayanagi, J. Chem. Soc. Perkin Trans. 1, 1244 (1973); (c) J. A. Barltrop and J. D. Coyle, J. Chem. Soc. B, 251 (1971); (d) J. G. Pacifici and J. A. Hyatt, Mol. Photochem., **3**, 267, 271 (1971).

(5) (a) C. E. Kalmus and D. M. Hercules, J. Amer. Chem. Soc., **96**, 449 (1974); (b) W. Adam, J. A. DeSanabia, and H. Fischer, J. Org, Chem., **38**, 2571 (1973); (c) D. Belluš, Advan. Photochem., **8**, 109 (1971), and references therein.

(6) H. E. Zimmerman and V. R. Sandel, J. Amer. Chem. Soc., **85**, 915 (1963).

(7) J. G. Pacifici, J. S. Zannucci, G. R. Lappin, J. C. Ownby, and C. A. Kelley, Mol. Photochem., **3**, 349 (1972), and references therein.

(8) Photochemical rearrangement of benzyl benzoates to benzylbenzoic acids has been reported, M. Afzal, Chem. Ind. (London), 37 (1974).

(9) For each run 250 ml of solution was degassed with purified nitrogen for 40 min prior to and during irradiation for 30 min with a 450-W Hanovia lamp through a Corex filter.

(10) Yields were determined by pmr analysis of product after rotary evaporation of hexane. Essentially all resonances could be assigned to indicated compounds.

(11) S. Ludwinowsky and J. Tambor, Chem. Ber., **39**, 4037 (1906).

(12) J. P. Brown, N. J. Cartwright, A. Robertson, and W. B. Whalley, J. Chem. Soc., 859 (1949).

(13) T. Petrzilka, W. Haefliger, and C. Sikemeier, Helv. Chim. Acta, **52**, 1102 (1969).

(14) The pmr, ir, and mass spectra were consistent with the structural assignment, and carbon and hydrogen analyses were within 0.3 % of theory.

(15) H. E. Zimmerman and V. R. Sandel found[6] that in 50% (v/v) aqueous dioxane **1a** undergoes photosolvolysis to yield 3,5-dimethoxybenzyl alcohol; **2a** is not formed.