

bromo-3,3-difluoropropene by bromine abstraction with photochemically generated diethylphosphonyl radicals.⁶ The esr spectra were interpreted in terms of nonequivalent substituents in the 1 and 3 positions (Table I).

While the coupling constants of the terminal protons in the allyl radical are essentially constant over a broad temperature range, the magnitude of the coupling to the 2 proton has a notable *positive* temperature coefficient. Similar temperature coefficients are observed for all the allylic radicals of Table I. They are attributed to out-of-plane vibronic motions of the hydrogens in the 2 position. The signs of these coefficients are opposite to that of the protons in the methyl radical indicating a *positive* sign for $a(\text{H}_2)$ ⁷ and therefore a negative π spin density on C_2 in agreement with theory.⁸ The greater temperature dependence of all couplings in the substituted radicals compared to the allyl radical imply greater amplitudes for torsional motion about the allylic bonds and therefore a reduced rigidity of the planar structures.

It is noteworthy that 1,1-difluoro and 1,1-dimethoxy substitution *increases* the π spin density on C_3 judging by the increase in the average magnitude of the H_3 couplings for these radicals relative to the allyl radical. The fluorine hyperfine couplings⁹ can be compared with those for α,α -difluorobenzyl¹⁰ (51.4 G) since in the parent hydrocarbon radicals the unpaired π spin densities on the benzylic and the terminal allylic carbon atoms are comparable.^{11,12} The larger α -fluorine coupling in the former indicates either some degree of nonplanarity at the benzylic carbon atom or out-of-plane vibronic and torsional motions of greater amplitudes than in the difluoroallyl radical. Thus, a coplanar vinyl group is more effective than a coplanar phenyl group in counteracting the strong inherent propensity of the $-\dot{\text{C}}\text{F}_2$ radical fragment toward a pyramidal structure.^{6a,13}

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(7) J. K. Kochi, P. Bakuzis, and P. J. Krusic, *J. Amer. Chem. Soc.*, **95**, 1516 (1973).

(8) H. M. McConnell, *J. Chem. Phys.*, **28**, 1188 (1958); C. Heller and T. Cole, *ibid.*, **37**, 243 (1962); A. Hinchliffe and N. M. Atherton, *Mol. Phys.*, **13**, 89 (1967); J. R. Bolton, "Radical Ions," Wiley-Interscience, New York, N. Y., 1968, Chapter 1.

(9) Cf. L. D. Kispert, C. U. Pittman, Jr., D. L. Allison, T. B. Patterson, Jr., C. W. Gilbert, Jr., C. F. Hains, and V. Prather, *J. Amer. Chem. Soc.*, **94**, 5979 (1972).

(10) L. D. Kispert, H. Liu, and C. U. Pittman, Jr., *ibid.*, **95**, 1657 (1973).

(11) Cf. (a) R. V. Lloyd and D. E. Wood, *J. Amer. Chem. Soc.*, **96**, 659 (1974); (b) M. Raimondi, M. Simonetta, and G. F. Tantaridini, *J. Chem. Phys.*, **56**, 5091 (1972).

(12) The unpaired π spin densities on the fluorinated carbon atoms of $\text{CH}_2=\text{CH}\dot{\text{C}}\text{F}_2$ and $\phi\dot{\text{C}}\text{F}_2$ have been calculated by the INDO method.^{9,10} For the former radical $\rho_{\text{C}} = 0.59^9$ and for the latter $\rho_{\text{C}} = 0.65$.¹⁰ A portion of the difference in fluorine splittings for these radicals may, therefore, be due to a small difference in unpaired spin density at carbon. The same authors, however, calculated a much flatter potential well for a torsional motion of the CF_2 group in $\phi\dot{\text{C}}\text{F}_2$ than in $\text{CH}_2=\text{CH}\dot{\text{C}}\text{F}_2$ in agreement with our conclusion. We thank a referee for these observations.

(13) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965); (b) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *ibid.*, **48**, 4802 (1968); (c) L. Pauling, *ibid.*, **51**, 2767 (1969); (d) R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **95**, 7180, 7182 (1973).

P. J. Krusic,* P. Meakin, B. E. Smart
Contribution No. 2166, Central Research Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

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Addition Reactions of Allenes. V.¹ 2,4-Dinitrobenzenesulfonyl Chloride²

Sir:

Addition of organic sulfonyl chlorides to olefins is well known, but the corresponding reaction of allenes has not been thoroughly explored.³ The recent paper on addition of 2,4-dinitrobenzenesulfonyl chloride to phenylallene⁴ leads us to give a preliminary report of our work on addition of this reagent to ten aliphatic allenes. Results are summarized in Table I.

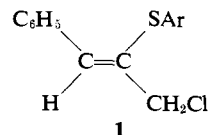
Table I. 2,4-Dinitrobenzenesulfonyl Chloride Adducts from $\text{RCH}=\text{C}=\text{CHR}'^a$

R	Allene	R'	% yield crystals	Oil	Mp, °C (crude)
CH_3		H^b	75	11.5	45–48.5
C_2H_5		H^b	73	17	72.5–75
<i>n</i> - C_3H_7		H^c	23	42	62–65
CH_3		CH_3^d	60	32	89–91
CH_3		C_2H_5^b	32	55	68–72
C_2H_5		$\text{C}_2\text{H}_5^{b,e}$		79	
	$-(\text{CH}_2)_6-f$		75	17	142–144
	$-(\text{CH}_2)_{10}-g$		35	35	109–113
Adm		Adm ^{b,h}	35	42	215–219

^a All of the allenes are known compounds and were synthesized by conventional methods. For 1,3-di(1-adamantyl)allene see T. L. Jacobs and R. C. Kammerer, *J. Amer. Chem. Soc.*, **94**, 7190 (1972). Additions were carried out in CHCl_3 at room temperature unless otherwise indicated. All crystalline adducts gave correct C and H values; Cl and either N or S values were obtained for most of them and all were correct. Expected nmr spectra were obtained on all adducts; chemical shifts for olefinic and allylic protons are given in Table II. Results for tetramethylallene are not included in the table. ^b At 0°. ^c Reaction time 48 hr, unreacted allene present. ^d In CH_2Cl_2 . ^e All attempts to obtain crystals failed. Analysis of the oil gave C, 45.96; H, 5.05. Calcd for $\text{C}_{13}\text{H}_{13}\text{ClN}_2\text{O}_4\text{S}$: C, 47.20; H, 4.57. ^f In HOAc, 3 hr. ^g About 15% of the crude product lost. ^h Adm, 1-adamantyl.

Equimolar amounts of the allene and sulfonyl chloride were allowed to react for 1–8 weeks at 0° or room temperature. Mixtures were obtained in every instance as shown by isolation of both crystals and oils or by the nature of the nmr spectra.

The major adduct from each monosubstituted allene had the type B structure,¹ $\text{RCHClC}(\text{Sar})=\text{CH}_2$, rather than type A, $\text{RCH}(\text{Sar})\text{CCl}=\text{CH}_2$. Neither this type A adduct nor any adduct in which attack occurred on the terminal double bond was detected by nmr of crude reaction mixtures or of the oils although presumably some of these were present in minor amounts. These results contrast with those for phenylallene⁴ which gives



as the only product. The general pattern in electrophilic additions to allenes is attack on the more elec-

(1) Paper IV: T. L. Jacobs and R. Macomber, *J. Org. Chem.*, **33**, 2988 (1968).

(2) From the Ph.D. Thesis of R. C. Kammerer, University of California, Los Angeles, 1972.

(3) For a brief review see M. C. Caserio, *Selec. Org. Transform.*, **1**, 259 (1970).

(4) K. Izawa, T. Okuyama, and T. Fueno, *J. Amer. Chem. Soc.*, **95**, 4090 (1973).

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-dinitrobenzenesulfonyl chloride are not greatly different^{5,6} ($k_2 \times 10^3 \text{ l. mol}^{-1} \text{ sec}^{-1}$; 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 sulfonyl 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 sulfonyl 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 $\text{ClCH}_2\text{C(SAr)=CH}_2$: R = CH_3 , δ 6.05, 6.45; C_2H_5 , 6.15, 6.45; $n\text{-C}_3\text{H}_7$, 6.10, 6.45. Signals for the -CHClR protons are also as expected: 4.60 (q), $J = 7 \text{ Hz}$; 4.35 (m); and 4.45 (t), $J = 6.5 \text{ Hz}$, 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 $\text{RCH=C=CHR}'$

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

^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, $=\text{CH}$, δ 6.40 (t), $J = 8.5 \text{ Hz}$, 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, $=\text{CH}$, δ 5.95 (s), CHClR, 5.20 (s).

Addition of an equimolar amount of tetramethylallene to 2,4-dinitrobenzenesulfonyl 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 $\text{H}_2\text{C=C(CH}_3\text{)C(SAr)}^d\text{=C(CH}_3\text{)}_2$, red needles, mp 88–89.5°, the expected product⁷: 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 mono-adduct.

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Thomas L. Jacobs,* R. Craig Kammerer

Contribution No. 3351, Department of Chemistry

University of California

Los Angeles, California 90024

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Tris(dimethylamino)tris(*N,N*-dimethylcarbamato)-tungsten(VI). The Product of the Remarkable Reaction between Hexakis(dimethylamino)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



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*-dialkyl-dithiocarbamate complexes² of the early transition elements, significant differences in their chemistry are apparent.¹ We wish at this time to report on the reaction between $\text{W(NMe}_2\text{)}_6$ and CO_2 which does not conform to eq A but rather leads to the novel compound $\text{W(NMe}_2\text{)}_3(\text{O}_2\text{CNMe}_2)_3$.

A hydrocarbon solution of $\text{W(NMe}_2\text{)}_6$ reacts rapidly with CO_2 (6 or more equiv) in a sealed tube at room temperature to give $\text{W(NMe}_2\text{)}_3(\text{O}_2\text{CNMe}_2)_3$ (**1**). When the reaction is carried out in an nmr tube the formation of **1** is seen to be quantitative, although the transient species $\text{W(NMe}_2\text{)}_5(\text{O}_2\text{CNMe}_2)$ and $\text{W(NMe}_2\text{)}_4(\text{O}_2\text{CNMe}_2)_2$ 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 $\text{W(NMe}_2\text{)}_3(\text{O}_2\text{-}^{12}\text{CNMe}_2)_3$ and of the ^{13}C labeled $\text{W(NMe}_2\text{)}_3(\text{O}_2\text{-}^{13}\text{CNMe}_2)_3$ show parent ions at 536 and 539, respectively (^{184}W), corresponding to loss of Me_2N .

(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).