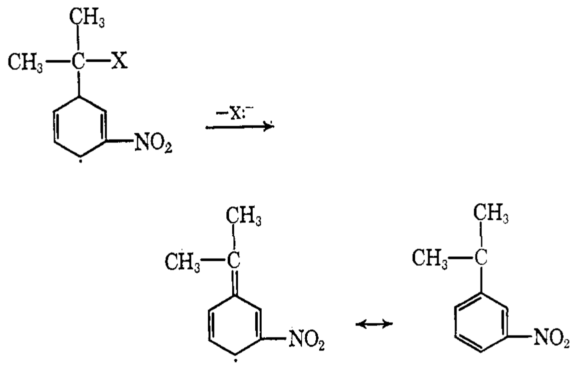


(5)

the *m*-nitro group, is a tertiary cumyl radical and, thus, is distinctly more stable than the benzylic radical of eq 3. Furthermore, in the *m*-nitrocumyl system, in contrast to the *m*-nitrobenzyl system,[3c] the SN2 displacement does not compete; consequently, the radical-anion sequence can proceed without interference.

Since the reactions of eq 4 do not occur when the *m*-nitro group is replaced by hydrogen,[1,2] it is clear that the *m*-nitro group plays a vital role in bringing about substitution at the tertiary carbon atom, and since the presence of a nitro group is also crucial in the *p*-nitrocumyl system (where considerable evidence has already been gathered supporting the intermediacy of radical anions[1,2]), it is reasonable to assume that the reactions of the *m*-nitrocumyl system also proceed *via* radical anions.[3c]

Acknowledgment. We thank the Petroleum Research Fund and the Explosives Department of Du Pont for generous support.

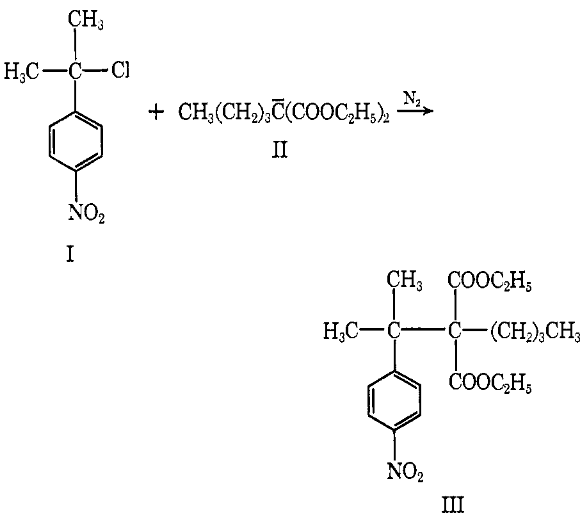
Nathan Kornblum, Thomas M. Davies, Gary W. Earl
Norman L. Holy, Joseph W. Manthey
Michael T. Musser, R. Thomas Swiger
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907
Received August 21, 1968

New and Facile Substitution Reactions at Tertiary Carbon. The Use of Oxygen as a Mechanistic Probe

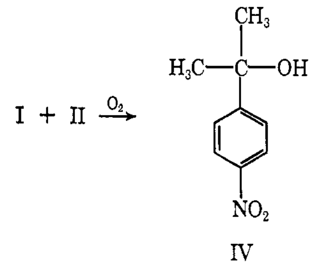
Sir:

In 1967 we reported that the chlorine of *p*-nitrocumyl chloride (I) is readily replaced by a variety of anions.[1] For example, treatment of I with the anion derived from *n*-butylmalonic ester (II) at 25° under nitrogen gives the alkylate III in 89% yield (eq 1). It has now been found that, when the reaction is conducted in the presence of oxygen, alkylation is completely suppressed. Not only is the alkylate III not formed, but, instead, *p*-nitrocumyl alcohol (IV) is isolated in 88% yield (eq 2). It is noteworthy that oxygen does not convert *p*-nitrocumyl chloride (I) to the alcohol IV in the absence of *n*-butylmalonate anion (II).

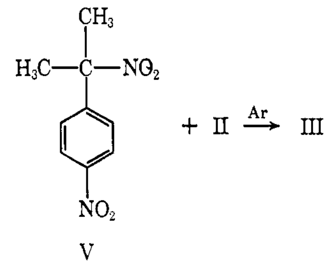
The results obtained with α,*p*-dinitrocumene (V) are also dramatic: treatment of V with the sodium salt of *n*-butylmalonic ester (II) results in a 98% yield of the alkylate III provided the reaction is carried out under argon (eq 3), but, under oxygen, *p*-nitrocumyl alcohol (IV) is the main product (80% yield) and the alkylate III is obtained in a mere 6% yield. α,*p*-Dinitrocumene is, of course, completely stable to oxygen when the *n*-butylmalonate anion (II) is absent.



(1)



(2)



(3)

Suppression of substitution at the tertiary carbon of *p*-nitrocumyl chloride[1] and α,*p*-dinitrocumene[2] by oxygen is not restricted to reactions which employ the anion of *n*-butylmalonic ester; it is clear from the data of Tables I and II that this is a general phenomenon. It is also evident from Tables I and II that the anion of *n*-butylmalonic ester is not unique in promoting the conversion of *p*-nitrocumyl chloride (I) and α,*p*-dinitrocumene (V) to *p*-nitrocumyl alcohol (IV).[3]

These facts are easily understood on the basis of the chain mechanism proposed for substitution at the tertiary carbon of the *p*-nitrocumyl system (eq 4–7).[1,2] Oxygen, a very efficient scavenger of carbon free radicals, intercepts the *p*-nitrocumyl radicals (VI) before they undergo reaction 6 and converts them into peroxy radicals (eq 8); substitution is thereby prevented. The peroxy radicals VIII are then usually converted into *p*-nitrocumyl alcohol.[4] However, with sodium azide in

---

(1) N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *J. Am. Chem. Soc.*, **89**, 725 (1967).

(2) N. Kornblum, T. M. Davies, G. W. Earl, G. S. Greene, N. L. Holy, R. C. Kerber, J. W. Manthey, M. T. Musser, and D. H. Snow, *ibid.*, **89**, 5714 (1967).

(3) The use of oxygen as a diagnostic was suggested to us by the work of G. A. Russell and W. C. Danen [*ibid.*, **88**, 5663 (1966)] who found that the 2-nitropropane anion is oxidized by molecular oxygen when *p*-nitrobenzyl chloride is present; they report, however, that the *p*-nitrobenzyl chloride is not consumed.

(4) G. A. Russell and A. G. Bemis [*ibid.*, **88**, 5492 (1966)] have shown that DMSO + $ROO^- \rightarrow DMSO_2 + RO^-$. Since most of the reactions

Table I. Reactions Employing *p*-Nitrocumyl Chloride (I)

Anion	Atm	Products, % yield: Substitution[1]	*p*-Nitrocumyl alcohol (IV)	Recovered I
$CH_3(CH_2)_3\bar{C}(COOC_2H_5)_2$	N_2	89	0	
	O_2	0	88	
$\bar{C}H(COOC_2H_5)_2$	Ar	95	0	
	O_2	0	94	1
1-Methyl-2-naphthoxide	Ar	63	0	*a*
	O_2	0	66	*a*
$(CH_3)_2\bar{C}$–NO_2[b]	N_2	85	10[c]	
	O_2	20	70	
$C_6H_5S^-$	Ar	95	0	
	O_2	4	83	*d*
N_3^- [b]	N_2	97	0	
	O_2	61	20[e]	4
$C_6H_5SO_2^-$ [b]	N_2	97	0	
	O_2	0	72	20

[a] *p*-Nitro-α-methylstyrene isolated in 30% yield. [b] In hexamethylphosphoramide. [c] *Cf.* footnote 7 of N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, J. W. Manthey, M. T. Musser, and R. T. Swiger, *J. Am. Chem. Soc.*, **90**, 6219 (1968). [d] *p*-Nitro-α-methylstyrene produced (10% yield). [e] Actually *p*-nitrocumene hydroperoxide.

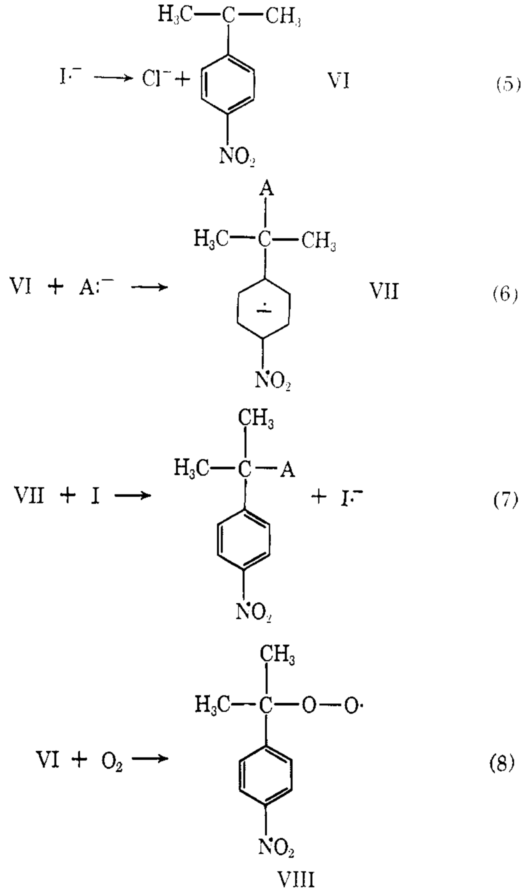
Table II. Reactions Employing α,*p*-Dinitrocumene (V)

Anion	Atm	Products, % yield: Substitution[2]	*p*-Nitrocumyl alcohol (IV)	Recovered V
$CH_3(CH_2)_3\bar{C}(COOC_2H_5)_2$	Ar	98	0	
	O_2	6	80	9
$\bar{C}H(COOC_2H_5)_2$	Ar	95	0	
	O_2	0	33	64
1-Methyl-2-naphthoxide	Ar	69	0	*a*
	O_2	0	69	*b*
$(CH_3)_2\bar{C}$–NO_2[c]	N_2	90	5[d]	
	O_2	0	80	15
$C_6H_5S^-$	Ar	96	0	
	O_2	82	11	3[e]
	O_2	2	4	92[f]
N_3^- [c]	N_2	97	0	
	O_2	4	84[g]	

[a] *p*-Nitro-α-methylstyrene isolated (23% yield). [b] *p*-Nitro-α methylstyrene isolated (22% yield). [c] In hexamethylphosphoramide. [d] *Cf.* footnote 7 of ref 8. [e] 2 mol of $NaSC_6H_5$/mol of V added all at once at beginning of reaction. [f] 3.5 mol of $NaSC_6H_5$/mol of V added over a 3-hr period. [g] This is actually 24% IV and 60% *p*-nitrocumene hydroperoxide.

hexamethylphosphoramide substantial amounts of *p*-nitrocumyl hydroperoxide are isolated. The isolation of *p*-nitrocumyl hydroperoxide provides strong support for the view that *p*-nitrocumyl radicals are intermediates in these substitution reactions.[5]

$$I + A:^- \longrightarrow I^{-} + A \qquad (4)$$



In the *m*-nitrocumyl series it is more difficult to obtain an insight into the ability of oxygen to affect reactions.[6] Nonetheless, sufficient is known to enable one to discern a striking difference: in the *meta* series oxygen is unable to prevent substitution by anions; furthermore, only very small amounts of *m*-nitrocumyl alcohol are produced. The data are given in Table III.

Table III. Reactions Employing *m*-Nitrocumyl Chloride (IX)

Anion	Atm	Products, % yield: Substitution[8]	*m*-Nitrocumyl alcohol	Recovered IX
$\bar{C}H(COOC_2H_5)_2$	Ar	92	0	
	O_2	70	3	22
$C_6H_5S^-$	N_2	94	0	
	O_2	82	2	12
N_3^- [a]	N_2	79	0	6[b]
	O_2	76	0	14[c]

[a] In hexamethylphosphoramide. [b] *m*-Nitro-α-methylstyrene also isolated in 8% yield. [c] *m*-Nitro-α-methylstyrene also isolated (9% yield).

We propose that in the *m*-nitrocumyl series radical anions are intermediates but that here, in contrast to the *p*-nitrocumyl system, a nonchain process[7] is the important pathway (eq 9–11).[8] In other words, cage collapse of radicals is the major process in the *m*-

---

reported herein were carried out in DMSO, it is not surprising that *p*-nitrocumyl alcohol is produced. Other pathways for the conversion of VIII to *p*-nitrocumyl alcohol are easily envisioned; this matter will be discussed presently. Furthermore, most of the anions employed are themselves attacked by oxygen, and, indeed, there are indications that the products of such oxidation augment scavenging of VI by molecular oxygen. It is of interest that from reactions involving the *n*-butylmalonate anion II the alcohol n-$C_4H_9C(OH)(COOC_2H_5)_2$ is isolated, and when the anion of 1-methyl-2-naphthoxide is employed, the corresponding alcohol, 1-hydroxy-2-keto-1-methyl-1,2-dihydronaphthalene, is obtained.

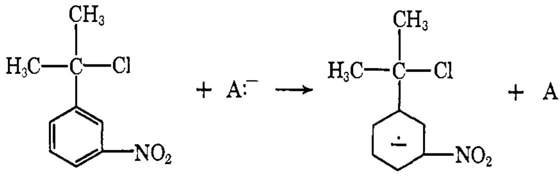
(5) It also becomes clear how anions induce the formation of *p*-nitrocumyl alcohol: *p*-nitrocumyl chloride and α,*p*-dinitrocumene, by reacting with anions according to eq 4 and 5, are transformed into *p*-nitrocumyl radicals (VI) which then react with oxygen (eq 8); in the absence of the anions *p*-nitrocumyl radicals are not produced, and, therefore, oxygen is without effect.

(6) This is true because ambident anions give mixtures of products and reaction rates are slower.[8]

(7) R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Am. Chem. Soc.*, **87**, 4520 (1965).

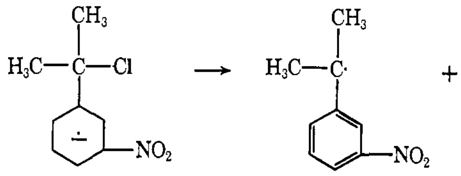
(8) Kornblum, *et al.*, Table I, footnote *c*.

nitrocumyl series. The failure of oxygen to stop substitution and its inability to convert *m*-nitrocumyl chloride into *m*-nitrocumyl alcohol are readily intelligible on this basis. Furthermore, cage combination of two radicals (eq 11) serves to explain the lack of selectivity observed with ambident anions in the *m*-nitrocumyl series, a lack of selectivity which is to be contrasted with the high degree of selectivity exhibited in the *p*-nitrocumyl system.[8,9]

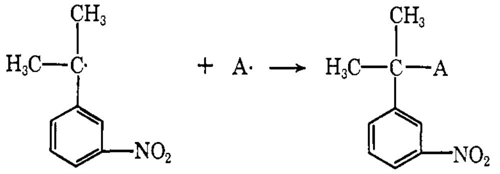


(9)

IX



(10)



(11)

Acknowledgment. We thank the Petroleum Research Fund and the Explosives Department of Du Pont for generous support.

[9] The allocation of a chain mechanism to the *p*-nitrocumyl system and a nonchain sequence to the *m*-nitrocumyl system is a matter which will be discussed in detail in the full paper.

Nathan Kornblum, Gary W. Earl, Norman L. Holy
Joseph W. Manthey, Michael T. Musser
Donald H. Snow, R. Thomas Swiger
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received August 21, 1968

The Vibrational Frequency of the O_2^+ Cation

Sir:

A new, easy preparation method for the dioxygenyl compounds of AsF_5 and SbF_5 was recently described by two of us.[1] We now report Raman spectra of the solid powders prepared in this way. The Raman equipment, details of which will be described elsewhere, includes a Spectra-Physics 125 He–Ne laser and a Spex 1400 II double monochromator.

A photograph of the Raman spectrum recorded for $O_2^+AsF_6^-$ is presented in Figure 1 with measured frequencies and assignments marked. By means of calibrations with nearby neon lines, we determined the frequencies to a probable error of about 1 cm^{-1}. Figure 1 clearly shows the three Raman-active vibrations of the octahedral AsF_6^- anion with frequencies close to those observed earlier for $Cs^+AsF_6^-$.[2] In addition, there is one intense band at 1858 cm^{-1}, which can only be assigned to the O_2^+ vibration. This has not, to our knowledge, been observed for solid complexes before, but corresponds quite well to the frequency of 1876 cm^{-1} determined from electronic band spectra of gaseous O_2^+.[3]

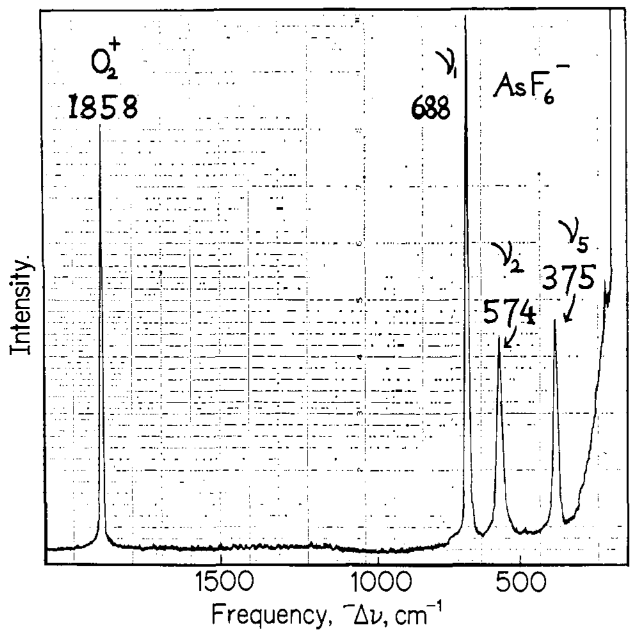


Figure 1.

Our observation of the O_2^+ vibration in the Raman spectrum is perhaps the most convincing or direct proof of the existence of the O_2^+ cation in a stable chemical compound.

We have also observed the O_2^+ vibration for solid $O_2^+SbF_6^-$, this time at 1862 cm^{-1}. It has also been possible to observe it in solution. This was done by dissolving $O_2^+SbF_6^-$ in excess liquid SbF_5. In the solution the O_2^+ vibration was observed at 1860 cm^{-1}.

Table I lists frequencies and force constants of a group of species related to O_2^+, isoelectronic species being in the same row. This table shows the marked decrease in force constant associated with increase of number of electrons.

Table I. Comparison of Frequencies and Force Constants for Related Species of Molecules or Ions

Species	Obsd frequency, cm^{-1}	Force constant, mdyn/Å	Species	Obsd frequency, cm^{-1}	Force constant, mdyn/Å
			NO^+	2387[d]	25.0
O_2^+	1860[a]	16.3	NO	1876[e]	15.5
O_2	1556[b]	11.4	NO^-	1100–1200[f]	5.52
O_2^-	1145[c]	6.18			

[a] Solid or liquid complex: this work. [b] Gas: A. Weber and E. A. McGinnis, *J. Mol. Spectry.*, **4**, 195 (1960). [c] Solid complex: J. A. Creighton and E. R. Lippincott, *J. Chem. Phys.*, **40**, 1779 (1964). [d] Solid complex: D. W. A. Sharp and J. Thorley, *J. Chem. Soc.*, 3557 (1963). [e] Gas: H. W. Thompson and B. A. Green, *Spectrochim. Acta*, **8**, 129 (1956). [f] Solid complexes, average value: W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 775 (1961).

For the isoelectronic pair, O_2^+ and NO, however, the force constant is nearly the same. This leads us to suggest that the frequency around 1150 cm^{-1} that

---

(1) J. Shamir and J. Binenboym, *Inorg. Chim. Acta*, **2**, 37 (1968).

(2) G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, **6**, 2212 (1967).

(3) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., New York, N. Y., 1950, p 560.