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THE EFFECT OF THE DIETHYLPHOSPHONATE GROUP ON FREE RADICAL STABILITIES

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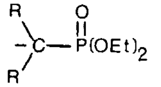
Abstract: The diethylphosphonate substituent is free radical stabilizing by a conjugation mechanism as judged by its effect on the rate of the methylenecyclopropane rearrangement.

The diethylphosphonate group is stabilizing to the carbanion 1.[1] Our recent studies[2] suggest that, contrary to naive expectations, this group is only weakly destabilizing when placed directly on a cationic center as in 2. In an attempt to shed further light on the properties of this electronegative substituent, we have carried out studies which allow an evaluation of the effect of this group on the stability of free radicals 3.[3]



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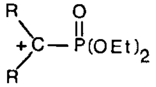

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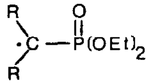

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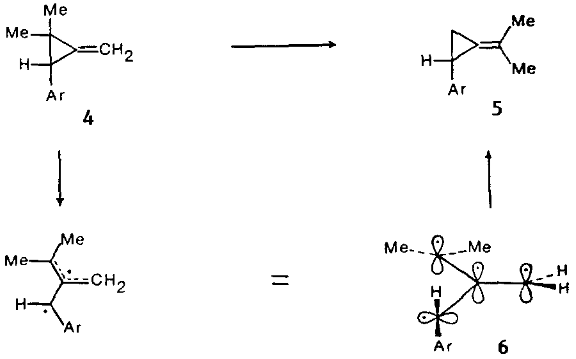
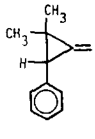
The methylenecyclopropane rearrangement shown below is a free radical process relatively devoid of polar character in the transition state.[4] The reaction of 4 proceeds thermally, in high yield, to give the isopropylidenecyclopropane 5, presumably via the singlet trimethylenemethane, 6. The rate is substituent dependent with free radical stabilizing groups on the aromatic ring leading to increased rates. We have previously used substituent effects on the rate of this reaction as a measure of purely radical stabilizing effects , in the absence of polar effects. Indeed, Arnold and Dust[5] have found that these rearrangement rates correlate with their free radical substituent constants based on benzyl radical hyperfine coupling constants.



We have now determined the effect of the diethylphosphonate substituent of the rate of this rearrangement.[6] Rate data[7] are summarized on the next page. A p-diethylphosphonate group increases the rearrangement rate by a factor of 1.48. This is similar to the rate increase induced by a p-methyl substituent , but smaller than the rate



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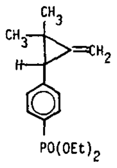

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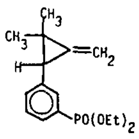

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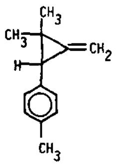

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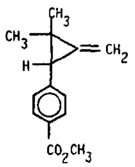

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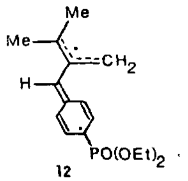


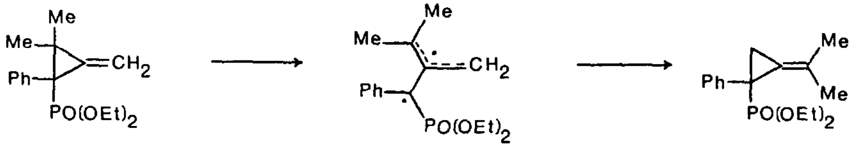
12

relative rearrangement rates in C_6D_6 at 80 °C

7	8	9	10	11
1.0	1.48	0.78	1.42	2.26

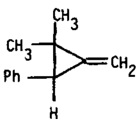
increase observed for the conjugating p-CO_2CH_3 group.[3a] One therefore concludes that the diethylposphonate group is also free radical stabilizing. Interestingly, this substituent in the meta position slightly retards the rate. This has been previously noted[3a] for other electronegative meta substituents (CF_3, CN, halogen) and attributed to the fact that a free radical is still an electron deficient intermediate which can be slightly destabilized by a purely electronegative substituent. The rate enhancing effect of the diethylphosphonate substituent in **8** is therefore a conjugative effect which increases the rate of formation of **12** despite the retardation expected for an electronegative substituent.

While the data suggest a radical stabilizing property of $PO(OEt)_2$, a problem is the relatively small rate spread observed. This is not unexpected since the true radical stabilizing effect of a substituent is attenuated by the aromatic ring in the intermediate. Hence we sought confirming data on the influence of $PO(OEt)_2$ attached directly to a free radical center where any radical stabilizing effect would not be greatly attenuated. Rearrangement rates[7] of **13** (where **14** is presumably the intermediate) to the corresponding isopropylidenecyclopropane **15** were therefore determined as well as rates of the analogs **16** and **17**. The rate trends parallel those seen in the p-substituted systems but with a much larger rate spread. The diethylphosphonate substituted system **13**



13 14 15

rearranges faster than the unsubstituted analog **7** but slower than the carboethoxy substituted analog **17**. However



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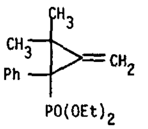

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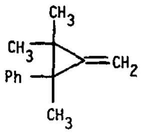

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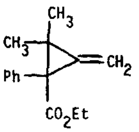


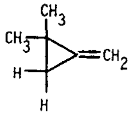
17

relative rearrangement rates at 60 °C

7	13	16	17
1.0	73	7.5	491

this data is much more difficult to interpret since steric factors are undoubtedly present and not a constant factor throughout the series. In any event, this data is consistent with a radical stabilizing effect of $PO(OEt)_2$ if one assumes that steric factors are not the only major factors influencing rearrangement rates in this series.

In an attempt to reduce steric factors in an unattenuated system, a third series of substrates (**18**-**20**) was



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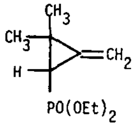

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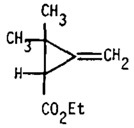


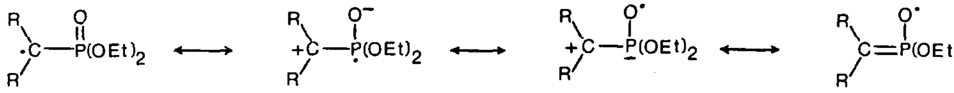
20

relative rearrangement rates in toluene-d_8 at 170 °C

1.0 32 560

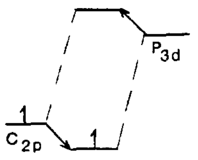
subjected to thermal methylenecyclopropane rearrangement.[8] Rates again implicate the diethylphosphonate group as free radical stabilizing, but somewhat less effective than carboethoxy. In systems **18**-**20**, steric effects are undoubtedly smaller than in the phenyl analogs **7**, **13**, and **17**. One should therefore have more confidence in using this data as evidence for the radical stabilizing nature of diethylphosphonate.

By what mechanism does the diethylphosphonate group, which contains an oxidized third row element, stabilize a free radical? The effect is presumably conjugative in that it is observed in the para but not in the meta position of an aromatic ring. A valence bond description of spin delocalization utilizing the vacant phosphorus d-orbitals is shown below. Forms such as **21b**, **21c**, and **21d** predict spin delocalization onto phosphorus and to oxygen.

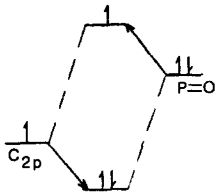


21a **21b** **21c** **21d**

A perturbation molecular orbital description would involve stabilization by interaction of the singly occupied carbon orbital of the radical with any vacant or any filled orbital of $PO(OEt)_2$ of appropriate symmetry and energy. Two such potential interactions, using a vacant phosphorus d-orbital or the filled phosphoryl orbital, are shown. Either of these two interactions would result in spin delocalization and net radical stabilization.



Stabilization of a radical by an adjacent vacant d-orbital



Stabilization of a radical by an adjacent filled phosphoryl orbital

In summary, the diethylphosphonate group is remarkably similar to the carbonyl and the cyano groups with respect to carbanions, carbocations and free radicals. All three groups are carbanion stabilizing. All three appear to interact with carbocationic centers in a fashion which minimizes the destabilizing inductive effect. Finally, all three groups are free radical stabilizing by conjugative interactions as judged by their effect on the methylenecyclopropane rearrangement.[9]

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References and Notes

1. Wadsworth, W. S., Jr.; Emmons, W. D. J. Am. Chem. Soc. **1961**, 33, 1733-38. The σ' value for this group is 0.52. See Tsvetkov, E. N.; Lobanov, D. I.; Isosenkova, L. A.; Kabachnik, M. I. J. Gen. Chem. USSR (engl. Transl.) **1969**, 39, 2126-32.

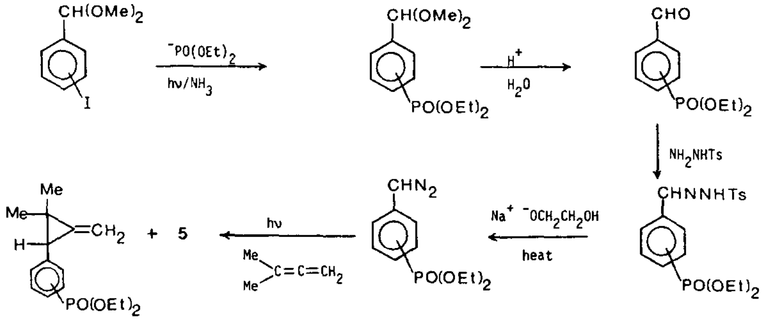
2. (a) Creary, X.; Geiger, C. C.; Hilton, K. J. Am. Chem. Soc. **1983**, 105, 2851-8. (b) Creary, X.; Underiner, T. J. Org. Chem. **1985**, 50, In Press.

3. Previous polymerization studies on diethyl vinylphosphonate imply that the diethylphosphonate group has some free radical stabilizing properties. See (a) Arcus, C. L.; Matthews, R. J. S. J. Chem. Soc. **1965**, 4607-12. (b) Pike, R. M.; Cohen, R. A. J. Polymer Sci. **1960**, 44, 531-8. CA 54:23410g. See also (c) Zenftman, H.; Calder, D. British Patent 812983. CA53:P15647f.

4. (a) Creary, X. J. Org. Chem. **1980**, 45, 280-4 and references therein. For further references, see also (b) Gajewski, J. J. J. Am. Chem. Soc. **1971**, 93, 4450-8. (c) Kirmse, W.; Marawski, H.-R. J. Chem. Soc., Chem. Commun. **1977**, 122-3. (d) Hehre, W. J.; Salem, L.; Willcott, M. R. J. Am. Chem. Soc. **1974**, 96, 4328-30.

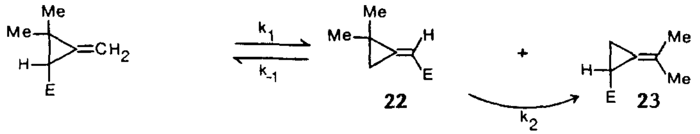
5. Dust, J. M.; Arnold, D. R. J. Am. Chem. Soc. **1983**, 105, 1221-7.

6. All of the substrates described were prepared by addition of the appropriate carbene to 1,1-dimethylallene. The specific substrates **8** and **9** were prepared as shown below.



7. Rearrangement rates of **7** in C_6D_6; k(80.0 °C)=5.65 x 10^{-5} s^{-1}; k(60.0 °C)=5.05 x 10^{-6} s^{-1}

8. Esters **19** and **20** rearrange to give initially a mixture of **22** and **23**, with **22** undergoing further rearrangement to **23** at a slower rate. The relative rates given represent rates of approach to equilibrium ($k_1 + k_{-1}$). The g.c. rate data is not of the precision necessary to extract the actual values of k_1.



19 E= $PO(OEt)_2$
20 E= CO_2Et

9. A recent thermolysis study on substituted azo compounds supports our contention that $PO(OEt)_2$ (as well as CN and COR) are radical stabilizing. See Luedtke, A. E.; Timberlake, J. W. J. Org. Chem. **1985**, 50, 268-70.

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