what slower rate. Both AgL^+ and AgL^{2+} have absorbance maxima in the ultraviolet at about 195 and 348 nm, respectively, making it possible to follow the course of the reaction and obtain an isobestic point at 312 nm.

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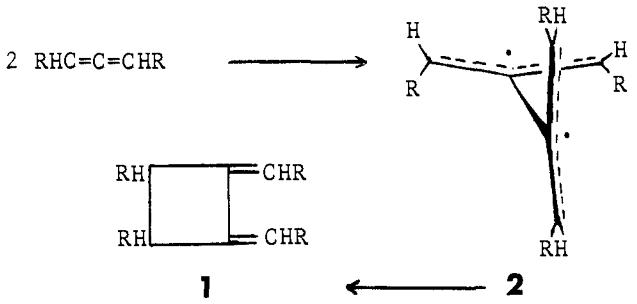
1,3-Diadamantylallene. Trapping of a Biradical Intermediate in Thermal Dimerization of Substituted Allenes

Sir:

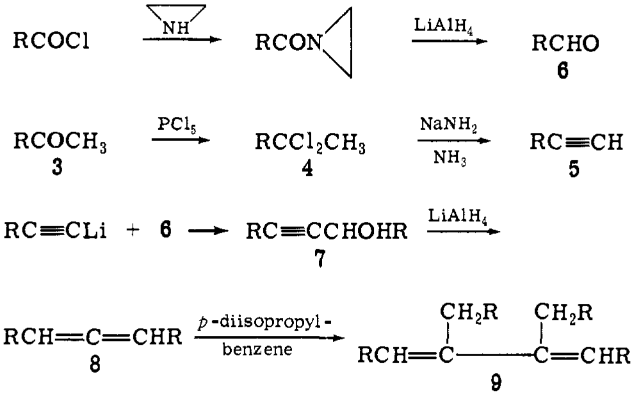
Evidence has accumulated[1-4] that thermal dimerization of many substituted allenes, which yields 1,2-dimethylenecyclobutanes (**1**), often involves formation of an intermediate bisallyl biradical **2**. Preference for those stereoisomers having larger groups on the double bonds inward[5] was explained by assuming that the most easily formed conformation for the biradical was that in which the two flat allylic ends were orthogonal and the larger substituents were inward; ring closure was assumed to be faster than rotation of the parts of the allylic system to form other conformers.



Adamantylallenes were chosen for further study because, on the basis of models, the bulky adamantyl group can occupy neither both inward positions on the double bonds of the 1,2-dimethylenecyclobutane system nor cis positions on the ring. Most adamantyl compounds are crystalline so it was hoped that it would be easier to establish the purity of the dimers obtained. Results with 3-adamantyl-1-chloroallene[1c] confirmed expectations. Several biradical conformations were required to account for the dimers formed, and these were the conformations which appeared least hindered on the basis of models.

The present paper reports the synthesis and attempted dimerization of 1,3-diadamantylallene. It was expected that dimerization would occur less readily with this allene but that if it did occur, only two of the six possible stereoisomers would be produced. Models suggested that the first step of the reaction, formation of the biradical, might occur fairly readily and it was hoped that it might live long enough to be trapped.

1,3-Diadamantylallene (**8**) was synthesized as shown in the equations. The yield of **3** was 95%[6] and adamantylacetylene (**5**) was obtained in 80% yield based on **3**. Dehydrohalogenation of **4** with powdered potassium hydroxide was unsuccessful. The spectral and analytical data for **5** agree with those in the literature.[7] Adamantyl aldehyde (**6**) was prepared as reported earlier;[8] this compound decomposes rapidly on storage and must be used at once. Addition of **6** to the lithium derivative of **5** gave **7**[9,10] in 80% yield by a procedure based on that for 2,2,6,6-tetramethyl-3,4-heptadiene.[11] Treatment of **7** with lithium aluminum hydride gave 30% of **8** and some **7** was recovered. White crystals of **8**, mp 226–232°, were isolated by column chromatography on alumina: ir (CCl_4) 2900 (s), 2850 (s), 1960 (m), 1440 (s), 1350 (m), 1340 (m), 1310 (m), 1100 (m), 985 (m), 980 (m), 875 (m) cm^{-1}; mass spectrum (70 eV) *m/e* 308 (parent ion); nmr (CCl_4) δ 1.80–2.10 (m, 30, adamantyl protons),[12] 4.95 (s, 2, allenyl protons).[9] Neither ir nor laser Raman spectra at full instrument sensitivity indicated any acetylenic impurity.



R = 1-adamantyl

8 gave a 1:1 adduct with 2,4-dinitrobenzenesulfenyl chloride, isolated by chromatography on silica gel: yellow crystals; mp 215–219°; nmr ($CDCl_3$) δ 1.50–2.20 (m, adamantyl protons), 5.20 (s, C*H*ClAd), 5.95 (s, =C*H*Ad), 7.95 (d), 8.30 (d of d), and 8.95 (d).[9]

When an attempt was made to dimerize **8**, neat in an evacuated sealed tube at 250° for 72 hr, pure unre-

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[1] (a) T. L. Jacobs, J. R. McClenon, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.*, **91**, 6038 (1969); (b) O. J. Muscio, Jr., and T. L. Jacobs, *Tetrahedron Lett.*, 2867 (1969); (c) T. L. Jacobs and O. J. Muscio, Jr., *ibid.*, 4829 (1970); (d) S. R. Byrn, E. Maverick, O. J. Muscio, Jr., K. N. Trueblood, and T. L. Jacobs, *J. Amer. Chem. Soc.*, **93**, 6680 (1971).

[2] J. J. Gajewski and C. N. Shih, *ibid.*, **89**, 4532 (1967); **91**, 5900 (1969); **94**, 1675 (1972); J. J. Gajewski and W. A. Black, *Tetrahedron Lett.*, 899 (1970).

[3] W. von E. Doering and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **89**, 4534 (1967); W. R. Dolbier, Jr., and S. H. Dai, *ibid.*, **92**, 1774 (1970).

[4] J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970), gives a review.

[5] 1,2-Cyclononadiene yields stereoisomers which do not follow this tendency [W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **91**, 5918 (1969)] perhaps because the allylic ends of the biradical can only be planar if the ring is strained, so an alternative, one-step, concerted pathway is followed. 1,3-Diarylallenes [E. V. Dehmlow and G. C. Ezimora, *Tetrahedron Lett.*, 1265 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 322 (1972); T. L. Jacobs, A. J. Brattesani, and O. J. Muscio, Jr., research in progress] also yield dimers that do not follow the stereochemical rules; these will be discussed in another paper.

[6] R. E. Bowman, *J. Chem. Soc.*, 322 (1950); H. Stetter and E. Rauscher, *Chem. Ber.*, **93**, 2054 (1960).

[7] H. Stetter and P. Goebel, *ibid.*, **95**, 1039 (1962).

[8] V. L. Narayanan, U. S. Patent 3,300,480 (1967); *Chem. Abstr.*, **66**, 85697 (1967); see also K. Bott, *Agnew. Chem., Int. Ed. Engl.*, **7**, 894 (1968).

[9] Satisfactory elemental analyses were obtained.

[10] Ir ($CHCl_3$) 3580, 3425, 2960, 2840, 2240, 1450, 1360, 1310, 1225, 1100, 1040, 1000 cm^{-1}; nmr ($CDCl_3$) δ 1.65–1.90 (m, 30), 2.15 (s, 1, OH), 3.80 (s, 1).

[11] W. T. Borden and E. J. Corey, *Tetrahedron Lett.*, 313 (1969).

[12] R. C. Fort, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

acted **8** was recovered. At 340 and 305° for 72 and 35 hr, respectively, only black carbonized, insoluble material was obtained; combustion analysis of this showed *ca.* 95% carbon. Heating of **8** as a 3% solution in *p*-diisopropylbenzene in an evacuated sealed tube for 50 hr at 250° gave a 60% yield of **9**: white crystals; mp 250–255°;[9] nmr (CCl$_4$) δ 1.30–2.10 (m, adamantyl and allylic protons), 5.20 (ill-defined t, olefinic protons), ratio *ca.* 30:1; mass spectrum (70 eV) parent ion at *m/e* 618, not 616 as would be expected for **1**; ir 2890 (s), 2850 (s), 2630 (m), 1445 (s), 1350 (m), 1340 (m), 1310 (m), 1100 (m), 1090 (m), 970 (s); uv$_{\max}$ (pentane) 209 nm (shoulder). Ultraviolet spectra of bent butadienes often have no maxima above 210 nm, *e.g.*, 2,3-di-*tert*-butyl-1,3-butadiene[13] and 2,3,4,5-tetramethyl-2,4-hexadiene.[14] These results are in agreement with structure **9**, the product expected for hydrogen transfer to **2** from *p*-diisopropylbenzene. A mixture of aromatic products was also obtained from the reaction but the components have not yet been identified. Although it is possible to account for **9** by other mechanisms than that involving **2**, these seem less likely, and isolation of **9** constitutes added evidence for the two-step, biradical mechanism for allene dimerization. Further attempts are underway to find conditions which will give even low yields of dimers from 1,3-diadamantylallene and an attempt will be made to prepare the optically active allene.

Acknowledgment. We wish to thank the National Science Foundation for generous support in the form of a grant to T. L. J., a research assistantship to R. C. K., and grants to the Department of Chemistry for purchase of spectral equipment.

[13] H. Wynberg, A. DeGroot, and D. W. Davies, *Tetrahedron Lett.'* 1083 (1963).

[14] W. F. Forbes, R. Shilton, and A. Balasubramanian, *J. Org. Chem.*, **29**, 3527 (1964).

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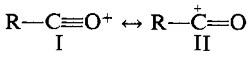
Electron Spectroscopy of Organic Ions. III.[1] Alkyl- and Aryloxocarbenium Ions (Acyl Cations)

Sir:

Since the first stable acyl cations were observed,[2] considerable effort has been directed toward elucidating their structure. Nmr, ir, and X-ray studies[3] have indicated that they are resonance hybrids of the oxonium (I) and oxocarbenium ion (II) forms without evaluating



$$\underset{\text{I}}{\mathrm{R{-}C{\equiv}O^+}} \leftrightarrow \underset{\text{II}}{\mathrm{R{-}\overset{+}{C}{=}O}}$$

the relative contributions of these forms. An important forward step in structural investigations of acyl cations in now provided by X-ray electron spectroscopy (es). Core electron binding energies (E_b) are closely related to molecular charge distribution, reflecting important changes in the valence shell.[4,5] Es has been particularly useful in studying both carbocationic[1,6] and oxonium ion[7] species.

We wish now to report the results of the es study of a series of alkyl- and aryloxocarbenium ions as thermally stable salts.[8] All samples were prepared under dry nitrogen atmosphere using the previously described powder technique.[6] The spectra were recorded with a Varian VIEE-15 instrument equipped with a spherical electrostatic analyzer. The analyzer energy was 100 V. Peak positions were taken as the intensity maxima. Because the salts were extremely sensitive to moisture and in some cases slowly decomposed under vacuum, the spectra were sometimes complicated by lines belonging to minor hydrolysis and/or decomposition products.[9] Impurity (as well as vacuum oil contamination) lines overlap with the lower E_b lines of the ionic species, altering the expected intensity ratios.

Figure 1 shows the C 1s spectrum of methyloxocarbenium and phenyloxocarbenium ions as hexafluoroantimonate salts. In both cases, the higher binding energy signal is assigned to the carbonyl carbon. Table I lists the differences in C 1s binding energies, ΔE_b, between the two principal types of carbon atoms present in the oxocarbenium ions studied. Also included are the relative intensities of the two signals indicating the extent of hydrolysis and/or decomposition processes in the case of alkyloxocarbenium ions.

A comparison between ΔE_b of the acetyl cation (6.0 eV) and that of acetaldehyde (2.6 eV)[10] reveals the substantial effect of formal hydride abstraction from the aldehyde. Since the oxonium ion form (I) of the acetyl cation is isoelectronic with acetonitrile, we have measured the es spectrum of the latter and found $\Delta E_b = 3.0$ eV. The difference $\Delta E_b(\mathrm{CH_3CO^+}) - \Delta E_b(\mathrm{CH_3CN}) = 3.0$ eV mainly accounts for the effect of the positive charge (the effect of the smaller electronegativity of N as compared with that of O should also be taken into consideration, but this effect is expected to be significantly smaller).

Veillard and Weiss[11] have calculated a ΔE_b value of 5.1 eV for the methyloxocarbenium ion and 4.9 eV

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[2] (a) H. Meerwein, K. Bodenbenner, P. Boener, F. Kunert, and K. Wunderlich, *Justus Liebigs Ann. Chem.*, **632**, 38 (1960), and references cited therein; (b) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *J. Amer. Chem. Soc.*, **84**, 2733 (1962).

[3] (a) G. A. Olah and A. M. White, *ibid.*, **89**, 7072 (1967); (b) B. T. Susz and J. J. Wuhrmann, *Helv. Chim. Acta*, **40**, 722 (1957); (c) D. Cook, *Can. J. Chem.*, 37, 48 (1959); (d) F. P. Boer, *J. Amer. Chem. Soc.*, **90**, 6706 (1968).

[4] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. Karlson, I. Lindgren, and B. Lindberg, "ESCA, Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist & Wiksells Boktryckerj, AB, Uppsala, 1967, p 108.

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[6] G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, *J. Amer. Chem. Soc.*, **92**, 7231 (1970); G. A. Olah, G. D. Mateescu, and J. L. Riemenschneider, *ibid.*, submitted for publication.

[7] G. D. Mateescu, J. L. Riemenschneider, and G. A. Olah, manuscript in preparation.

[8] (a) G. A. Olah, *et al.*, *J. Amer. Chem. Soc.*, **85**, 1328 (1963); (b) G. A. Olah and J. J. Svoboda, *Synthesis*, 306 (1972).

[9] The acetyl and isobutyryl cations are subject to proton elimination from the α carbon with subsequent acylation of the resulting ketene. The new acyl ions broaden the lines and alter their relative intensities. The aryloxocarbenium ions are significantly more stable (there is no α hydrogen to allow the above described secondary reactions). Therefore, their spectra show the expected intensity ratios.

[10] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland, London, 1969, p 119.

[11] We thank Professors A. Veillard and R. Weiss for communicating their results prior to publication.