in the proportions 7:2:1, respectively. Because of its relevance to our work and also because of the abnormally high level of Stevens product (**8**, R = Ph) we have reexamined this report. To avoid the ambiguities inherent in glpc analysis (*vide supra*) of these 1,5-dienes we separated products by adsorption chromatography over silica gel. The products[8] **12–19** (Table I) were stable to the reaction conditions and to the separation procedure.[9] Furthermore, those compounds **14–17** containing the vinyl sulfide residue all have the *trans* configuration (J = 14.5–16 Hz),[7] and also we have shown that *cis*- and *trans*-vinyl sulfides do not interconvert under the reaction and work-up conditions. Thus the suggestion[2b] that **14** arises from an electrocyclic reaction (**20**) is excluded since this mechanism demands the formation of a *cis*-vinyl sulfide only. In order to demonstrate beyond any doubt that unusual products **13–19** originated from the ylide **11** we prepared the parent salt **6** (R = Ph)[10] and studied its base-catalyzed decomposition. At 65° in tetrahydrofuran, the same conditions of temperature and solvent as the benzyne reaction, **6** (R = Ph) was transformed by potassium *t*-butoxide in the same product mixture as was obtained in the benzyne run. The product distribution (Table I) was almost identical, in accord with the view that the ylide **11** is the common precursor in both reactions. However at −45° it was converted almost quantitatively into the 1,5-rearrangement product (**11**). A reasonable interpretation of these results is that, along with the 1,5 process, there is a competing homolytic dissociation of the ylide which is of higher activation energy and yields the recombination products of the radical pair **21** and **22**.[11] Apparently the S-phenyl group assists this process since, as we observed, in the S-alkyl series the unusual products are much less favored under similar reaction conditions. Spin delocalization into the phenyl moiety is probably the source of this effect. In summary, therefore, vinylsulfonium ylides rearrange preferentially by the 1,5 pathway, but there is also a competing mechanism, whose importance is a function of the molecular environment and temperature and which is most simply viewed as a homolytic dissociation–recombination reaction.[12]

Table I. Product Composition (wt %)

Method	Temp, °C	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Benzyne[2b,c]	65	69	12	6	6	2	3	2	0.2
Salt + KO-*t*-Bu	65	74	11	5	4	2	3	1	0.2
	−45	99	0.3	0.3	0.3				

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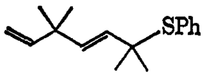
[8] All new compounds have correct (±0.3%) elemental analyses and spectral properties. The dimer **18** occurs as an approximately equal mixture of two diastereoisomers. An excellent materials balance has been achieved in these reactions.

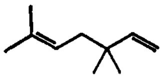
[9] Blank experiments showed that sulfide **11**, on prolonged contact with silica gel, was isomerized to a small extent to compound a.



a

[10] This salt was obtained by the reaction of phenyl 3-methyl-2-butenyl sulfide and 3-methyl-2-butenyl chloride with silver fluoroborate at −45° in tetrahydrofuran.

[11] We could not find hydrocarbon b, but since its isomer was the least abundant product it could have escaped our separation procedure. In the original benzyne work[6] there is a brief note that a dimeric type material was obtained in small amount from dibenzyl sulfide, which is in keeping with our present results.



b

[12] It is significant that a similar radical dissociation–recombination mechanism has been suggested for certain Wittig reactions (*cf.* P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Am. Chem. Soc.*, **88**, 78 (1966)), and more recently direct physical evidence from the same pathway in a Stevens nitrogen reagent has been reported (A. R. Lepley, *ibid.*, **91**, 1237 (1969).

[13] National Science Foundation Predoctoral Fellow, 1968–1969.

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Nuclear Polarization in a Thermal 1,3-Sigmatropic Rearrangement. Evidence for a Radical Pathway

Sir:

In principle a concerted 1,3 shift of a carbon–carbon bond in an allyl system, *i.e.*, **1** to **2**, may proceed with conservation of orbital symmetry by two geometrical pathways, either as a suprafacial migration with inversion in R or as an antarafacial migration with retention in R.[1,2] An alternative, stepwise process could be a radical dissociation–recombination mechanism, proceeding through an intermediate radical pair such as **3**. Since the recombination of a radical pair would, under conditions of favorable electron and nuclear spin relaxation, lead to a nuclear polarized product,[3] we have examined a suitable system in the hope of observing such an effect.

The thermal conversion of the *exo*-methylenecyclohexadienamine (**4**) to the aromatic isomer **5** was discovered and studied by Hauser and Van Eenam,[4] who showed that the reaction was unimolecular and proceeded readily under homogeneous conditions at rates which were compatible with our experimental facilities.[5] A gas–liquid partition chromatographic analysis of the products of this thermolysis, in the temperature range 140–170°, showed that under these conditions **4**

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[1] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965), and references cited there. Reviewed by (a) R. B. Woodward in "Aromaticity," Special Publication No. 21, The Chemical Society, London; (b) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); G. B. Gill, *Quart. Rev.* (London), 22, 338 (1968).

[2] Concerted 1,3- and 1,5-sigmatropic rearrangements have been extensively studied by J. A. Berson, who has reviewed the area in *Accounts Chem. Res.*, **1**, 152 (1968).

[3] H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5518 (1967); (b) R. G. Lawler, *ibid.*, **89**, 5519 (1967); (c) J. Bargon, H. Fischer, and H. Johnson, *Z. Naturforsch.*, **22a**, 1551, 1556 (1967); (d) A. R. Lepley, *J. Am. Chem. Soc.*, **90**, 2710 (1968); (e) H. R. Ward, R. G. Lawler, and H. Y. Loken, *ibid.*, **90**, 7359 (1968); (f) R. Kaptein, *Chem. Phys. Letters*, **2**, 261 (1968); (g) A. R. Lepley, *Chem. Commun.*, 64 (1969); (h) H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Am. Chem. Soc.*, **91**, 747 (1969); (j) A. R. Lepley and R. L. Landau, *ibid.*, **91**, 748 (1969); (j) A. R. Lepley, *ibid.*, **91**, 749, 1237 (1969).

[4] C. R. Hauser and D. N. Van Eenam, *ibid.*, **79**, 5512, 5520, 6274, 6277 (1957).

[5] These studies were carried out on a Varian A-60 instrument with a variable-temperature probe.

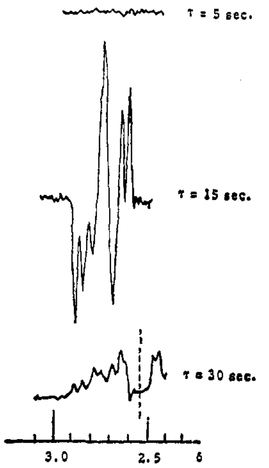
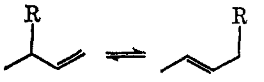
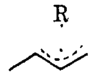


Figure 1. Emission and absorption in the CH_2^A multiplet observed at 160° during conversion of **4** to **5**.

proceeded almost quantitatively to **5**, contaminated by a small amount (5%) of the dimeric hydrocarbon **6**.[6] Since chemically induced dynamic nuclear polarization (CIDNP)[3] was most probable in those protons directly attached to the carbon atoms involved in the rebonding process, *i.e.*, the residue $ArCH_2^ACH_2^BN$ in **5**, we scrutinized this spectral region prior to the experiment. The expected symmetrical A_2B_2 structure (Figure 1c) was partially obscured in the higher field multiplet by the N- and C-methyl resonances. This higher field portion was shown to be due to the group CH_2^B by conversion of the amine to its trifluoroacetate salt, whereupon it underwent the expected downfield shift of 0.7 ppm. By inserting a neat sample of **4** into the probe at 160° and scanning the region δ 2.5–3.0 repeatedly, we obtained the enhanced emission and absorption in the CH_2^A multiplet, shown in Figure 1b. Enhancement factors in both emission and absorption were in the range of 5–20 at the time of maximum effect, 15 sec after insertion of the sample. After 30 sec the normal spectrum of product **5** was established (Figure 1c). Although the greater part of the upper field multiplet CH_2^B was obscured by the methyl signals, we were able to record a strong emission from the first line. These dynamic effects are reproducible and can be readily observed in the range 170–120°; however, for this particular system the practical requirements of repeated scanning and minimal viscosity broadening are best met by a temperature of 160°. We could not observe any polarization in either of C- or N-methyl groups or in the aryl protons using this technique;[7] instead only the normal growth of lines expected of increasing chemical concentration during the course of the reaction[8] were observed.



1 **2**



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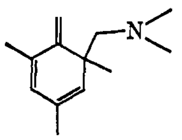

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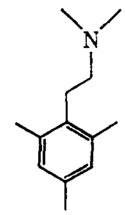
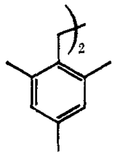
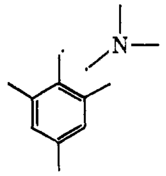


5



6



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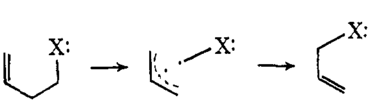

8 **9** **10**

This observation of stimulated absorption–emission in the visible components of the multiplet from CH_2^A, and in the one visible line of CH_2^B, we believe is very strong evidence for a formation mechanism which creates this carbon–carbon bond from species having abnormal nuclear polarizations. The radical pair **7** appears to be a suitable candidate for this process.

There are a number of related thermal reactions[9] which may be described by the sequence **8** to **10**, and all have in common the presence of a lone electron pair on the heteratom X. In at least two cases,[9a,b] with X = O, the geometrical requirements of the system do not allow a concerted process to occur with conservation of orbital symmetry. In another case,[9h] X = S, direct chemical evidence from the radical intermediates has been recently obtained. It seems likely from these observations that, at least in some instances,[10] the delocalization of the lone pair of electrons in the intermediate radical pair[11] makes a strong contribution to the ease of the homolytic pathway.

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[6] W. J. Humphlett and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 3289 (1950).

[7] In respect of the protons attached to the aryl residue this result is perhaps not surprising since esr studies of the benzyl radical have shown that a predominance of electron spin density is concentrated at the benzylic methylene group; *cf.* A. Carrington and J. C. P. Smith, *Mol. Phys.*, **9**, 137 (1965).

[8] Insertion of product **5** into the hot probe under the same conditions gave no abnormal spectral effects.

[9] (a) J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, **86**, 5017, 5019 (1964); (b) R. K. Lustgarten and H. G. Richey, *Tetrahedron Letters*, 4655 (1966); (c) H. Prinzbach, M. Arguelles, and E. Druckrey, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1039 (1966); (d) H. Prinzbach and J. Rivier, *Tetrahedron Letters*, 3713 (1967); (e) M. Israel, L. C. Jones, and E. J. Modest, *ibid.*, 4811 (1968); (f) Y. Hayashi and R. Oda, *ibid.*, 5381 (1968); (g) personal communication from Professor W. D. Ollis, University of Sheffield, Sheffield, England, who has observed an aliphatic analog of the conversion **4** to **5**; (h) J. E. Baldwin and R. E. Hackler, unpublished work on the sulfur analog of the conversion **8** to **10**.

[10] J. A. Berson and E. J. Walsh, Jr., *J. Am. Chem. Soc.*, **90**, 4729, 4730, 4732 (1968). These authors have made a quantitative estimate of the extent of this effect.

[11] This type of delocalization has been discussed at length by J. W. Linnett in "The Electronic Structure of Molecules," Methuen, London, 1964.

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