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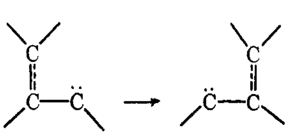
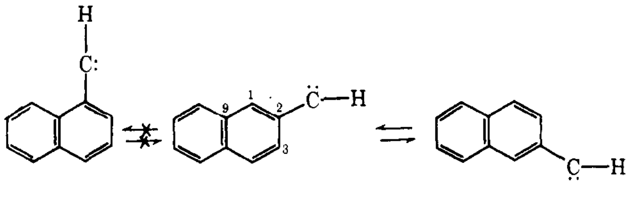
Carbene-Carbene Rearrangements. Importance of Bond Order

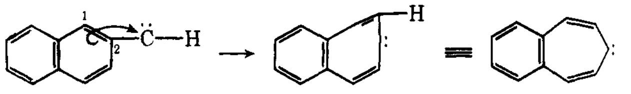
Sir:

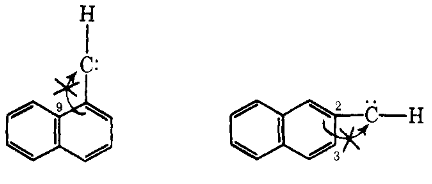
Carbene-carbene rearrangements[1] differ from carbonium ion, carbanion, and free-radical rearrangements in that the overall reaction requires cleavage of a bond with significant double bond character.[6]



In an attempt to assess the importance of bond order in this rearrangement, we have now studied the gas-phase[2] carbene-carbene rearrangement of a series of substituted naphthylcarbenes and report here our finding that scrambling of the carbene occurs *only* between positions 2 and 3 with none occurring between positions 1 and 2. These results point to facile net cleavage of the bond of highest bond order (the 1,2 bond)[9] with initial rearrangement of C-1 from C-2 to the carbene center. We found no evidence of rearrangement of either C-9 from C-1 to the carbene center or C-3 from C-2 to the carbene center.







As in a number of other studies of carbene-carbene rearrangements,[3] a methyl group was used as an internal trap for rearranged carbene (actually two rearrangements) with formation of vinylnaphthalene as proof that rearrangement had occurred.

To illustrate the method used, consider the rearrangement of 3-methyl-2-naphthylcarbene (**1**). Migration of C-1 from C-2 to the carbene center on C-2 (cleavage of a 1,2-double bond)[10] would give cycloheptatrienylidene (**2**) which, by further rearrangement would give methylnaphthylcarbene (**3**). This should undergo rapid rearrangement to 2-vinylnaphthalene. On the other

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[1] To date, carbene-carbene rearrangements have been reported in benzenoid (carbocyclic[2,3] and heterocyclic[4]), tropylium,[2] and carbonylcarbene[5] systems. Other nonaromatic multiple bond carbenes are currently under investigation.

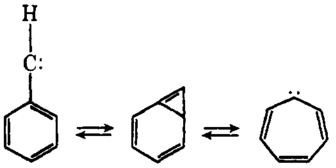
[2] R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969); J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, **92**, 4740 (1970); and references cited therein.

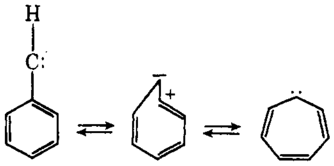
[3] G. G. Vander Stouw, *Diss. Abstr.*, **25** (12), 6974 (1965); *Chem. Abstr.*, **63**, 13126b (1965), under the direction of H. Shechter; P. O. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *J. Amer. Chem. Soc.*, **92**, 2147 (1970); E. Hedaya and M. E. Kent, *ibid.*, **93**, 3283 (1971); W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *ibid.*, **92**, 4739 (1970); C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970).

[4] C. Wentrup, *Tetrahedron*, **27**, 367 (1970); C. Wentrup and W. D. Crow, *ibid.*, **27**, 361 (1971); and references cited therein.

[5] G. Frater and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 6654 (1970), and previous references; R. L. Russell and F. S. Rowland, *ibid.*, **92**, 7508 (1970).

[6] Carbene-carbene rearrangements in cyclic conjugated systems[2-4] can be visualized as occurring by at least three different mechanisms, all of which have been alluded to for nitrene-carbene rearrangements.[4] In one case, rearrangement takes the form of a simple closure of a vinylcarbene to a cyclopropene[7] followed by or concomitant with ring opening to give the new carbene. This mechanism which has been assumed by most authors[2,3] and which probably takes place from an orientation of the vinylcarbene in which the vacant orbital is conjugated with the π system[7,8] (although to date, there is no firm evidence for this) would be favored by high double bond character. Another mechanism which is intuitively less attractive for carbocyclic systems than for heterocyclic analogs[4] takes the form of a Wolff rearrangement in which the vacant orbital of the carbene is presumably[8] orthogonal to the π system and therefore properly oriented for migration of a σ bond. This mechanism, which is limited to cyclic conjugated systems, would lead to, or take place from, an intermediate zwitterion and should be favored by low double bond character. Finally, rearrangement could occur by ring opening to a diradical followed by closure to a cyclic allene which can give the carbene.



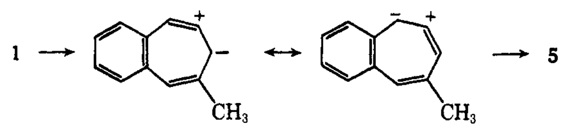


[7] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 99 (1963), and references cited therein.

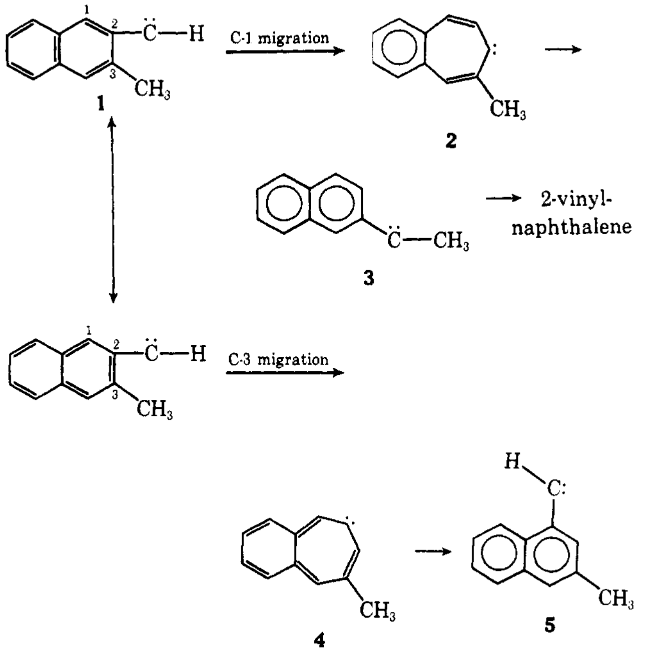
[8] R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *ibid.*, **90**, 1485 (1968).

[9] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N.Y., 1961.

[10] A Wolff type of rearrangement of C-3 of carbene **1** with cleavage of a 2,3-single bond would give a zwitterion ion which could undergo futher rearrangement to carbene **5**, while retaining the benzenoid aromaticity.

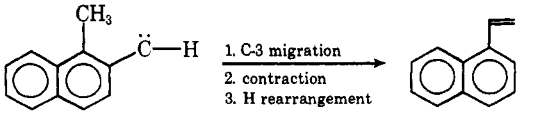


hand, migration of C-3 from C-2 to the carbene center (cleavage of a 2,3-double bond)[16] would give carbene **4** which, upon further rearrangement, would move the methyl away from the carbene center and thus preclude formation of vinylnaphthalene.



1 **2** **3** **4** **5**

By similar reasoning, migration of C-1 to the carbene center on C-2 (cleavage of the 1,2 bond) in 1-methyl-2-naphthylcarbene would move the methyl away from the carbene center whereas migration of C-3 to the carbene center on C-2 would lead to 1-vinylnaphthalene. Finally, migration of C-9 to a carbene center on C-1 of 2-methyl-1-naphthylcarbene would ultimately lead to 2-vinylnaphthalene while migration of C-2 would not.



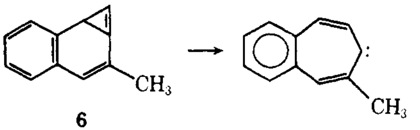
As will be noted in Table I, 3-methyl-2-naphthylcarbene gives 2-vinylnaphthalene in yields up to 70% with formation of only small amounts of naphthocyclobutene, a C–H insertion product of the unrearranged carbene. On the other hand, 1-methyl-2-naphthyl- and 2-methyl-1-naphthylcarbene give no trace of 1- or 2-vinylnaphthalene, respectively. Furthermore, 4-methyl-1-naphthylcarbene affords neither vinylnaphthalene nor naphthocyclobutene.

Table I. Pyrolysis of the Sodium Salts of Monomethylnaphthaldehyde *p*-Toluenesulfonylhydrazones

Aldehydes[a]	Temp, °C	Yield,[b] % I[c]	II[c]	III[c]	IV[c]
4-Methyl-1-naphthaldehyde[d]	350	0		0	
2-Methyl-1-naphthaldehyde[d]	350		0	17.5	
1-Methyl-2-naphthaldehyde[d]	350	0		16	
3-Methyl-2-naphthaldehyde[e]	350		55		2.2
	300		53		4.2
	250		70.5		5.6
	200		48.5		5.9
2-Methylbenzotropone[f]	350		24		2.5

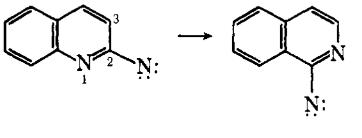
[a] All new compounds gave acceptable analyses. [b] Determined by nmr and vpc. [c] Compared with authentic samples: 1-vinylnaphthalene (I); 2-vinylnaphthalene (II); naphtho[*a*]cyclobutene (III); naphtho[*b*]cyclobutene (IV). [d] Synthesized from the corresponding bromomethylnaphthalene according to the procedure of Ziegler and Tiemann (K. Ziegler and P. Tiemann, *Ber.*, **55**, 3410 (1922)). [e] Synthesized by the method of Sultamow, Rodiomow, and Schemiakan (A. S. Sultamow, W. M. Rodiomow, and M. W. Schemiakan, *Zh. Obshch. Khim.*, **16**, 2073 (1946)). [f] Synthesized by the method of Meuche, Strauss, and Heilbronner (D. Meuche, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, **41**, 2220 (1958)).

These results clearly point to facile rearrangement resulting from net cleavage of the 1,2 bond with no detectable cleavage of either the 1,9 bond or the 2,3 bond and are rationally explainable by the mechanism[6] in which the carbene–carbene rearrangement proceeds through a bicycloheptatriene **6** either as an intermediate or a transition state. The intermediacy of benzocycloheptatrienylidiene (**7**) in the overall reaction is supported by the fact that 2-methylbenzocycloheptatrienylidene (from the sodium salt of 2-methylbenzotropone tosylhydrazone) gives the same products as 3-methyl-2-naphthylcarbene.



6 **7**

The absence of 1-vinylnaphthalene from 1-methyl-2-naphthylcarbene is in striking contrast to the recent report of Wentrup[4] that 2-quinolylnitrene readily rearranges to isoquinolylnitrene—a rearrangement that requires migration of C-3 of the quinoline ring[11] to the nitrene on C-2 with cleavage of the 2,3 bond. This surprising result may signal a different mechanism (perhaps a Wolff type[6]) from phenylcarbenes although further work is required before this possibility is secure.



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[11] In like manner, we found it intuitively surprising that phenylpyridylcarbene undergoes exclusive insertion into the pyridine ring[12] (at least 94%) to give products that require migration of C-3 of the pyridine.

[12] W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 6149 (1968).

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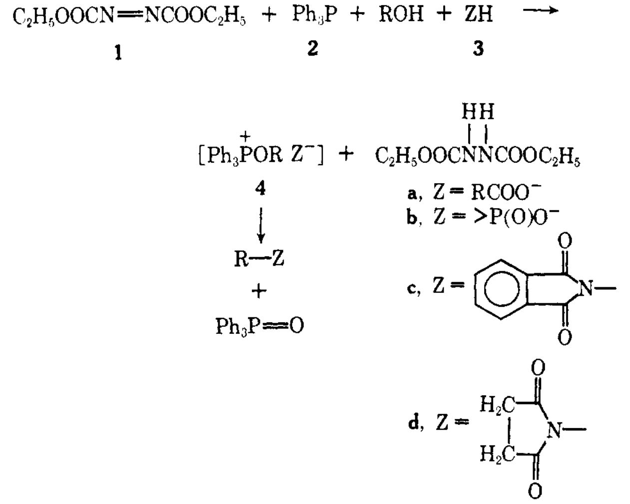
Stereospecific and Stereoselective Reactions. I. Preparation of Amines from Alcohols

Sir:

Syntheses of amines under mild conditions have received much attention and many methods have been devised.[1] Generally, the hydroxyl group of an alcohol must first be converted to another functional group such as the halogens before an amine can be synthesized from an alcohol. While many kinds of two-step routes are widely used, they may involve stereochemical uncertainties because of the displacement nature of the steps.[2] Recently, White, *et al.*,[3] and Burgess, *et al.*,[4] have reported a one-step route for the preparation of amines and urethanes from alcohols.

In this communication, we wish to report a stereospecific one-stage formation of *N*-alkylphthalimides and *N*-alkylsuccinimides from alcohols.

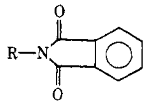
The preceding papers describe how the reaction of alcohols or nucleosides with either carboxylic acids or hydrogen phosphate esters in the presence of equimolar amounts of diethyl azodicarboxylate (**1**) and triphenylphosphine (**2**) afforded carboxylic esters or phosphoric esters.[5] High stereospecificity was observed in the formation of carboxylic esters.[5c] An alkoxyphosphonium salt (**4**) was assumed to be the intermediate of the reaction, from which the alkyl group was presumably transferred to carboxylate or phosphate anions.



These results and those obtained in other laboratories[6] show that alkoxyphosphonium salts are powerful alkyl group donors and anions such as carboxylate, phosphate, or halide act as alkyl group acceptors. These considerations suggested the possibility that various nucleophiles might be alkylated by the alkoxyphosphonium salt under proper conditions. Thus, alkylation of phthalimide by means of an alcohol, **1**, and **2** was tried.

When various alcohols (1–1.5 mmol) were allowed to react with 1 mmol each of phthalimide (**3c**), **1**, and **2** in tetrahydrofuran (THF) at room temperature, the corresponding *N*-alkylphthalimides[7] were obtained in good yields as expected (Table I). Similarly, the reaction of (±)-ethyl lactate (1 mmol) with equimolar amounts of **1**, **2**, and **3c** resulted in the formation of (±)-phthalylalanine ethyl ester[8] in a 58% yield (mp 59–61°).[9]

Table I. Preparation of *N*-Alkylphthalimides

Alcohol ROH R =	Product  R =	Yield, %
C_2H_5	C_2H_5	91
n-C_3H_7	n-C_3H_7	93
n-C_4H_9	n-C_4H_9	81
$(\pm)$-$CH_3\overset{\vert}{C}HC_2H_5$	$(\pm)$-$CH_3\overset{\vert}{C}HC_2H_5$	75
$(\pm)$-$CH_3\overset{\vert}{C}HC_6H_{13}$	$(\pm)$-$CH_3\overset{\vert}{C}HC_6H_{13}$	82
$(\pm)$-$CH_3\overset{\vert}{C}HCO_2C_2H_5$	$(\pm)$-$CH_3\overset{\vert}{C}HCO_2C_2H_5$	58

The reaction of *n*-butyl alcohol (1 ml) with 10 mmol each of succinimide (**3d**), **1**, and **2** in THF at room temperature gave *N*-*n*-butylsuccinimide in a 76% yield (bp 140° (23 mm)).

When *n*-butyl *N*,*N*′-tetraethylphosphorodiamidite and **3d** were treated with **1** in THF at room temperature, *N*-butylsuccinimide was isolated in a 95% yield by distillation (bp 72–75° (3 mm)).

Although only a few investigations have been reported on the stereochemistry of the decomposition of alkoxyphosphonium salts, they show that there is a

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(1) (a) Houben-Weyl, "Methoden der Organischen Chemie," Vol. XI, Part 1, Georg Thieme Verlag, Stuttgart, 1957; (b) S. R. Sandler and W. Kars, "Organic Functional Group Preparation," Academic Press, New York, N. Y., 1968; (c) C. A. Buehler and D. E. Pearson, "Survey of Organic Syntheses," Wiley-Interscience, New York, N. Y., 1970.

(2) Streitwieser and Schaeffer have demonstrated that the direct displacement reaction of sulfonate esters with azide ion proceeds with nearly complete inversion: A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **78**, 5597 (1956).

(3) E. H. White and C. A. Elliger, *ibid.*, **87**, 5261 (1965), and references therein.

(4) E. M. Burgess, H. R. Penton, Jr., and E. A. Taylor, *ibid.*, **92**, 5224 (1970).

(5) (a) O. Mitsunobu and M. Yamada, *Bull. Chem. Soc. Jap.*, **40**, 2380 (1967); (b) O. Mitsunobu, K. Kato, and J. Kimura, *J. Amer. Chem. Soc.*, **91**, 6510 (1969); (c) O. Mitsunobu and M. Eguchi, *Bull. Chem. Soc. Jap.*, **44**, 3427 (1971); (d) O. Mitsunobu, J. Kimura, and Y. Fujisawa, *ibid.*, in press.

(6) (a) R. G. Harvey and E. R. De Sombre, *Top. Phosphorus Chem.*, **1**, 57 (1964); (b) R. F. Hudson, "Structure and Mechanism in Organo-phosphorus Chemistry," Academic Press, New York, N. Y., 1965; (c) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967.

(7) The *N*-alkylphthalimides were separated by means of preparative thin-layer chromatography on silica gel (Wakogel B-5) utilizing benzene or chloroform as eluent. Satisfactory infrared and nmr data were obtained for these products.

(8) Satisfactory analytical, infrared, and nmr data were obtained for this product.

(9) As it is well known that, on hydrolysis or hydrazinolysis, *N*-alkylphthalimides and phthalylamino acids afford corresponding primary amines and amino acids, we made no attempts to cleave these products.