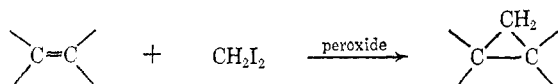


## Cyclopropane Formation via Radical-Induced Methylene Transfer to Olefins<sup>1</sup>

Sir:

We wish to report a new type of free-radical reaction, transfer of a methylene group to an olefin to give a cyclopropane.



Results of a preliminary study involving a few olefins are given in Table I. Table II contains more complete data for the reaction of 1,1-diphenylethylene.

Table I. Peroxide-Induced Reaction of Methylene Iodide with Olefins

	% yield <sup>a</sup> of the corresponding cyclopropane			
	$(t\text{-BuO})_2$ 166°		$(\text{PhCO}_2)_2$ 115°	
	135°	81°	81°	
1-Octene	38	17	33	23
PhCH=CH <sub>2</sub>	17	5	8	4
Ph <sub>2</sub> C=CH <sub>2</sub>	14	<i>b</i>	18	2
Cyclohexene	<1		<1	
<i>cis</i> -Stilbene <sup>c</sup>	54		17	9
<i>trans</i> -Stilbene <sup>c</sup>	58		17	9
<i>cis</i> -4-Octene <sup>d</sup>	16		18	
<i>trans</i> -4-Octene <sup>d</sup>	13		19	

<sup>a</sup> Based on starting olefin. <sup>b</sup> The yield at 135° was very much lower than that at 166°. <sup>c</sup> *cis*-Stilbene is isomerized to *trans*-stilbene under the reaction conditions. The product obtained from either olefin is *trans*. <sup>d</sup> See ref 4.

Table II. Peroxide-Induced Reaction of Methylene Iodide with 1,1-Diphenylethylene

Reactants <sup>b</sup>	Weight, mmole at	
	166°, 1 hr <sup>a</sup>	115°, 1.5 hr <sup>a</sup>
Ph <sub>2</sub> C=CH <sub>2</sub>	0.957	0.264
$(t\text{-BuO})_2$ <sup>c</sup>	1.510	
$(\text{PhCO}_2)_2$ <sup>c</sup>		0.398
CH <sub>2</sub> I <sub>2</sub> <sup>d</sup>	0.988	0.254
Products <sup>e</sup>		
1,1-Diphenylcyclopropane	0.13	0.047
Ph <sub>2</sub> C=CHCH <sub>3</sub>	0.078	
Ph <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> I	0.024	0.004
Ph <sub>2</sub> C=CHOCOPh		0.033
Ph <sub>2</sub> CH <sub>2</sub>	0.005	
PhCH <sub>2</sub> I	0.011	
CH <sub>2</sub> I <sub>2</sub>	0.22	0.062
CH <sub>3</sub> I	1.59	Trace
PhI	0.010	0.34
CH <sub>3</sub> COCH <sub>3</sub>	1.54	
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	0.78	
$(\text{CH}_3)_3\text{COH}$	0.77	

<sup>a</sup> No significance should be attached to the reaction time with the exception that it is long enough so that no detectable reaction occurred on further heating. <sup>b</sup> In benzene as solvent. <sup>c</sup> No reaction occurred in the absence of peroxide. <sup>d</sup> Use of a large excess of methylene iodide did not improve, and often greatly decreased, the yield of 1,1-diphenylcyclopropane. <sup>e</sup> Yields were estimated by use of nmr spectroscopy and gas chromatographic analysis. This reaction resulted in very many products many of which formed also in the absence of methylene iodide and not all of which have been identified. Material balances on di-*t*-butyl peroxide derived products and iodine are good, however.

(1) This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation.

In view of the present lack of mechanistic information, we do not feel justified in invoking reaction paths more involved than reaction between iodomethyl radical and olefin to give a cyclopropane. This process must proceed with loss of iodine either before,<sup>2</sup> during,<sup>4</sup> or after<sup>5</sup> carbon-carbon bond formation.

Our observations are clearly relevant to the question of the mechanism<sup>10</sup> of the photolytic reaction of methylene iodide with cyclohexene,<sup>8,11</sup> 3-hexene,<sup>8</sup> and 2-butene<sup>8</sup> to give the corresponding cyclopropanes.

(2) Strong evidence against this route is provided by a crudely estimated endothermicity of 70–85 kcal/mole for the reaction  $\cdot\text{CH}_2\text{I} \rightarrow \cdot\text{CH}_2 + \text{I}\cdot$ . Our formulation of this possibility must remain vague because we are unable to predict with confidence the relative amounts of singlet and triplet  $\cdot\text{CH}_2$  that would be initially produced by loss of iodine from  $\cdot\text{CH}_2\text{I}$ . It should be noted that the reactions  $\cdot\text{CCl}_3 \rightarrow \text{Cl}\cdot + \cdot\text{CCl}_2$ <sup>3a</sup> and  $\cdot\text{CF}_3 \rightarrow \cdot\text{CF}_2 + \text{F}\cdot$ <sup>3b</sup> have been invoked.

(3) (a) G. P. Semeluk and R. B. Bernstein, *J. Am. Chem. Soc.*, **79**, 46 (1957); G. Archer and C. Hinshelwood, *Proc. Roy. Soc. (London)*, **A261**, 293 (1961); M. Seakins, *ibid.*, **A274**, 413 (1963). However, see also: A. E. Shilov and R. D. Sabirova, *Zh. Fiz. Khim.*, **33**, 1365 (1959); **34**, 860 (1960); J. W. Engelsma, *Rec. Trav. Chim.*, **84**, 187 (1965); D. J. Clark and J. M. Tedder, *Trans. Faraday Soc.*, **62**, 393, 399, 405 (1966). (b) J. W. Hodgins and R. L. Haines, *Can. J. Chem.*, **30**, 473 (1952). However, see E. Tschuikow-Roux, *J. Chem. Phys.*, **43**, 2251 (1965).

(4) This is an unprecedented (in free-radical chemistry), but not *a priori* unreasonable, process. An analog in carbonium ion chemistry would be the proposed  $\pi$  route to "nonclassical" cations, an idea which does not lack supporters. Similar processes have been proposed as models for the reaction of carbenoids with olefins to give cyclopropanes,<sup>6</sup> the Simmons-Smith reaction,<sup>7</sup> and the photolytic reaction of methylene iodide with olefins.<sup>8</sup> We have obtained preliminary results under conditions such that there is no *cis-trans* interconversion among the olefins or the cyclopropanes, which indicates that the reaction of *cis*- and *trans*-4-octenes to give 1,2-dipropylcyclopropane is not stereospecific, both *cis*- and *trans*-4-octenes leading to a *trans:cis* ratio of 1,2-dipropylcyclopropane of ~20. This observation cannot be readily accommodated to a mechanism whereby ring formation and iodine loss are concerted.

(5) This possibility is very reasonable in view of our recent radical-induced conversion of 1,3-diiodopropane to cyclopropane.<sup>9</sup> In this communication we also mentioned the above conversion of 1,1-diphenylethylene to 1,1-diphenylcyclopropane.

(6) G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964); G. L. Closs and L. E. Closs, *Angew. Chem. Intern. Ed. Engl.*, **1**, 334 (1962).

(7) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958).

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(9) L. Kaplan, *J. Am. Chem. Soc.*, **89**, 1753 (1967).

(10) It was concluded<sup>8</sup> that the intermediacy of iodomethyl radicals is unlikely.

(11) R. C. Neuman, Jr., and R. S. Wolcott, *Tetrahedron Letters*, 6267 (1966).

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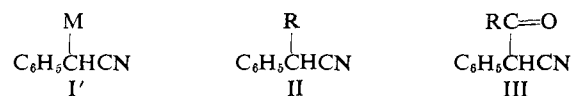
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## Influence of Metallic Cation in Carbonyl Addition Reactions of Certain Nitriles and Sulfones with Benzophenone

Sir:

It has previously been shown that sodiophenyl-acetonitrile (I', M = Na), prepared from phenyl-acetonitrile and sodium amide in liquid ammonia, can be alkylated<sup>1</sup> and acylated<sup>2</sup> in this medium to form II and III, respectively.



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(2) R. Levine and C. R. Hauser, *J. Am. Chem. Soc.*, **68**, 760 (1946).