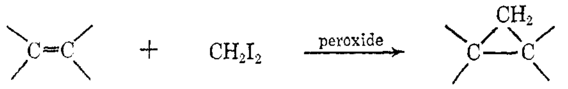
Cyclopropane Formation *via* Radical-Induced Methylene Transfer to Olefins[1]

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[a] of the corresponding cyclopropane			
	$(t\text{-BuO})_2$		$(PhCO_2)_2$	
	166°	135°	115°	81°
1-Octene	38	17	33	23
$PhCH{=}CH_2$	17	5	8	4
$Ph_2C{=}CH_2$	14	*b*	18	2
Cyclohexene	<1		<1	
cis-Stilbene[c]	54		17	9
trans-Stilbene[c]	58		17	9
cis-4-Octene[d]	16		18	
trans-4-Octene[d]	13		19	

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

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

	Weight, mmole at	
	166°, 1 hr[a]	115°, 1.5 hr[a]
Reactants[b]		
$Ph_2C{=}CH_2$	0.957	0.264
$(t\text{-BuO})_2$[c]	1.510	
$(PhCO_2)_2$[c]		0.398
CH_2I_2[d]	0.988	0.254
Products[e]		
1,1-Diphenylcyclopropane	0.13	0.047
$Ph_2C{=}CHCH_3$	0.078	
$Ph_2CHCH_2CH_2I$	0.024	0.004
$Ph_2C{=}CHOCOPh$		0.033
Ph_2CH_2	0.005	
$PhCH_2I$	0.011	
Ch_2I_2	0.22	0.062
CH_3I	1.59	Trace
PhI	0.010	0.34
CH_3COCH_3	1.54	
$(CH_3)_2C{=}CH_2$	0.78	
$(CH_3)_3COH$	0.77	

[a] 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. [b] In benzene as solvent. [c] No reaction occurred in the absence of peroxide. [d] Use of a large excess of methylene iodide did not improve, and often greatly decreased, the yield of 1,1-diphenylcyclopropane. [e] 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.

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,[2] during,[4] or after[5] carbon–carbon bond formation.

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

---

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

(2) Strong evidence against this route is provided by a crudely estimated endothermicity of 70–85 kcal/mole for the reaction $\cdot CH_2I \rightarrow :CH_2 + I\cdot$. Our formulation of this possibility must remain vague because we are unable to predict with confidence the relative amounts of singlet and triplet $:CH_2$ that would be initially produced by loss of iodine from $\cdot CH_2I$. It should be noted that the reactions $\cdot CCl_3 \rightarrow Cl\cdot + :CCl_2$[3a] and $\cdot CF_3 \rightarrow :CF_2 + F\cdot$[3b] 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 π 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,[6] the Simmons–Smith reaction,[7] and the photolytic reaction of methylene iodide with olefins.[8] 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.[9] 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).

(8) D. C. Blomstrom, K. Herbig, and H. E. Simmons, *J. Org. Chem.*, 30, 959 (1965).

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

(10) It was concluded[8] that the intermediacy of iodomethyl radicals is unlikely.

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

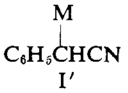
Leonard Kaplan
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

Received May 5, 1967

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

Sir:

It has previously been shown that sodiophenylacetonitrile (I′, M = Na), prepared from phenylacetonitrile and sodium amide in liquid ammonia, can be alkylated[1] and acylated[2] in this medium to form II and III, respectively.

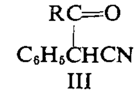


$C_6H_5\overset{M}{\overset{|}{C}}HCN$

I′

$C_6H_5\overset{R}{\overset{|}{C}}HCN$

II



$C_6H_5\overset{RC=O}{\overset{|}{C}}HCN$

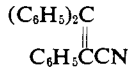
III

---

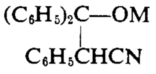
(1) A. C. Cope, H. L. Holmes, and H. O. House, *Org. Reactions*, **9**, 107 (1957); W. G. Kenyon, E. M. Kaiser, and C. R. Hauser, *J. Org. Chem.*, 30, 4135 (1965).

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

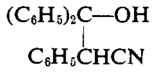
Sodionitrile I′ has also been condensed with benzophenone in refluxing ether to form the α,β-unsaturated nitrile IV,[3] which presumably arose through intermediate sodio adduct V′ (M = Na); the neutral adduct V was not isolated. In fact, hydroxy nitrile V has not been reported previously.


$(C_6H_5)_2C{=}C(C_6H_5)CN$

IV


$(C_6H_5)_2C(OM){-}CH(C_6H_5)CN$

V′

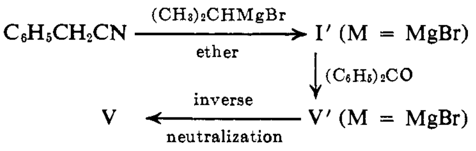

$(C_6H_5)_2C(OH){-}CH(C_6H_5)CN$

V

Apparently, the equilibrium of the addition reaction of sodio or lithio nitrile I′ with benzophenone in liquid ammonia is on the side of I′ and the ketone. Thus, we have observed that, not only are phenylacetonitrile and benzophenone recovered on treating the sodio or lithio nitrile I′ with the ketone and neutralizing the reaction mixture inversely, but the nitrile and ketone are also obtained on treating the hydroxy nitrile V (prepared as described below) with sodium amide under similar conditions.

We now wish to report that the hydroxy nitrile V can be prepared from phenylacetonitrile and benzophenone if M of the intermediate I′ is a metal possessing a sufficiently greater coordinating (chelating) capacity than sodium and the reaction is effected in an inert solvent. Thus, adduct V was obtained in yields of 40–63% when M of intermediate I′ was MgBr[4] or an aluminum chloride moiety, and in 11% yield when M was lithium. One procedure is illustrated in Scheme I.

Scheme I

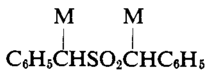

$$\begin{tikzcd}
C_6H_5CH_2CN \arrow[r, "(CH_3)_2CHMgBr", "\text{ether}"'] & I' \ (M = MgBr) \arrow[d, "(C_6H_5)_2CO"] \\
V & V' \ (M = MgBr) \arrow[l, "\text{inverse}"', "\text{neutralization}"]
\end{tikzcd}$$

Other procedures involved preparation of lithiophenylacetonitrile (I′, M = Li) from phenylacetonitrile and *n*-butyllithium in tetrahydrofuran–hexane and treatment of it with either magnesium bromide followed by benzophenone or preferably with a preformed 2:1 complex of magnesium bromide–benzophenone in THF. The aluminum chloride type intermediate I′ was prepared by a procedure analogous to the latter one.

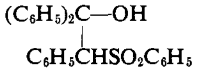
Similarly, the magnesium bromide salt VI′ of benzyl phenyl sulfone and the dimagnesium bromide salt VII″ of dibenzyl sulfone (M = MgBr), prepared from the sulfone and isopropylmagnesium bromide or from the sulfone, *n*-butyllithium, and magnesium bromide, underwent carbonyl addition reactions with benzophenone to form hydroxy sulfones VIII and IX in yields of 50–52 and 42–56%, respectively. In contrast to these results, the lithium, sodium, or potassium salts VI′ and VII″ (M = Li, Na, or K) failed to afford these products on treatment with the ketone.


$C_6H_5CH(M)SO_2C_6H_5$

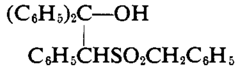
VI′


$C_6H_5CH(M)SO_2CH(M)C_6H_5$

VII″

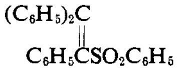

$(C_6H_5)_2C(OH){-}CH(C_6H_5)SO_2C_6H_5$

VIII


$(C_6H_5)_2C(OH){-}CH(C_6H_5)SO_2CH_2C_6H_5$

IX

The structures of the hydroxy nitrile V and the hydroxy sulfones VIII and IX were supported by analyses, infrared and nmr spectra, and dehydration to afford the corresponding α,β-unsaturated nitrile IV and sulfones X and XI, respectively.


$(C_6H_5)_2C{=}C(C_6H_5)SO_2C_6H_5$

X


$(C_6H_5)_2C{=}C(C_6H_5)SO_2CH_2C_6H_5$

XI

However, the corresponding benzophenone adducts of malonic ester and acetylacetone failed to be isolated on preparing their respective magnesium bromide derivatives and treating them with the ketone under similar conditions. Instead, only starting materials were recovered.

These results support the hypothesis that, although the main driving force in such carbonyl addition reactions of carbanions is considered to be the formation of a weaker base or nucleophile[5] (*i.e.*, the alkoxide type ion, as in V′), an additional driving force can arise through coordination (chelation) within the product.[6–8] This additional factor appears to be ineffective, however, when the difference between the strengths of the starting carbanion and the resulting alkoxide type ion is relatively great, since even the magnesium salts of the more weakly basic or nucleophilic carbanions failed to afford adducts (see above).

Studies are in progress to ascertain the relative importance of weaker base formation, chelation, and steric factors[8] and to determine the generality and usefulness of the method in synthesis. Also, the mechanism of such addition reactions is being investigated.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research at the University of Missouri, and to the National Science Foundation for partial support at Duke University.

Edwin M. Kaiser
Department of Chemistry, University of Missouri
Columbia, Missouri 65201
Charles R. Hauser
Department of Chemistry, Duke University
Durham, North Carolina 27706

Received June 27, 1967

---

[3] S. Wawzonek and E. M. Smolin, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 387.

[4] This reagent (I′, M = MgBr) has a formal similarity to the Ivanov reagent, $C_6H_5CH(MgCl)COONa$, which is known to react with carbonyl compounds; however, disodio- or dilithiophenyl acetate are preferable since they give better yields of β-hydroxy acids. See P. J. Hamrick, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, **82**, 1957 (1960).

[5] This hypothesis is supported by the fact that cleavage of such a benzophenone adduct occurs in the presence of a catalytic amount of base to form the thermodynamically more stable neutral starting materials; see P. J. Hamrick and C. R. Hauser, *J. Am. Chem. Soc.*, **81**, 3146 (1959).

[6] See C. R. Hauser and W. R. Dunnavant, *J. Org. Chem.*, **25**, 1300 (1960).

[7] A similar shift in equilibrium has been observed in the reactions of nitroparaffins and carbon dioxide in the presence of magnesium and aluminum ions; see H. L. Finkbeiner and M. Stiles, *J. Am. Chem. Soc.*, **85**, 616 (1963).

[8] A steric factor may also be involved since certain adducts appear to be obtained more readily from benzaldehyde than from benzophenone.