

Table I. Carbon-Carbon Mulliken Overlap Populations in Bicyclobutane<sup>a</sup>

	Orbital pair				Bond order
	2s <sub>C<sub>a</sub></sub> -2s <sub>C<sub>b</sub></sub>	2s <sub>C<sub>a</sub></sub> -2p <sub>C<sub>b</sub></sub>	2s <sub>C<sub>b</sub></sub> -2p <sub>C<sub>a</sub></sub>	2p <sub>C<sub>a</sub></sub> -2p <sub>C<sub>b</sub></sub>	
Central bond ( <i>a</i> = 1, <i>b</i> = 3)	-0.0712	0.0166	0.0166	0.3844	0.3464
Side bond ( <i>a</i> = 1, <i>b</i> = 2)	0.0254	0.1956	0.1134	0.3026	0.6330

<sup>a</sup> Cyclopropane values for the 2s-2s, 2s-2p, and 2p-2p overlaps are -0.0020, 0.1248, and 0.321, respectively.

subsequent arguments. As regards the orbital energies, bicyclobutane is predicted to (adiabatically) valence ionize<sup>10</sup> more easily than cyclopropane and ethylene, but to less readily core ionize, with little ESCA chemical shift between the bridge and bridgehead carbons.

The unusual bonding in bicyclobutane is first encountered in the overlap populations (Table I). Unlike most carbon-carbon bonds with overlap populations containing substantial contributions from 2s and adjacent 2p orbital overlaps (for example, 48% for the side bond of bicyclobutane, 44% for cyclopropane<sup>11</sup>), for the central bicyclobutane bond this contribution is not appreciable (<10%). Moreover, the contribution from adjacent 2s pairs is also small. The central bond is therefore nearly pure p in character, and since the p-σ and p-π contributions partition approximately in the ratio 5:1, the central bond is best described as arising from largely σ interaction of two unhybridized p orbitals.<sup>12</sup> Such bonding might be anticipated to occur in II (as yet unknown), which may be viewed as a substituted ethane formed from two methyl radicals unable to rehybridize.<sup>13</sup> That such bonding occurs in bicyclobutane with two "free" ligands is somewhat surprising.

Turning to the CH bonds, the method of Yonezawa, *et al.*,<sup>14</sup> indicates that the *exo*, *endo*, and bridgehead hydrogens are attached to sp<sup>2.02</sup>, sp<sup>2.08</sup>, and sp<sup>1.55</sup> hybrids, respectively (cyclopropane is sp<sup>1.96</sup>). The bridgehead value, between that of ethylene and acetylene, is in accord both with the high bridgehead acidity and the large <sup>13</sup>C-H coupling constant<sup>15</sup> (but does not require the C-C bond to be olefinic).

Several significant chemical consequences attend this bonding scheme. First, use of unhybridized p orbitals implies a high density of electrons behind the central bond and slightly below it.<sup>16</sup> The resulting external lobe may play an important role in bicyclobutane chemistry, for example, accounting for the ready decarboxylation of *endo*-1,3-diphenylbicyclobutane-2-carboxylic acid (85°) relative to the *diexo* isomer of 1,3-diphenyl-4-carbomethoxybicyclobutane-2-carboxylic acid (200°).<sup>17</sup> The *endo* acid proton can reach the external lobe to give a cyclic transition state, whereas the *exo* proton cannot.<sup>5</sup> Similarly, an incoming proton may first attack bicyclobutane from behind the central bond (fixing the stereochemistry at that center) rather than from above it. This former path is in accord with the observed stereochemistry<sup>18</sup> and it need not preclude the initial "p-σ

complex" continuing on to, say, an edge-protonated cyclopropane. A somewhat analogous mode of attack has been suggested for the reaction of bicyclobutane with benzyne.<sup>19</sup>

The σ p-p-bond model also suggests why bicyclobutane is reluctant to undergo Diels-Alder reaction. Unlike the π bond of an olefin, with electrons oriented toward the incoming diene, the central bond of bicyclobutane is not disposed to overlap early in the reaction coordinate. The transition state is therefore of relatively high energy although the reaction would be very exothermic.

Finally, consider the uv band of 1,3-diphenylbicyclobutanes at *ca.* 270 mμ,<sup>20</sup> suggesting phenyls in conjugation. To interact through the p-p bond the benzene rings must align themselves face to face. Space-filling models suggest substantial steric hindrance to such orientation in the presence of a large *exo* substituent. It is, in fact, observed that the 270-mμ maximum is absent in esters of *exo*-1,3-diphenylbicyclobutane-carboxylic acids.<sup>20</sup>

however, and since the latter predicts the stereochemically incorrect top-side attack to be preferred, the question must be considered still open.

(19) (a) M. Pomerantz, G. W. Gruber, and R. N. Wilke, *ibid.*, **90**, 5040 (1968); (b) P. G. Gassman and G. D. Richmond, *ibid.*, **92**, 2090 (1970).

(20) R. B. Woodward and D. L. Dalrymple, *ibid.*, **91**, 4612 (1969).

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### Mechanism of the Wolff Rearrangement. III

Sir:

With regard to the intermediacy of the cyclic oxirene structure in the photochemical Wolff rearrangement of diazo ketones, recent investigations have led to conclusions which were in apparent conflict with those derived from earlier studies.

Nearly 30 years ago Huggett, *et al.*,<sup>1</sup> converted benzoic acid, <sup>13</sup>C labeled in the carboxyl group, into phenylacetic acid by the Arndt-Eistert method, C<sub>6</sub>H<sub>5</sub>\*-COOH → C<sub>6</sub>H<sub>5</sub>\*COCl → C<sub>6</sub>H<sub>5</sub>\*COCHN<sub>2</sub> → C<sub>6</sub>H<sub>5</sub>-CH=\*C=O → C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>\*COOH (oxidation) → \*CO<sub>2</sub>, and found that all the originally present heavy isotope, which amounted to only 2.5%, appeared after oxidation in the CO<sub>2</sub> product, indicating that no scrambling took place during rearrangement.

Later Franzen<sup>2</sup> applied the <sup>14</sup>C-labeling technique for the elucidation of the mechanism of the photolytic and thermal Wolff rearrangement of azibenzil. Experiments were carried out in dioxane-water-tri-

(1) C. Huggett, R. T. Arnold, and T. S. Taylor, *J. Amer. Chem. Soc.*, **64**, 3043 (1942).

(2) V. Franzen, *Justus Liebigs Ann. Chem.*, **614**, 31 (1958).

(10) T. Koopmans, *Physica*, **1**, 104 (1933).

(11) Unpublished results.

(12) It is about as bent as the cyclopropane bond which partitions 10:1.

(13) Similar calculations are currently being performed on II.

(14) T. Yonezawa, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968).

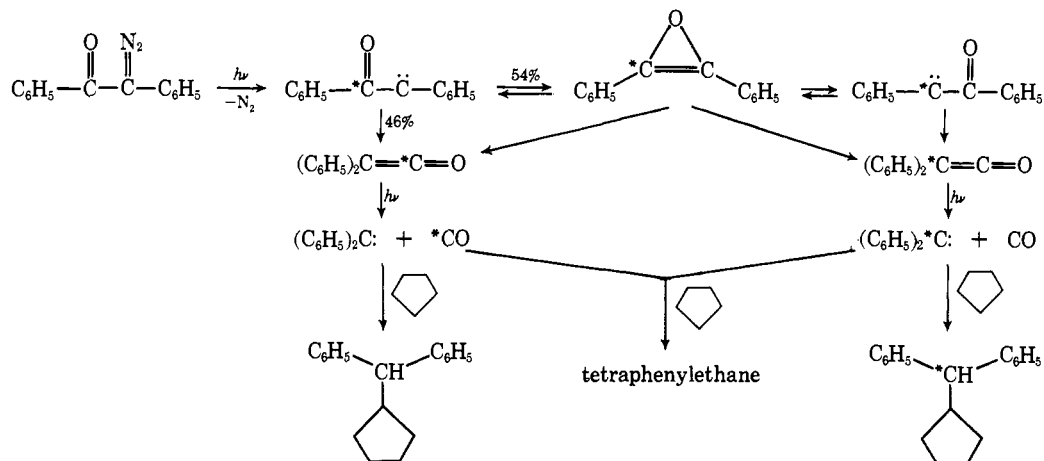
(15) J. N. Shoolery, *J. Chem. Phys.*, **30**, 1427 (1959).

(16) Or, what is operationally equivalent, a highly polarizable p-p bond.

(17) S. Masamune, *Tetrahedron Lett.*, **14**, 945 (1965).

(18) K. B. Wiberg and G. Szeimes, *J. Amer. Chem. Soc.*, **92**, 571 (1970). Our path conflicts with the CNDO results of this reference,

Scheme I



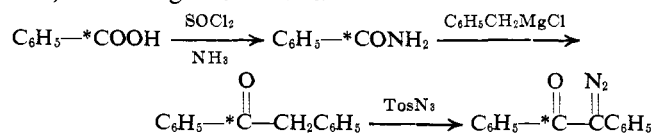
ethylamine and dioxane-water solutions and the position of the  $^{14}\text{C}$  atom in the resulting diphenylacetic acid was determined through oxidative decarboxylation and measurements of the radioactivity of the  $\text{CO}_2$ . It was concluded that oxirene was not an intermediate and the reaction proceeds *via*  $\text{C}_6\text{H}_5^{14}\text{COCN}_2\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5^{14}\text{COCC}_6\text{H}_5 \rightarrow \text{O}=\text{C}=\text{C}=(\text{C}_6\text{H}_5)_2 \rightarrow \text{HOO}^{14}\text{C}-\text{CH}(\text{C}_6\text{H}_5)_2 \rightarrow ^{14}\text{CO}_2 + \text{C}_6\text{H}_5\text{COC}_6\text{H}_5$ , since all radioactivity appeared in the carbon dioxide.

Largely on the basis of Franzen's paper it has since been generally accepted in the literature that oxirene is not an intermediate of the Wolff rearrangement.

In two recent communications<sup>3,4</sup> from this laboratory, however, it had been shown that oxirene formation is a principal reaction path in the gas-phase photochemical Wolff rearrangement of 3-diazobutanone-2 (100%), 3-diazopropanone-2 ( $\geq 16\%$ ), ethyl diazoacetate ( $\geq 32\%$ ), and methyl diazoacetate ( $\geq 28\%$ ). This posed the question if the difference between these and the azibenzil results is due to structural effects or a phase effect. For this reason we have extended our studies to the solution phase.

Photolysis of 3-diazobutanone-2 in both a polar and a nonpolar solvent has led to a somewhat diminished, but still substantial, yield ( $>60\%$ ) of oxirene formation. From comparison of this result with that of Franzen it appeared that phenyl substituents in the molecule play a vital role in preventing ring closure in the carbene intermediate. But before accepting this hypothesis we wanted to convince ourselves of the validity of Franzen's earlier results and repeated the photolysis of azibenzil in cyclopentane and in dioxane-water (2:1) solvents, using the  $^{13}\text{C}$ -labeling technique.

$^{13}\text{C}$ -Azibenzil was prepared from  $^{13}\text{C}$ -benzoic acid (61 atom %  $^{13}\text{C}$  in the carboxylic C atom, Merck Co.) according to the scheme<sup>5,6</sup>



The intermediate benzyl phenyl ketone was identified by nmr, ir, and mass spectroscopic analyses. The latter indicated 61%  $^{13}\text{C}$  labeling in the carbonyl carbon.

(3) I. G. Csizmadia, J. Font, and O. P. Strausz, *J. Amer. Chem. Soc.*, **90**, 7360 (1968).

(4) D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *ibid.*, **92**, 1768 (1970).

(5) S. S. Jenkins, *ibid.*, **55**, 703 (1933).

(6) M. Regitz, *Chem. Ber.*, **98**, 1210 (1965).

The properties of  $^{13}\text{C}$ -azibenzil agreed with those reported in the literature.<sup>6</sup> The isotopic and normal carbonyl stretching vibrations in the ir ( $\text{CH}_2\text{Cl}_2$ ) appeared at 1600 and 1622  $\text{cm}^{-1}$ , respectively. In the mass spectrum the parent peak does not appear but from the  $(M - 28)^+$  fragment the sample was found to contain 60.5%  $^{13}\text{C}$ -labeled material.

Irradiation of  $10^{-2} M$  solutions was carried out in carefully degassed and sealed quartz tubes at room temperature using a 450-W medium-pressure mercury lamp with a 2200-Å cutoff filter.

The noncondensable gases from the cyclopentane solution were collected and analyzed by an MS-9 mass spectrometer. The yield of nitrogen was 70–92% with a ratio of  $\text{N}_2$ -CO of unity. From three experiments the isotopic composition of CO indicated scrambling of the oxygen atom to an extent corresponding to 54% oxirene participation in the reaction.

Two hydrocarbon products were also isolated from the solution and identified as diphenylcyclopentylmethane and tetraphenylethane.<sup>7,8</sup> They both showed substantial  $^{13}\text{C}$  labeling.

The mechanism proposed to account for these observations is outlined in Scheme I.

In order to secure comparable data with Franzen's experiments the photolysis was repeated in dioxane-water solvent, under otherwise identical conditions as described above. The resulting diphenylacetic acid was isolated and subjected to high-resolution mass spectrometric analysis. By monitoring the intensities of the 212 and 213 parent ions the overall isotopic substitution was found to correspond to that of the starting material, 61%. The position of the  $^{13}\text{C}$  in the molecule was determined from the  $\text{COOH}^+$  and  $^{13}\text{COOH}^+$  fragment ion intensities, which led to a value of 46% for oxirene participation in the reaction. The difference from that found for cyclopentane (54%) as solvent may be real or may reflect scatter in the isotopic analysis.

Thus we conclude that oxirene formation is an important reaction path in the solution-phase photochemical Wolff rearrangement of azibenzil and 3-diazobutanone-2 and the credibility of earlier literature claiming to the contrary should be discounted.

(7) B. A. Kazanskii and V. Ya. Temkina, *Vestn. Mosk. Univ., Ser. Fiz.-Mat. Estest. Nauk*, **9** (6), 91 (1954); *cf.*, *Chem. Abstr.*, **49**, 5336 (1955).

(8) H. Nozaki, M. Nakano, and K. Kondo, *Tetrahedron*, **22**, 477 (1966).

A more detailed report will be forthcoming at a later date.

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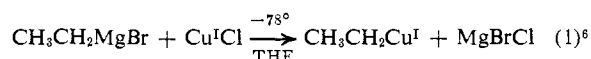
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### Autocatalytic Decomposition of Alkylcopper(I) Species. Electron Spin Resonance Spectrum of Binuclear Copper(0) Intermediates

Sir:

We have examined alkyl derivatives of transition metal complexes formed by metathesis between various Grignard reagents and transition metal halides and other salts in tetrahydrofuran (THF) solutions.<sup>1</sup> In this report we wish to present evidence for the *autocatalytic* decomposition of organocopper(I) species in homogeneous solutions. We also wish to show catalysis by other "zero"valent metal complexes and the presence of novel mixed valence copper(0) species during the decomposition.

The studies were carried out by mixing a solution of the Grignard reagent (*e.g.*, ethylmagnesium bromide) and copper(I) chloride in stoichiometric amounts in THF at  $-78^\circ$ .<sup>2</sup> The resulting homogeneous and colorless solution was stable for prolonged periods at this temperature. From the negative Gilman color test I,<sup>3</sup> we deduce that the ethylcopper(I)<sup>4</sup> species was formed according to eq 1.<sup>5</sup>



When the Grignard reagent and copper(II) chloride were mixed (in a 2:1 molar ratio) under the same conditions, a transitory orange color was observed and 0.5 mol of *n*-butane was generated spontaneously. The properties of the resulting colorless solution were indistinguishable from that formed directly from copper(I) chloride. We infer that alkylcopper(II) species under these conditions were only formed as highly metastable species,<sup>7</sup> and afforded alkylcopper(I).

(1) M. Tamura and J. Kochi, to be published.

(2) The reaction can also be carried out practically by using an excess of Grignard reagent. House, *et al.*, have shown that dialkylcuprate(I) is not formed from a Grignard reagent and copper(I) iodide in diethyl ether [H. O. House, W. L. Respass, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966)].

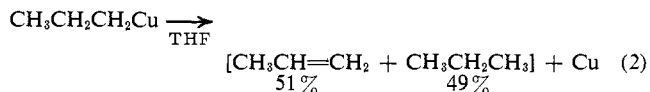
(3) H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, **47**, 2002 (1925).

(4) The oxidation state of copper is given only as a formalism.

(5) For some studies of organocopper(I) species see: (a) G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, **92**, 1426 (1970); **91**, 6542 (1969); (b) G. Costa, A. Camus, L. Gatti, and N. Marsich, *J. Organometal. Chem.*, **5**, 568 (1966); **8**, 339 (1967); G. Costa, G. de Alti, L. Stefani, and G. Boscarato, *Ann. Chim. (Rome)*, **52**, 289 (1962); (c) K. H. Thiele and J. Köhler, *J. Organometal. Chem.*, **12**, 225 (1968); (d) R. J. DePasquale and C. Tamborski, *J. Org. Chem.*, **34**, 1736 (1969); (e) A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 2186 (1968); (f) A. Camus and N. Marsich, *J. Organometal. Chem.*, **14**, 441 (1968); **21**, 249 (1970); (g) H. Gilman and J. M. Straley, *Recl. Trav. Chim. Pays-Bas*, **55**, 821 (1936); (h) C. E. H. Bawn and F. J. Whitby, *J. Chem. Soc.*, 3926 (1960); C. E. H. Bawn and R. Johnson, *ibid.*, 4162 (1960).

(6) Coordination by THF around copper is assumed, but not specifically included.

The decomposition of *n*-propylcopper(I) in THF solution produced propylene and propane in approximately equal amounts consistent with the results obtained from *n*-butyl(tri-*n*-butylphosphine)copper(I) in



diethyl ether.<sup>8a</sup> Careful examination of the rate of decomposition of ethylcopper(I) at  $0^\circ$  (Figure 1) revealed an induction period followed by a rapid decomposition (dark circles). The induction period was removed when a solution of partially decomposed ethylcopper(I) was deliberately added<sup>8</sup> to a solution of ethylcopper(I) (open circles). Other alkylcopper(I) compounds have varying degrees of stability but otherwise showed the same kinetic behavior.<sup>9</sup>

We attribute the autocatalytic decomposition of alkylcopper(I) species to the presence of copper(0) intermediates during decomposition. This induced decomposition can be shown in an alternative experiment illustrated in Figure 2, in which catalytic amounts of soluble silver(0), palladium(0), and copper(0) species<sup>11</sup> stimulated the decomposition of *n*-propylcopper(I) in a rather dramatic way.<sup>10</sup> This behavior is not restricted to organocopper species since the more stable alkylmanganese compounds also show a marked catalytic decomposition.<sup>1</sup>

The visible absorption spectrum and the electron paramagnetic resonance (epr) spectrum of organocopper species in THF solution showed interesting changes during these transformations. If a solution of ethylcopper(I) in THF was held at  $-10^\circ$  for approximately 30 min, it gradually turned purple<sup>12,13</sup> and remained homogeneous, but no decomposition was apparent. The change is probably due to association of the organocopper(I) species into clusters.<sup>14,15</sup> No epr (microwave) absorption occurred during this period of color change. Raising the temperature to  $0^\circ$  shortened the period of quiescence and accelerated the rate of decomposition of ethylcopper(I) [Figure 1]. The epr

(7) Dialkylcopper(II) may be an intermediate which decomposes to alkylcopper(I) with the liberation of dialkyl. Alternatively, the reaction may proceed *via* prior reduction of copper(II) followed by subsequent reaction of the Grignard reagent with copper(I).

(8) These reactions were carried out in an all-glass apparatus consisting of two compartments.

(9) (a) For example, 15 and 100 hr are required for the decomposition of methyl- and neopentylcopper(I), respectively, at room temperature. The induction periods for the decomposition of *n*-propyl-, ethyl-, and isopropylcopper(I) at  $0^\circ$  are 200, 30, and  $<5$  min, respectively.

(b) The induction period varied somewhat with different batches of copper salts due to small but variable amounts of iron impurities which are also exceedingly efficient catalysts.<sup>1,10</sup> The rate of the decomposition was, however, independent of the presence of excess Grignard reagent (up to fivefold excess) or magnesium bromide (twofold).

(10) The decomposition of *n*-butyl(tri-*n*-butylphosphine)copper(I)<sup>8a</sup> in diethyl ether also shows a slight induction period which is removed by catalytic amounts of iron(0) species.<sup>1</sup>

(11) The preparation of soluble silver(0), palladium(0), and copper(0) species will be described separately.<sup>1</sup>

(12) (a) Colored (red) solutions of alkylcopper species in di-*n*-butyl ether were originally investigated by Noller, *et al.*; (b) V. D. Parker, L. H. Piette, R. M. Salinger, and C. R. Noller, *J. Amer. Chem. Soc.*, **86**, 1110 (1964).

(13) Solutions of *n*-propylcopper(I) showed a broad absorption band centered at 575 nm. The apparent absorptivity ( $\log \epsilon \cong 2$ ) based on the copper charged was difficult to reproduce and changed with time.

(14) Further studies of these species are in progress.

(15) (a) Arylcopper(I) clusters have been recently described; (b) A. Cairncross and W. A. Sheppard, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1967, Abstract ORGN-118; (c) *cf.* also L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Amer. Chem. Soc.*, **90**, 7357 (1968).