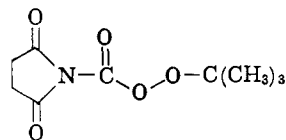
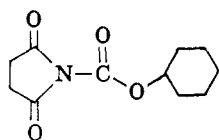


clusions cannot be made until more is known about percarbamate decompositions. No evidence of acyl isocyanate<sup>15</sup> or any similar fragmentation was found in any of our studies.



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**Acknowledgment.**—This work was supported by a grant (Type G) from the Petroleum Research Fund administered by the American Chemical Society.

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(16) National Science Foundation Undergraduate Research Participant, 1963–1964.

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RECEIVED APRIL 29, 1964

### Concerning the Mechanism of the Reaction of Phenyl(trihalomethyl)mercurials with Olefins

Sir:

We have reported a facile synthesis of *gem*-dihalo-cyclopropanes by the reaction of phenyl(trihalomethyl)-mercurials with olefins.<sup>1,2</sup> Several comments concerning the possible mechanism of this reaction have appeared.<sup>3</sup>

Studies of the stereochemistry of the haloform-butoxide-olefin reaction<sup>7</sup> and of the relative reactivities of olefins toward this reagent system<sup>8</sup> led to the conclusion that the reaction of a free, electrophilic dihalocarbene with the olefin was involved. Qualitative studies of relative reactivities of olefins toward sodium trichloroacetate in 1,2-dimethoxyethane suggested that there also a reaction between a free carbene and an olefin was taking place.<sup>9</sup> It therefore was of interest to investigate the stereochemistry of the C<sub>6</sub>H<sub>5</sub>Hg-CX<sub>3</sub>-olefin reaction and to determine relative reactivities of various olefins toward C<sub>6</sub>H<sub>5</sub>HgCX<sub>3</sub>.

We have compared olefin reactivities toward C<sub>6</sub>H<sub>5</sub>HgCCl<sub>2</sub>Br<sup>10</sup> in benzene at 80° with the reactivities of the same olefins toward sodium trichloroacetate in 1,2-dimethoxyethane at 80°, thus avoiding complications due to temperature effects.<sup>11</sup> In the standard ex-

periment 15 ml. of benzene was added to 10.0 mmoles of mercurial under argon, then 50.0 mmoles each of cyclohexene and olefin A. The flask was immersed in a preheated oil bath and the mixture was stirred for 3 hr. and filtered. The filtrate was distilled *in vacuo* into a receiver at -78°. Gas chromatographic analysis of an aliquot of the distillate containing *n*-butyrophenone as internal standard followed.<sup>12</sup> The relative rates (cyclohexene = 1) were calculated by Doering's method.<sup>8b</sup> The reactions with sodium trichloroacetate were carried out in a similar fashion.

The results of these experiments are given in Table I. The following are worthy of special comment. (1) Especially noteworthy is the near identity of the relative reactivities of all olefins toward C<sub>6</sub>H<sub>5</sub>HgCCl<sub>2</sub>Br and CCl<sub>3</sub>CO<sub>2</sub>Na. (2) The relative reactivity of olefins toward C<sub>6</sub>H<sub>5</sub>HgCCl<sub>2</sub>Br does not appear to be solvent dependent (note the experiments with (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C=CHCH<sub>3</sub> and *trans*-*n*-C<sub>3</sub>H<sub>7</sub>CH=CHC<sub>2</sub>H<sub>5</sub>). (3) The relative reactivities parallel reasonably well those measured for similar (but not identical) olefins toward the CHCl<sub>3</sub>-*t*-BuOK system,<sup>8b</sup> but with a greater spread of reactivities being observed in the latter case. Other subtle differences are apparent. These may reflect the effect of lower temperature in the latter system, as well as minor differences in steric factors in the olefins. (4) The relative reactivities do not parallel those observed for iodomethylzinc iodide reactions with comparable olefins,<sup>13</sup> where the relative reactivities indicated electrophilic attack on the olefin but with a pronounced steric factor also operative. (5) The relative reactivities do not parallel those observed for oxymercuration of olefins.<sup>14</sup> (6) The stereochemistry of the olefin is retained. *cis*- and *trans*-3-heptene gave 1,1-dichloro-2-ethyl-3-*n*-propylcyclopropanes which were identical with the cyclopropanes prepared from the respective olefins by the Doering-Hoffmann method.<sup>15</sup> Similar results were obtained in the reactions of C<sub>6</sub>H<sub>5</sub>HgCBr<sub>3</sub> with *cis*- and *trans*-2-butene.

The results of our studies lead us to the following conclusions. A "methylene transfer" system of the type discussed by Simmons, *et al.*,<sup>16</sup> does not appear to be involved in the mercurial-olefin reaction: the steric factor associated with iodomethylzinc iodide is absent. Secondly, if in both systems studied by us structures such as I were involved in transition states such as II, then for a number of reasons one would not expect to find such close correspondence in the relative

(1) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

(2) D. Seyferth, R. J. Minasz, A. J. H. Treiber, J. M. Burlitch, and S. R. Dowd, *ibid.*, **28**, 1163 (1963).

(3) For example, one paper<sup>4</sup> quotes a referee who asserts that "the mercury reagents most probably do not generate anything approaching free dihalocarbene, but are analogous to the Simmons-Smith reagent." On the other hand, a carbene mechanism is favored by Hine<sup>5</sup> and by Landgrebe.<sup>6</sup>

(4) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 56 (1964), footnote 16b.

(5) J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, p. 54.

(6) J. A. Landgrebe and R. D. Mathis, *J. Am. Chem. Soc.*, **86**, 524 (1964).

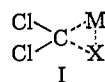
(7) (a) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956); (b) W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956).

(8) (a) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (b) W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958).

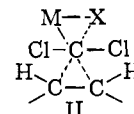
(9) W. M. Wagner, H. Kloosterziel, and S. Van Der Ven, *Rec. trav. chim.*, **80**, 740 (1961).

(10) D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **84**, 1757 (1962).

(11) The relative reactivities of olefins toward the CHCl<sub>3</sub>-*t*-BuOK system were measured at -20 to -10°. <sup>8b</sup>



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reactivities of the olefins studied toward C<sub>6</sub>H<sub>5</sub>HgCCl<sub>2</sub>Br (M = C<sub>6</sub>H<sub>5</sub>Hg) and CCl<sub>3</sub>CO<sub>2</sub>Na (M = Na). Nor would one expect such good correspondence in relative reactivities for these olefins if CCl<sub>3</sub>CO<sub>2</sub>Na

(12) The dichlorocyclopropanes were identified by comparison of their g.l.c. retention times and infrared spectra with those of authentic samples. They will be described in a later paper.

(13) E. P. Blanchard and H. E. Simmons, *J. Am. Chem. Soc.*, **86**, 1337 (1964).

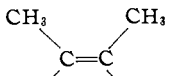
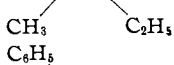
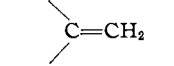
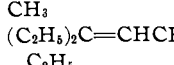
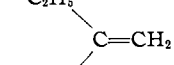

(14) C.-E. Döring and H. G. Hausthal, *J. prakt. Chem.*, [4] **22**, 59 (1963).

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(16) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

TABLE I

RELATIVE REACTIVITIES OF OLEFINS TOWARD PHENYL(BROMODICHLOROMETHYL)MERCURY AND TOWARD SODIUM TRICHLOROACETATE

Olefin A	$k_A/k$ , for $C_6H_5HgCCl_2Br$ (duplicate) <sup>a, b, e</sup>	$k_A/k$ , for $CCl_3CO_2Na$ <sup>c, e</sup>	Over-all yields of dichlorocyclopropanes for $C_6H_5HgCCl_2Br$ reactions <sup>d, f</sup>	Over-all yields of dichlorocyclopropanes for $CCl_3CO_2Na$ reactions <sup>h</sup>
	21.5 (23.5)	24.8	93.6 (94.4)	87.7
	7.16 (7.34)	7.35	93.0 (95.2)	85.7
	3.53 (3.55) 3.55 <sup>e</sup>	3.52	93.4 (93.2)	80.9
	2.05 (2.09)	2.08	92.0 (92.1)	80.1
	1.23 (1.22)	1.26	92.8 (94.2)	72.7
	1.00	1.00		
<i>cis</i> - $n$ - $C_3H_7CH=CHC_2H_5$	0.826 (0.831)	0.800 <sup>a</sup>	82.9 (86.4)	49.7
<i>trans</i> - $n$ - $C_3H_7CH=CHC_2H_5$	0.523 (0.526) 0.512 <sup>e</sup>	0.523	91.2 (93.4)	63.6
$n$ - $C_8H_{11}CH=CH_2$	0.236 (0.236)	0.219	89.6 (91.5)	60.6
$Cl_2C=CHCl$	0.0146 (0.0158) <sup>f</sup>		85.4 (84.7)	

<sup>a</sup> Reaction time 3 hr. at  $80 \pm 2^\circ$ . <sup>b</sup> Solvent, benzene. <sup>c</sup> Solvent, 1,2-dimethoxyethane. <sup>d</sup> Reaction time 8 hr. at  $80 \pm 2^\circ$ . <sup>e</sup> Compared with cyclohexene; both in fivefold excess unless otherwise specified. <sup>f</sup> Olefins in sevenfold excess. <sup>g</sup> Per cent based on  $C_6H_5HgCCl_2Br$ . <sup>h</sup> Per cent based on  $CCl_3CO_2Na$ . <sup>i</sup> Yields of  $C_6H_5HgBr$  isolated: 95–97%.

involved free dichlorocarbene as an intermediate and  $C_6H_5HgCCl_2Br$  reacted as shown in II.

The elimination of the "methylene transfer" mechanism leaves for discussion mechanisms involving attack on the olefin by  $:CCl_2$  or by  $:CCl_2Br$  in the case of our mercury reagent. The reaction of cyclohexene with the  $CHCl_2Br-t$ -BuOK system has been shown to give (*via*  $:CCl_2Br$ ) 7,7-dichlorobicyclo[4.1.0]heptane and 7-bromo-7-chlorobicyclo[4.1.0]heptane in 6:1 molar ratio.<sup>17</sup> In contrast, the reaction of  $C_6H_5HgCCl_2Br$  with cyclohexene gave *only* 7,7-dichlorobicyclo[4.1.0]heptane and phenylmercuric bromide.<sup>10</sup> This suggests that  $:CCl_2Br$  is not involved in mercurial-olefin reactions. For these reasons we favor a mechanism for the  $C_6H_5HgCX_3$ -olefin reaction which involves a free dihalocarbene intermediate. By implication we also favor a free dichlorocarbene intermediate in the sodium trichloroacetate-olefin reaction. It is to be noted that both of these systems, mercurials<sup>18</sup> and sodium trichloroacetate,<sup>19</sup> insert  $CX_2$  into C-H bonds, a reaction currently thought to be one characteristic of free carbenes.

A kinetic study of the mercurial-olefin reaction is in progress. We present the results above at this time because of the current interest in the mechanism of these reactions and because we wish to point out that not all reactions of olefins leading to cyclopropane formation which involve a metal-containing "divalent carbon carrier" necessarily proceed *via* transition state II.

**Acknowledgment.**—We are grateful for support of this work by the Directorate of Chemical Sciences, Air

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Force Office of Scientific Research Grant No. AF-AFOSR-502-64.

(20) (a) Alfred P. Sloan Foundation Fellow, 1962–1966; (b) National Institutes of Health Predoctoral Fellow, 1963–1964.

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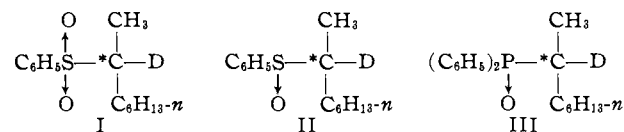
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RECEIVED APRIL 25, 1964

### Structural Requirements for Second-Row-Element Functional Groups to Preserve Asymmetry of Carbanions

Sir:

In previous work three functional groups centered about second-row elements have been examined with regard to their effect on the stereochemical capabilities of carbanions. The benzenesulfonyl group has been demonstrated to preserve the asymmetry of attached carbanions<sup>1</sup> whereas the benzenesulfinyl and diphenylphosphinoxy groups have not exhibited this property.<sup>2</sup> Thus,  $k_e/k_a$  (ratio of rate constants of base-catalyzed hydrogen isotopic exchange to that of racemization) for I was  $\geq 10$  in a variety of solvents,<sup>1b</sup> whereas the



(1) (a) D. J. Cram, W. D. Nielsen, and B. Rickborn, *J. Am. Chem. Soc.*, **82**, 6415 (1960); (b) D. J. Cram, D. A. Scott, and W. D. Nielsen, *ibid.*, **83**, 3696 (1961); (c) D. J. Cram and A. S. Wingrove, *ibid.*, **85**, 1100 (1963); (d) E. J. Corey and E. T. Kaiser, *ibid.*, **83**, 490 (1961); (e) E. J. Corey, H. König, and T. H. Lowry, *Tetrahedron Letters*, **12**, 515 (1962); (f) H. L. Goering, D. L. Towns, and B. Dittmar, *J. Org. Chem.*, **27**, 736 (1962).

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