

which the substituent exerts its influence on the shieldings of these carbons. An attenuation factor of about 4 seems to apply to the substituent effects at these two carbons; this does not seem unreasonable for a mechanism that is propagated through a  $\sigma$ -carbon network.<sup>14</sup>

In view of the relationship between the shieldings of  $C_2$  and  $C_3$ , it is noteworthy that the  $C_4$  shieldings do not follow the same order. Indeed, except for  $X = H$ , the  $C_4$  shieldings follow the opposite order from that of  $C_2$  and  $C_3$ . These results seem to point toward one of two possibilities: either there is a through-bond, substituent-effect mechanism that is merely attenuated between  $C_2$  and  $C_3$  but changes sign between  $C_3$  and  $C_4$ , or else a substantially different mechanism is operative at  $C_4$ , perhaps a field effect. Additional experiments and theoretical approaches aimed at clarifying this point are under way.

(14) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4506 (1970), and references therein.

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### Catalysis of Symmetry-Restricted Reactions by Weak Lewis Acids

Sir:

We report evidence that, for a sufficiently strained system, reactions which are thermally symmetry restricted ( $\sigma_{2a} + \sigma_{2a}$  and  $\sigma_{2s} + \sigma_{2s}$ ) can be catalyzed, quite dramatically in some cases, by a large number of substances which all share the features of being moderate to weak Lewis acids.

These reactions have been investigated for the tri-*tert*-butylprismane I<sup>1</sup> which, together with the tri-*tert*-butyl(Dewar benzene) II,<sup>1</sup> the tri-*tert*-butylbenzvalene III,<sup>1</sup> and 4-methoxy-2,4,6-tri-*tert*-butylbicyclo[3.1.0]hex-2-ene (VII) have been prepared and characterized by Kaplan and Wilzbach and their collaborators.<sup>2-4</sup>

In the absence of acid or other catalysts the prismane was relatively stable thermally; it decomposed only slowly in pyridine at 110° to give the benzenes IV and V in a 1:1 ratio ( $t_{1/2} = 18$  hr).

In contrast, catalytic quantities (*ca.* 0.01 *M*) of a large number of metal complexes at 25–30° in methanol converted I into the Dewar benzene II, the benzvalene III, and, probably, also into the benzvalene VI<sup>1</sup> (see Table I and Scheme I). Some of the catalysts ( $AgNO_3$ ,  $SnCl_2$ ,  $Na_2PdCl_4$ , and  $[Rh(CO)_2Cl]_2$ ) also isomerized II and III to IV in slower subsequent steps. These reactions are also thermally symmetry restricted and will be discussed later.

The benzvalene VI is unstable and isomerizes readily to V, or, in the presence of methanol, gives the bicyclo-

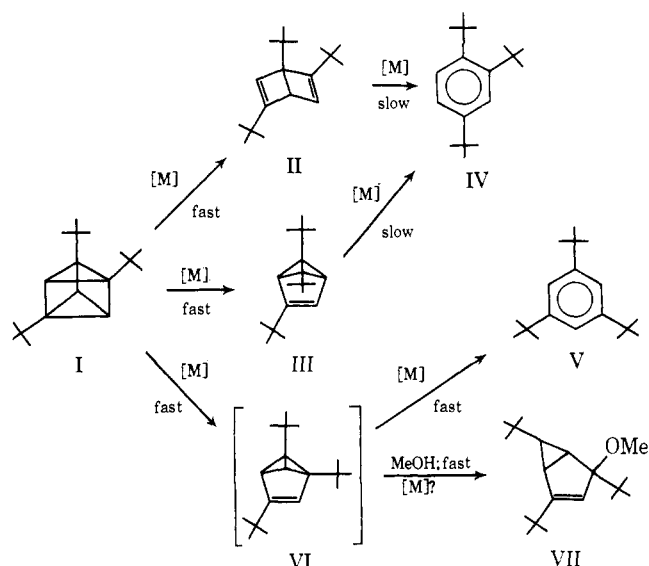
(1) The systematic names for the compounds are 1,3,5-tri-*tert*-butyl-tetracyclo[2.2.0.0.2<sup>a</sup>.0.3<sup>b</sup>]hexane (I), 1,2,5-tri-*tert*-butylbicyclo[2.2.0]hexa-2,4-diene (II), 1,3,6-tri-*tert*-butyltricyclo[3.1.0.0.2<sup>a</sup>]hex-3-ene (III), and 1,2,4-tri-*tert*-butyltricyclo[3.1.0.0.2<sup>a</sup>]hex-3-ene (VI).

(2) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 4004 (1965).

(3) L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *ibid.*, **88**, 2881 (1966).

(4) I. E. Den Besten, L. Kaplan, and K. E. Wilzbach, *ibid.*, **90**, 5868 (1968).

Scheme I



hexene VII.<sup>4</sup> Since the latter was frequently detected in the catalyzed reactions and the benzene V was obtained in the  $AgNO_3$ -catalyzed reactions, we presume that both of these compounds arose from VI here too. These isomerizations may also have been accelerated by the catalysts used.

The prismane I also reacted with protonic acids; however, 0.003 *M* hydrochloric acid in methanol at 30° only isomerized I to IV ( $t_{1/2} = 35$  min). Since both II and III were unchanged under these conditions, they cannot be intermediates in the formation of IV which presumably involves a protonation step. As the asymmetric benzene IV was formed in only negligible amounts in the other reactions (see Table I), these isomerizations were not due to the adventitious presence of traces of acid.

All the metal-catalyzed reactions (except, possibly, those where  $t_{1/2} < 1$  min, which were not studied) appear, from our preliminary data, to be first order in I. This has been rigorously established for the  $\{Rh(CO)_2Cl\}_2$ -catalyzed reaction in methanol, which is also approximately first order in catalyst (pseudo-first-order rate constant for the disappearance of I is  $4.4 \pm 0.6 \times 10^{-4} \text{ sec}^{-1}$  at 37°,  $[\{Rh(CO)_2Cl\}_2] = 3 \times 10^{-4} \text{ mol l}^{-1}$ ,  $[I] = 6 \times 10^{-2} \text{ mol l}^{-1}$ ).

The most remarkable feature of the results is that such a wide variety of catalysts, including  $Hg(II)$ ,  $Sn(II)$ ,  $Zn(II)$ , and  $Pb(II)$  salts and *sym*-trinitrobenzene, are effective. Although pyridine, when used as solvent, deactivated some catalysts completely ( $ZnCl_2$ ,  $Pb(OAc)_2$ ,  $[Cu(OAc)_2]_2$ , and  $Co(acac)_3$ ), others, such as  $HgCl_2$ ,  $AgNO_3$ , or  $SnCl_2$ , were still active, though at a somewhat reduced rate. This inhibition is not unexpected; since pyridine is a good ligand to most metals there will be competition between it and I for the catalyst.

The product distribution varied with the catalyst; some ( $HgCl_2$ ,  $SnCl_2$ ) favored formation of the Dewar benzene II, others ( $AgNO_3$ ,  $Co(acac)_3$ ), the benzvalene III (or VI). If concerted, these reactions would be examples of ( $\sigma_{2s} + \sigma_{2s}$ ) and ( $\sigma_{2a} + \sigma_{2a}$ ) reactions, respectively.

A number of examples of the catalysis of symmetry-restricted ( $\sigma_{2s} + \sigma_{2s}$ )<sup>5-11</sup> and ( $\sigma_{2a} + \sigma_{2a}$ )<sup>12,13</sup> reactions

(5) H. Hogeveen and H. C. Volger, *ibid.*, **89**, 2486 (1967).

Table I. Products from Catalyzed Decomposition of Tri-*tert*-butylprismane (I)<sup>a</sup>

Catalyst	Solvent	$t_{1/2}$ , min	I, %	II, %	III, %	IV, %	V, %	VII, %
HgCl <sub>2</sub> <sup>b</sup>	MeOH	<1	0	90	10	0	0	0
HgCl <sub>2</sub> <sup>b</sup>	Pyridine	<1	0	87	13	0	0	0
SnCl <sub>2</sub> ·2H <sub>2</sub> O	MeOH	0.5	0	71	14	0	0	14
SnCl <sub>2</sub> ·2H <sub>2</sub> O	Pyridine	1320	50	42	8	0	0	0
ZnCl <sub>2</sub>	MeOH	4	50	36	14	0	0	0
Na <sub>2</sub> PdCl <sub>4</sub>	MeOH	10	50	35	5	0	0	10
[Rh(CO) <sub>2</sub> Cl] <sub>2</sub>	MeOH	20	50	34	13	0	0	3
[Pd(OAc) <sub>2</sub> ] <sub>3</sub>	MeOH	4	50	33	17	0	0	0
[1,5-C <sub>8</sub> H <sub>12</sub> RhCl] <sub>2</sub>	MeOH	31	50	32	18	0	0	0
[Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O] <sub>2</sub>	MeOH	18	50	19	22	0	0	11
Ru <sub>3</sub> (CO) <sub>12</sub>	MeOH	12	50	20	26	0	0	4
Pb(OAc) <sub>2</sub> ·3H <sub>2</sub> O	MeOH	9	50	10	27	0	0	13
[C <sub>6</sub> Me <sub>2</sub> RhCl] <sub>2</sub>	MeOH	120	50	6	27	1	0	16
AgNO <sub>3</sub>	MeOH	<1	0	5	51	6	38	0
AgNO <sub>3</sub>	Pyridine	5	50	2	22	4	22	0
C <sub>6</sub> Me <sub>2</sub> Rh(OAc) <sub>2</sub> H <sub>2</sub> O	MeOH	300	50	4	33	0	0	13
1,3,5-Trinitrobenzene <sup>c</sup>	MeOH	460	50	2	28	2	8	10
Co(acac) <sub>3</sub>	MeOH	13	50	2	26	0	0	21

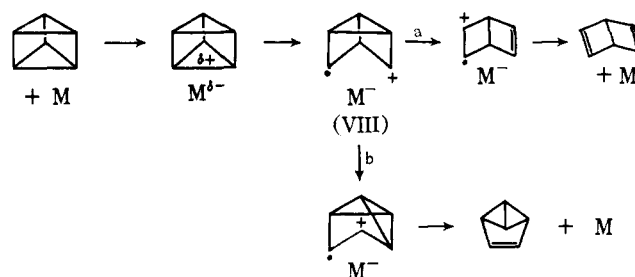
<sup>a</sup> The experiments were carried out in an nmr tube containing approximately 10 mg of a mixture of I (50–80%), II (20–40%), and III (5–10%) in 0.5 ml of methanol or pyridine. The molar ratio of I to catalyst used was *ca.* 100:1 except where stated. The mixture of I, II, and III used was obtained by vpc of the photolysis products of IV in an all-glass chromatograph. The rates of change in the concentrations of I, II, and III and the formation of IV, V, and VI were followed by nmr at 30°. The percentages of product quoted are for the half-completed reaction (initial prismane concentration normalized to 100), to minimize further reactions of II or III, except for those where  $t_{1/2} < 1$  min, where the product distribution was determined after 2 min when little I remained. <sup>b</sup> There was no significant change in product composition for ratios of I:HgCl<sub>2</sub> from 1 to 100. <sup>c</sup> The molar ratio [I]:[trinitrobenzene] was 5 here. The reaction was significantly slower in CDCl<sub>3</sub>.

have been reported. Two types of explanation have been offered: (i) that the symmetry-restricted reactions become allowed in the presence of metals which have d orbitals of energy such that interaction can occur,<sup>6,14,15</sup> and (ii) that these reactions are not concerted but proceed *via* a  $\sigma$ -bonded metal complex intermediate.<sup>8,9</sup>

Since there is no sharp change in product distribution or rate which can be correlated with the stereochemistries or electronic configurations of the catalysts, we propose that all the reactions described in Table I proceed by similar routes. However, it is clear that neither of the above explanations suffices to explain the results. A number of the better catalysts do not have d orbitals at readily accessible energies and the formation of metal-carbon bonds, particularly by an oxidative addition mechanism, can be ruled out for the majority of the cases described here.

A common feature of all the catalysts is that they are moderate to weak Lewis acids which can be fairly easily reduced. We suggest that the first step is the formation of a very short-lived charge-transfer complex between the catalyst and I, which gives the prismane radical cation VIII, where a cyclopropane bond has been opened (Scheme II).<sup>16</sup> Rapid rearrangements to

give the Dewar benzene (path a) or the benzvalenes (path b) then occur, their relative rates determined by the nature of the catalyst.

Scheme II<sup>17</sup>

Analogous to this process is the ring opening of quadricyclene to norbornadiene which is induced by excited singlet-state naphthalene *via* a charge-transfer complex.<sup>18,19</sup>

A consequence of this proposed mechanism is that any substituent which makes the removal of an electron from the skeleton of the strained hydrocarbon more difficult should decrease the rate of the catalyzed rearrangement.

The intermediates with metal-carbon  $\sigma$  bonds which have been reported to arise in some Rh(I)-catalyzed ( $\sigma_2 + \sigma_2$ ) reactions<sup>8,9</sup> can be derived from intermediates analogous to VIII when the Lewis acid, in that case a d<sup>8</sup> metal complex, is also able to back-donate electrons.<sup>20</sup>

(17) For clarity, localized structures have been written and *tert*-butyl groups omitted.

(18) B. S. Solomon, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969).

(19) We thank Dr. J. J. McCullough for drawing our attention to this work.

(20) No intermediate complex could be detected during the Rh(I)-catalyzed decomposition of I.

(6) W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4788 (1967).

(7) H. Hogeveen and H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **86**, 830 (1967); *Chem. Commun.*, 1733 (1967).

(8) T. J. Katz and S. Cereface, *Tetrahedron Lett.*, 2509 (1969); *J. Amer. Chem. Soc.*, **91**, 2405, 6519 (1969).

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(10) H. Dietl and P. M. Maitlis, *ibid.*, 759 (1967).

(11) K. L. Kaiser and P. M. Maitlis, *ibid.*, 942 (1970).

(12) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970).

(13) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970).

(14) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967); F. D. Mango, *Tetrahedron Lett.*, 4813 (1969).

(15) R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969).

(16) Although no metal is formed during any of the catalyzed reactions of I, we have found that hexamethylprismane undergoes a stoichiometric silver nitrate induced isomerization in which silver is precipitated.

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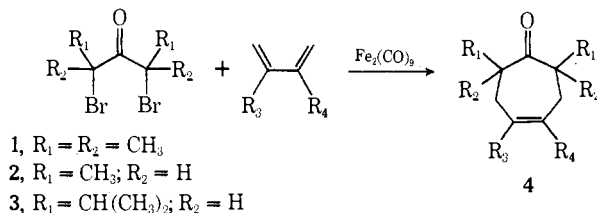
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### Reaction of $\alpha,\alpha'$ -Dibromo Ketones with Iron Carbonyls in the Presence of 1,3-Dienes. A New Route to Troponoid Compounds

Sir:

Cycloadditions and cyclocondensations are the most widely used reactions for constructing the framework of organic molecules, and an enormous number of publications on these subjects have been presented. However, only a few examples are known of the formation of carbocyclic seven-membered rings by combining three- and four-carbon units.<sup>1</sup> We wish to describe a dehalogenation of  $\alpha,\alpha'$ -dibromo ketones with iron carbonyls in the presence of 1,3-dienes, which provides a novel, direct route to seven-membered cyclic ketones including troponoid compounds.

When a solution of 2,4-dibromo-2,4-dimethylpentan-3-one (**1**), diiron nonacarbonyl ( $\text{Fe}_2(\text{CO})_9$ ), and 2,3-dimethylbutadiene (1.0:1.2:9.0 mole ratio) in dry benzene was heated at 60° for 40 hr under nitrogen atmosphere, 2,2,4,5,7,7-hexamethyl-4-cycloheptenone (**4**,  $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{CH}_3$ ) was obtained in 71% yield after work-up.<sup>2</sup> The spectral data were in accord with the assigned structure: mass  $m/e$  194 ( $\text{M}^+$ ); nmr ( $\text{CCl}_4$ , TMS)  $\delta$  1.07 (s, 12 H,  $\text{CH}_3$ ), 1.79 (s, 6 H,  $\text{CH}_3$ ), and 2.25 (s, 4 H,  $>\text{CH}_2$ ); ir (neat liquid) 1685  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ) characteristic of di-*tert*-alkyl ketones.<sup>3</sup> Butadiene, isoprene, or cyclopentadiene as the diene component afforded similar adducts in moderate to good yields. Secondary dibromides **2** and **3** were also



employable, but  $\alpha,\alpha'$ -dibromoacetone failed to give the corresponding cycloheptenones. Iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) could be used as the reducing agent, but less effectively. The use of the butadieneiron tricarbonyl complex (**5**)<sup>4</sup> in place of  $\text{Fe}_2(\text{CO})_9$  and free

(1) (a) R. A. Raphael, "Chemistry of Carbon Compounds," Vol. IIA, E. H. Rodd, Ed., Elsevier, New York, N. Y., 1953, p 249; E. S. Waight, "Rodd's Chemistry of Carbon Compounds," Vol. IIB, S. Coffey, Ed., Elsevier, New York, N. Y., 1968, p 347. (b) Cycloaddition of allyl cation to cyclic conjugate dienes was recently reported: H. M. R. Hoffmann and D. R. Joy, *J. Chem. Soc. B*, 1182 (1968). (c) For the reaction of 1-diethylamino-1,3-butadiene with diphenylcyclopropanone, see J. Ciabattini and G. A. Berchtold, *J. Amer. Chem. Soc.*, **87**, 1404 (1965).

(2) All new compounds gave correct elemental analyses and/or molecular peaks in mass spectra. Ir, nmr, and uv spectra were consistent with the structures assigned.

(3) J. Lascombe, P. Grange, and M. L. Josien, *Bull. Soc. Chim. Fr.*, 773 (1957).

(4) R. B. King, *Organometal. Syn.*, **1**, 128 (1965).

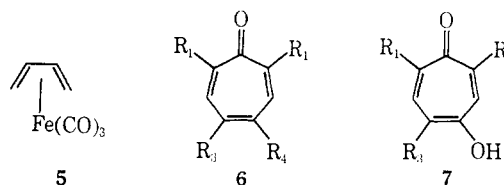
butadiene resulted in notably increased yields of cycloheptenones. Some examples of the new annelation reaction are summarized in Table I.

**Table I.** Reaction of  $\alpha,\alpha'$ -Dibromo Ketones with  $\text{Fe}_2(\text{CO})_9$  in the Presence of 1,3-Dienes

Di-bromide <sup>a</sup>	Diene	Product	Yield, <sup>b,c</sup> %
1	2,3-Dimethylbutadiene	2,2,4,5,7,7-Hexamethyl-4-cycloheptenone	71
1	Butadiene	2,2,7,7-Tetramethyl-4-cycloheptenone	33 (84)
1	Isoprene	2,2,4,7,7-Pentamethyl-4-cycloheptenone	47
1	Cyclopentadiene	2,2,4,4-Tetramethylbicyclo[3.2.1]oct-6-en-3-one	82
2	Butadiene	2,7-Dimethyl-4-cycloheptenone	44 (55)
2	Isoprene	2,4,7-Trimethyl-4-cycloheptenone	36
2	2,3-Dimethylbutadiene	2,4,5,7-Tetramethyl-4-cycloheptenone	47
2	Cyclopentadiene	2,4-Dimethylbicyclo[3.2.1]oct-6-en-3-one	86
3	Butadiene	2,7-Diisopropyl-4-cycloheptenone	44 (77)
3	Isoprene	2,7-Diisopropyl-4-methyl-4-cycloheptenone	31
3	2,3-Dimethylbutadiene	2,7-Diisopropyl-4,5-dimethyl-4-cycloheptenone	50
3	Cyclopentadiene	2,4-Diisopropylbicyclo[3.2.1]oct-6-en-3-one	93

<sup>a</sup> Dibromo ketones **2** and **3** were used as mixtures of *meso* and *dl* isomers. <sup>b</sup> Isolated yield (preparative tlc on silica gel followed by distillation). <sup>c</sup> Yield obtained by the use of butadieneiron tricarbonyl (**5**) (dibromo ketones:**5** = 1:2, in benzene, 60–80°) is given in parentheses.

4-Cycloheptenones derived from secondary bromides and open-chain 1,3-dienes serve as potential intermediates for the synthesis of various seven-membered ketones, especially of troponoid compounds. For example, treatment of **4** ( $\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$ ) with 4 equiv of pyrrolidone hydrotribromide in tetrahydrofuran (30°, 12 hr)<sup>5</sup> followed by dehydrobromina-



tion with lithium chloride in *N,N*-dimethylformamide (DMF) (140°, 1 hr) gave the known 2,7-dimethyltropone (**6**,  $\text{R}_1 = \text{CH}_3$ ,  $\text{R}_3 = \text{R}_4 = \text{H}$ ) in 64% yield, which was identified by comparison of the spectral data with those reported.<sup>6</sup> Bromination of **4** ( $\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$ ) with 5.5 equiv of pyridine hydrotribromide in acetic acid (25°, 12 hr)<sup>7</sup> was followed by treatment with lithium chloride in DMF (130°, 1 hr) and hydrolysis of the resulting 4-bromo-2,7-dimethyltropone in a mixture of 48%  $\text{HBr}-\text{H}_2\text{O}$ -acetic acid (3:4:3) in a sealed tube (130°, 8 hr) to afford 2,7-dimethyl- $\gamma$ -tropone (**7**,  $\text{R}_1 = \text{CH}_3$ ;  $\text{R}_3 = \text{H}$ ) in 53% overall yield. Physical properties of troponoid de-

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