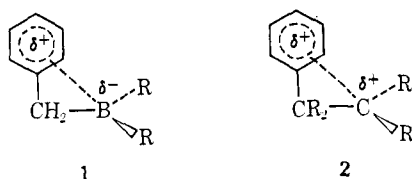


### Tribenzylborane. A Charge-Transfer Model for Benzyl-Group Va Metalloid Electronic Transitions and Phenonium Ion Transition States

Sir:

The ultraviolet spectra of aryl derivatives of trivalent group V elements (M) such as  $C_6H_5M(CH_3)_2$  exhibit intense transitions in the region 240–300 nm, and there has been substantial difference of opinion as to whether these transitions should be regarded as  $^1L_a$ ,  $^1L_b$ ,  $n \rightarrow \pi^*$ , or intramolecular charge transfer.<sup>1</sup> A similar controversy<sup>2,3</sup> has arisen around the intense 300-nm transition of triarylboranes. The energy of an intramolecular charge-transfer transition is well approximated<sup>4</sup> by the relation in eq 1 where  $I_p$  is the donor ionization poten-

$$E_{CT} = I_p - E_a - e^2/r \quad (1)$$



tial,  $E_a$  is the acceptor electron affinity, and  $r$  is the distance between positive and negative charge in the excited state. From eq 1 we estimate that the difference in charge-transfer transition energy of  $(C_6H_5)_3M$  and  $(C_6H_5CH_2)_3M$  due to change in  $r$ , measured as distance between M and the center of phenyl ring, should be a blue shift of the order of 1.2–1.3 eV. A correction must be subtracted from this, however, to accommodate a decrease in the  $+I\pi$  effect<sup>5</sup> of electrostatic repulsion between electron density remaining on M and increased electron density in the ring. For aniline the  $+I\pi$  effect amounts<sup>5</sup> to  $\sim 0.6$  eV, and our additional correction should be about 0.1 eV. An unknown correction of a few tenths of an electron volt for the change in  $I_p$  of M with a change in the inductive effect from  $C_6H_5$  to  $C_6H_5CH_2$  as the M substituent should also be subtracted from the value 1.2–1.3 eV. These qualitative arguments are meant to show that if the first intense transitions of  $C_6H_5MR_2$  (R = alkyl or aryl) are charge transfer ( $^1A_1 \rightarrow ^1A_1$ , local  $C_{2v}$  symmetry), then it is not unreasonable that a similar but weaker blue-shifted charge-transfer transition should appear in the spectra of  $C_6H_5CH_2MR_2$  (R = alkyl or  $CH_2C_6H_5$ ). In fact, we find reported,<sup>1d,6</sup> but unassigned, transitions for  $(C_6H_5CH_2)_3M$  in the literature:  $\lambda_{max}$  for  $(C_6H_5)_3P$  262 nm (4.7 eV);  $(C_6H_5CH_2)_3P$  247 nm (5.0 eV) ( $\epsilon 2.9 \times 10^3$ ), and  $(C_6H_5)_3N$  297 nm (4.2 eV);  $(C_6H_5CH_2)_3N$  248 nm (sh) (5.0 eV)

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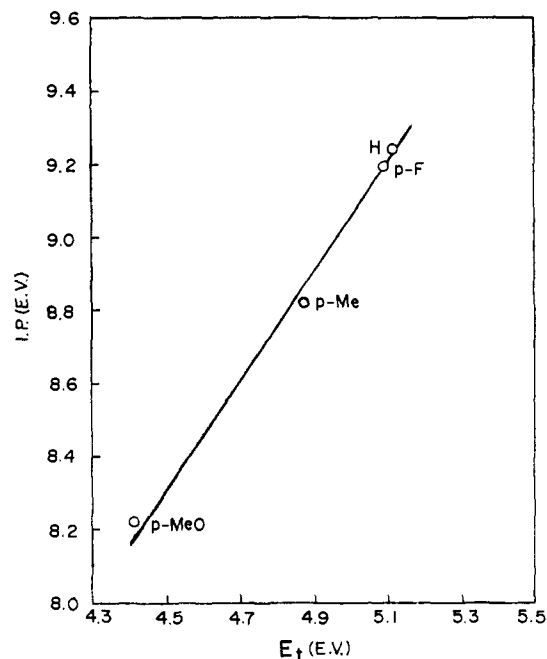


Figure 1. A plot of the charge-transfer transition energy (eV) of  $(p-RC_6H_4CH_2)_3B$  against the first ionization potentials (eV) of  $RC_6H_5$  (R = H, F,  $CH_3$ ,  $CH_3O$ ).

with increasing absorption in the region of 240 nm. Clearly it is not unreasonable to assign these 240-nm transitions of  $(C_6H_5CH_2)_3M$  to intramolecular charge transfer from the M lone pair to the lowest vacant  $C_6H_5CH_2 \pi$  orbital.

We now wish to report the observation of a similar but reverse charge-transfer transition in the spectra of *para*-substituted tribenzylboranes,  $(p-RC_6H_4CH_2)_3B$ , where R is H, F,  $CH_3O$ , and  $CH_3$ . These molecules, in addition to the usual  $^1L_a$  and  $^1L_b$  transitions near 200 and 260 nm, exhibit a third medium-intensity ( $\epsilon \sim 10^3$ ) broad absorption maximum in the region 240 to 280 nm. The transition disappears in the spectrum of  $(C_6H_5CH_2)_3BNH_3$ , and an excellent linear correlation of the charge transfer transition energy ( $E_{CT}$ ) of  $(p-RC_6H_4CH_2)_3B$  with the ionization potential of  $C_6H_5R$  is observed in Figure 1, as required by eq 1. The molar extinction coefficient of the transition in  $(C_6H_5CH_2)_3B$  is found to obey Beer's law. We feel that these results firmly establish these transitions in the spectra of  $(C_6H_5CH_2)_3B$  and the corresponding transition at 300 nm in the spectra of triarylboranes as intramolecular charge transfer.

Controversy<sup>7</sup> over the nature of the transition state in the solvolysis of  $\beta$ -aryl-substituted alkyl halides, tosylates, and similar derivatives continues unabated.

The use of organoboranes as models for carbonium ions has been noted before,<sup>2,8</sup> and the charge-transfer excited state of  $C_6H_5CH_2BR_2$  (1) may serve as a useful model for structure 2 proposed by Brown<sup>7c</sup> for the transition state in these solvolyses. We believe, therefore, it is significant that for systems  $p-RC_6H_4CH_2CH_2OTs$

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in formic acid,<sup>9</sup>  $p$ - $\text{RC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{CH}_2\text{OBs}$  in acetic acid,<sup>10</sup> and  $p$ - $\text{RC}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_2\text{Cl}$  and  $p$ - $\text{RC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{Cl}$  in 80% aqueous ethanol,<sup>7c</sup> where R is H,  $\text{CH}_3$ , and  $\text{OCH}_3$ , a virtually perfect correlation is found between  $\log k$  (rate constant) and the ionization potential of  $\text{RC}_6\text{H}_5$ . These correlations are gathered into a single Figure 2 by plotting  $\log(k/k^0)$  where  $k^0$  is the rate for R = H. Since we have established the linear re-

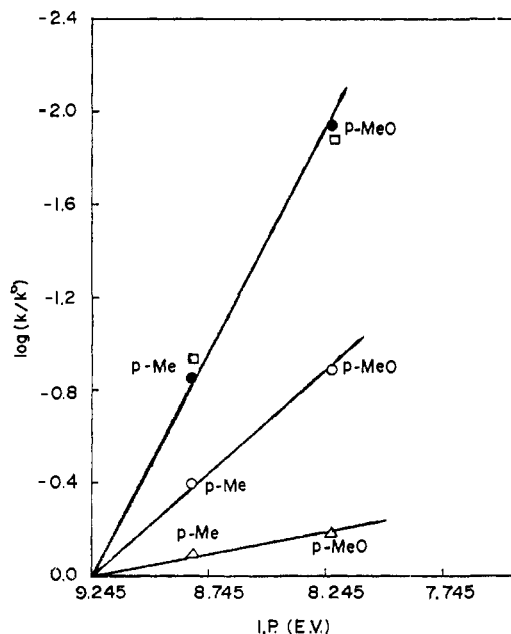


Figure 2. A plot of  $\log(k/k^0)$  for the solvolysis rates of  $p$ - $\text{RC}_6\text{H}_4\text{-C}(\text{CH}_3)_2\text{CH}_2\text{OBs}$  (●),  $p$ - $\text{RC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OTs}$  (□),  $p$ - $\text{RC}_6\text{H}_4\text{-C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{Cl}$  (○), and  $p$ - $\text{RC}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_2\text{Cl}$  (△) against the ionization potential (eV) of  $\text{RC}_6\text{H}_5$  (R = H,  $\text{CH}_3$ ,  $\text{OCH}_3$ ).

lationship for R = H,  $\text{CH}_3$ , and  $\text{CH}_3\text{O}$  between the ionization potential and ( $p$ - $\text{RC}_6\text{H}_5\text{CH}_2$ )<sub>3</sub>B charge-transfer transition energy, Figure 2 is also a correlation of  $\log(k/k^0)$  with  $E_{\text{CT}}$ . It should be noted that the slopes of the correlation lines in Figure 2 correspond to that expected from relative importance of neighboring group participation by the phenyl ring in the solvolysis transition states. The correlation in Figure 2, which involves 12 points, implies that the mechanism by which R stabilizes the excited state of ( $p$ - $\text{RC}_6\text{H}_4\text{CH}_2$ )<sub>3</sub>B is similar to that by which the solvolysis transition state of the  $\beta$ -phenylalkyl tosylates, etc., are stabilized. Although each of the four linear relationships in Figure 2 is defined by only three points, no other substituent parameter such as Hammett  $\sigma$  or  $\sigma^+$  places the  $\text{CH}_3\text{O}$  on the lines defined by H and  $\text{CH}_3$ .

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(12) Author to whom inquiries should be addressed: Department of Chemistry, San Francisco State College, San Francisco, Calif.

Brian G. Ramsey<sup>11,12</sup> Nirmal K. Das

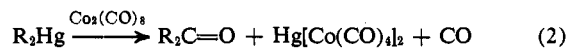
Department of Chemistry  
University of Akron, Akron, Ohio

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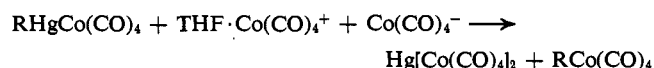
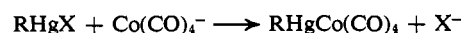
## A Convenient High Yield Dicobalt Octacarbonyl Catalyzed Synthesis of Diaryl Ketones from Diarylmercury Compounds and Carbon Monoxide

Sir:

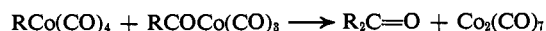
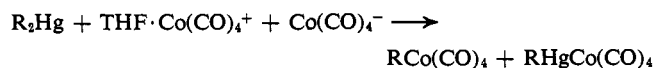
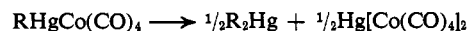
Recently we reported a synthesis of symmetrical ketones by the reaction of organomercuric halides or diorganomercurials with dicobalt octacarbonyl at room temperature in THF solution.<sup>1</sup> The yields of ketones were in general quite good, and in the case of diaryl



ketones they were excellent. A mechanism involving organocobalt intermediates was indicated



or



Reactions 1 and 2 represent a stoichiometric utilization of dicobalt octacarbonyl. More practical and economical would be a reaction in which the stoichiometric reagent is carbon monoxide and the relatively expensive dicobalt octacarbonyl is used in only catalytic quantities (eq 3). We report here concerning the realization of such a ketone synthesis.



Our new catalytic ketone synthesis is based upon our previously developed reaction of diorganomercurials with dicobalt octacarbonyl (eq 2). In order to make this process catalytic, a method for the conversion of the unreactive  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  to the active reagent,  $\text{Co}_2(\text{CO})_8$ , must be available. Italian workers<sup>2</sup> have reported photochemical reactions of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  with acetylenes, in which photolysis of the mercury compound served to release dicobalt octacarbonyl; e.g., eq 4. This observation suggested to us that reaction 1 or 2 could be made catalytic in dicobalt octacarbonyl by irradiating the reaction mixture with an ultraviolet source while the reaction progressed. Our subsequent experiments showed that such was the case.

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