Table I. Resolution *via* the Pfeiffer Effect

Initial racemic complex	Environment compd	Pfeiffer rotation (P_{obsd}),[a] deg	Concn of complex,[b] M	Rotation[b] α_{obsd}	[M],[a] deg	% resolution
$[\mathrm{Ni}(o\text{-phen})_3]^{2+}$ (0.05 M)	*l*-Malic acid (0.2 M)	2.345	0.048	−1.599	334.2	2.8
$[\mathrm{Ni(dipy)_3}]^{2+}$ (0.05 M)	*l*-Malic acid (0.2 M)	0.396	0.048	−0.151	31.46	1.5

[a] 25°, 589 mμ. [b] After resolution.

complexes as well. However, a better test would be to "freeze" the supposedly displaced equilibrium and then study the racemization of the enantiomer trapped in greater concentration. Since the alteration of the equilibrium does not give any indication of the rate at which the interconversion occurs, an attempt was made to find complexes which exhibit the effect but which take some time to achieve the maximum Pfeiffer rotation. The tris(*o*-phenanthroline) and tris(2,2′-dipyridyl) complexes of nickel(II) fall into this category. Dwyer indicated that since the former takes several days to achieve the maximum Pfeiffer rotation, it should be capable of being resolved by conventional means, and this is correct.[7,8] In addition, although the tris(2,2′-dipyridyl) complex of nickel(II) takes only 20 min to achieve its maximum Pfeiffer rotation, it is also capable of being resolved by conventional means.[9]

Most systems which exhibit the Pfeiffer effect attain the maximum Pfeiffer rotation practically instantaneously, and it is interesting to note that none of the racemates of optically active complexes which exhibit an instantaneous Pfeiffer effect has yet been resolved.

In the present work the authors have succeeded in freezing out the nonequimolar mixture of enantiomers from the Pfeiffer-active systems composed initially of DL-$[\mathrm{Ni}(o\text{-phen})_3]^{2+}$ (0.05 M) and *levo*-malic acid (0.2 M) in aqueous solution, in one case, and DL-$[\mathrm{Ni(dipy)_3}]^{2+}$ (0.05 M) and *l*-malic acid (0.2 M) in the other. The removal of the displaced-equilibrium mixtures from the environment was achieved by precipitation of the complexes as the relatively insoluble perchlorates, by use of sodium perchlorate. The insoluble perchlorates were then redissolved by placing them (as aqueous suspensions) in contact with Amberlite IRA-400 anion-exchange resin in the chloride form. In each case the solution containing the soluble complex (as the chloride) was filtered and its rotation was read by means of a Perkin-Elmer Model 141 photoelectric polarimeter.

Table I lists the observed and Pfeiffer rotations. The observed Pfeiffer rotation is defined[4] as $P_{\mathrm{obsd}} = \pm(\alpha_{\mathrm{e+c}} - \alpha_{\mathrm{e}})$, where $\alpha_{\mathrm{e+c}}$ is the observed rotation of the Pfeiffer-active system containing both the added racemic complex and the environment compound, α_{e} is the observed rotation of the environment compound in solution before addition of the racemic complex, and the symbol ± indicates that the sign to be placed in front of the parentheses while calculating the observed Pfeiffer rotation is the same as the sign of α_{e}.

Figure 1 is a comparison of the first-order racemization curves of the complexes which have been partially resolved by this Pfeiffer-effect technique with the racemization curves of the compounds resolved by conventional means. That these curves are identical provides strong support, in the authors' opinion, for the "equilibrium displacement" mechanism proposed by Gyarfas and Dwyer[3] for the occurrence of the Pfeiffer effect.

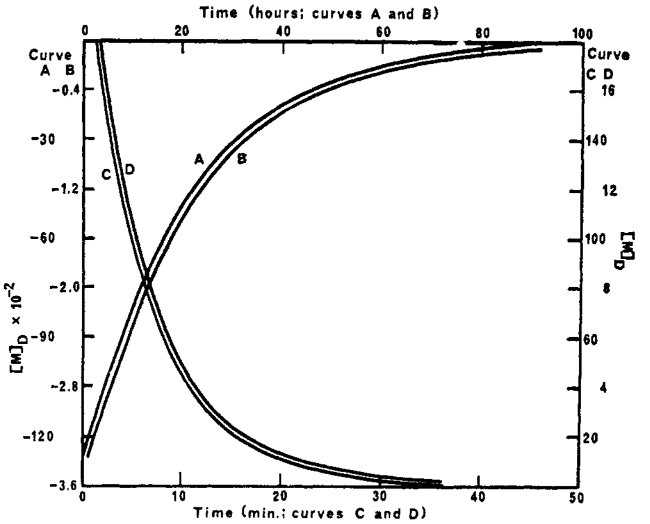

Figure 1. The racemizations in aqueous solution at 25° (1-dm cell) of (A) L-$[\mathrm{Ni}(o\text{-phen})_3]^{2+}$ (0.001 M); (B) L-$[\mathrm{Ni}(o\text{-phen})_3]^{2+}$ partially resolved by the Pfeiffer-effect technique (0.048 M); (C) L-$[\mathrm{Ni(dipy)_3}]^{2+}$ (0.02 M); (D) L-$[\mathrm{Ni(dipy)_3}]^{2+}$ partially resolved by the Pfeiffer-effect technique (0.048 M).

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Mono- and Dialkylation of Ethyl Dihaloacetates by Reaction with Organoboranes under the Influence of Potassium *t*-Butoxide. Convenient Procedures for the Conversion of Olefins into the α-Haloalkanoic or Dialkylacetic Acid Esters *via* Hydroboration

Sir:

We wish to report that the facile reaction of organoboranes with ethyl bromoacetate under the influence of potassium *t*-butoxide,[1] which provides a remarkably

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(8) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 232 (1949).

(9) G. Morgan and F. Burstall, *J. Chem. Soc.*, 2213 (1931).

(1) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *J. Am. Chem. Soc.*, **90**, 818 (1968).

Table I. Conversion of Olefins into Ethyl 2-Bromoalkanoates, 2-Chloroalkanoates, and Dialkylacetates by Reaction of the Corresponding Organoboranes with α-Haloalkanoates under the Influence of Potassium *t*-Butoxide

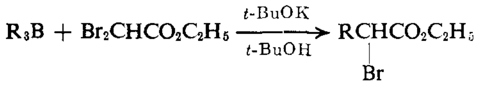
Organoboranes from Olefin	R_3B, mmol	Halogen derivative	RX, mmol	$t\text{-BuO}^-K^+$, mmol	Temp, °C	Product	Yield, %[a]
Ethene[b]	10.0	Br_2CHCO_2Et	10.0	10.0	0	$C_2H_5CHBrCO_2Et$	97
	50.0	Cl_2CHCO_2Et	50.0	50.0	0	$C_2H_5CHClCO_2Et$	98
1-Hexene	100	Br_2CHCO_2Et	100	100	0	$CH_3(CH_2)_5CHBrCO_2Et$	98
	50.0	Cl_2CHCO_2Et	50.0	50.0	0	$CH_3(CH_2)_5CHClCO_2Et$	98
1-Decene	100	Br_2CHCO_2Et	100	100	0	$CH_3(CH_2)_9CHBrCO_2Et$	92
2-Butene	50.0	Br_2CHCO_2Et	50.0	50.0	0	$C_2H_5(CH_3)CHCHBrCO_2Et$	80
Isobutylene	50.0	Br_2CHCO_2Et	50.0	50.0	0	$(CH_3)_2CHCH_2CHBrCO_2Et$	85
Cyclopentene	50.0	Br_2CHCO_2Et	50.0	50.0	0	$(CH_2)_4CHCHBrCO_2Et$	93
	50.0	Cl_2CHCO_2Et	50.0	50.0	0	$(CH_2)_4CHCHClCO_2Et$	54[c]
Cyclohexene	50.0	Br_2CHCO_2Et	50.0	50.0	0	$(CH_2)_5CHCHBrCO_2Et$	47
Ethene[b]	20.0	Br_2CHCO_2Et	10.0	20.0	0	$(C_2H_5)_2CHCO_2Et$	60
	20.0	Br_2CHCO_2Et	10.0	20.0	50	$(C_2H_5)_2CHCO_2Et$	69
	10.0	$C_2H_5CHBrCO_2Et$	10.0	10.0	50	$(C_2H_5)_2CHCO_2Et$	87
	10.0	$CH_3(CH_2)_5CHBrCO_2Et$	10.0	10.0	50	$CH_3(CH_2)_5(C_2H_5)CHCO_2Et$	72
1-Hexene	100	$C_2H_5CHBrCO_2Et$	100	100	50	$CH_3(CH_2)_5(C_2H_5)CHCO_2Et$	63

[a] By glpc analysis. The yield is based on halogen derivative. [b] Commercial triethylborane was used. [c] 30% of the α-*t*-butoxy derivative formed.

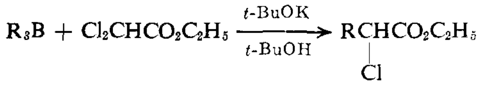
simple synthesis of esters with the addition of a two-carbon moeity to the structure (1), can now be extended

$$R_3B + BrCH_2CO_2C_2H_5 \xrightarrow[t\text{-BuOH}]{t\text{-BuOK}} RCH_2CO_2C_2H_5 \qquad (1)$$

to ethyl dibromoacetate or ethyl dichloroacetate to provide an exceedingly simple synthesis of the corresponding α-halocarboxylic acid esters (2 and 3).



$$R_3B + Br_2CHCO_2C_2H_5 \xrightarrow[t\text{-BuOH}]{t\text{-BuOK}} \underset{\displaystyle Br}{\underset{|}{RCHCO_2C_2H_5}} \qquad (2)$$

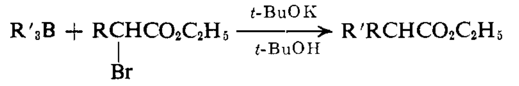


$$R_3B + Cl_2CHCO_2C_2H_5 \xrightarrow[t\text{-BuOH}]{t\text{-BuOK}} \underset{\displaystyle Cl}{\underset{|}{RCHCO_2C_2H_5}} \qquad (3)$$

Moreover, the use of 2 molar equiv of potassium *t*-butoxide achieves the dialkylation of ethyl dibromoacetate (4). The dialkylation can be achieved

$$2R_3B + Br_2CHCO_2C_2H_5 \xrightarrow[t\text{-BuOH}]{2t\text{-BuOK}} R_2CHCO_2C_2H_5 \qquad (4)$$

in two successive stages, permitting the introduction of two different organic groups into the acetic acid moeity (2 and 5). Consequently, these developments also



$$R'_3B + \underset{\displaystyle Br}{\underset{|}{RCHCO_2C_2H_5}} \xrightarrow[t\text{-BuOH}]{t\text{-BuOK}} R'RCHCO_2C_2H_5 \qquad (5)$$

provide an alternative to the commonly used malonic ester synthesis for the preparation of disubstituted acetic acids.

The procedure involved is both simple and rapid. The olefin in tetrahydrofuran is converted into the organoborane by the addition of the calculated quantity of diborane in the same solvent. The α-halo ester (ethyl dibromoacetate, ethyl dichloroacetate, or ethyl α-bromoalkanoate) is added, followed by the addition of the appropriate quantity of potassium *t*-butoxide in *t*-butyl alcohol. As in the case with ethyl bromoacetate,[1] the reactions are exceedingly rapid, being essentially over as soon as the addition of base has been completed. (The monoalkylations are generally carried out at 0°, with the synthesis of the disubstituted products providing improved yields at 50°.) The product can be distilled directly from the reaction mixture. However, in this case we have observed that the product contains minor amounts of organoborane moieties as impurities. Consequently, we have found it preferable to subject the reaction mixture to oxidation by alkaline hydrogen peroxide prior to isolation of the product by distillation.

These reactions presumably proceed through mechanisms which are quite similar to that previously described.[1]

The yields are usually quite high, generally in the range of 80–100%. With some of the more hindered trialkylboranes, such as tricyclohexylborane, the yields dropped considerably, to approximately 50%. This was especially true for ethyl dichloroacetate, where in these hindered cases we observed the formation of a side product, the corresponding α-*t*-butoxy ester. The results are summarized in Table I.

The following procedure is representative. A dry 500-ml flask, equipped with a septum inlet, thermometer well, pressure-equalizing dropping funnel, and magnetic stirrer, was flushed with nitrogen and maintained under a static pressure of the gas. The flask was charged with 100 ml of tetrahydrofuran and 37.7 ml (300 mmol) of 1-hexene, and then cooled in an ice bath. Hydroboration was achieved by dropwise addition of 50 ml of a 2.0 *M* solution of borane (300 mmol of hydride) in tetrahydrofuran. The solution was stirred for 1 hr at room temperature and again cooled in an ice bath, and 50 ml of dry *t*-butyl alcohol was added, followed by 13.0 ml (100 mmol) of ethyl dibromoacetate. Potassium *t*-butoxide in *t*-butyl alcohol (100 ml of 1.0 *M* solution) was added over a period of 30 min. There was an immediate precipitate of potassium bromide. Glpc analysis of the reaction mixture, following addition of *n*-octane as internal standard, indicated a 98% yield of ethyl α-bromooctanoate. To the reaction mixture was then added 30 ml of 3 *N* sodium acetate, followed by dropwise addition of 12 ml of 30% hydrogen peroxide, maintaining the temperature below 10°. The reaction mixture was stirred at room temperature for 30 min and then saturated with sodium chloride. The organic layer was separated, dried over magnesium sulfate, filtered, and distilled. There was obtained 21.3 g (85% yield) of ethyl α-bromooctanoate, bp 112–114°

(9 mm). The product exhibited ir and nmr spectra in accordance with its structure.

The α-halocarboxylic acids and esters are exceedingly valuable intermediates, providing routes to the corresponding α-amino acids and a host of other α-substituted derivatives. The dialkylacetic acids are also valuable intermediates. This new synthesis evidently provides a highly convenient route to these intermediates which should greatly enhance their synthetic utility. Of even greater significance may be the implication that this new method of forming carbon–carbon bonds is of considerable generality for α-halogen-substituted carbanions.

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[3] Graduate Research Assistant on Grant GM 10937 from the National Institutes of Health.

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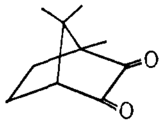
Mechanisms of Photochemical Reactions in Solution. LII.[1] Photoreduction of Camphorquinone

Sir:

Camphorquinone (**1**) is of potential interest in photochemistry because it is optically active, is nonenolizable, and has its carbonyl functions in a rigid *cis* configuration. In addition, a recent report[2] indicated that, in the absence of oxygen, the compound has little or no reactivity in photoreduction reactions. These properties suggest that the diketone would be of interest as an optically active sensitizer and also raise interesting questions concerning structure–reactivity relationships in the photoreduction reaction. In the course of an investigation of **1**, we have found that the compound does in fact undergo photoreduction and that an interesting, symmetrical radical is an intermediate.



1

Table I. Coupling Constants of Radicals in Gauss

	A_{CH_3}	A_{H_4}	A_{H_5}	A_{H_6}	$A_{H(endo)}$
2[a]	0.55, 0.15	2.08	3.01	3.01	0.221
3	0.7	2.0	3.4	3.4	. . .

[a] From ref 3.

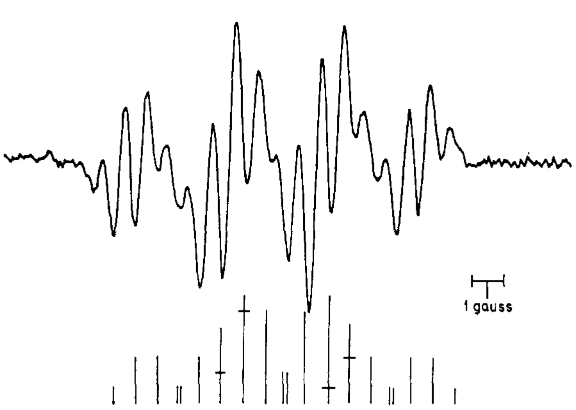
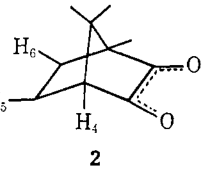


Figure 1. Esr spectrum of radical produced from camphorquinone on irradiation in isopropyl alcohol (top); calculated spectrum based on splitting constants (bottom) given in Table I.



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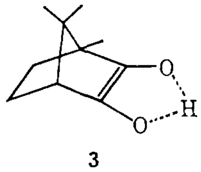

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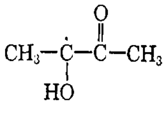

$$CH_3-\underset{HO}{\overset{\cdot}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

4

Irradiation of **1** was carried out in the cavity of an epr spectrometer with samples degassed by five freeze–thaw cycles under high vacuum. In methanol solution the signal was of an intensity too low to be resolved. However, in isopropyl alcohol, a species having a spin resonance signal with an easily resolvable hyperfine structure was observed. The spectrum is shown in Figure 1, along with a theoretical reconstruction based on the splitting constants listed in Table I. Symmetrical structure **3** is assigned to the radical because of the simplicity of the spectrum and the good agreement of the splitting constants for **3** with those of semidione **2**, produced by reduction of **1** with alkali metals.[3] In this connection it should be noted that, for the corresponding radicals derived from biacetyl,[4] the two methyl groups are not equivalent, showing very different A_{CH_3} values. An additional splitting of 2.07 gauss, assigned to the hydroxyl hydrogen, is observed. While it is possible that the splitting constant assigned to H_4 in the spectrum of **3** is due to the hydroxyl proton, it is unlikely in view of the similarity of the splitting constants for H_5 and H_6, and that for one of the methyl groups of **2**. It seems reasonable to propose that these differences stem from the fact that **4** probably has its carbonyl group in the *trans* configuration, while those of **3** are held rigidly *cis*. Under our experimental conditions a splitting constant as low as 0.5 gauss would most likely not have been observed. Thus we believe that the simplicity of the hyperfine pattern would be compatible with two unsymmetrical structures that interconvert rapidly by oscillation of the bridging hydrogen atom between two positions, which might explain our failure to observe an interaction with the hydroxyl hydrogen. We note that Prichett[5] has observed conversion of the spectrum of **4** to a symmetrical splitting pattern at pH 0.5. This must be associated with protonation to form a conjugate acid of **4** without disturbing the *trans* configuration since the one value of A_{CH_3} in strong acid is 8.3 gauss.

The reaction has every characteristic of a normal photoreduction reaction with isopropyl alcohol serving as a hydrogen donor. The triplet state of the diketone is probably involved because the reaction can be sensitized by benzophenone.[6] Irradiation of a solution of

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[1] Part LI: G. Ziegler and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 513 (1968).

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[4] H. Zeldes and R. Livingston, *J. Chem. Phys.*, **47**, 1465 (1967).

[5] R. J. Prichett, *Mol. Phys.*, **12**, 481 (1967).

[6] Interesting kinetic complications arise from the chemical crossing of the paths of reduction of the substrate and sensitizer. These results will be described later in a full report. The inference concerning mechanism is drawn from experiments under conditions that lead to essentially complete energy transfer to the diketone.