

silanes (e.g., **1a**, **1b**, and **1c**) resulted in a stereoselective route to  $\alpha$ -C-glycosides containing terminally oxygenated propenyl units. Given the high facial selectivities and the versatility of the enol double bonds, these C-glycosides should prove quite useful in asymmetric synthesis. The combined use of the two-dimensional homo- and heteronuclear correlation methods has provided a reliable protocol for the determination of stereochemistry of C-glycosides. The  $^1J_{C_1,H_1}$  values should be particularly useful for the stereochemical evaluation of a variety of C-glycosides where the vicinal proton coupling constants are unmeasurable due to resonance overlap. The continued exploration of the utility of heteroatom-substituted allylic silanes and their applications are currently underway and will be reported in due course.

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**Supplementary Material Available:** General experimental procedures for the C-glycosidations, oxidative cleavage sequences, and catalytic hydrogenations, along with spectroscopic data (8 pages). Ordering information is given on any current masthead page.

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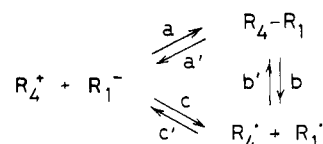
## The Hydrocarbon Cation–Anion System in Which Ionic, Radical, and Covalent Species Coexist in Equilibria

**Summary:** A new hydrocarbon salt prepared from 1,3,5-tricyclopopyltropylium ion ( $R_4^+$ ) and Kuhn's carbanion ( $R_1^-$ ) undergoes both coordination and single-electron transfer in THF affording the ionic, radical, and covalent species coexisting in equilibria.

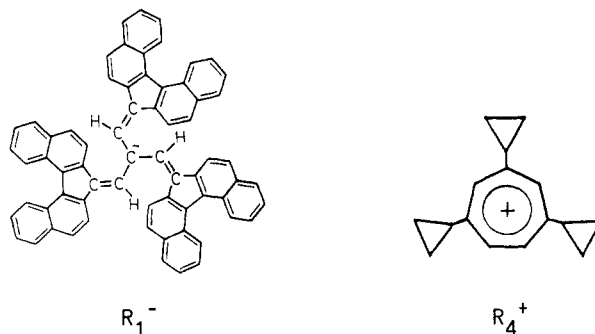
**Sir:** Following our first synthesis of the hydrocarbon salt,<sup>1</sup> i.e., a completely dissociated salt composed of Agranat's cation ( $R_2^+$ ; tri-3-guaiazulenylcyclopropenyl ion)<sup>2</sup> and Kuhn's anion ( $R_1^-$ ; tris(7H-dibenzo[c,g]fluorenylidene-methyl)methyl anion),<sup>3</sup> we reported the syntheses of first heterolytically dissociative hydrocarbons prepared by combination of  $R_1^-$  with tropylium ion<sup>1</sup> and with tricyclopopyltropylium ion ( $R_3^+$ ).<sup>4</sup> On the other hand, in a series of their systematic studies on thermodynamics of carbocation–carbanion reactions, Arnett and co-workers reported a system in which a carbocation (4,4'-bis(dimethylamino)triphenylmethyl cation) and a carbanion (4,4',4''-trinitrotriphenylmethyl anion) are in equilibrium with their corresponding radicals by way of single-electron transfer (SET) process.<sup>5</sup> The present paper now describes another new hydrocarbon system in which three types of elementary organic species, i.e., ions (a carbocation and a carbanion), radicals, and a covalent hydrocarbon, can all coexist in equilibria. To our knowledge this represents the first example of such system.

For the purpose of clarifying a limit of cation stability for preparation of hydrocarbon salts using  $R_1^-$ , we have investigated the reaction of 1,3,5-tricyclopopyltropylium ion ( $R_4^+$ )<sup>6</sup> with  $R_1^-$  under various conditions. The cation  $R_4^+$  has the  $pK_{R^+}$  value about 1 unit lower, and the reduction potential 0.6 and 1.3 V lower than  $R_2^+$  and  $R_3^+$ , respectively. When 1 mL of a 0.0856 M solution of  $R_4^+$ - $BF_4^-$  (0.0856 mmol) in MeCN was mixed with an equimolar amount of  $K^+R_1^-$  generated from 0.147 mL of 0.546 M t-BuOK/THF and  $R_1H$  (73.0 mg; 0.0848 mmol) in 1 mL

Scheme I



of THF and the solvents immediately evaporated under vacuum, there remained a dark green solid, which was then taken up in 1 mL of THF, filtered with a membrane filter (0.2  $\mu$ m) to remove  $KBF_4$ , and reprecipitated directly in pentane to give  $R_4^+R_1^-$  as a dark green powder (40.5 mg; 45.3% yield). The whole operation was conducted under an argon atmosphere and was completed within 5 min to suppress the progress of cation–anion reaction (vide infra) to minimum. The salt  $R_4^+R_1^-$  gave satisfactory elemental analyses and was characterized by UV–vis (in  $Me_2SO$ ) and IR (KBr) spectra consisting of those of  $R_4^{+6}$  and  $R_1^{-3}$  superimposed.



Although  $R_4^+R_1^-$  dissolved in  $Me_2SO$  (dielectric constant  $\epsilon$ , 46.5) without any reaction giving a deep green solution ( $\lambda_{max}$  696 nm), it underwent rapid coordination (path a in Scheme I) in less polar chloroform ( $\epsilon$ , 4.81) to give an orange solution ( $\lambda_{max}$  363 nm,  $\lambda_{sh}$   $\sim$  383 nm)<sup>7</sup> of the covalent compound  $R_4-R_1$ . The compound  $R_4-R_1$  freshly prepared in chloroform heterolytically dissociated again (path a') by dilution with 10 volumes of  $Me_2SO$  as shown

(7) For comparison, the covalent hydrocarbons  $R_1-H$  and  $R_1$ -cycloheptatrienyl exhibit  $\lambda_{max}$  363 and 365 nm, respectively, with  $\lambda_{sh}$  for both compounds at 380–390 nm in chloroform.

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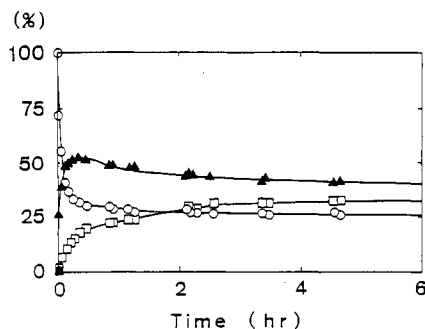
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**Figure 1.** Time dependence of concentrations of  $R_1^-$  (O),  $R_1^*$  (□), and  $R_4-R_1$  (▲) in the reaction of  $R_1^-$  ( $1 \times 10^{-4}$  M) with  $R_4^+$  ( $1 \times 10^{-4}$  M) in THF at  $\sim 20^\circ\text{C}$  under vacuum.

by UV-vis spectroscopy, and also regenerated the salt  $R_4^+R_1^-$  upon reprecipitation in pentane or simply by evaporation under vacuum just as had already been observed in the case of  $R_3-R_1$ .<sup>4</sup> However, when the chloroform solution of  $R_4-R_1$  was let stand for longer than 1 min under vacuum, generation of the radical  $R_1^*$  ( $\lambda_{\text{max}}$  546 nm)<sup>8</sup> became evident, reaching 93% after 6 h at  $\sim 20^\circ\text{C}$ . This suggests the occurrence of homolytic dissociation of  $R_4-R_1$  (path b).

In contrast, in a solvent with intermediate polarity such as THF ( $\epsilon$ , 7.58), the coordinative (path a) and SET pathways (path c) are now shown to be occurring concurrently. Thus, either when  $R_4^+R_1^-$  was redissolved in THF or when  $R_4^+BF_4^-$  was mixed with  $K^+R_1^-$  in THF under vacuum, the visible spectrum indicated rapid decrease in  $R_1^-$  ( $\lambda_{\text{max}}$  690 nm;  $t_{1/2} \sim 3$  min) with concomitant increase in  $R_1^*$  reaching an apparent equilibrium as shown

in Figure 1. After 48 h, the usual workup of the reaction mixture afforded the dimer of 1,3,5-tricyclopropylcycloheptatrienyl radical,  $R_4-R_4^8$  in 20% yield. The difference between the amounts of consumed anion  $R_1^-$  and of produced radical  $R_1^*$  was shown to be due to the covalent compound  $R_4-R_1$ , since the corresponding amount of  $R_1^-$  was regenerated by 10-fold dilution with  $\text{Me}_2\text{SO}$ .

The occurrence of SET process in the present cation-anion system seems to be attributed to the presence of three cyclopropyl substituents on the tropylium ring, which bring about steric congestion in the covalent hydrocarbon and also stabilization of the radical species due to possible  $\sigma$ -conjugation between the cyclopropyl group and the  $\pi$ -system.<sup>9</sup>

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(8) The same dimer was obtained by one-electron reduction of  $R_4^+$  with zinc powder in MeCN. For the example of similar equilibria of cycloheptatrienyl and triphenylmethyl radicals with their homo- and cross-coupled covalent compounds, see: Okamoto, K.; Komatsu, K.; Kinoshita, T.; Shingu, H. *Bull. Chem. Soc. Jpn.* 1970, 43, 1901.

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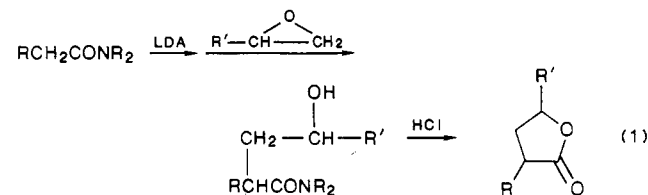
## Diastereoselective Reactions of Ester Enolates with Epoxides

**Summary:** Although epoxides do not undergo facile reactions with lithium enolates of esters, they do undergo highly diastereoselective reactions with aluminum enolates.

**Sir:** Diastereoselective aldol reactions have been found to be a significant value in organic synthesis.<sup>1</sup> The development of similar, selective enolate/epoxide chemistry has not been demonstrated despite the availability of a virtually unlimited number of optically active epoxides through the Sharpless epoxidation.<sup>2</sup> Development of this chemistry would provide a valuable method of carbon-carbon formation and a general method for the relatively rare 1,3-asymmetric induction.<sup>3a</sup>

Nitrogen-containing enolates (e.g. of amides,<sup>3</sup> enamines,<sup>4</sup> and ketimines<sup>5</sup>) do open epoxides. However, we have found that enolates of ketones and esters do not react with epoxides under conditions which favor selectivity.<sup>6</sup> To

get around the latter problem, epoxides have been combined with amide enolates, and the resulting hydroxy amide products have been hydrolyzed and cyclized to lactones (eq 1).<sup>3a</sup> This type of chemistry has recently been utilized in the synthesis of a segment of the immunosuppressant FK-506.<sup>7</sup>



The diastereoselectivity of the reaction of amide enolates with epoxides has been studied.<sup>3a</sup> The trouble with this approach is that highly hindered amide enolates (e.g. of *N,N*-diisopropylamides) are required to achieve high diastereoselectivity. Furthermore, the sterically hindered hydroxy amide products of such reactions are difficult to hydrolyze.<sup>8</sup>

If the enolates of *tert*-butyl esters could be used to open epoxides, hydrolysis of the products (eq 2) could be achieved under mild acidic conditions.<sup>9</sup> Accordingly, we set out to develop this type of chemistry.

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