

(log $S_E = 0.51-0.69$; log $S_N = 1.7-2.3$), 1-adamantyl (log $S_E = -0.075$ to -0.25 ; log $S_N = 0.4-1.30$), and 2-adamantyl (log $S_E = -0.48$ to -0.78 ; log $S_N = 0.82-1.51$), we arbitrarily plotted in Figure 1 the points corresponding to the lowest S_N values. However, we also added the points with the highest S_N values for these compounds (see Table I) in order to demonstrate the uncertainty in the values.⁹

Our conclusion is that by use of the presently available data the selectivity-selectivity plot shows a scatter of points rather than being linear. If a linearity is enforced on the plot, the "best" slope is lower than unity. Whether a mechanistic conclusion concerning the product-determining step for various R^+ 's can be drawn from such a plot is not clear.¹⁹

Acknowledgment. This research was supported by the Israel commission for Basic Research, the Israel Academy for Sciences and Humanities, to which we are indebted.

- (9) The errors in the S_E values were not taken into account.
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 (16) Goering, H. L.; Levy, J. F. *J. Am. Chem. Soc.* 1964, 86, 120.
 (17) Humski, K.; Sendjarevic, V.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* 1973, 95, 7722.
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 (19) We want to emphasize that the purpose of this paper is not to criticize previous workers who based their correlations mainly on literature data from various sources. We have three aims: (a) to point out that the linearity of the log S_E vs. log S_N plot does not give additional information over that already embodied in the log S_N and log S_E vs. log k_{sol} plots; (b) to point out the inherent inconsistency in a slope of unity for the log S_E vs. log S_N plot; (c) to offer an explanation to point b. Other explanations, e.g., different extents of capture of different cationoid species (free ions, ion pairs), are also possible.

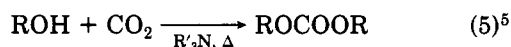
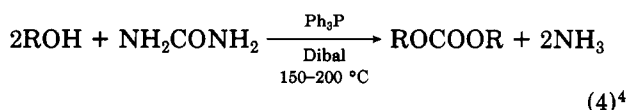
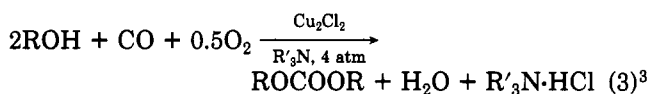
Convenient Preparation of Carbonates from Alcohols and Carbon Dioxide

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Received November 19, 1981

Various routes are available to produce dialkyl carbonates, but, except for the chloroformate approach (eq 1),

$$\text{ROCOCl} + \text{ROH} + \text{NaOH} \rightarrow \text{ROCOOR} + \text{NaCl} \quad (1)^1$$


(1) E. Abrams in "Kirk-Othmer Encyclopedia of Chemical Technology", 4th ed., Wiley, New York, 1978.

Table I

starting alcohol	reaction ^b		product
	method	yield, ^a %	
1-pentanol	A	88 (81)	dipentyl carbonate
2-butanol	A	80 (47)	di- <i>sec</i> -butyl carbonate
2-ethylhexanol	A	74 (45)	bis(2-ethylhexyl)-carbonate
2-ethylhexanol	B	97 (61)	bis(2-ethylhexyl)-carbonate
allyl alcohol	A	75 (40)	diallyl carbonate

^a By GC analysis, based on unrecovered alcohol. Values in parentheses are isolated yields, after column chromatography. Most of the differences are due to losses during evaporative workup. ^b Reaction time was 18 h in all cases.

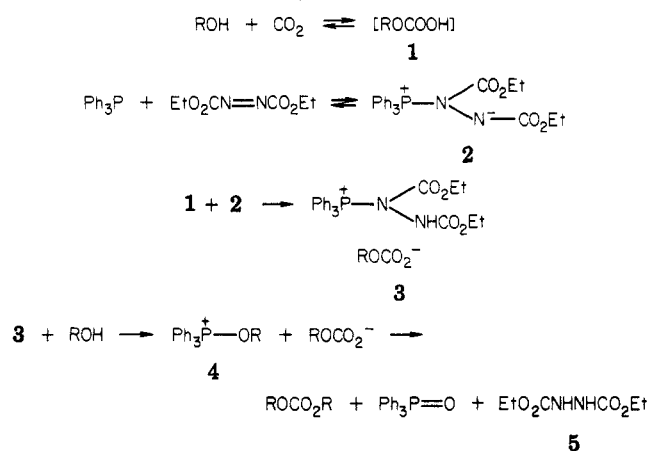
they usually result in low conversions making them inconvenient for laboratory preparations. Moreover, oxidative conditions (eq 3) and high temperatures (eq 4) are frequently incompatible with remote functionalities, as are the strong bases favored in the chloroformate route. These conditions are imposed to overcome or avoid the especial instability of the hemicarbonic acids, which otherwise might be viewed as simple carboxylic acids, subject to ordinary esterification conditions.

The view of carbonate formation as esterification of hemicarbonic acid led me to consider application of the conditions first described by Mitsunobu and Eguchi^{6a} in 1971. Their preparation of carboxylic esters from alcohols, carboxylic acids, triphenylphosphine (Ph_3P), and diethyl azodicarboxylate (DEADC) in tetrahydrofuran (THF) solution is characterized by mildness, simplicity, and high yields. The net effect of the reaction is displacement of the alcoholic hydroxyl group, and the displacement has been accomplished by imides,^{6b} phenols,^{6c,e} and other species,^{6f} having $\text{p}K_a < 10$ and solubility in THF.

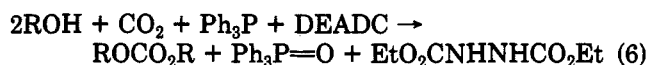
Hemicarbonic acids fit these latter requirements, and I now report that they undergo esterification, affording carbonates in good yield under ambient conditions. The

- (2) J. W. Shepherd, U.S. Patent 2983749 (1961).
 (3) E. Perrotti and G. Cipriani, U.S. Patent 3846468 (1974).
 (4) P. Ball, H. Fullmann, and W. Heitz, *Angew. Chem., Int. Ed. Engl.*, 19, 718 (1980).
 (5) H.-J. Buysch, H. Krimm, and H. Rudolph, European Patent 1777 (1979).
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 (7) (a) H. Kunz and P. Schmidt, *Chem. Ber.*, 112, 3886 (1979). (b) G. Gryniewicz, J. Jurczak, and A. Zamojski, *J. Chem. Soc., Chem. Commun.*, 413 (1974). Sugar ethyl carbonates were produced in good yields when a large excess of DEADC/ Ph_3P was introduced. (c) A referee pointed out that Bittner et al. [*Chem. Ind. (London)*, 526 (1976)] derived carbonates from DEADC/ Ph_3P and alcohols without CO_2 . This is similar to the earlier paper by Gryniewicz et al.^{7b} and only loosely related to my findings: Bittner's carbonates are formed without CO_2 , at the expense of destruction of DEADC, with evolution of N_2 , and in the presence of the reaction alcohol as the solvent. DEADC is used in 100% excess over that needed to form the DEADC/ Ph_3P "bifunctional catalyst". Carbonates reported in this paper are formed only with added CO_2 , there being no detectable reaction of dilute THF solutions of small (1 or 2) molar ratios of alcohols to the 1/1 DEADC/ Ph_3P . DEADC is not destroyed, only hydrogenated to H_2DEADC which is usually recovered in ~90% yield. Far from generating pressure as Bittner describes (N_2 ↑), this reaction occurs with pressure loss as CO_2 is consumed (particularly visible in method B, with a pressure gauge or even with a balloon reservoir).

Scheme I

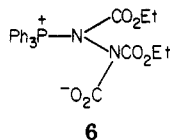


overall reaction is shown in eq 6, and examples listed in Table I.



A mechanism which is consistent with that proposed previously for reactions mediated by DEADC/ Ph_3P ⁸ is shown in Scheme I.

An alternative mechanism, involving betaine **6** (from 2



and CO_2) was considered. However, production of dialkyl carbonate from **6** would require 1 mol of DEADC and Ph_3P for each mole of alcohol, rather than the 1:1:2 molar ratio used, or would result in a maximum conversion of 50% and recovery of half the charged alcohol. In the present work, very little starting alcohol was observed in the crude product. The high recovery (ca. 90% of theory) of dicarbethoxyhydrazine adds support to the proposed mechanism, as does the absence of ethyl alkyl carbonates, which would be expected if the alternative mechanism were operative.

An interesting prediction may be made, as a consequence of the mechanism in Scheme I: that carbonates of enantiomerically pure alcohols should be *R,S* diastereoisomers. Moreover, 1,2- and 1,3-diols and diols in larger "puckered" rings should undergo regioselective⁸ inversions, of potential value in sugar, steroid, macrolide,⁹ and prostaglandin work.

Experimental Section

All products were identical (IR, NMR, GC/MS) with authentic samples made by the method of Ball et al.⁴ or from the corresponding alcohol and phosgene. GC-determined yields were corrected for response factors. Chromatographic grade THF was sufficiently dry when freshly opened and remained dry when stored over 4A molecular sieves.

Method A. To 100 mL of anhydrous THF in a 250-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, drying tube, and submerged gas inlet capillary tube were added 100 mmol of alcohol and 50 mmol (13.1 g) of Ph_3P . Stirring was started, and a slow, steady stream of "Bone-Dry" CO_2 (Matheson) was begun. After 10 min, 50 mmol (8.17 g, 99% of theory) of DEADC was added in two or three portions. After 4-6 h, the CO_2 was shut off and the solution allowed to stir for 18

(8) See ref 6c,d. Axial hydroxyl groups, for example, are frequently not reactive to ester- or ether-forming DEADC/ Ph_3P conditions.

(9) See, for example, B. Seuring and D. Seebach, *Justus Liebig's Ann. Chem.*, 2044 (1978).

h. THF was removed on a rotary evaporator and the semisolid residue chromatographed over Brockmann 1 neutral alumina (30 g) by using benzene and monitoring by IR. Careful handling, especially during THF removal, is required for the lower-boiling carbonates.

Method B. To 50-mL of anhydrous THF in a 250-mL Parr bottle equipped with magnetic stirrer and pressure closure were added 5.0 g (38.5 mmol) of 2-ethylhexyl alcohol, 5.6 g (21.4 mmol) of Ph_3P (in 25 mL of anhydrous THF), and 4.35 g (25 mmol) of DEADC (in 25 mL of anhydrous THF). The closure was seated, and the vessel was evacuated (10 mmHg) briefly, weighed, and refilled with "Bone-Dry" CO_2 (1 g, 0.0227 mol). The mixture was vigorously stirred for 18 h and worked up as in method A, yielding 3.4 g of bis(2-ethylhexyl) carbonate (61%) after chromatography.

Acknowledgment. I thank Mr. S. Griff for GC/MS results and comparisons with authentic samples.¹⁰ The technical assistance of Mr. L. Criscione is gratefully acknowledged.

Registry No. Dipentyl carbonate, 2050-94-4; di-*sec*-butyl carbonate, 623-63-2; bis(2-ethylhexyl)carbonate, 14858-73-2; diallyl carbonate, 15022-08-9; 1-pentanol, 71-41-0; allyl alcohol, 107-18-6; CO_2 , 124-38-9; Ph_3P , 603-35-0; DEADC, 1972-28-7.

(10) Previously unreported fragmentation patterns will be presented in a future paper by Mr. Griff.

On the Possibility of New Families of ($4n + 2$)- π -Electron Biradicaloid Hydrocarbons¹

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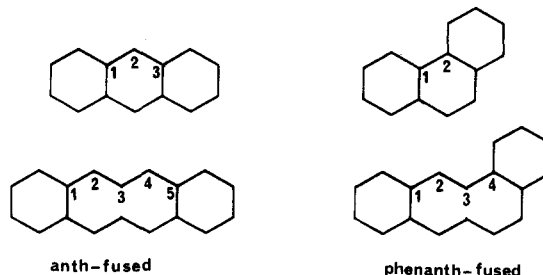
Received April 9, 1982

We report evidence, both experimental and from calculations, that anth-fused² dibenzannelated [$4n + 2$]-annulenes might exist as biradicaloid hydrocarbons, having either a triplet ground state or a low-lying thermally accessible triplet state.

In 1973, Kolc and Michl³ used the "biradicaloid hydrocarbon" for a molecule whose ground state has two orbitals which are approximately nonbonding and which are occupied by two electrons, regardless of the actual electronic configuration of this state. They used this term because

(1) Benzannelated Annulenes. 9. For part 8 see R. H. Mitchell, R. V. Williams, R. Mahadevan, Y. H. Lai, and T. W. Dingle, *J. Am. Chem. Soc.*, 104, 2571 (1982).

(2) We use the term anth-fused to describe molecules like anthracene which are 1,3-, 1,5-, 1,7-, etc. fused as opposed to phenanth-fused, which are 1,2-, 1,4-, 1,6-, etc. fused.



(3) J. Kolc and J. Michl, *J. Am. Chem. Soc.*, 95, 7391 (1973).