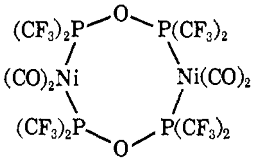
and 2060 cm^{-1}. It can be argued that a very wide P–O–P bond angle would make Ni–(CO)–Ni bridging impossible because the nickel atoms would be too far apart. We suggest an eight-membered ring structure such as



in which the Ni(CO)$_2$ units could be situated on either the same or opposite sides of the (POP)$_2$ plane. The argument for a very wide P–O–P bond angle relates to the known 144° Si–O–Si angle in $(SiH_3)_2O$.[6] In the present case the widening effect of O_{2p}–P_{3d} π bonding should be even more important. In contrast, a weaker S_{3p}–P_{3d} π bonding in $(CF_3)_2PSP(CF_3)_2$[3b] would permit a narrower P–S–P bond angle and allow CO bridging in $Ls_2Ni_2(CO)_3$.

A quantitative synthesis in hexane at 25° is described by the following equation with millimole stoichiometry.

$$\begin{array}{llll} 2Lo\ + & 2Ni(CO)_4 \rightarrow & 4CO\ + & Lo_2Ni_2(CO)_4 \\ 1.004 & 1.002 & 1.954 & \text{(not detmd)} \end{array}$$

The molecular weight of a recrystallized sample (by differential tensimetry in *n*-pentane) was 964 or 966; calculated for the binuclear formula, 937. Analysis of a vacuum-sublimed sample by the iodine method gave 12.7% Ni (calcd, 12.5). The pure white crystals darkened with decomposition at 45°, or turned green during 24 hr in the open air. Whenever the synthesis was done with excess Ni(CO)$_4$, a red product began to form just as the CO displacement approached two per Lo. Obviously, some by-products are possible with all three of the bisphosphines here employed.

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Received September 9, 1966

The Formolysis of *exo*-2-*t*-2-Norbornyl Brosylate[1]

Sir:

The problem of 3,2 hydride shifts during solvolysis of norbornyl derivatives can be investigated with a singly labeled substrate, and the results from such a study on the acetolysis of *exo*- and *endo*-2-*t*-2-norbornyl brosylates (*exo*- and *endo*-I-2-*t*) have been reported.[2] In a well-known review, Berson[3] has discussed 3,2 hydride shifts and has referred to the analysis of Dill[4] on the data of Roberts and co-workers[5] obtained from solvolyses of norbornyl brosylates labeled with ^{14}C at both C-2 and C-3. It may be of interest to point out that the contributions of various processes, including 3,2 (and 7,1) hydride shifts, assigned by Dill,[4] as quoted by Berson,[3] for the acetolysis of *exo*-I-2,3-$^{14}C_2$ at 45° do not fit the more recent data obtained with *exo*-I-2-*t*.[2] Reference to Dill's work has again been made in a very recent review by Sargent[6] in regard to the necessity of postulating 3,2 hydride shifts during formolysis. In order to provide some clarification on the rearrangement processes involved in formolysis, we now report the results from the formolysis of *exo*-I-2-*t*.

Roberts and co-workers[5] were unable to explain the isotopic distribution in the product obtained from formolysis, at reflux temperature, of a mixture of *exo*- and *endo*-I-2,3-$^{14}C_2$. We believe that one of the chief factors responsible for this difficulty resulted from complications arising from the subsequent ionization and rearrangement of the *exo*-2-norbornyl formate in the reaction mixture at reflux temperature.[5] In order to minimize these complications, the present work was carried out at 25°.

exo-I-2-*t*[2] was solvolyzed in anhydrous formic acid in the presence of sodium formate at 25° for 20 hr. The resulting product was degraded and the tritium distribution determined as described in the analogous acetolysis studies.[2] The results are given in Table I. The presence of about 6% of the activity at C-3 indicates a substantial involvement of 3,2 hydride shifts during the formolysis of *exo*-I-2-*t*. Since the rates of the Wagner–Meerwein rearrangement and the 6,2 (and 6,1) hydride shift are very much faster than the rate of the 3,2 hydride shift in the norbornyl cation in a highly acidic medium,[7] it is also likely that the 3,2 shift is the slowest rearrangement under solvolytic conditions. Thus 3,2 shifts together with the Wagner–Meerwein rearrangement and 6,2 (and 6,1) hydride shifts will result in the complete equivalence of all seven carbon positions of the norbornyl cation.[5]

Table I. Tritium Distribution in the Product from Formolysis of *exo*-I-2-*t* at 25°

	Tritium content, %[a]			
	C-2	C-3	C-1,4,7	C-5,6
Run 1	31.0	6.5	39.1	23.3
Run 2	30.8	6.2	39.2	23.8

[a] Activities were measured by a liquid scintillation counter; 100% corresponded to specific activities of 29,587 and 31,125 counts/min mmole, respectively, for runs 1 and 2.

As discussed previously for the acetolysis of *exo*-I-2-*t*,[2] the isotopic distribution shown in Table I can be attributed to three processes, namely (1) complete equivalence of all carbon positions resulting from 3,2 hydride shifts together with Wagner–Meerwein and 6,2 (and 6,1) hydride shifts; (2) equivalence of C-1 and C-2 from reaction with the initially formed nornornonium ion; and (3) equivalence of C-1, C-2, and C-6 from the equilibration of norbornonium ions *via* 6,2 and 6,1 hydride shifts. If the contributions of these processes were as shown in Table II, the calcu-

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(1) Supported by a grant from the National Research Council of Canada.

(2) C. C. Lee and L. K. M. Lam, *J. Am. Chem. Soc.*, 88, 2831 (1966).

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(7) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, 86, 5679 (1964); M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, 86, 5680 (1964).

lated tritium distribution is in very good agreement with the observed results (Table I). Of particular interest is the observation that the process with all carbon positions equivalent, which involves the 3,2 hydride shift, is responsible for 35.2% of the formolysis product, while in the acetolysis under analogous conditions, the contribution of this process is only 10%. This result confirms all previous assumptions[3-6] that more 3,2 shifts occur during formolysis than acetolysis. The finding is in agreement with expectation as the norbornyl cation should have a longer life in formic acid than in acetic acid, thus providing a greater opportunity for the slower 3,2 hydride shifts to take place.

Table II. Calculated Tritium Distribution for the Formolysis of *exo*-I-2-*t* at 25°

Process	% contribution^a	Calcd % *t* C-2	C-3	C-1,4,7	C-5,6
Complete equivalence	35.2	3.2	6.4	12.8	12.8
C-1, C-2 equivalent	43.2	21.6		21.6	
C-1, C-2, C-6 equivalent	21.6	5.4		5.4	10.8
Calcd *t* content		30.2	6.4	39.8	23.6

[a] The analogous contributions for the acetolysis of *exo*-I-2-*t* at 25° are 10, 45, and 45%, respectively, for the three processes of complete equivalence, C-1, C-2 equivalent, and C-1, C-2, C-6 equivalent.[2]

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Received September 6, 1966

Low-Temperature Kinetics in Protic Solvents. Reactions of *p*-Nitrophenyl Acetate in Methanol and Methanol-*d* at −78°

Sir:

The possibility that water structures resembling crystalline gas hydrates exist in protein cavities and are important in enzyme action[1] has prompted recent measurements of reaction rates in ice.[2] Interesting rate enhancements are found in this medium, but their nature is unclear because of uncertainties associated with the heterogeneity of the systems. We have extended these studies of the chemistry in cold protic solvents by examining kinetically some nucleophilic reactions of an ester in liquid methanol at low temperature, and we report the results here.

The rate constants for the reaction of methoxide ion with *p*-nitrophenyl acetate (*p*-NPA) in methanol and methanol-*d*[3] at −78.2° are given in Table I. The data indicate that the reaction is first order in ester and in methoxide, and that the reaction proceeds 2.6 times faster in methanol-*d* than in methanol.[4] The rate constants for the reaction of excess *n*-butylamine with *p*-NPA in methanol and methanol-*d* at −78.2° are given in Table II. A plot of k_{obsd} *vs.* [*n*-butylamine] is linear and has a zero intercept, indicating a simple one-term rate expression which is first order in amine. The small amount of methoxide ion present in *n*-butylamine–methanol solutions was shown not to contribute significantly to the reaction because buffering with *n*-butylamine hydrochloride does not change the rate constants. Furthermore, analysis of the reaction products by vapor phase chromatography shows that methyl acetate is produced in less than 10% yield. The observed reaction is mainly nucleophilic attack on the ester by an amine, with little methoxide reaction or general base catalyzed methanolysis. The aminolysis of *p*-nitrophenyl acetate proceeds only 1.12 times faster in methanol-*d* than in methanol, a rate difference which approaches the size of the experimental error.

Table I. The Observed Rate Constants for the Reaction of Methoxide Ion with *p*-Nitrophenyl Acetate in Methanol and Methanol-*d* at −78.2°

[Methoxide],^{a,d} M	[*p*-NPA]^a × 10^4, M	k_{obsd} × 10^4, sec^{-1}	k_2^b × 10^3, M^{-1} sec^{-1}
		Methanol	
0.236	2.18	11.8	5.00
0.236	2.18	12.2	5.17
0.236	2.18	11.9	5.04
0.117	2.18	6.41	5.48
0.108	2.18	5.82	5.39
0.0694	2.18	3.45	4.97
0.234	4.33	12.1	5.17
			$\bar{k}_2$ = 5.17
		Methanol-*d*^{c}	
0.0970	2.18	12.9	13.3
0.0798	2.18	11.1	13.9
0.0554	2.18	7.34	13.2
			$\bar{k}_2$ = 13.5

[a] At −78.2 ± 0.3°. [b] $k_2 = k_{obsd}$/[methoxide]. [c] >99% deuterium content. [d] Sodium methoxide.

Table II. The Observed Rate Constants for the Reaction of *n*-Butylamine with *p*-Nitrophenyl Acetate in Methanol and Methanol-*d* at −78.2°

[*n*-Butylamine],^{a} M	[*p*-NPA]^a × 10^4, M	k_{obsd} × 10^4, sec^{-1}	k_2^b × 10^3, M^{-1} sec^{-1}
		Methanol	
1.52	4.33	15.4	1.01
1.13	4.33	10.8	0.956
1.13^d	4.33	10.4	0.920
0.904	4.33	8.69	0.961
0.565	4.33	5.46	0.966
0.225	4.33	2.09	0.929
			$\bar{k}_2$ = 0.957
		Methanol-*d*^{c}	
0.226	4.33	2.44	1.08
0.228	4.33	2.41	1.06
			$\bar{k}_2$ = 1.07

[a] At −78.2 ± 0.3°. [b] $k_2 = k_{obsd}$/[*n*-butylamine]. [c] >97% deuterium content. [d] +0.122 M *n*-butylamine hydrochloride.

Nucleophilic reactions of nitrogen bases with carboxylic acid derivatives in aqueous solutions are not subject to solvent isotope effects.[5] In this respect the

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(2) H. E. Alburn and N. H. Grant, *J. Am. Chem. Soc.*, **87**, 4174 (1965), and references cited therein.

(3) The purity of these dried solvents was assayed by vapor phase chromatography and found to be satisfactory. Addition of 3% water to the methanol does not perturb the rate constants.

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