

Table I. Rate Constants^a and Activation Parameters^b for the Reaction of Ni(C¹⁶O)₄ with C¹⁸O and Ph₃P in Hexane Solution

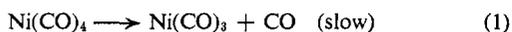
Temp, °C	Rate constant: 10 ⁴ k sec ⁻¹	
	C ¹⁸ O exchange ^c	Ph ₃ P substitution ^d
0.5	2.50	2.45
10.0	12.5	11.0
20.0	52.0	49.8
30.0	210	206
ΔH [‡] , kcal mole ⁻¹	24.3 ± 0.4	24.2 ± 0.2
ΔS [‡] , eu	14 ± 2	13 ± 1

^a First-order rate law. ^b Errors given represent probable error estimated from experimental errors. ^c Standard deviation, 2%. ^d Standard deviation, 1%.

five species will be published separately). The Ph₃P substitution reactions were also followed by infrared spectrophotometry, and also obey a first-order rate law.

In competition experiments in which C¹⁸O and Ph₃P were allowed to react simultaneously with Ni(C¹⁶O)₄, both Ni(C¹⁶O)₃(C¹⁸O) and Ni(C¹⁶O)₃(Ph₃P) formed more slowly than in the single-ligand experiments at the same temperature. However, the sum of their rates of formation, which was equal to the rate of reaction of Ni(C¹⁶O)₄, was approximately equal to the rate of either of the single-ligand reactions. With equimolar quantities of C¹⁸O and Ph₃P, the latter reacted about five times as fast. A tenfold excess of Ph₃P over C¹⁸O virtually eliminated the exchange reaction.

We conclude, therefore, that the description of the reaction mechanism requires at least two steps. The first, which is rate determining, does not involve the reacting nucleophile and is the same for CO exchange and Ph₃P substitution. This is followed by rapid reaction of the nucleophile with the reactive intermediate formed in step 1. It seems likely that the reactive intermediate is the species Ni(CO)₃, e.g.



We have also studied the gas-phase exchange reaction (Ni(C¹⁸O)₄-C¹⁶O) and find it to be first order in Ni(CO)₄ and zero order in CO. The rate constants are about three times greater than in hexane solution, and the activation energies are very similar in the gas phase and in hexane. This creates a conflict with the postulated⁶ mechanism for Ni(CO)₄ decomposition in the gas phase, where step 1 is also supposed to be rate controlling, at low CO pressure, but is about 1% of the rate of CO exchange. We are studying the gas-phase thermal decomposition reaction further to resolve this conflict.

Results from Previous CO Exchange. We have considered possible sources of error in the original ¹⁴CO-exchange experiments. In these, a mixture of ¹²CO and ¹⁴CO was pumped through a solution of Ni(¹²CO)₄, and the reaction was assumed to occur in, and at the temperature of, the solution. The radioactivity of a substantial gas phase (at laboratory temperature) was measured. It is now clear that some exchange always occurred in the gas phase, because of the volatility of Ni(CO)₄. Approximate calculations, using measured values of the vapor pressure of Ni(CO)₄ over solutions, show that up to 50% of the observed exchange could have occurred in the gas phase in the most unfavorable case. This effect would be greatest at the lowest solution

(6) R. K. Chan and R. McIntosh, *Can. J. Chem.*, **40**, 845 (1962).

temperature and would result in an "observed" activation energy much lower than the "true" activation energy. If we take our present (infrared) results to be correct, then the deviation of the previous results can be understood. Exchange studies by the ¹⁴CO method for other volatile metal carbonyls such as CoNO(CO)₃ may also be in error due to gas-phase reaction.⁷

Acknowledgment. The work done at Northwestern was supported in part by a National Science Foundation Grant.

(7) E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.*, **88**, 3929 (1966).

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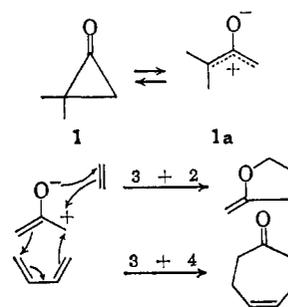
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Cycloaddition Reactions of 2,2-Dimethylcyclopropanone¹

Sir:

The application of orbital symmetry considerations has provided an important stimulus to the study of electrocyclic,² sigmatropic,³ and cycloaddition⁴ reactions. Cyclopropanones possess the unusual property of being capable of undergoing numerous cycloaddition reactions.⁵ In order to employ the Woodward-Hoffmann rules²⁻⁴ to predict the selection rules for cycloaddition reactions of cyclopropanones, it is useful to consider the reactive intermediate as a dipolar ion⁶ (e.g., **1a**). This description indicates that two symmetry-allowed cycloadditions are possible: (a) 3 + 4 → 7 additions of cyclopropanones and dienes,⁵ and (b) 3 + 2 → 5 additions of cyclopropanones and monoolefins.



We wish to report the first examples of 3 + 2 → 5 cycloaddition reactions of cyclopropanones.

(1) (a) Cyclopropanones. VII. Paper VI: N. J. Turro and W. B. Hammond, *Tetrahedron Letters*, 3085 (1967). (b) The generous support of this research by the Air Force Office of Scientific Research (Grant AFOSR-1000-66) and the National Science Foundation (Grant NSF-GP 4280) is gratefully acknowledged.

(2) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2046 (1965); H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

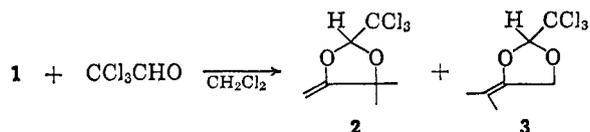
(3) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).

(4) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4388 (1965).

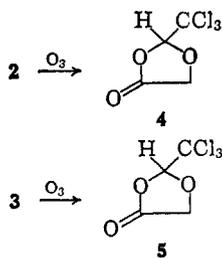
(5) Cycloaddition reactions of the carbonyl group; the 1,2 bond and the 2,3-bond of cyclopropanones are known: (a) W. B. Hammond and N. J. Turro, *ibid.*, **88**, 2880 (1966); (b) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *ibid.*, **87**, 2613 (1965).

(6) J. G. Burr, Jr., and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

Addition of trichloroacetaldehyde (50% excess) to a methylene chloride solution (reflux) of 2,2-dimethylcyclopropanone (**1**) followed by refluxing yields the cyclic enol ethers **2** (16%) (nmr⁷ (CCl₄) δ 1.46 (3 H, s), 1.57 (3 H, s), 3.90 (1 H, d, *J* = 3 Hz), 4.40 (1 H, d, *J* = 3 Hz), 5.53 (1 H, s); ir λ_{max}^{CCl₄} 5.90 μ (C=C); mass spectra at 75 eV, *m/e* (relative intensity) 234 (1.1), 232 (3.6), 230 (M⁺, 3.7) 121 (1.8), 119 (5.0), 117 (5.1), 113 (84), 84 (82), 67 (100), 56 (89), 49 (99), 41 (80)) and **3** (1.5%) (nmr (CCl₄) δ 1.57 (3 H, s), 1.74 (3 H, m), 4.43–4.97 (2 H, m) 5.54 (1 H, s); ir λ_{max}^{CCl₄} 5.78 μ (C=C); mass spectra (75 eV) 234 (3.1), 232 (9.7), 230 (M⁺, 10.3), 113 (33)).



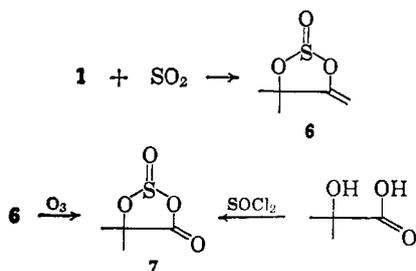
Spectral evidence indicates that PhCHO and CH₃CHO form adducts similar to **2**. Compounds **2** and **3** were further characterized by ozonolysis to the lactones **4** (nmr (CH₂Cl₂) δ 1.51 (3 H, s), 1.58 (3 H, s), 5.78 (1 H, s); ir λ_{max}^{CH₂Cl₂} 5.50 μ (C=O); mass spectra (75 eV) 121 (0.89), 119 (2.8), 117 (3), 115 (24), 87 (45), 59 (100)) and



5 (nmr (CCl₄) δ 4.48 (2 H, AB, *J*_{AB} = 14 Hz, Δ*V*_{AB} = 10 Hz, second order splitting), 5.85 (1 H, second-order splitting); ir λ_{max}^{CCl₄} 5.44 μ (C=O)).

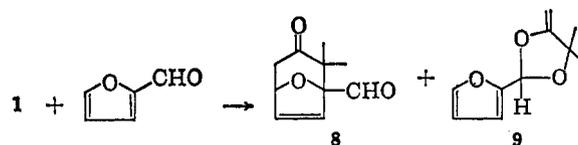
Addition of SO₂ to methylene chloride solutions of **1** yields the adduct **6** (nmr (neat) δ 1.49 (3 H, s), 1.87 (3 H, s), 4.33 (1 H, d, *J* = 3.0 Hz), 4.66 (1 H, d, *J* = 3.0 Hz); ir λ_{max}^{neat} 3.22 μ (C=CH), 5.99 μ (OC=C); mass spectra, *m/e* 148 (M⁺), 84 (24), 69 (20), 56 (68), 48 (20)).

The structure of **6** was proven by ozonolysis to the ketone **7** which was compared with authentic material.⁸

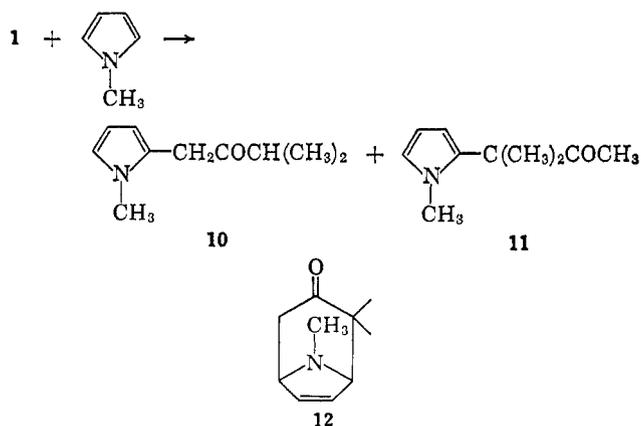


Furfural and **1** yield the cycloadducts **8** (nmr (CCl₄) δ 1.11 (3 H, s), 1.23 (3 H, s), 2.59 (2 H, AB, *J*_{AB} = 16 Hz, Δ*V*_{AB} = 39.2 Hz, low-field half split *J* = 5 Hz, high-field half split *J* = 1.5 Hz), 5.13 (1 H, d of t, *J* = 5 Hz, 1.5 Hz), 6.36 (2 H, AB, *J*_{AB} = 6 Hz, Δ*V*_{AB} = 7.75 Hz, low-field half split *J* = 1.5 Hz), 9.77 (1 H, s); ir λ_{max}^{CCl₄} 5.88 μ, 5.93 μ; mass spectra (75 eV), *m/e* 180 (M⁺) and **9** (nmr (CCl₄) δ 1.42 (3 H, s), 1.48 (3 H, s), 3.82 (1 H, d,

J = 2.5 Hz), 4.24 (1 H, d, *J* = 2.5 Hz), 6.13 (1 H, s), 6.28–6.53 (2 H, m), 7.43 (1 H, m); mass spectra (75 eV), *m/e* 180 (M⁺)).



Addition of N-methylpyrrole to **1** results in formation⁹ of the substitution adducts **10** (nmr (CCl₄) δ 0.97 (1 H, d, *J* = 7 Hz), 2.7 (1 H, septet, *J* = 7 Hz), 3.4 (3 H, s), 3.56 (2 H, s), 5.88 (2 H, m), 6.43 (1 H, t, *J* = 2 Hz); ir λ_{max}^{CCl₄} 5.85 μ; mass spectra (75 eV), *m/e* 165 (M⁺) and **11** (nmr (CCl₄) 1.43 (6 H, s), 1.87 (~3 H, s), 5.89 (~2 H, m), 6.45 (~1 H, t) *J* = 2 Hz); ir λ_{max}^{CCl₄} 5.86 μ; mass spectra (75 eV), *m/e* 165 (M⁺) as the major 1:1 products (ratio of **10**:**11** was 5:1).



The mechanisms of these reactions are presently under investigation.

(9) A mixture of CH₂Cl₂ and excess N-methylpyrrole was cooled to -78°. A CH₂Cl₂ solution of **1** was added and the resulting mixture was left standing at -78° for several days. The solvent was then stripped off at room temperature and the residue was worked up by preparative vpc. At this time it is uncertain whether **10** and **11** are primary products or are products of the rearrangement of **12**.

(10) Alfred P. Sloan Fellow.

(11) National Science Foundation Predoctoral Fellow, 1966–present. National Science Foundation Predoctoral Trainee, 1965–1966.

(12) National Institutes of Health Postdoctoral Fellow, 1967–1968.

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Topography of Nucleic Acid Helices in Solutions. VIII. Selective Interactions of L-Amino Acids and Peptides with Nucleic Acid Helices¹

Sir:

One of the intriguing problems in biochemistry is the universality of the L-amino acids in proteins and D-ribose and D-deoxyribose in nucleic acids. Two basic questions may be asked: (a) "how were these particular isomers selected originally?" and (b) "what is the basic relationship, if any, between the protein helical conformation based on a chain structure composed of

(1) For part VII in this series see E. J. Gabbay and R. R. Shimshak, *Chem. Commun.*, submitted for publication.

(7) TMS internal standard. Satisfactory mass spectral or elemental analyses were obtained for all new compounds reported.

(8) E. Blaise and A. Montagne, *Compt. Rend.*, **174**, 1553 (1922).