contraction being of the same order of magnitude as those found in the other heteroaromatics.[10] The phosphorus d orbitals may be involved in this situation. The C—C and C=C bonds in the phosphole ring have similar lengths to those of the other heteroaromatics, although the average C=C distance of 1-benzylphosphole is closer to the ethylene value[11] (1.334 Å) and not significantly different from it (1.5σ). The ring angles are very similar to those in thiophene.

Microwave spectral studies have indicated that furan, pyrrole, and thiophene are planar species and that the nitrogen proton in pyrrole is in the plane of the ring.[10b] Significant differences of the phosphole ring are a slight puckering of the ring and retention of pyramidal configuration at phosphorus. The latter feature is consistent with the conclusion of other workers[12] based on nmr studies of the barrier to inversion about phosphorus in 1-isopropyl-2-methyl-5-phenylphosphole. The phosphorus and C_6 are displaced by 0.21 and 1.36 Å, respectively, to opposite sides of the least-squares plane through C_2–C_5 which are accurately planar (root-mean-square deviation 0.0018 Å). The significant increase in the PC_6C_7 angle to 116.4 (±0.4°) from tetrahedral (109° 28′) may be ascribed to intramolecular van der Waals repulsions between the phosphole and phenyl rings. The puckering at phosphorus may result, at least in part, from this interaction. The difference between the phosphole and pyrrole systems with regard to the noncoplanarity of the hetero substituent with the ring atoms in the former may be associated with the configurational stability of phosphorus, whereas nitrogen inverts rapidly. Clearly, quantitative treatment of the bonding in the phosphole system would be desirable.

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(10) See, for example (a) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, England, 1969, pp 30–39; (b) R. M. Acheson, "Introduction to the Chemistry of Heterocyclic Compounds," 2nd ed, Interscience, New York, N. Y., 1967, Chapter 3, and references cited therein.

(11) L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **27**, 1414 (1957).

(12) W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 1442 (1970).

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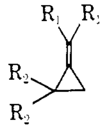
Nickel(0)-Catalyzed Reaction of Methylenecyclopropanes with Olefins. A Novel [$_\sigma 2 + _\pi 2$] Cycloaddition

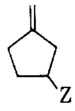
Sir:

The [2 + 2] cycloaddition reaction is not readily attainable in noncatalyzed, ground-state reactions,[1] and few examples of the addition of cyclopropane to olefins to form carbocyclic five-membered rings are known.[2] We wish to report a novel cycloaddition of methylenecyclopropanes across carbon–carbon double bonds under the influence of nickel(0) catalyst.

A solution of methylenecyclopropane (**1a**)[3] (10 mmol) in excess methyl acrylate (15 ml) in the presence of bis(acrylonitrile)nickel(0)[4] (0.3 mmol) was heated in a sealed tube at 60° for 48 hr under a nitrogen atmosphere. The usual work-up and distillation gave the 1:1 adduct, methyl 3-methylenecyclopentanecarboxylate (**2a**), in 82% yield.[5,6] The spectral data were in accord with the assigned structure: mass m/e 140 (M^+); ir (neat) 1735 (C=O) and 880 cm^{-1} (exocyclic methylene); nmr (CCl_4, TMS) δ 1.7–2.9 (m, 7 H, $\geqslant$CH and >CH_2), 3.67 (s, 3 H, $COOCH_3$), and 4.90 (m, 2 H, =CH_2). Ozonolysis of **2a** afforded known methyl 3-oxocyclopentanecarboxylate (**3**).[7] $Ni(CH_2{=}CHCN)_2[P(C_6H_5)_3]_n$ (n = 1 or 2)[4] also effects the cycloaddition, but in lower yield. No reactions were observed in the absence of the nickel catalysts even at 100°. Employing methyl vinyl ketone[6] or acrylonitrile as substrates gave rise to the corresponding methylenecyclopentanes **2b** and **2c** in moderate yields. Both **2b** and **2c** were identified by converting to **3** using ordinary procedures.

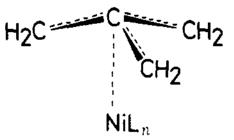


1a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = H$



2a, $Z = COOCH_3$
b, $Z = COCH_3$
c, $Z = CN$

The fixation of trimethylenemethane, a highly reactive bond isomer of **1a**, on transition metals is well known,[8] and treatment of methylenecyclopropane derivatives with diiron nonacarbonyl produces the corresponding trimethylenemethaneiron tricarbonyl complexes.[9] Recently photolysis of trimethylenemethaneiron tricarbonyl in cyclopentene was reported to afford 3-methylenebicyclo[3.3.0]octane though in poor yield.[10] These facts led us to consider as a mechanism for this cycloaddition the intervention of the nickel(0) complex **4** (L = $CH_2{=}CHZ$) in which the trimethylenemethane ligand has a C_{3v} symmetry.[11] This possibility, however, was ruled out by the following experiments. Reaction of 2,2-dimethylmethylenecyclopropane (**1b**)[12] with methyl acrylate afforded the adduct



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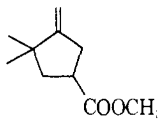

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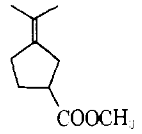

6

5 in 60% yield: mass m/e 168 (M^+); ir (neat) 1735

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(1) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(2) Very recently cycloaddition of 1,1-diphenylcyclopropane to tetracyanoethylene was reported: Th. Martini and J. A. Kampmeier, *ibid.*, **82**, 216 (1970). For metal-catalyzed intramolecular cycloaddition, see H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *J. Amer. Chem. Soc.*, **91**, 218 (1969); T. J. Katz and S. A. Cerefice, *ibid.*, **91**, 2405 (1969); T. J. Katz and S. A. Cerefice, *Tetrahedron Lett.*, 2561 (1969); T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **91**, 6519 (1969).

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(5) All new compounds gave satisfactory elemental analyses.

(6) A trace amount of the acrylonitrile adduct **2c** was obtained.

(7) D. S. Noyce and J. S. Fessenden, *J. Org. Chem.*, **24**, 715 (1959).

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(9) R. Noyori, T. Nishimura, and H. Takaya, *Chem. Commun.*, 89 (1969).

(10) A. C. Day and J. T. Powell, *ibid.*, 1241 (1968).

(11) (a) M. R. Churchill and K. Gold, *ibid.*, 693 (1968); (b) A. Almenningen, A. Haaland, and K. Wahl, *ibid.*, 1027 (1968).

(12) W. Rahman and H. G. Kuivila, *J. Org. Chem.*, 31, 772 (1966).

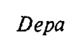
(C=O) and 883 cm^{-1} (=CH$_2$); nmr (CCl$_4$) δ 1.00 and 1.10 (s, 3 H each, C(CH$_3$)$_2$), 1.6–2.9 (m, 5 H, >CH and >CH$_2$), 3.58 (s, 3 H, COOCH$_3$), and 4.74 (m, 2 H, =CH$_2$). Ozonolysis gave the previously reported methyl 3,3-dimethyl-4-oxocyclopentanecarboxylate.[13] Similar cycloaddition using isopropylidenecyclopropane (**1c**)[14] furnished the isomeric adduct **6** (61%), which upon ozonolysis gave **3**: mass m/e 168 (M$^+$); ir (neat) 1735 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.60 (s, 6 H, =C(CH$_3$)$_2$), 1.7–3.0 (m, 7 H, >CH and >CH$_2$), and 3.60 (s, 3 H, COOCH$_3$). If a trimethylenemethane complex such as **4** were involved as the intermediate, these two reactions should give the same adduct or an identical mixture of isomers. The lack of crossover of the products suggests that methylenecyclopropanes enter into the cycloaddition with olefins at C-2 and C-3 or C-1 and C-3.[15]

Thus the present reaction, which would formally be analyzed as a [$_\sigma 2 + {}_\pi 2$] process, serves as a single-step synthesis of methylenecyclopentane derivatives starting with readily available materials.[16] Further studies on the scope and the detailed mechanism including the stereochemistry of the addition will be published at a later time.

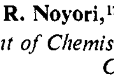
[13] J. C. Bardhan, S. K. Banerji, and M. K. Bose, *J. Chem. Soc.*, 1127 (1935).

[14] (a) K. Sisido and K. Utimoto, *Tetrahedron Lett.*, 3267 (1966); (b) E. E. Schweizer and J. G. Thompson, *Chem. Commun.*, 666 (1966).

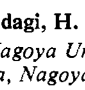
[15] σ complexes i or ii or simple π complex ii (L = CH$_2$=CHZ) could be the possible intermediate.



i



ii



iii

[16] Difficulty in Wittig condensation between cyclopentanone and phosphoranes is well known. See A. Maercker, *Org. React.*, **14**, 270 (1965).

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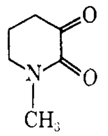
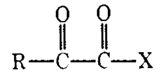
Rearrangement of Pyruvates to Malonates[1]

Sir:

Although α-ketocarboxylic acids are known to react with periodate to give carbon dioxide and the carboxylic acid with one less carbon,[2] the reaction of α-keto acyl derivatives with periodate has not been reported. We have synthesized the pyruvyl derivatives **1** and **2a–c**[3-5] and now report their reaction with periodate which leads to skeletal rearrangement.

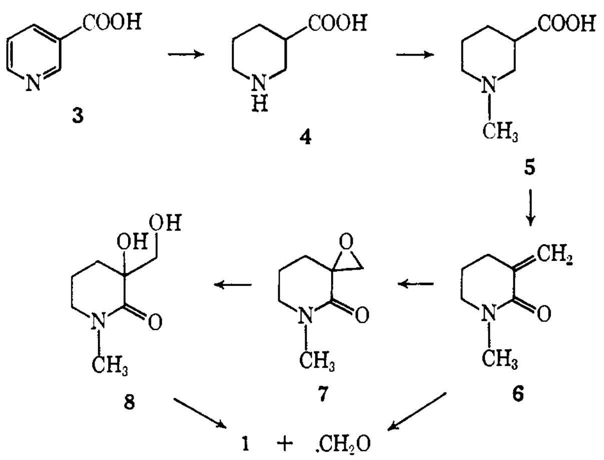

1


$$R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-X$$

2a, R = CH$_3$CH$_2$; X = OC$_2$H$_5$
b, R = CH$_3$CH$_2$; X = N(CH$_3$)$_2$
c, R = CH$_3$(CH$_2$)$_4$; X = NH$_2$

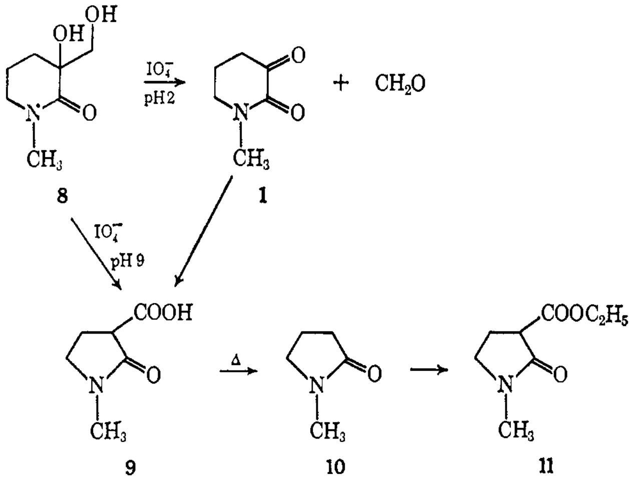
1-Methyl-2,3-piperidinedione (**1**) was synthesized as shown in Scheme I. Nicotinic acid (**3**) was catalytically (PtO$_2$) hydrogenated to nipecotic acid (**4**) which was reductively methylated to give N-methyl derivative **5** (100%).[6] Reaction of **5** in refluxing acetic anhydride for 3 hr gave 1-methyl-3-methylene-2-piperidone (**6**) in 93% yield.[7] Ozonolysis of **6** at −78° followed by addition of trimethoxyphosphine[8] or dimethyl sulfide[9] and chromatography gave the piperidinedione **1** in 65% yield. Alternately, **6** was epoxidized (m-chloroperbenzoic acid) to **7** (88%), epoxide **7** was hydrolyzed with 6% HClO$_4$ to **8**,[10] and glycol **8** was oxidized with NaIO$_4$ in dilute HCl, giving **1** (83%).[11]

Scheme I



Although reaction of glycol **8** with excess periodate at pH 2 gave piperidinedione **1** and formaldehyde, the reaction (Scheme II) of either **8** or **1** with 6 equiv of NaIO$_4$ at pH 7 or 9 for 10 hr gave 3-carboxy-1-methyl-2-pyrrolidinone (**9**) in 80% yield. Heating **9** at 150°

Scheme II



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[1] This work was supported in part by Grant No. MH12797 from the National Institute of Mental Health, U. S. Public Health Service.

[2] D. B. Sprinson and E. Chargraff, *J. Biol. Chem.*, **164**, 433 (1964).

[3] All compounds reported in this communication have been characterized spectrally (uv, ir, nmr) and analytically (elemental, mass spectrum).

[4] E. Vogel and H. Schinz, *Helv. Chim. Acta*, **33**, 116 (1950).

[5] M. Igarashi and H. Midorikawa, *J. Org. Chem.*, **28**, 3088 (1963).

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[7] M. Ferles, *Collect. Czech. Chem. Commun.*, **29**, 2323 (1964).

[8] W. S. Knowles and Q. E. Thompson, *J. Org. Chem.*, **25**, 1031 (1960).

[9] J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Lett.*, 4273 (1966).

[10] E. E. Van Tamelen, A. Storni, E. J. Hessler, and M. Schwarz, *J. Amer. Chem. Soc.*, **85**, 3295 (1963).

[11] Due to the high water solubility of most of the compounds reported here, continuous extraction with methylene chloride has been used for isolation from aqueous solution.