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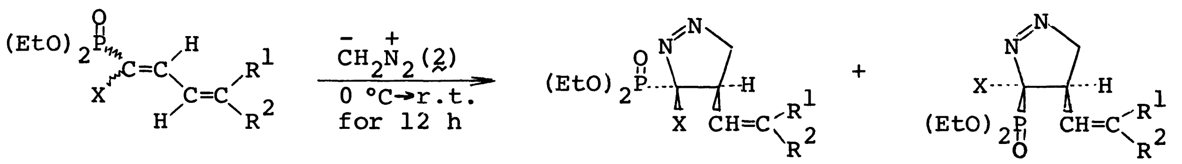
CYCLOADDITION OF DIAZOMETHANE TO BUTADIENYLPHOSPHONATES. A NEW APPROACH TO FUNCTIONALIZED PENTADIENYLPHOSPHONATES AND PYRAZOLES

Toru MINAMI,* Shigehumi TOKUMASU, Rikako MIMASU, and Ichiro HIRAO
Department of Industrial Chemistry, Kyushu Institute of Technology,
Sensuicho, Tobata, Kitakyushu 804

The cycloaddition reaction of diazomethane with diethyl 1,3-butadienylphosphonates containing electronegative substituents on the α-carbon atom gave diethyl (4-alkenyl-Δ^1-pyrazolin-3-yl)phosphonates in high yields. Thermolysis and the base-catalyzed reaction of the pyrazolinylphosphonates produced functionalized 2,4-pentadienylphosphonates and pyrazoles, respectively, in good yields.

1,3-Dipolar cycloadducts of diazoalkanes to vinyl- and alkenylphosphonium salts have been reported as useful intermediates for the synthesis of pyrazoles.[1)] Similar cycloaddition of diazoalkanes to vinylphosphonates and related phosphoryl compounds have been well studied.[2)] However, to our knowledge, the reaction of diazoalkanes with their homologues, butadienylphosphonates has not been reported. On the other hand, we have recently reported some reactions of butadienylphosphonates.[3)] In connection with our continuing interest in the synthetic utilization of butadienylphosphonates, we investigated the cycloaddition reaction of diazomethane with butadienylphosphonates bearing electronegative substituents.

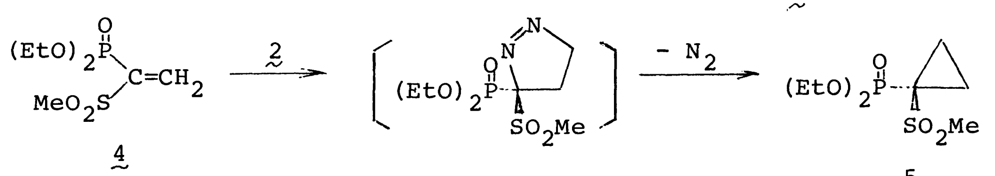
Cycloaddition of diazomethane (2) to butadienylphosphonates 1b,d,e[3),4)] in ether gave mixtures of (E)- and (Z)-4-alkenyl-3-diethoxyphosphinyl-3-ethoxycarbonyl-Δ^1-pyrazolines 3b,d,e[5)] (88-91% yields) in the same ratios as those in starting 1b,d,e, while the reaction using a single (1E,3E)-1-methylsulfonyl-1,3-butadienylphosphonate 1a[3)] exclusively produced the corresponding (E)-3-diethoxyphosphinyl-3-methylsulfonyl-Δ^1-pyrazoline 3a[5)] in 86% yield. Although similar treatment of (1E,3E)-1-cyanobutadienylphosphonate 1c[3)] provided Δ^1-pyrazoline 3c, this adduct 3c could not be isolated in a pure form due to thermolability. However, its presence was



1a-e (E)-3b,d,e (E)-3a (Z)-3b,d,e (1)

1a, 3a: X=SO_2Me, R^1=H, R^2=Ph
1b, 3b: X=CO_2Et, R^1=H, R^2=Ph
1c : X=CN, R^1=H, R^2=Ph
1d, 3d: X=CO_2Et, R^1=H, R^2=Me
1e, 3e: X=CO_2Et, R^1=R^2=Me

demonstrated by the base-catalyzed reaction as mentioned below.
In contrast, similar reaction of diethyl (1-methylsulfonylethenyl)phosphonate (4)[6] with 2 exclusively led to diethyl (1-methylsulfonylcyclopropyl)phosphonate (5): 76%; Oil; ^{13}C NMR(CDCl$_3$) δ 12.0($^2J_{pc}$=2.6 Hz), 16.3($^3J_{pc}$=6.0 Hz), 35.3($^1J_{pc}$=185.7 Hz), 41.2, and 63.6($^3J_{pc}$=6.0 Hz). The structure of 5 was confirmed by comparison of its ^{1}H NMR and ^{13}C NMR spectra with those of an authentic sample prepared from 4 and dimethyloxosulfonium methylide. The formation of 5 would be explained by

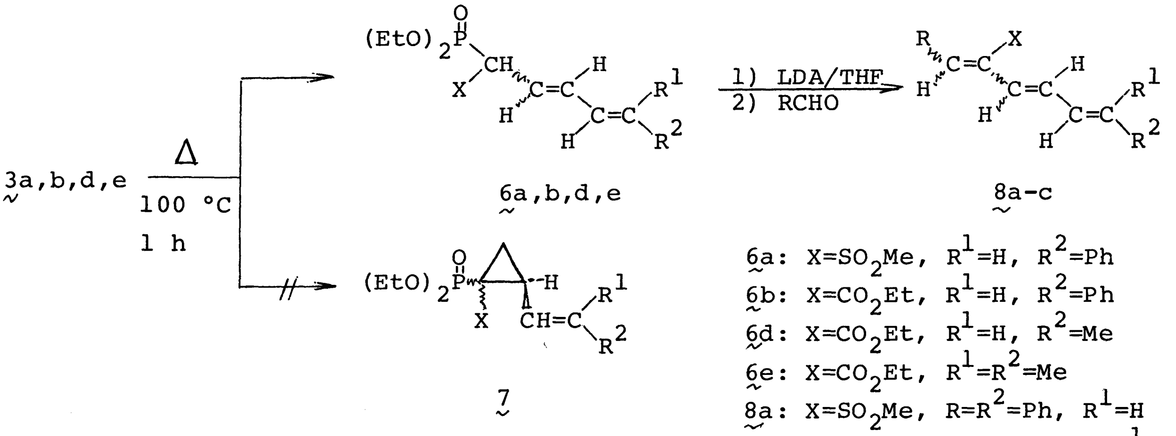


4 (2)

5

the extrusion of N$_2$ from an initially produced unstable Δ^1-pyrazoline.

On the other hand, thermolysis of the pyrazolines 3a,b,d,e at 100 °C for 1 h did not afford expected cyclopropylphosphonates 7, but exclusively led to one-carbon homologation products, diethyl 2,4-pentadienylphosphonates 6a,b,d,e,[7] which are not easily obtainable by existing methods, in good yields. Treatment of 6a,e with lithium diisopropylamide (LDA), followed by the reaction with aldehydes, readily led to Wittig-Horner reaction products, 1,3,5-trienes 8a,c and 1,3,5,7-tetraene 8b having functionality in good yields.[8]

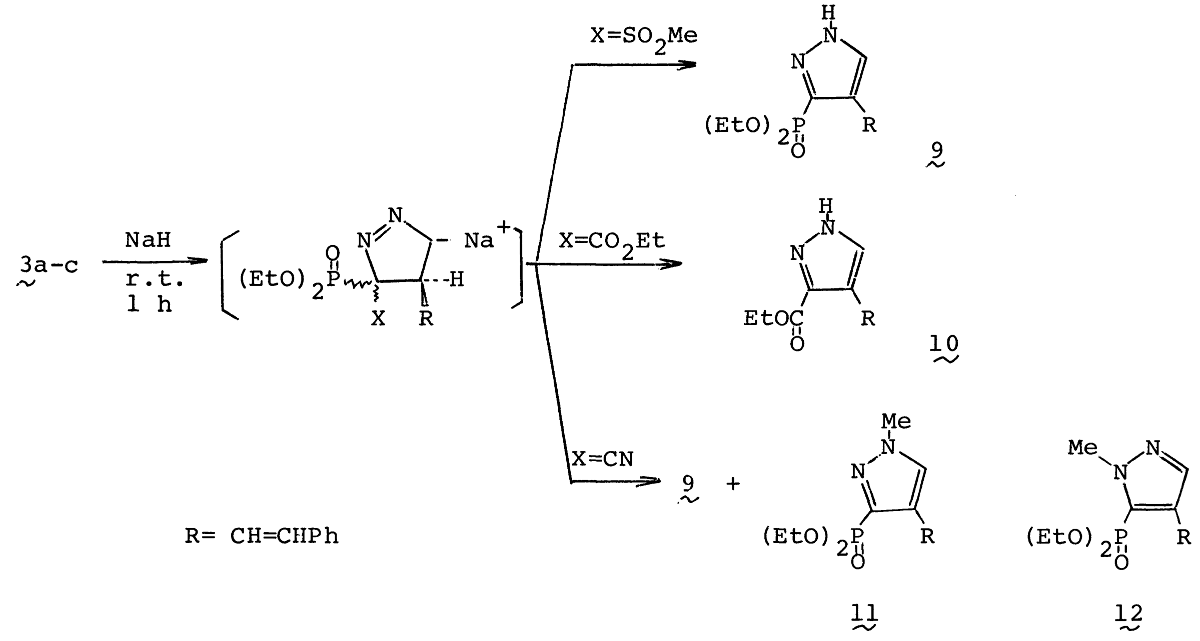


6a: X=SO$_2$Me, R^1=H, R^2=Ph
6b: X=CO$_2$Et, R^1=H, R^2=Ph
6d: X=CO$_2$Et, R^1=H, R^2=Me
6e: X=CO$_2$Et, R^1=R^2=Me
8a: X=SO$_2$Me, R=R^2=Ph, R^1=H
8b: X=SO$_2$Me, R=CH=CHPh, R^1=H
R^2=Ph
8c: X=CO$_2$Et, R=Ph, R^1=R^2=Me

Scheme 1.

The compounds 8a and 8b showed their ^{1}H NMR signals at δ 3.02(3H, s, SO$_2$Me) and at δ 6.15-7.80(15H, m), and at δ 3.00(3H, s, SO$_2$Me) and at δ 6.40-7.80(17H, m), respectively. These results suggest that the products 8a and 8b are single isomers, although their stereochemistry is not determined. On the other hand, the product 8c was a mixture of two stereoisomers (isomer ratio, ca. 2.2:1 by ^{13}C NMR).

Treatment of the Δ^1-pyrazolines 3a and 3b with base such as sodium hydride and triethylamine in benzene easily gave 3-diethoxyphosphinyl-(9) (mp 62-64 °C) and 3-ethoxycarbonyl-4-styrylpyrazoles (10)[9] (mp 146-147 °C) in 83% and 67% yields with the accompanying elimination of the methylsulfonyl and diethoxyphosphinyl moieties, respectively. The structural assignment of the product 9 rests upon its spectral



Scheme 2.

data: ^{1}H NMR(CDCl$_3$) δ 1.34(6H, t), 3.80-4.60(4H, m), 6.60-7.70(7H, m), 8.19(1H, d, J=2.20 Hz, C5-H), and 11.34(1H, br.s, NH); ^{13}C NMR δ 16.3($^3J_{pc}$=6.0 Hz), 62.8($^2J_{pc}$= 5.2 Hz), 117.6, 125.0($^2J_{pc}$=20.6 Hz, C4), 126.3, 127.6, 128.7, 129.8, 132.0($^3J_{pc}$= 12.0 Hz, C5), 134.7($^1J_{pc}$=225.2 Hz, C3), and 137.3. The structure of 10 was determined by comparison of ^{1}H NMR and ^{13}C NMR spectral data with those of 9. Similar treatment of 3c, in-situ prepared from 1c and 2, with sodium hydride led to a mixture of 9 (33%), and N-methylated pyrazoles 11 (19%) and 12 (20%).10) Structural assignment of 11 and 12 was similarly made by comparison of their ^{13}C NMR spectra with that of 9. The formation of 11 and 12 would be reasonably accounted for by the reaction of 9, which would be similarly produced by the facile elimination of a cyanide anion from 3c, and its isomer, 5-diethoxyphosphinyl-4-styrylpyrazole, with 2 which is present in the reaction system (Scheme 2). These results show that the reaction products are dependent upon the substituents X.

Thus, the 1,3-dipolar cycloadducts of diazomethane to butadienylphosphonates can serve as versatile synthons not only for 2,4-pentadienylphosphonates, which are used in the synthesis of unsaturated systems, but also for functionalized pyrazoles.

References

1) E. E. Schweizer and C. S. Kim, J. Org. Chem., 36, 4033, 4041(1971); E. E. Schweizer and C. S. Labaw, ibid., 38, 3069(1973).

2) For examples, R. D. Gareev, G. M. Loginova, and A. N. Pudovik, Zh. Obshch. Khim., 49, 493(1979); Chem. Abstr., 91, 4894w(1979); R. D. Gareev and A. N. Pudovik, Zh. Obshch. Khim., 49, 728(1979); Chem. Abstr., 91, 56196q(1979); R. D. Gareev and A. N. Pudovik, Zh. Obshch. Khim., 52, 2637(1982); Chem. Abstr., 98, 143529p (1983); E. Öhler and E. Zbiral, Monatsh. Chem., 115, 493(1984).

3) T. Minami, T. Yamanouchi, S. Tokumasu, and I. Hirao, Bull. Chem. Soc. Jpn., 57, 2127(1984).

4) Mixtures of Diethyl (1E,3E)- and (1Z,3E)-(1-ethoxycarbonyl-1,3-pentadienyl)-(**1d**)(bp 95 °C/1 Torr)(isomer ratio, ca. 4:1), and (1-ethoxycarbonyl-4-methyl-1,3-pentadienyl)phosphonates (**1e**)(bp 95 °C/1 Torr)(isomer ratio, ca. 3:1) were respectively prepared in 78% and 55% yields by the condensation of diethyl (ethoxycarbonylmethyl)phosphonate with crotonaldehyde and 3-methylcrotonaldehyde in the presence of titanium tetrachloride according to a modification of the reported procedure [W. Lehnert, Tetrahedron, 30, 301(1974)].

5) All the new compounds gave satisfactory, spectral data and analytical data (±0.4% for C, H, N). Physical and spectral data for the selected compounds are as follows, (E)-**3b**: Oil; ^{1}H NMR($CDCl_3$) δ 1.17(3H, t, Me), 1.34(6H, t, Me), 3.20-5.00(9H, m,>CH-, OCH_2, and NCH_2), 5.48-6.0(1H, dd, J=8.57, 15.67 Hz, olefinic H), 6.52(1H, d, J=15.67 Hz, olefinic H), and 7.26(5H, s, Ph); (Z)-**3b**: Oil; ^{1}H NMR($CDCl_3$) δ 1.0-1.60(9H, m, Me), 2.92-5.40(9H, m,>CH-, OCH_2, and NCH_2), 6.10-6.60(1H, dd, J=7.76, 15.56 Hz, olefinic H), 6.65(1H, d, J=15.56 Hz, olefinic H), and 7.33(5H, s, Ph). The stereochemistries of (E)- and (Z)-**3b** were tentatively assigned on the basis of comparison of their styryl ^{1}H chemical shifts with those in diethyl (E)- and (Z)-(1-ethoxycarbonyl-2-styrylcyclopropyl)phosphonates$^{3)}$[5.70-6.20(1H, dd, J=8.61, 15.93 Hz) and 6.68(1H, d, J=15.93 Hz) in the (E)-isomer, and 6.10-6.65(1H, dd, J=6.78, 15.93 Hz) and 6.71(1H, d, J=15.93 Hz) in the (Z)-isomer].

6) T. Minami, H. Suganuma, and T. Agawa, Chem. Lett., 1978, 285.

7) **6a**: 87% yield; Mp 77-79 °C; ^{1}H NMR($CDCl_3$) δ 1.36(6H, t), 3.16(3H, s), 3.75-4.50(5H, m), 5.40-7.00(4H, m), 7.34(5H, s). Found: C, 53.27; H, 6.63%. Calcd for $C_{16}H_{23}O_5SP$: C, 53.62; H, 6.47%. **6b**: 83% yield; Oil; ^{1}H NMR($CDCl_3$) δ 1.32(9H, t), 3.20-3.70(1H, m), 3.80-4.50(6H, m), 5.50-7.00(4H, m), 7.34(5H, s). **6d**: quant. yield; Oil; ^{1}H NMR($CDCl_3$) δ 1.00-1.50(9H, m), 1.70(3H, dd, J=2.71, 5.20 Hz), 3.30-4.50(7H, m), 5.20-6.70(4H, m). **6e**: quant. yield; Oil; ^{1}H NMR ($CDCl_3$) δ 1.00-1.50(9H, m), 1.76(6H, s), 3.40-4.50(7H, m), 5.30-6.80(3H, m).

8) **8a**: quant. yield; Mp 86-88 °C. Found: C, 73.13; H, 6.13%. Calcd for $C_{19}H_{18}O_2S$: C, 73.52; H, 5.85%. **8b**: 79% yield; Mp 143-145 °C. **8c**: 66% yield; Oil; ^{1}H NMR($CDCl_3$) δ 1.30(3H, t), 1.74(6H, s), 4.25(2H, q), 5.60-7.50(9H, m).

9) **10**: ^{1}H NMR($CDCl_3$) δ 1.45(3H, t), 4.00-4.80(2H, q), 6.60-8.20(8H, m), 11.78(1H, br.s, NH); ^{13}C NMR($CDCl_3$) δ 14.5, 61.2, 118.5, 122.6(C4), 126.3, 127.6, 128.7, 130.0, 131.3(C5), 135.9(C3), 137.3, 161.9.

10) **11**: Oil; ^{1}H NMR($CDCl_3$) δ 1.24(6H, t), 3.70-4.20(4H, m), 3.83(3H, s, N-Me), 6.40-7.70(8H, m); ^{13}C NMR($CDCl_3$) δ 16.0($^3J_{pc}$=6.0 Hz), 39.3, 62.1($^2J_{pc}$=5.2 Hz), 117.6, 125.8($^2J_{pc}$=23.2 Hz, C4), 125.9, 127.1, 128.3, 128.9, 136.9, 138.6($^1J_{pc}$=228.7 Hz, C3). The C5 resonance was obscured by another peak.
12: Oil; ^{1}H NMR($CDCl_3$) δ 1.32(6H, t), 3.80-4.60(4H, m), 4.08(3H, d, J=0.55 Hz, N-Me), 6.80-7.80(7H, m), 7.83(1H, d, J=1.83 Hz); ^{13}C NMR($CDCl_3$) δ 16.0($^3J_{pc}$=6.0 Hz), 39.3, 62.4($^2J_{pc}$=6.0 Hz), 118.0, 126.0, 126.7($^1J_{pc}$=211.5 Hz, C5), 127.2, 128.3, 129.2, 135.2($^3J_{pc}$=17.2 Hz, C3), 137.0. The C4 resonance was obscured by another peak.

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