Communications to the Editor

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A FACILE SYNTHESIS OF 2-METHOXY-4,4-DIMETHYL-2,5-CYCLOHEXADIENONE VIA 5,5-DIMETHYL-2-NITRO-1,3-CYCLOHEXADIENOL[1]

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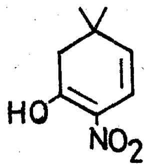
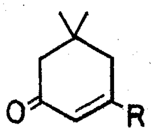
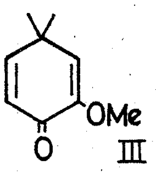
5,5-Dimethyl-2-nitro-1,3-cyclohexadienol(I), which was prepared from 5,5-dimethyl-2-cyclohexenone(IIa), afforded 5,5-dimethyl-2-hydroxyimino-3-cyclohexenone(VIII) by reaction with diazomethane. VIII was hydrolyzed to 2-hydroxy-5,5-dimethyl-2,5-cyclohexadienone(Vb) via nitrone(X). Vb was methylated to III by treating with dimethyl sulfate. The yield of III from VIII was satisfiable.

KEYWORDS ——— 2-nitro-1,3-cyclohexadienol; 2-nitro-2-cyclohexenone; 2-hydroxyimino-3-cyclohexenone; 2-methoxy-2,5-cyclohexadienone; diazomethane; hydrolysis

Recently synthetic uses for nitro olefins were examined mainly by Corey et al.[2] In this communication, the reaction with diazomethane of 5,5-dimethyl-2-nitro-1,3-cyclohexadienol(I), which was prepared from 5,5-dimethyl-2-cyclohexenone(IIa)[3], and a facile synthesis of 2-methoxy-4,4-dimethyl-2,5-cyclohexadienone(III) starting from I was described. IIa was nitrated with potassium metal and isoamylnitrate in liquid ammonia to give potassium salt(IV) in 52.6% yield. IV: mp288-289°C[4] IR(nujol): ν1630cm^{-1}. NMR(D_2O, internal standard: DSS)δ: 1.00(6H, s), 2.42(2H, s), 5.76 and 6.75(each 1H, d, J=11Hz). Efforts to hydrolyze IV with a cold diluted sulfuric acid to 5,5-dimethyl-3-cyclohexene-1,2-dione(Va) or its enol isomer, 2-hydroxy-4,4-dimethyl-2,5-cyclohexadienone(Vb) were unsuccessful(Nef reaction[5]) and gave only the corresponding neutralized product. It was suggested from the following data that the structure of the product was not 5,5-dimethyl-2-nitro-2-cyclohexenone(VIa) but I. I: IR(film):ν1585cm^{-1}. NMR(CCl_4)δ: 1.13(6H, s), 2.60(2H, s), 5.58 and 6.55(each 1H, d, J=9.5Hz), 14.7(1H, br.s). I was an unstable oil and its purification could only be performed through its salt,IV. On the other hand, the nitrated product from 3,5,5-trimethyl-2-cyclohexenone(IIb) proved by its physical data to be 3,5,5-trimethyl-2-nitro-2-cyclohexenone(VIb). VIb: mp48-50°C IR(nujol)cm^{-1}:$\nu_{C=O}$1685, ν1530, 1380. NMR(CCl_4)δ: 1.08(6H, s), 1.97(3H, s), 2.36 and 2.45(each 2H, s). Then the reactions of I or VIb with an excess of diazomethane were examined. Though VIb gave only unchanged starting material, I gave mainly two compounds. It was concluded from the following physical data and the mechanistical consideration that they are 3a-hydroxy-5,5-dimethyl-1-oxy-3,3a,4,5-tetrahydro[2,1]benzisoxazole(VII) and 2-hydroxyimino-5,5-dimethyl-3-cyclohexenone(VIII). VII: mp71-73°C IR($CHCl_3$)cm^{-1}:ν_{OH}3600-3200, $\nu_{C=N}$1690(weak), ν_{NO}1520 (strong). NMR(CCl_4)δ: 1.10(6H, s), 2.41 and 3.81(each 2H, s), 6.01 and 6.50(each 1H, d, J=10.5Hz). MS, m/e(%): 183(M^+, 65), 110($>\overset{+}{C}$-CH=CH-C$\equiv\overset{+}{N}$-O^-, base peak). VIII: mp132-134°C IR($CHCl_3$)cm^{-1}: ν_{OH}3220, $\nu_{C=O}$ 1710. NMR($CDCl_3$)δ: 1.12(6H, s), 2.60(2H, s), 6.37 and 6.95(each 1H, d, J=10.5Hz). MS,m/e(%): 94($>\overset{+}{C}$-CH=CH-C$\equiv$N, 94), 153(M^+, base peak). The isolated yields of VII and VIII were 2.9 and 36.8%, respectively. VII was unstable and changed gradually to crystals of VIII on standing at room temperature. Therefore VII is considered to be an intermediate of VIII. VIII was also obtained from the reaction of IIa with potassium metal and isoamylnitrite in a yield of 38.6%. The mechanism for the formation of VIII from I was considered to be as shown in the scheme. From the literature[6], the former product may be epoxymethylenimine N-oxide(IX). But the structure must be rejected according to the MS data, that is, the base peak, m/e 110, could not be explained by the structure of IX. Efforts to hydrolyze the oxime, VIII with titanium trichloride[7] were unsuccessful. So VIII was further treated with diazomethane[8] to give quantitatively nitrone, 5,5-dimethyl-2-methylnitrono-3-cyclohexenone(X). X: mp51-54°C NMR(CCl_4)δ: 1.16 (6H, s), 2.50(2H, s), 4.06(3H, s), 6.00 and 6.83(each 1H, d, J=10Hz). X was hydrolyzed to Vb by treating with 5% HCl at room temperature. Vb: oil NMR($CDCl_3$)δ: 1.30(6H, s), 5.97(1H, d, J=3.5Hz), 6.24(1H, d, J=10Hz), 6.87(1H, d, J=10 and 3.5Hz). III was obtained from X in a quantitative yield by treating Vb with dimethyl sulfate in basic medium. By the treatment of Vb with diazomethane, a large amount of Vb was recovered together with a small amount of the desired product, III. III[9]: oil NMR(CCl_4)δ: 1.27(6H, s), 3.58(3H, s), 5.69(1H, d, J=2Hz), 6.08(1H, d, J=9.5Hz), 6.73(1H, d.d, J=9.5 and 2Hz). III was identified by comparison with an authentic sample prepared from 4,4-dimethyl-2-cyclohexenone[10] by means of IR, NMR, and GLC.


I


IIa: R=H
b: R=Me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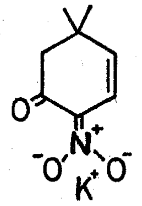
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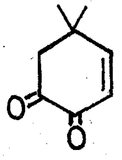
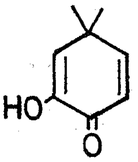

Va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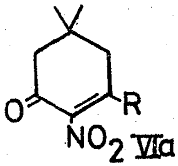
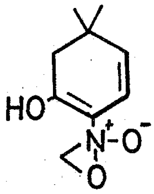

VIa: R=H
b: R=Me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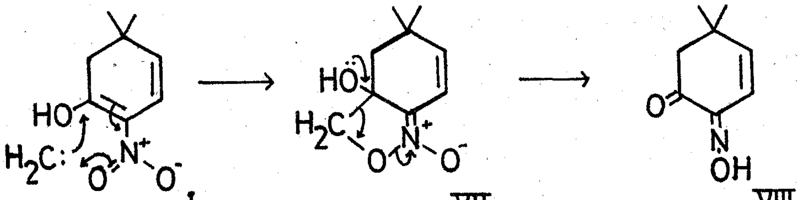
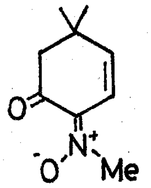

I VII VIII


X

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