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ONE-STEP SYNTHESIS OF A NEW HETEROCYCLE, 6-METHYLENE-4,7-DIOXABICYCLO[3.2.1]OCT-2-ENE

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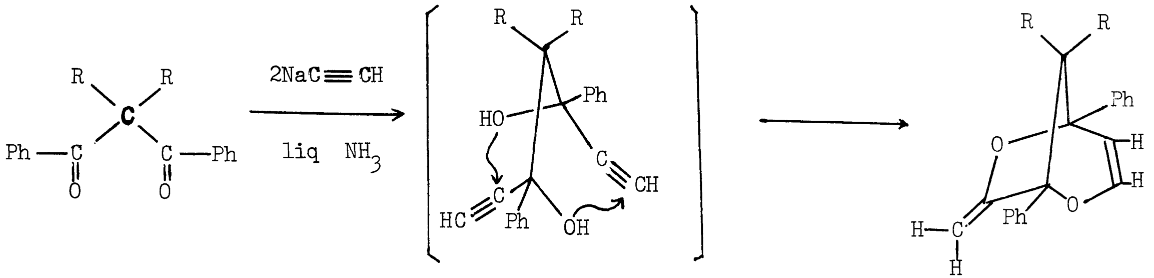
The reactions of 2,2-dibenzoylpropane (Ia) and 1,1-dibenzoylcyclopentane (Ib) with two molar amounts of sodium acetylide in liquid ammonia afforded 8,8-dimethyl-6-methylene-1,5-diphenyl-4,7-dioxabicyclo[3.2.1]oct-2-ene (IIIa) and 6-methylene-1,5-diphenyl-4,7-dioxabicyclo[3.2.1]oct-2-ene-8-spirocyclopentane (IIIb), respectively. Some reactions of III were described.

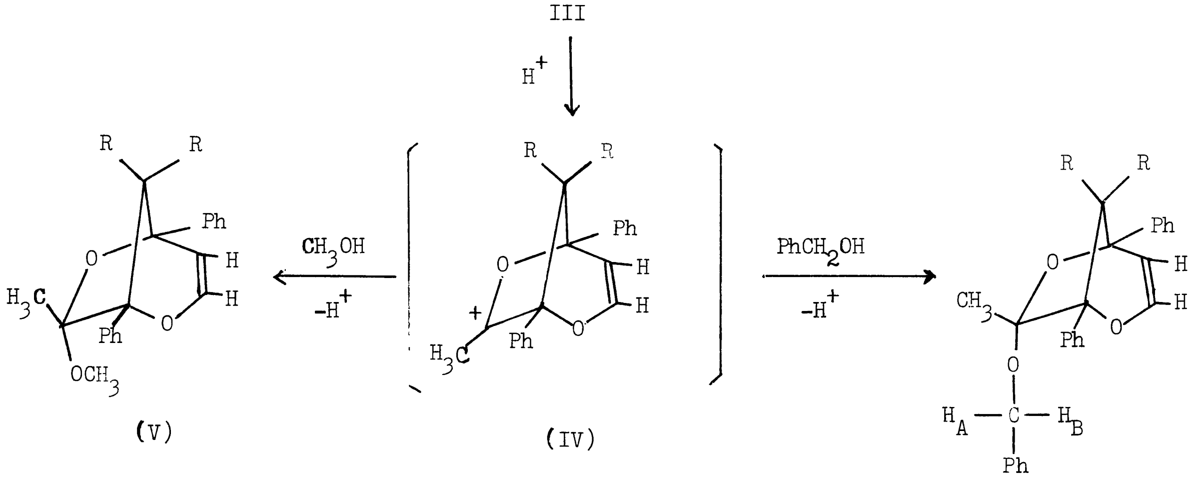
The reaction of 2,2-dibenzoylpropane (Ia) with two molar amounts of sodium acetylide in liquid ammonia afforded a new heterocyclic compound, 8,8-dimethyl-6-methylene-1,5-diphenyl-4,7-dioxabicyclo[3.2.1]oct-2-ene (IIIa) in a 24% yield (colorless prisms; mp 154-156°C). The same treatment of 1,1-dibenzoylcyclopentane (Ib) with sodium acetylide as of Ia afforded 6-methylene-1,5-diphenyl-4,7-dioxabicyclo[3.2.1]oct-2-ene-8-spirocyclopentane (IIIb) in a 20% yield (colorless prisms; mp 194°C). The structure of IIIa and IIIb was identified by means of spectral data (Table 1). The spectral data of IIIa and IIIb are comparable each other.

A possible precursor of III is a meso-diacetylenediol (II), in which one oxygen attacks the terminal carbon of one acetylene moiety and another one does the internal carbon of another acetylene moiety. Such the base-catalyzed cyclization reactions of acetylene alcohol as proceed by the former1) and the latter fashion2) have been reported. However, neither the cyclization product of II by the two former fashions nor that by the two latter fashions could be detected.

Heating of IIIa in MeOH in the presence of a catalytic amount of concd HCl for a few min afforded 6-methoxy-6,8,8-trimethyl-1,5-diphenyl-4,7-dioxabicyclo[3.2.1]oct-2-ene (Va) in an 80% yield (colorless prisms; mp 124-126°C). The same treatment of IIIb as of IIIa afforded 6-methoxy-6,8,8-trimethyl-1,5-diphenyl-4,7-dioxabicyclo[3.2.1]oct-2-ene-8-spirocyclopentane (Vb) in a 75% yield (colorless prisms; mp 127-129°C). Heating of a solution of IIIa, benzyl alcohol, and a catalytic amount of concd HCl in acetone for a few min afforded the benzyloxy analog of Va (VIa)

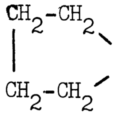


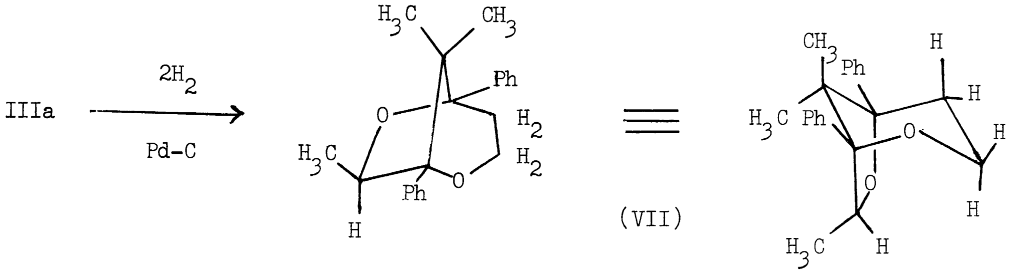
(I) (II) (III)



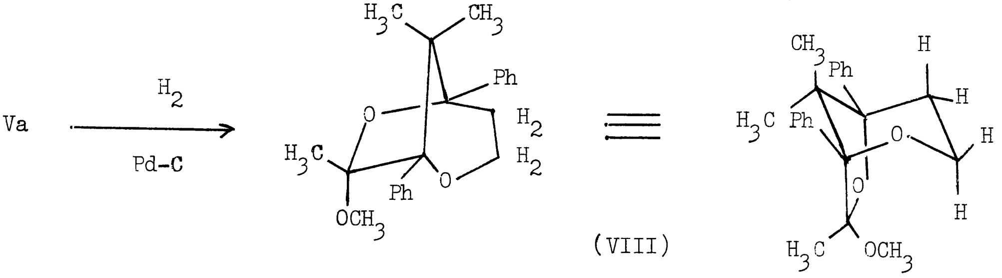
(V) (IV) (VI)

a: R=CH_3; b: R,R=


$\begin{array}{l}CH_2\text{-}CH_2\diagdown\\ |\\ CH_2\text{-}CH_2\diagup\end{array}$



(VII)



(VIII)

Table 1 The spectral data[a] of III and V[b]

Compounds	IR cm^{-1}	NMR τ	MS m/e (rel intensity)
IIIa	1685 (C=C), 1640 (C=C), 1235 (=C-O), 820 (=CH$_2$)	2.1-2.7 (m, Ph, 10H), 3.42 (d, J=10 Hz, =CH, 1H), 4.22 (d, J=10 Hz, =CH, 1H), 5.83 (d, J=2 Hz, =CH$_2$, 1H), 6.47 (d, J=2 Hz, =CH$_2$, 1H), 8.76 (s, CH$_3$, 3H), 9.10 (s, CH$_3$, 3H)	304 (M$^+$, 14), 289 (M$^+$-CH$_3$, 4), 262 (M$^+$-CH$_2$=C=O, 2), 247 (M$^+$-(CH$_2$=C=O + CH$_3$), 60), 105 (PhCO, 100)
IIIb	1670 (C=C), 1630 (C=C), 1230 (=C-O), 820 (=CH$_2$)	2.1-2.6 (m, Ph, 10H), 3.51 (d, J=10 Hz, =CH, 1H), 4.11 (d, J=10 Hz, =CH, 1H), 5.83 (d, J=2 Hz, =CH$_2$, 1H), 6.46 (d, J=2 Hz, =CH$_2$, 1H), 7.7-9.5 (m, cyclopentane, 8H)	330 (M$^+$, 16), 288 (M$^+$-CH$_2$=C=O, 10), 274 (M$^+$-C$_4$H$_8$, 13), 183 (M$^+$-(PhCO+CH$_2$=C=O), 30), 105 (PhCO, 100)
Va	1640 (C=C), 1255 (=C-O), 1080 (C-O-C), 1040 (C-O-C)	2.1-2.7 (m, Ph, 10H), 3.86 (d, J=10 Hz, =CH, 1H), 4.40 (d, J=10 Hz, =CH, 1H), 7.10 (s, OCH$_3$, 3H), 8.33 (s, CH$_3$, 3H), 8.89 (s, CH$_3$, 3H), 9.11 (s, CH$_3$, 3H)	336 (M$^+$, 29), 305 (M$^+$-OCH$_3$, 6), 262 (M$^+$-(OCH$_3$+CH$_3$CO), 42), 247 (M$^+$-(OCH$_3$+CH$_3$CO+CH$_3$), 100), 105 (PhCO, 62)
Vb	1630 (C=C), 1260 (=C-O), 1050 (C-O-C), 1020 (C-O-C)	2.1-2.7 (m, Ph, 10H), 3.90 (d, J=10 Hz, =CH, 1H), 4.25 (d, J=10 Hz, =CH, 1H), 7.18 (s, OCH$_3$, 3H), 8.40 (s, CH$_3$, 3H), 7.7-9.5 (m, cyclopentane, 8H)	362 (M$^+$, 30), 331 (M$^+$-OCH$_3$, 10), 288 (M$^+$-(OCH$_3$+CH$_3$CO), 67), 105 (PhCO, 100)

a) The IR and NMR spectra were measured in Nujol mull and CDCl$_3$ respectively. The Mass spectra were measured with an ionization energy of 75 eV.

b) The UV spectra of the compounds showed only benzenoid bands.

in a 24% yield (colorless prisms; mp 115-117°C). The same treatment of IIIb as of IIIa afforded VIb in a 25% yield (colorless prisms; mp 148-150°C). These reactions probably proceed via the carbonium ion (IV) initially formed by the protonation on the exo-methylene carbon of III, and the alcohols attack IV from the sterically less hindered endo-direction. Study on a molecular model supported that the attack from the endo-direction is favorable. The NMR and Mass spectra of VI were comparable to those of V. However, magnetic nonequivalence of the two benzyl protons H_A and H_B of VI due to a restricted rotation around the O-CH$_2$ bond of the benzyl group was observed. On the basis of the spectral data of the benzyl protons of VIa in CDCl$_3$ (two doublets centered at 5.66 and 5.94 τ, J=12 Hz; coalescence temperature 81°C) and of VIb in CDCl$_3$ (two doublets centered at

5.63 and 5.87 τ, J=12 Hz; coalescence temperature 84°C), the activation energies of the free rotation of the benzyl groups of VIa and VIb were estimated to be 17.9 and 18.7 Kcal/mole, respectively.

The catalytic reduction of IIIa and Va on Pd-C afforded 6,8,8-trimethyl-1,5-diphenyl-4,7-dioxabicyclo[3.2.1]octane (VII) (90% yield; colorless prisms; mp 90-92°C) and its 6-methoxy derivative (VIII) (86% yield; colorless needles; mp 105-107°C), respectively. The structures of VII [2.2-2.7 (m, Ph, 10H), 6.18 (q, J=6 Hz, CH, 1H), 7.55-8.35 (m, CH_2, 4H), 8.61 (d, J=6 Hz, CH_3, 3H), 9.02 (s, CH_3, 3H), and 9.15 τ (s, CH_3, 3H)] and VIII [2.5-3.1 (m, Ph, 10H), 7.28 (s, OCH_3, 3H), 8.05-8.60 (m, CH_2, 4H), 8.35 (s, CH_3, 3H), 9.02 (s, CH_3, 3H), and 9.17 τ (s, CH_3, 3H)] were identified by the NMR spectral data in $CDCl_3$ shown in parentheses. The hydrogenation of IIIa and Va probably occurs from their sterically less hindered endo-directions.

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