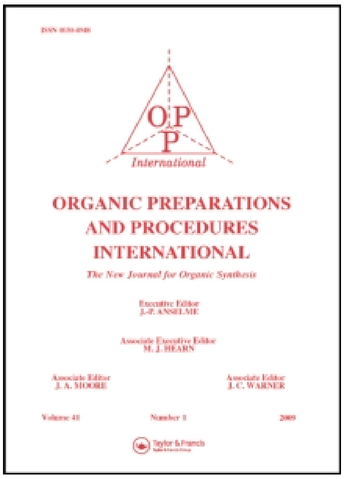

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A FACILE ROUTE TO
BENZO[b]BICYCLO[3.2.2]NONENE DERIVATIVES

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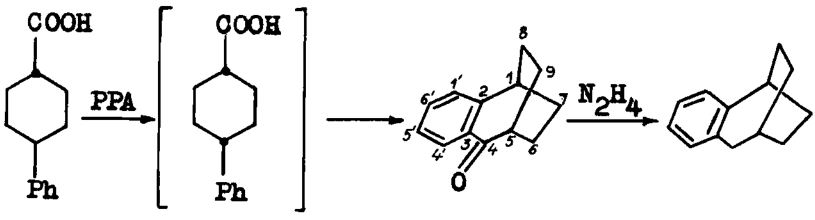
The benzo[b]bicylco[3.2.2]nonene system (III) has not been studied extensively. Derivatives of this type (containing many substitutents) have been prepared by the Diels-Alder reaction[1] and by more complex reaction sequences.[2] The benzo[b]bicyclo[3.2.2]nonene-4-yl acetate was formed in 24% yield during the acetolysis of 7-(β-tosyloxyethyl)-benzo[a]cyclohepta-1,3-diene.[3] To our knowledge, besides this acetate and the corresponding alcohol and ketone (II) prepared from it[3] , no other simple benzo[b]bicyclo[3.2.2]nonene derivatives have yet been described.

We now report a convenient synthesis of the benzo[b]bicyclo[3.2.2]nonene-4-one (II) by cyclization of 4-phenyl-



trans-I **cis**-I II III

cyclohexanecarboxylic acid (I) in the presence of polyphosphoric acid (PPA).

Evidently, only cis-4-phenylcyclohexanecarboxylic acid could be cyclized to the ketone II. The synthesis of cis-I is tedious[4] but it was pointed out[4,5] that vigorous acid treatment (conc. HCl, 185°) of trans-I (more easily available) afforded the cis-isomer in 10% yield. On this basis, we felt that the polyphosphoric acid (PPA) could simultaneously be used as an isomerization catalyst and as a cyclization agent.

The trans-4-phenylcyclohexanecarboxylic acid (trans-I) was prepared essentially by the Nenitzescu procedure[6] but the methyl 4-phenylcyclohexyl ketone was purified through the semicarbazone[7] and then oxidized[8] to trans-I.[9] PPA treatment of trans-I gave II in 66% yield, because the subsequent cyclization of cis-I continually shifted the equilibrium between the two isomeric acids towards the unstable cis form; if crude trans-I was used, the yield dropped to 60-62%. Wolff-Kishner reduction of ketone II afforded hydrocarbon III. The corresponding alcohol and acetate[3] could be readily synthesized from the ketone II by conventional methods.

EXPERIMENTAL[11]

Benzo[b]bicyclo[3.2.2]nonen-4-one (II). A mixture of trans-4-phenylcyclohexanecarboxylic acid (3 g; 14.7 mmol) and PPA (prepared from 87 g of P_2O_5 and 60 ml of 89% H_3PO_4, stirred at 100° for 1.5 hr) was heated with stirring at 130° for 3.5 hrs. The mixture was then poured into 100 ml ice-water and allowed to stand overnight. After extraction with 100 ml of ether and removal of the acidic material by washing with 5%

NaOH, the solution was dried and evaporated to yield 1.8 g (66%) of a yellow oil. Purification by chromatography (30 g neutral alumina, eluent a mixture of 95% petroleum ether and Et_2O) afforded 1.65 (91%) II as a colorless liquid. IR (CCl_4; cm^{-1}): 1680 (vs), 2888 (s), 2961 (vs), 3040 (w), 3089 (w). NMR (CCl_4; δ): 1.0-2.25 (8H, m, H_6-H_9), 2.91 (1H, m, H_1), 3.18 (1H, m, H_5), 7.1-7.55 (3H, m, $H_{1',5',6'}$), 7.9-8.1 (1H, m, $H_{4'}$). In the NMR spectrum of the complex $Eu(DPM)_3$ - II (molar ratio 0.281), H_9 as well as the aromatic proton $H_{5'}$ give rise to distinct signals.

Oxime, mp. 200-202° (MeOH). Anal. Calcd for $C_{13}H_{15}NO$: C, 77.57; H, 7.51; N, 6.96. Found: C, 77.19; H, 7.59; N, 6.90.

2,4-Dinitrophenylhydrazone, mp. 223-225° (dioxane-H_2O). Anal. Calcd for $C_{19}H_{18}N_4O_4$: C, 62.28; H, 4.95; N, 15.29. Found: C, 62.41; H, 5.05; N, 15.10. UV-VIS ($CHCl_3$, λ_{max} nm, log ε): 384.9 (4.41).[12]

Benzo[b]bicyclo[3.2.2]nonene (III). Ketone II (0.3 g; 1.61 mmol), KOH (1.8 g; 32.2 mmol), 85% hydrazine (3.6 ml; 54 mmol) and diethylene glycol (18.1 ml) were refluxed for 2 hrs. The condenser was then set for distillation and the temperature raised to 200°; water was distilled, carrying some organic product. The mixture was heated at 200° for a further 3 hrs, then poured into 15 ml dil. HCl. The distillate was added and the mixture extracted with ether (50 ml). The ethereal extract was washed with water, dried ($MgSO_4$) and evaporated to give a colorless oil (0.2 g; 72%). Purification (7 g alumina, eluent n-pentane) yielded 0.15 g (54%) of III.

IR (CS_2 and CCl_4; cm^{-1}): 728 (s), 2865 (s), 2935 (vs), 3016 (w), 3060 (w).

NMR (CCl_4: δ): 1.4-2.05 (8H, m, H_6-H_9), 2.13 (1H, m, H_5), 2.71 (1H, m, H_1), 3.07 (2H, d, H_4), 6.75-7.15 (4H, m, $H_{1'}$, $H_{4'}$, $_{5',6'}$); $J_{4,5}$ = 4 Hz.

REFERENCES

1. W. Davey and H. Gottfried, J. Org. Chem., 26, 3699 (1961).
2. M. Takeshi and S. Akira, Bull. Chem. Soc. Japan, 34, 276 (1961).
3. I. Dragutan, C. Draghici and E. Cioranescu, Rev. Roumaine Chim., 20, 283 (1975).
4. H. E. Zimmerman and H. J. Giallombardo, J. Am. Chem. Soc., 78, 6259 (1956).
5. R. Rassow, Ann., 282, 147 (1894).
6. C. D. Nenitzescu and I. G. Gavat, ibid., 519, 260 (1935).
7. Methyl 4-phenylcyclohexyl ketone was isolated as a semicarbazone from the fraction[6] bp. 163-168°/12 mm (49% of this ketone, vpc analysis). Crystallization (EtOH) of the semicarbazone mixture afforded a derivative mp. 190-191° (lit.[6,8] 190-191° and 191°) which on acidic hydrolysis gave the pure ketone, mp. 53-55° (lit. 55°).
8. W. S. Johnson and R. D. Offenhauer, J. Am. Chem. Soc., 67, 1045 (1945).
9. The resulted acid has mp. 208° (AcOH or MeOH) indicating that it is the trans-isomer (lit.[4,10] 201-203° and 205-208°). Vpc analysis of its methylic ester showed a homogeneous product.
10. L. F. Fieser and M. T. Leffler, J. Am. Chem. Soc., 70, 3186 (1948).
11. Spectra were recorded with Zeiss Jena UR 20 (IR), a Specord UV-VIS (UV) and a Varian A-60A (NMR; TMS as internal standard). Vpc analyses were performed on a Carlo Erba model D; column: Carbowax 20 M (20% on Chromosorb W, 30-60 mesh), 2 m x 4 mm; 178°; H_2 rate flow 80 ml/min.
12. This maximum is consistent with a C=O group included in a seven-membered ring, for the DNPH of the related, perfectly conjugated, benzo[b]bicyclo[3.3.1]nonen-4-one displays a strong absorption at 390 nm (R. Huisgen and G. Seidl, Tetrahedron, 20, 231 (1964)).

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