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FORMYLATION OF β-TETRALONES

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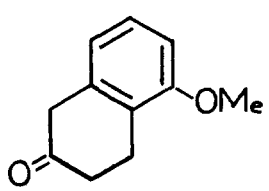
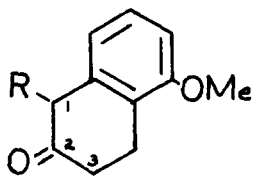
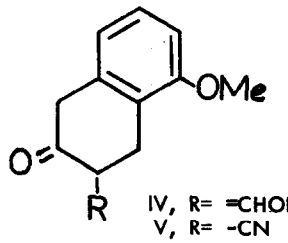
Recently we described a simple method for the preparation of β-tetralone-3-carboxylates[1] using magnesium methyl carbonate.[2,3] In connection with this work we reported the synthesis from 5-methoxy-2-tetralone (I) of a hydroxymethylene derivative and a cyano derivative (via the isoxazole) to which we assigned structures II and III, respectively.[4] This paper reports evidence showing that these compounds are actually 3-substituted β-tetralones of structure IV and V, respectively; therefore, formylation of simple β-tetralones, like carboxylation[1], and oxalylation,[6] occurs preferentially at the 3-position.



I



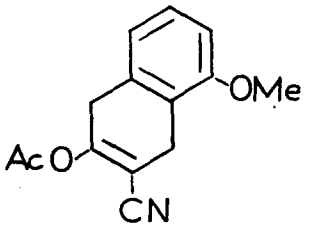
II, R= =CHOH
III, R= -CN



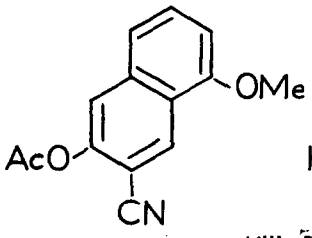
IV, R= =CHOH
V, R= -CN

The structures of the formylation product (IV) and the cyano derivative (V) were demonstrated by conversion of V to the cyanonaphthalene (VII) which was synthesized by an independent route. Treatment of V with acetic anhydride and a trace of p-toluenesulfonic acid gave the enol acetate (VI)[5], m.p. 123-124°, ν max (nujol) 2230 cm.$^{-1}$ (CN), 1760 cm.$^{-1}$ (enol acetate), 1680 cm.$^{-1}$ (C=C); λ max 202 mμ (29,000), 275 mμ (2100), 281 mμ (2400); τ 6.17 (3H-singlet, -OC$\underline{H}_3$), τ 7.72 (3H-singlet, OCOC$\underline{H}_3$), τ 6.37 (4H-triplet, -C$\underline{H}_2$). Conversion of VI to the

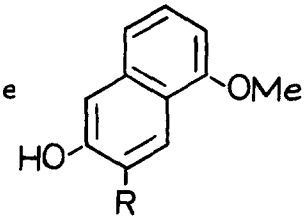
naphthalene derivative (VII) was effected by treatment with selenium dioxide in acetic acid, m.p. 120-121°, ν max (nujol) 2237 cm.$^{-1}$ (-CN), 1764 cm.$^{-1}$ (aromatic acetate); λ max 215 mμ (38,000), 252 mμ (41,000), 290 mμ (2800), 299 mμ (3400), 310 mμ (3000), 352 mμ (5200).



VI



VII

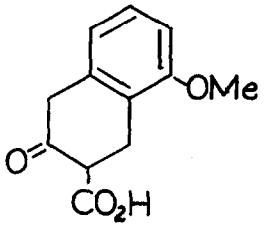


VIII, R= $\overset{|}{\underset{|}{C}}$HOH / CO_2H XI, R= $-CO_2H$

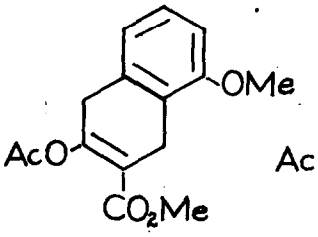
IX, R= $\overset{|}{\underset{|}{C}}$HOH / CH_2OH XII, R= $-CH{=}NOH$

X, R= -CHO

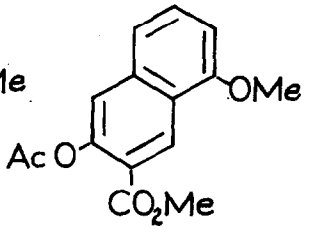
Treatment of I with dimethyl oxalate-sodium methoxide gave the glycolate (VIII)[6], m.p. 126-127°, ν max (nujol) 3570, 3320 cm.$^{-1}$ (OH), 1748 cm.$^{-1}$ ($-CO_2Me$); λ max 222 mμ (49,000), 249 mμ (32,000), 279 mμ (3800), 288 mμ (4300), 298 mμ (3500), 326mμ (1850), 336 mμ (2100). Reduction of VIII with lithium aluminum hydride gave the glycol IX, m.p. 123-124°, ν max (nujol) 3546, 3268 cm.$^{-1}$ (OH), λ max 222 mμ (40,000), 244 mμ (27,000), 248 mμ (26,000), 279 mμ (23,000), 287 mμ (3800), 296 mμ (3200), 318 mμ (1520), 332 mμ (1580). Cleavage of IX with periodic acid gave the aldehyde (X), m.p. 148.5-149.5°, ν max 3300 cm.$^{-1}$ (OH), 1664 cm.$^{-1}$ (-CHO); λ max 233 mμ (30,000), 257 mμ (30,000), 270 mμ (21,000),



XIII



XIV



XV

315 mμ (6900), 323 mμ (7600), 398 mμ (2500). Oxidation of X with silver oxide gave the corresponding acid XI, m.p. 228.5-230.5°, ν max 3300, 1667 cm.$^{-1}$; λ max 227 mμ (34,000), 236 mμ (41,000), 260 mμ (22,000), 292 mμ (4200), 301 mμ (5500), 310 mμ (4500), 368 mμ (2800), identical with a sample prepared from carboxylation product (XIII)[1] via the enol acetate (XIV), m.p. 97.5°, ν max (nujol) 1760 cm.$^{-1}$ (enol acetate), 1712 cm.$^{-1}$ (conj. ester), 1686 cm.$^{-1}$ (C=C); λ max 203 mμ (46,000), 273 mμ (2300), 280 mμ (2300); τ 6.30 (4H-singlet, $2CH_2$-), τ 6.15, 6.20 (3H-singlets, $-OCH_3$ and CO_2CH_3), τ 7.75 (3H-singlet, $-OCOCH_3$) and naphthalene derivative (XV), m.p. 123-124°, ν max 1754, 1730 cm.$^{-1}$; λ max 214 mμ (40,000), 249 mμ (48,000), 288 mμ (4900), 297 mμ (5600), 307 mμ (4600), 347 mμ (6400); τ 6.00, 6.07 (3H-singlets, $-OCH_3$ and $-CO_2CH_3$); τ 7.62 (3H-singlet, $-OCOCH_3$).

Conversion of aldehyde X to the oxime (XII), m.p. 198-200° and dehydration of the latter with acetic anhydride - sodium acetate gave the cyanonaphthalene (VII), m.p. 119-120°, identical with compound prepared from VI by dehydrogenation with selenium dioxide.

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REFERENCES

1. S. W. Pelletier and P. C. Parthasarathy, Tetrahedron Letters, No. 2, 103 (1964).
2. M. Stiles, J. Am. Chem. Soc., 81, 2598 (1959); Ann. N. Y. Acad. Sci., 88, 332 (1960).
3. H. L. Finkbeiner and M. Stiles, J. Amer. Chem. Soc., 85, 616 (1963).
4. Professor Richard Turner has informed us that in repeating this sequence of reactions they have been able to isolate an isomeric isoxazole from the mother liquors which can be converted to 1-methyl-5-methoxy-2-tetralone. This would suggest that either a small amount of the 1-hydroxymethylene derivative is formed when I is treated with ethyl formate or some rearrangement occurs during formation of the isoxazole. Moreover, they have synthesized 1-cyano-5-methoxy-2-tetralone and shown it to be different from our 3-cyanoderivative. We thank Professor Turner for communicating these results to us prior to publication.
5. New compounds reported gave correct analytical values.
6. For an analogous reaction with β-tetralone see: M. D. Soffer, R. A. Stewart and G. L. Smith, J. Amer. Chem. Soc., 78, 1556 (1952).