

OXIDATIONS WITH LEAD TETRAACETATE. I. CYCLIZATION OF KETOCARBOHYDRAZONES
TO 3-KETIMINO- Δ^1 -1,2,4-TRIAZOLIN-3-ONES

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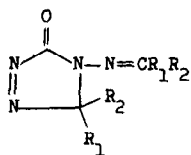
Lead tetraacetate (LTA) in methylene chloride oxidizes some compounds of the type $R_1R_2C=NNHR_3$ to the corresponding azoacetates, $R_1R_2C(OAc)N=NR_3$. The reaction has been reported for N-alkyl and N-aryl ketohydrazones (3), for carbethoxyhydrazones (4), and for acetylhydrazones (5). Even N,N-disubstituted ketohydrazones, $(C_6H_5)_2C=NNR_1R_2$ (6) can give azoacetates, $(C_6H_5)_2C(OAc)N=NR_1$.

Other systems with the structural unit $>C=NNH-$ may form azoacetates as intermediates. For example, N,N-dialkylsemicarbazones are converted to carbamates (7), benzoyl hydrazones yield oxdiazolines (8), and tosylhydrazones are oxidized to the parent ketones (9).

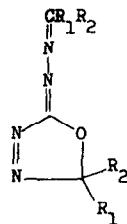
For a study of some aspects of cage-effects in radical processes, we wished to prepare compounds of the type $(R_1R_2C(X)-N=N)_2CO$, I, in which $X = CN$ or $X = OAc$. Oxidation of ketocarbohydrazones $(R_1R_2C=NNH)_2CO$ (10), II, with LTA did not give the anticipated I ($X = OAc$) however, but led instead to a new class of compounds formed by oxidative ring closure.

Treatment of II ($R_1 = R_2 = CH_3$) with twice the molar equivalent of LTA at 0° in CH_2Cl_2 , followed by addition of water, drying and evaporation of CH_2Cl_2 gave a yellow oil, III, which failed to show acetate (5.75, 8.03 μ) or NH stretching absorption in the IR. Similar oxidation with only one equivalent of LTA gave the same material in 76% yield. Rapid distillation

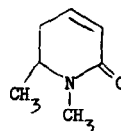
at 89° (5 mm) gave purified material, 62%, as a yellow oil; $n_D^{25} = 1.5124$; λ_{\max} (95% EtOH, log ϵ in brackets) 291 $m\mu$ (3.74); IR (CCl₄) 3.32, 3.40, 5.97, 6.14 sh, 6.63, 6.93 and 6.98 μ ; NMR (CCl₄, rel. to $\tau_{TMS} = 10$, s = singlet, t = triplet, q = quartet, m = multiplet), 8.38 s (6H), 7.99 s (3H), 8.05 s (3H); calc. for C₇H₁₂N₄O: C 49.98, H 7.19, N 33.31, found: C 50.17, 49.22, 49.03, 49.14, H 7.07, 7.32, 7.12, 6.91, N 34.03, 33.11, 33.14, 32.97; m.w. 168, found 168 by vapour pressure osmometry (Mechrolab, model 301A). These data as well as other evidence (vide infra) identify the material as 4-isopropylimino-5,5-dimethyl- Δ^1 -1,2,4-triazolin-3-one (III, R₁=R₂=CH₃).



III



IV



V

Analogous procedures gave, from the appropriate carbohydrazone II:

- (a) 4-sec.-butylimino-5-ethyl-5-methyl- Δ^1 -1,2,4-triazolin-3-one (III, R₁=CH₃, R₂=CH₂CH₂), oil; $n_D^{25} = 1.5062$; λ_{\max} 295 $m\mu$ (3.73); IR (neat) 3.35, 3.40, 3.46, 5.99, 6.11 sh, 6.65 and 6.87 μ ; NMR (CDCl₃)^{*} 9.27 t (3H), 8.90 t (3H), 8.47 s (3H), 8.10 s over 7.72 m (7H); calc. for C₉H₁₆N₄O: C 55.08, H 8.22, N 28.55, found: C 53.79, H 8.14, N 28.92;
- (b) 4-acetophenonimino-5-methyl-5-phenyl- Δ^1 -1,2,4-triazolin-3-one (III, R₁ = CH₃, R₂ = C₆H₅), oil; $n_D^{25} = 1.6260$; λ_{\max} 245 $m\mu$ (3.88), 314 $m\mu$ (3.91); IR (neat) 3.26, 3.40, 3.48,

* Where R₁ ≠ R₂, geometric isomers are possible. Carbohydrazones of unsymmetrical ketones were shown by NMR to be predominantly one isomer (>90%). The expected minor component was not detected in the NMR spectra of the purified triazolinone.

- 6.01, 6.25 weak, 6.41 weak, 6.67 and 6.92 μ ; NMR(CDC1₂)^{*}
 8.05 s (3H), 7.52 s (3H), 2.0-2.6 m (10H); and
- (c) 4-benzophenonimino-5,5-diphenyl- Δ^1 -1,2,4-triazolin-3-one
 (III, R₁ = R₂ = C₆H₅), yellow solid, mp. 112^od; λ_{\max} 252 m μ
 (4.08), 322 m μ (3.96); IR (KBr) 6.02, 8.33, 9.78 13.31 and
 14.44 μ ; NMR (CDC1₂) only 2.2-2.9 m; mass spectrum (strong
 peaks) m/e 360, 332, 283, 194, 180, 165, 152; calc. for
 C₂₇H₂₀N₄O: C 77.86, H 4.84, N 13.45, found: C 78.37, 77.71,
 76.74, H 4.85, 4.38, 5.01, N 13.93, 12.83, 13.49; m.w. 416,
 found 411.

Each of the new compounds appears to be the product of oxidative cyclization. In the infrared, diacetone carbohydrazone absorbs at 2.98 and 3.14 μ (NH) and at 5.88 μ (CO)^{**}. The oxidation product of diacetone carbohydrazone lacks NH absorption and shows absorption at 5.97 μ , attributable to an α,β -unsaturated carbonyl function. In the NMR spectrum (CCl₄) the two methyl singlets at 7.99 and 8.05 τ correspond closely to those of the parent carbohydrazone (7.97 and 8.09 τ , CHCl₃) and the 6H singlet at 8.38 τ indicates that the two other methyl groups have become equivalent. Finally, molecular weight and analytical data are consistent with the loss of 2H in the overall reaction. These data are consistent with a cyclized structure, such as III or IV (R₁ = R₂ = CH₃). Structure IV is unlikely on the basis of the infrared spectra of the new compounds, all of which show a strong band in the region 5.97 - 6.02 μ . This band is expected for the carbonyl group in III, but is probably at too high frequency for a C = N vibration of an

^{**} Neither the carbohydrazones nor their oxidation products have strong absorption near 6.1 μ . Most compounds containing C = N absorb in that region but systematic examination of the spectra of hydrazones indicate that C = N absorption is not observable in this class of compounds (11).

unsaturated azine like IV.† Mass spectral data also support the structural assignment. The first intense peak in the mass spectrum of these compounds is at M-56. This feature is readily explained as due to loss of N₂ and CO from III but it is difficult to accommodate in terms of IV. Further, the mass spectrum of the product in which R₁ = R₂ = C₆H₅ resembles that of benzophenone azine which should be a good model for the M-56 ion from III (R₁ = R₂ = C₆H₅).

Good model systems to which the UV spectra of the triazolones might be referred do not seem to be available. A guide to what might be expected for a Δ^1 -1,2,4-triazolin-3-one is obtained by referring to an α,β -unsaturated lactam. Although α,β -unsaturated amides, C=C-CON have no UV maximum above 210 m μ the lactam V has λ_{\max} 251, log ϵ 3.05 (13). The lactam should be a qualitatively satisfactory model, for it has been shown that 1,2-diazabutadienes retain the intense $\pi-\pi^*$ absorption of conjugated dienes (14). Absorption in III is expected at longer wavelength than that shown by the model V, because of extended conjugation into the side chain. The importance of extended conjugation through amide nitrogen has been amply demonstrated in other systems (15,16). For example, H₂NCON=NCONH₂ has λ_{\max} 240, while C₆H₅NHCON=NCONHC₆H₅ has λ_{\max} 335 m μ (16). Any weak $n-\pi^*$ azo absorption (17) that might be present in the UV of III is probably masked by the stronger $\pi-\pi^*$ band. In III (R₁ = R₂ = alkyl), for example, the band near 290 m μ tails into the visible with $\epsilon > 100$ at 300 m μ . The band at shorter wavelength in each of the phenylated compounds is probably due to the phenyl-conjugated imino chromophore. Benzophenone oxime for example, has

† Conjugated azines generally absorb in the region 6.05-6.5 μ of the infrared (11). Assignment of the 5.97-6.02 μ band to a conjugated CO group finds support from the IR spectra of the products of LTA oxidation of N-substituted ketosemicarbazones, R₂C=NNHCONHR'. In such products, which appear to be analogous to III, there is a strong band at 5.88 μ , which can not be a C=N absorption (12).

λ_{\max} 252 $m\mu$, in good agreement with the value observed for III ($R_1=R_2=C_6H_5$). In alkyl systems the corresponding maximum is probably below 210 $m\mu$ and may be a cause of the strong end absorption observed.

Each new compound reported is readily reduced, either catalytically on Pd/C in EtOH (25°, 50 psi) or by $LiAlH_4$ (2 moles) in ether, to the carbohydrazone(II) from which it was made. Identity of the reduction product was established in each case by comparison of mp and IR spectrum with those of the known carbohydrazone. Yields were 75-85% in the catalytic procedure and 30-50% with $LiAlH_4$, which also caused reduction to the carbonylhydrazide stage (R_1R_2NHNH)₂CO. The course of the hydrogenation constitutes strong evidence that there are no migrations of alkyl or aryl groups in the LTA oxidations of II.

A trace of acid rapidly destroys the compounds which also deteriorate on standing in air or in the light at room temperature, making it difficult to obtain highly pure samples.

Other aspects of the oxidations described here, as well as thermal and photochemical reactions of the triazolinones, are under investigation.

References

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- (2) We are indebted to the Petroleum Research Foundation for support of this work (PRF 1396-A4).
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