## INTRAMOLECULAR REACTIONS OF NITROOLEFIN-β-DIKETONE MICHAEL ADDUCTS FORMATION OF 3-OXO-2,3-DIHYDRO-4*H*-1,2-BENZOXAZINE AND 4(5*H*)-BENZOFURANONE DERIVATIVES

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Abstract—1,3-Cyclohexanedione (3) undergoes Michael addition to  $\beta$ -nitrostyrene in methanolic sodium methoxide to form 3,5-dioxo-4-phenyl-2,3,5,6,7,8-hexahydro-4H-1,2-benzoxazine (5a). With 1-nitro-propene 3 forms the corresponding 4-methyl derivative (5b). These substances had been designated as 4-substituted 5-oxo-5,6,7,8-tetrahydro-4H-1,2-benzoxazine-2-oxides (4a, b) by other workers. 5,5-Dimethyl-1,3-cyclohexanedione (9) under similar conditions adds to  $\beta$ -nitrostyrene to form 2-(2-nitro-1-phenylethyl)-5,5-dimethyl-1,3-cyclohexanedione (10); 9 and 2-nitro-1-phenylpropene yield 3-phenyl-2,6,6-trimethyl-6,7-dihydro-4(5H)-benzofuranone (12). In other reactions various  $\beta$ -diketones add to nitroolefins to yield normal Michael adducts, 4-nitro-1-alkanones (1, 2). Molecular ion fragmentation patterns and mechanisms of formation of the abnormal addition products are presented and their rationalizations discussed.

MICHAEL addition of a variety of β-diketones to nitroolefins usually occurs in a normal manner to yield 1:1 adducts, 4-nitro-1-alkanones (1);<sup>1-6</sup> β-keto esters behave similarly.<sup>4, 7-9</sup> β-Diketones previously employed in these additions include acyclic (RCO)<sub>2</sub>CH<sub>2</sub> + R'CH=C(R'')NO<sub>2</sub> -<sup>B</sup>→ (RCO)<sub>2</sub>CHCH(R')CH(R'')NO<sub>2</sub>

and cyclic types such as acetylacetone, benzoylacetone, dimedon, 1,3-indanedione and 1,3-cyclopentanedione. Reaction of two molecules of nitroolefin with one of  $\beta$ -diketone to yield a bis-adduct, a 1,5-dinitroalkane (2), has been observed with certain nitroolefins lacking a 1-substituent (nitroethylene and 2-aryl-1-nitroethylenes).<sup>4, 10</sup>

> $O_2NCH_2CH(R')C(COR)_2CH(R')CH_2NO_2$ 2

Products other than normal Michael adducts (1, 2) resulting from  $\beta$ -diketones and nitroolefins are described in only one previous report.<sup>10</sup> (1-Halo-1-nitroolefins react with  $\beta$ -diketones and  $\beta$ -keto esters to produce 1:1 Michael adducts or furanone derivatives.<sup>11-16</sup>) Whereas 1,3-cyclohexanedione (3) adds to nitroethylene to give a normal bis-adduct [2,2-bis(2-nitroethyl)-1,3-cyclohexanedione], addition to  $\beta$ -nitrostyrene and 1-nitropropene in methanolic sodium methoxide has been reported to produce crystalline products designated as 4-substituted-5-oxo-5,6,7,8-tetrahydro-4H-1,2-benzoxazine-2-oxides (4a, b).<sup>10</sup>

We have reexamined this reaction and find the products to be 3,5-dioxo-4-substituted-2,3,5,6,7,8-hexahydro-4H-1,2-benzoxazines (**5a**, **b**) (equation 1).

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Attempts to find additional examples of this reaction were unsuccessful. Normal Michael adducts usually resulted, except in the reaction of dimedon with 1-phenyl-2-nitro-1-propene which led to a 4(5H)-benzofuranone derivative.

Support for the cyclic hydroxamic ester structure 5 rests on chemical and spectral evidence. The gross structural features of 5a were established previously by its hydrolysis to 4-oxo-2-phenyloctanedioic acid and hydrogenation to 3-phenyl-4-oxo-2,3,5,6tetrahydroindole.<sup>10</sup> Compounds 5a, b are insoluble in saturated aqueous sodium bicarbonate solution. They decompose rapidly in 10% aqueous potassium hydroxide; acidification of the alkaline solutions usually gave polymeric material. Attempts to prepare derivatives of 5a, b were unsuccessful, owing, in part, to the extreme sensitivity of these compounds to nucleophilic and electrophilic reagents.

Structures **5a**, **b** are in agreement with their spectra. The IR spectrum of **5a** (KBr) reveals strong bands at 1700 (C=O, conjugated), 1640 (C=O, amide) and 3400 cm<sup>-1</sup> (NH); no C=N band is apparent. Absorption maxima appear at 216 ( $\varepsilon$  7720) and 271 mµ ( $\varepsilon$  11,200, ethanol) in the ultraviolet spectrum of **5a**. The NMR spectrum measured in dimethyl sulfoxide- $d_6$  shows an acidic proton at  $\tau$  -0.80 and no vinyl proton. The spectra of **5b** are similar. These data rule out nitronic ester structure **4** and any significant contribution of tautomer **6**. They are in agreement with the known acidic properties and spectra of hydroxamic acid esters.<sup>17</sup>



The mass spectra of 5a, **b** are consistent with the structure assignments (Table 1). The rationalization for the primary fragmentation of the molecular ion involves cleavage of the cyclohexanone ring with loss of cyclopropanone (Scheme 1). Also evident is the loss of hydroxyl followed by hydrogen cyanide in the case of 5b (meta-stable peaks at 148.6 and 114.2; calculated 148.60, 114.44).

It was of interest to compare the mass spectra of 5a, b with that of the only other known six-membered cyclic hydroxamic acid ester, 3-0x0-2,3,4,5-cis-4a,7a-hexa-

2395

 $R = C_6 H_5$ ; m/e 128  $R = CH_3$ ; m/e 66

$\sum_{40}^{+} \frac{1}{76} + \frac{1}{100} + \frac{1}{1$
$b \sum_{40}^{+} \frac{m/e}{\%} \frac{42}{4.5} \frac{55}{5.1} \frac{66}{4.6} \frac{80}{3.2} \frac{94}{3.2} \frac{108}{3.3} \frac{125}{10.7} \frac{137}{1.6} \frac{164}{3.2} \frac{166}{3.2} \frac{181}{7.3} (M^{\bullet})$ $\sum_{40}^{+} \frac{m/e}{\%} \frac{40}{6.6} \frac{66}{77} \frac{77}{78} \frac{79}{78} \frac{80}{79} \frac{81}{81} \frac{107}{122} \frac{122}{138} \frac{139}{139} (M^{\bullet})$
$\sum_{n=1}^{\infty} \frac{m}{e} = 40$ 66 77 78 79 80 81 107 122 138 139 (M*)
$\sum_{40} \frac{1}{6} 2.9  9.5  11.0  3.4  15.4  7.3  5.6  8.5  4.5  0.2  10.2$

TABLE 1. MASS SPECTRA OF CYCLIC HYDROXAMIC ACID ESTERS (3-0X0-2,3-DIHYDRO-4H-1,2-0XAZINES)

SCHEME 1

hydrocyclopent[e]-1,2-oxazine (8), a product of rearrangement of norbornene-5nitronic acid (7).<sup>18,\*</sup>



The fragmentation of the molecular ion of 8 differs from that of 5a, b in that the initial cleavage occurs in the oxazine ring with loss of  $H_2NO \cdot$ ; loss of a hydrogen radical and  $C_2H_3NO$  are also apparent (Scheme 2).

Attempts were made to extend the scope of the reaction of equation (1) by reaction of 1,3-cyclohexanedione, 5,5-dimethyl-1,3-cyclohexanedione (dimedone), 1,3-indanedione, and acetylacetone, each under various conditions, with various conjugated nitroolefins including 1-nitropropene, 1-nitrobutene,  $\beta$ -nitrostyrene, 2-nitro-1-

<sup>\*</sup> We are indebted to Professor W. E. Noland for generously providing us with a sample of 3-oxo-2,3,4,5-cis-4a,7a-hexahydrocyclopent[e]-1,2-oxazine.



phenylpropene and 2-nitro-1-phenyl-1-butene. Nitroethylene has been reported to yield 2-bis-(2-nitroethyl) derivatives with these ketones.<sup>4, 10</sup> With other nitroolefins we find, in agreement with other workers,<sup>1-6, 10</sup> that dimedone and acetylacetone provide normal 4-nitro-1-alkanone 1:1 Michael adducts (1), 1,3-indanedione gives 2:1 adducts (2), and 1,3-cyclohexanedione does not yield normal Michael adducts. No cyclic hydroxamic acid esters other than 5a, b could be isolated as products of these reactions. For example, the addition of dimedone (9) to  $\beta$ -nitrostyrene gave the normal 1:1 Michael adduct 10 which did not cyclize under various reaction conditions.

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array} \rightarrow \begin{array}{c} C_{\kappa}H_{3}CH = CHNO_{2} \\ 9 \end{array} \xrightarrow{NaOCH_{3}} \\ CH_{3}OH \\ CH_{3} \\ CH_{3} \\ \end{array} \xrightarrow{CH(C_{\kappa}H_{3})CH_{2}NO_{2}} \\ 10 \end{array}$$

Exceptional behaviour was exhibited in the addition of dimedon (9) to 2-nitro-1phenylpropene (11). The product obtained in refluxing methanolic sodium methoxide is 3-phenyl-2,6,6-trimethyl-6,7-dihydro-4(5H)-benzofuranone (12); 23% yield (equation 2). Its structure is in agreement with its spectra which are nearly identical with IR,



UV, and NMR spectra reported for 2,6,6-trimethyl-6,7-dihydro-4(5H)-benzofuranone.<sup>19</sup> Its mass spectrum reveals an initial fragmentation of the cyclohexanone ring with loss of isobutylene, and ultimate formation of acetylium ion characteristic of 2-methylfurans (Scheme 3). Attempts to extend the reaction of equation 2 to other nitroolefins were unsuccessful.

Numerous derivatives of 6,6-dimethyl-6,7-dihydro-4(5H)-benzofuranone have been prepared from dimedone.<sup>14–16,19</sup> One synthesis involves a reaction with 2-aryl-1-



bromo-1-nitroethylenes in refluxing benzene containing triethylamine catalysts to yield 3-aryl derivatives (13).<sup>15</sup>

One mechanism for formation of 5a, b would involve intramolecular addition of nitronate oxygen to carbonyl in 14 leading to ketol 15, followed by dehydration to 4. Covalent hydration of C=N in 4, followed by dehydration of the hydrate 16,



yields 6, which tautomerizes to 5. Certain cyclic nitronic esters and many other heteroaromatics are known to undergo facile C—N hydration.<sup>20, 21</sup> Formation of 5 is allowed only when the 3-substituent in 15 is hydrogen. Intramolecular nitronate addition to carbonyl is found in the closely related formation of cyclic nitronic ester 17 from cyclohexanone and 1-phenyl-2-nitropropene (11).<sup>22, 23</sup>



1,3-Cyclohexanedione (3) and 2-nitro-1-phenylpropene (11) failed to produce any isolable crystalline condensation product under various conditions. Also, the normal 1:1 Michael adduct (1) derived from 3 and  $\beta$ -nitrostyrene could not be isolated. Nitronate anion 14 fails to yield isolable C-protonation products and is unstable with respect to reactants nitroolefin and 3 anion, or cyclization product 5.

A mechanism leading to benzofuranone 12 could depart from nitronic acid enolate anion 18, followed by intramolecular addition of enolate anion to C = N and dehydration leading to a nitrosofuran (19). A bright emerald green color which developed



during the reaction could be that of 19. Elimination of nitroxyl, or oxidation of nitroso to nitro followed by nitrous acid elimination, would produce 12. Elimination of nitrous acid from 2-nitro-2,3-dihydro-4(5H)-benzofuranones (precursors of 13) is known to occur with great ease.<sup>11-16</sup>

The stability of the abnormal Michael adducts isolated in the present work undoubtedly facilitates their isolation. The complete scope of these reactions has not been determined but could probably be extended to include other examples. The difference in behaviour exhibited by 1,3-cyclohexanedione (3) and dimedone (9) with respect to products formed by addition to nitroolefins is of interest. It may be a consequence in part, of the existence of adduct anions of 3 principally as ketonitronates (14), and those of 9 as nitronic acid enolates (18). It is known that 2,5,5-trimethyl-1,3cyclohexanedione (p $K_a$  5.6) is a stronger acid than 2-methyl-1,3-cyclohexanedione  $(pK_a 6.5)$ ;<sup>24</sup> alkanenitronic acids have a  $pK_a \cong 5$ .<sup>25</sup> Also, C-protonation of nitronate anions may be considered essentially irreversible in these reactions since nitroalkanes are weak acids  $(pK_a 8-10)$ <sup>25</sup> and the reaction media employed are nearly neutral or weakly acidic. Furthermore, C-protonation of  $\alpha$ -alkylnitronates is much slower than with non-substituted nitronates;  $\alpha, \beta, \beta$ -substituted nitronic acids are relatively stable.<sup>25</sup> Considering these facts it is to be expected that a ketonitronate anion (like 14) is not likely to form from dimedone in high concentration, and the nitronate enolate bisanion of 18 (R' = H) should undergo rapid nitronate C-protonation to 10, rather than cyclize to 5.

## EXPERIMENTAL

Melting points were determined on a Kofler block and are corrected. UV spectra were determined on a Cary Model 11 spectrophotometer (95% ethanol), IR spectra on a Perkin-Elmer Model 137 spectrophotometer, and NMR spectra on a Varian A-60 spectrometer. Mass spectra were determined on a Hitachi model RMU-6E, 80 eV. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

3,5-Dioxo-4-phenyl-2,3,5,6,7,8-hexahydro-4H-1,2-benzoxazine (5a). A solution of 140 g (0.10 mole) of 1,3-cyclohexanedione (Aldrich, in 20% saturated aqueous sodium chloride solution) in 30 ml of methanolic sodium methoxide (prepared from 0.5 g of sodium) was added to 14.9 g (0.10 mole) of  $\beta$ -nitrostyrene dissolved in 30 ml of methanol. A slightly exothermic reaction ensued with the appearance of a reddish color. After standing at 25° for 30 min, the solution was cooled to 5° and filtered to yield 21.5 g (88%) of 5a; the melting point (decomposition) is sharp but varies with the solvent employed in recrystallization and the rate of

heating from 145–147° (ethanol) to 178–180° (acetone), with most values being near 170°; lit<sup>10</sup> 165–167°, methanol; (Found: C, 69·26; H, 5·50; N, 5·76; mol wt, 243. (mass spectra).  $C_{14}H_{13}NO_3$  requires: C, 69·12; H, 5·39; N, 5·76; mol wt, 243·25).

The NMR spectrum determined in acetone- $d_6$  shows a phenyl proton signal centered at  $\tau 2.5$  (m, 5 protons), and complex methylene signals centered at 7.2 (2) and 7.6 (4). An interesting feature is a splitting of the C-4 benzyl proton signal into two triplets of nearly equal intensity centered at  $\tau 4.76$  and  $\tau 5.00$  (J = 2 Hz, 1), apparently due to two slowly interconverting conformers. In dimethyl sulfoxide- $d_6$  this splitting is not apparent and this signal appears as one triplet at  $\tau 4.88$  (J = 1.5 Hz); the long-range coupling of this proton to the C-8 methylene protons produces the triplet; a phenyl singlet appears at  $\tau 2.58$  (5), a multiplet at 7.5 (6), and a singlet acidic protod at  $\tau - 0.80$  (1).

Compound 5a was insoluble in saturated aqueous sodium bicarbonate solution. It dissolved readily in 10% aqueous potassium hydroxide; instantly acidifying the solution with hydrochloric acid (10%) gave an amorphous solid which was recrystallized from ethanol to yield recovered 5a. Acidifying an alkaline solution of 5a after allowing it to stand for 2 min gave an amorphous high-melting solid containing to 5a; no constant elemental analysis could be obtained for this substance which appears to be polymeric. A solution of 10 g of 5a in 20 ml of ethanol and 5 ml of 10% aqueous hydrochloric acid was allowed to stand at 25° for 12 hr; evaporation of the solution produced a black tar from which no crystalline product could be isolated.

Treatment of 5a in benzene solution with benzyl bromide  $(25^\circ, 1 \text{ week})$ , or with 1-naphthyl isocyanate in methylene chloride  $(25^\circ, 3 \text{ days}; 0^\circ, 2 \text{ days})$  gave recovered 5a (80%) and no isolable crystalline product. Reaction of 5a with diazomethane in benzene-ether  $(25^\circ, 3 \text{ days})$  gave a brown oil, unidentified. With bromine in methylene chloride, hydrogen bromide was slowly evolved and a black tar produced. Attempts to prepare a 2,4-dinitrophenylhydrazone (ethanolic hydrochloric acid) or oxime (ethanolic hydroxylamine-pyridine) of 5a gave black tars and no crystalline products.

3,5-Dioxo-4-methyl-2,3,5,6,7,8-hexahydro-4H-1,2-benzoxazine (5b). A procedure similar to that employed for preparation of 5a with 20 g (0·14 mole) of 1,3-cyclohexanedione and 12·0 g (0·18 mole) of 1-nitropropene gave, after 2 days at 0°, 5·5 g (24%) of 5b; m.p. 160–162° (dec) after crystallization from acetone; lit.<sup>10</sup> m.p. 164–166°, dec, methanol; as with 5a the melting point is variable. (Found: C, 59·86; H, 6·25; N, 7·69%; mol wt, 181 (mass spectra); C<sub>9</sub>H<sub>11</sub>NO<sub>3</sub> requires: C, 59·66; H, 6·12; N, 7·73%; mol wt, 181·19). v (KBr) 1720 (C==O, conjugated), 1640 (C==O, amide), and 3390 (NH) cm<sup>1</sup>;  $\lambda_{max}$  218 mµ ( $\varepsilon$  = 3340), 269 ( $\varepsilon$  = 12,200). The NMR spectrum (dimethylsulfoxide-d<sub>6</sub>) showed an acidic proton singlet at  $\tau$  – 1·32 (1), a quartet at 6·02 (J = 7 Hz, 1), multiplet at 7·5 (6), and a methyl doublet at 8·65 (J = 7 Hz, 3).

Attempted reaction of 1,3-cyclohexanedione with 1-phenyl-2-nitropropene. A solution of 5.8 g (0.050 mole) of 1,3-cyclohexanedione and 7.8 g (0.050 mole) of 1-phenyl-2-nitropropene in 50 ml of ethanol containing 1 ml of 10% aqueous potassium hydroxide heated under reflux for 25 min, and allowed to stand at 25° for 4 hr and a 0° for 12 hr, gave unreacted 1-phenyl-2-nitropropene. Repetition of the experiment, but employing a 10 hr reflux time, followed by standing at 0° for 24 hr, again gave unreacted 1-phenyl-2-nitropropene (54% recovery). No other crystalline product could be isolated from the reaction mixtures.

5,5-Dimethyl-2-(2-nitro-1-phenylethyl)-1,3-cyclohexanedione (10). A solution of 7-0 g (0-050 mole) of 5,5dimethyl-1,3-cyclohexanedione in 20 ml of methanolic sodium methoxide (prepared from 0.5 g of sodium) was added to 74 g (0-050 mole) of  $\beta$ -nitrostyrene in 40 ml of methanol. The solution was allowed to stand at 25° for 24 hr and at 0° for 1 week; the solid which precipitated was removed by filtration and recrystallized from acetone to yield 7.9 g (55%) of 10, m.p. 149–150°, dec; the melting point (decomposition) varies with the solvent of recrystallization; m.p. 155–157° from ethanol; lit.<sup>4</sup> m.p. 137·2° from methanol. (Found: C, 66·50; H, 6·58; N, 4·64%; mol wt, 299 (vapor osmometry, benzene); C<sub>16</sub>H<sub>19</sub>NO<sub>4</sub> requires C, 66·42; H, 6·62; N, 4·84%); mol wt, 289·32). v (KBr) 1370, 1540 cm<sup>-1</sup> (NO<sub>2</sub>); broad, strong bands characteristic of enolic 1,3-diketones are found at 1600 and 3100 cm<sup>-1</sup>. The NMR spectrum in dimethyl sulfoxide-d<sub>6</sub> showed a phenyl complex at  $\tau$  2·6 (5 protons), a multiplet at 4·8 (3), ring methylene singlet at 7·70 (4), a methyl singlet singlet at 9·05 (6), and an acidic proton signal at  $\tau$  -0·05 (1, very broad) which disappeared upon addition of D<sub>2</sub>O.

Compound 10 gave a reddish color in ferric chloride solution. It slowly turned reddish brown on storage in air. It is soluble in aqueous sodium bicarbonate solution and precipitates unchanged from this solution upon acidification with aqueous hydrochloric acid.

A solution of 5,5-dimethyl-1,3-cyclohexanedione (10 g) in 30 ml of 10% aqueous potassium hydroxide was added to 10 g of  $\beta$ -nitrostyrene and the mixture heated to produce a dark red-brown solution. After 15 min the solution was acidified by addition of 10 ml of glacial acetic acid; polynitrostyrene and tar, but no crystalline material could be isolated from the reaction mixture. A similar experiment conducted in hexane solvent (100 ml) containing 0.5 ml of diethylamine gave only polynitrostyrene (m.p.  $> 300^{\circ}$ ).

3-Phenyl-2,6,6-trimethyl-6,7-dihydro-4(5H)-benzofuranone (12). A solution of 7-0 g (0.050 mole) of 5,5dimethyl-1,3-cyclohexanedione and 7-5 g (0.050 mole) of 1-phenyl-2-nitropropene in 50 ml of methanolic sodium methoxide (prepared from 0-5 g of sodium) was heated under reflux for 2 hr during which time the color of the solution changed from bright emerald green, to olive green, to red-brown. The solution was cooled and treated with 2 ml of 10% aqueous sodium hydroxide solution and allowed to stand at 25° for 2 days and at 0° for 12 hr. The precipitate which formed was removed by filtration and crystallized from methanol to yield 2-88 g (23%) of furanone 12, m.p. 104–105°. (Found: C, 80-43; H, 7-26%; mol wt, 254 (mass spectra), 260 (vapor osmometry, benzene);  $C_{17}H_{18}O_2$  requires C, 80-28; H, 7-13%; mol wt, 254·31). v (KBr) 1670 (C=O, conjugated), 1050 (ether) cm<sup>-1</sup>;  $\lambda_{max}$  280 mµ ( $\varepsilon$  4350). The NMR spectrum (deuteriochloroform) showed a phenyl singlet at  $\tau$  2-49 (5 protons), methylene singlets at 7-20 (2) and 7-60 (2) and methyl singlets at 7-67 (3) and 8-85 (6).  $\sum_{k=0}^{\infty} 43$  (13-3), 127 (9-3), 170 (10-0), 198 (18-2), 254 (11-1) M<sup>\*</sup>.

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2400