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Formic Acid Reduction. VII.[1] Reduction of Carbon–Carbon Double Bonds adjacent to Carbonyls

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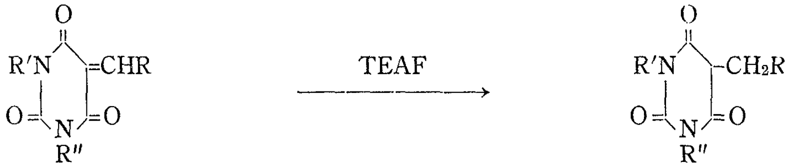
Triethylammonium formate, TEAF given by $5HCOOH\cdot 2N(C_2H_5)_3$ has been introduced as a reagent effective for reduction of carbon–carbon double bond adjacent to carbonyl group, preferably double bond of central methylene carbon of 1,3-diketone. The reduction is selective at the carbon–carbon double bond. Nitro group, carbonyl group and other carbon–carbon double bond such as cinnamyl of substrate are not affected by the reduction.

An improvement in the preparation of substrate compounds, α,β-unsaturated ketones, using boron trioxide as a dehydrating agent, is also given.

Previous papers[3] in this series have reported that the 5-methylidyne bonds attached to barbituric acids are smoothly reduced to the 5-methylene bonds on heating with triethylammonium formate, TEAF.[4]



R=phenyl, *o*-, *m*- or *p*-substituted phenyl, cinnamyl, benzyl
R′ and R″=H or methyl

This reaction involves formic acid reduction of carbon–carbon double bond, which may be refered to as a new type of reaction. Therefor, it was of interest to investigate extensively into the general applicability of this novel reduction.

The reduction appeared proper to such carbon–carbon double bond adjacent to carbonyl group, preferably double bond at central methylene carbon of 1,3-diketone. As substrates for the reduction reaction nine α,β-unsaturated ketones inclusive of four new compounds (see Table II) were prepared from corresponding ketones and aromatic aldehydes, but for a number of these which were not easily available an improvement in their preparations was made on the previously reported method. That is, adaptation of boron trioxide as a dehydrating agent in the reactions was found to be effective for raising the yields. Reaction procedures are that a benzene solution of 1,3-diketone, aldehyde and catalytic amount of piperidine with a suspension of a large excess of boron trioxide is refluxed with stirring. Details are given in Experimental. The results are summarized in Table I. In selected examples, benzoylacetone and 1,3-indandione in the absence of boron trioxide gave no benzylidene products but other reaction products. Of these prepared by the above procedures *p*-methoxy-, *m*-nitro- and *p*-nitro-benzylidene dibenzoylmethanes and cinnamylidenedibenzoylmethane have not been reported previously. They were identified from their analytical and infrared (IR) spectral data.

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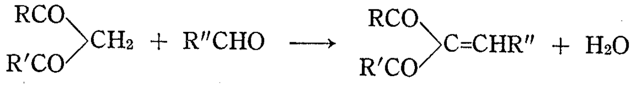
[1] Part VI: M. Sekiya and C. Yanaihara, *Chem. Pharm. Bull.* (Tokyo), **17**, 810 (1969).
[2] Location: *Oshika, Shizuoka.*
[3] M. Sekiya and C. Yanaihara, *Chem. Pharm. Bull.* (Tokyo), **17**, 747 (1969).
[4] Liquid, bp 95° (15 mmHg), given by $5HCOOH\cdot 2N(C_2H_5)_3$ [K. Ito, *Yakugaku Zasshi*, **86**, 1166 (1966)].

Table I. Preparation[a] of 2-Benzylidene- and 2-Cinnamylidene-1,3-diketones



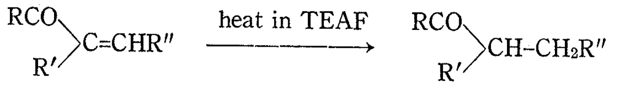
$$\begin{matrix}RCO\\R'CO\end{matrix}\rangle CH_2 + R''CHO \longrightarrow \begin{matrix}RCO\\R'CO\end{matrix}\rangle C{=}CHR'' + H_2O$$

R	R'	R''	Yield (%)
CH_3-	C_6H_5-	C_6H_5-	50
C_6H_5-	C_6H_5-	C_6H_5-	81
C_6H_5-	C_6H_5-	m-NO_2-C_6H_4-	49[b]
C_6H_5-	C_6H_5-	p-NO_2-C_6H_4-	70
C_6H_5-	C_6H_5-	p-$CH_3O{=}C_6H_4$-	75
C_6H_5-	C_6H_5-	C_6H_5-$CH{=}CH$-	56
o-$C_6H_4\langle$		C_6H_5-	90

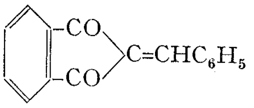
a) 1,3-Diketone, aldehyde and boron trioxide were used in 1:1.1:1.5 molar proportion. A benzene solution of 1,3-diketone, aldehyde and catalytic amount of piperidine with a suspension of boron trioxide was refluxed. Procedures are given in Experimental in details.

b) m-Nitrobenzylideneacetophenone was obtained as side product in 22% yield.

Table II. TEAF Reduction[a] of α,β-Unsaturaturated Ketones

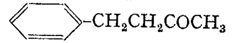


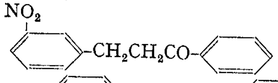
$$\begin{matrix}RCO\\R'\end{matrix}\rangle C{=}CHR'' \xrightarrow{\text{heat in TEAF}} \begin{matrix}RCO\\R'\end{matrix}\rangle CH{-}CH_2R''$$

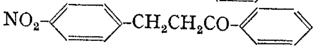
Run No.	Substrate	Reaction Temp(°C)	Reaction Time(hr)	Reaction Yield(%)
1	$\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\rangle C{=}CHC_6H_5$	145—150	3	72
2[b]	$\begin{matrix}CH_3CO\\C_6H_5CO\end{matrix}\rangle C{=}CHC_6H_5$	145—150	3	71
3	$\begin{matrix}C_6H_5CO\\C_6H_5CO\end{matrix}\rangle C{=}CHC_6H_5$	145—150	3	56
4[b]	$\begin{matrix}C_6H_5CO\\C_6H_5CO\end{matrix}\rangle C{=}CHC_6H_4\text{-}m\text{-}NO_2$	145—150	1.5	58
5[b]	$\begin{matrix}C_6H_5CO\\C_6H_5CO\end{matrix}\rangle C{=}CHC_6H_4\text{-}p\text{-}NO_2$	145—150	2	59
6	$\begin{matrix}C_6H_5CO\\C_6H_5CO\end{matrix}\rangle C{=}CHC_6H_4\text{-}p\text{-}OCH_3$	145—150	4	81
7	$\begin{matrix}C_6H_5CO\\C_6H_5CO\end{matrix}\rangle C{=}CH{-}CH{=}CH{-}C_6H_5$	145—150	3	74
8		145—150	0.5	55
9	$\begin{matrix}C_6H_5CO\\C_6H_5\end{matrix}\rangle C{=}CHC_6H_5$	165—170	8	84

a) Solution of substrate in TEAF in 1:12 (as HCOOH) molar proportion was heated. Procedures are given in Experimental in details.

b) In these runs, the following side products were obtained. Yields are given in parentheses.

run 2:  (20 %)

run 4:  (33 %)

run 5:  (40 %)

The α,β-unsaturated ketones thus prepared were then allowed to react with TEAF. In general, the reactions were carried out by means of heating a mixture of substrate and TEAF in 1:12 (as HCOOH) molar proportion in a flask fitted with a long air condenser tube. The reaction temperatures were decided by noting considerable emission of carbon dioxide. The results of the experiments are summarised in Table II. As can be seen from the Table the reductive hydrogenation of the carbon–carbon double bond adjacent to carbonyl was successfully performed with the reagent. That formic acid itself is inert to the reduction was confirmed by a number of selected examples. Consequently a component triethylamine in the reagent appeares as a basic catalyst. A side reaction affording β-phenylmonoketones was observed in the runs with 2-benzylidene-1,3-diketones which is presumably interpreted as acid fission of the reduction products, 2-benzyl-1,3-diketones, initially produced, by the influence of the triethylamine base in the reagent.

Structural requirement for the reaction is noticeable. A benzylidene compound of the monoketone, 2-benzylidenedesoxybenzoin was affected by the reduction at higher temperature as shown in Table II, but benzylideneacetone was inert to the reduction even at refluxing temperature (175—180°).

All the reduction products inclusive of four new compounds were identified mainly by elemental analyses and from their IR spectra.

As can be realized from Table II, the TEAF reduction is selective at the carbon–carbon double bond adjacent to carbonyl. With a variety of substrates, their carbonyl group, nitro group and cinnamyl double bond of the cinnamylidene compound did not suffer the reduction. Evidence for the retention of the cinnamyl double bond of the product, 2-cinnamyldibenzoylmethane was provided mostly by nuclear magnetic resonance (NMR) spectrum analysis, where the methine and methylene protons of $\rangle CH-CH_2-CH=CH-C_6H_5$ appeared respectively as triplet at τ 4.62 and triplet at τ 6.99, and the two protons of $-CH=CH-$ appeared in aromatic region, τ 1.89—2.95. An IR spectrum of the product also gave a band at 961 cm^{-1} suggesting trans relationship of the double bond.

In summary, the TEAF reagent has been known to be effective for selective reduction of such carbon–carbon double bond adjacent to carbonyl, preferably centered between two carbonyls, which is otherwise not easily accessible. The TEAF is easily available, but the known analogous trialkylammonium formates, given by $5HCOOH \cdot 2NR_3$,⁵⁾ would be also effective for the reduction.

Experimental

2-Benzylidene- and 2-Cinnamylidene-1,3-diketones. General Procedure——To a benzene solution of 1,3-diketone (0.02 mole) and piperidine (0.012 mole), suspended with boron trioxide (0.03 mole), aldehyde (0.022 mole) was added in small portions with stirring. The reaction was exothermic. The mixture was refluxed or maintained at appropriate temperature until no aldehyde was detected by Tollens' reagent. After filtration of the warm mixture, the filtrate was concentrated under reduced pressure. To the resulting residue MeOH was added so as to crystallize. After standing overnight, the crystals were filtered and washed. The materials obtained by the above procedures were almost pure without further recrystallization. Reaction conditions, yields and identities of the products are described in the following.

2-Benzylidenebenzoylacetone: Refluxing for 2 hr. Yield, 50%. Needles (from MeOH), mp 98—99°, lit.⁶⁾ mp 98—99°. IR ν_{max}^{KBr} cm^{-1}: 1655, 1689 (C=O), 1619 ($\rangle$C=CH–). UV λ_{max}^{MeOH} mμ (log ε): 257 (4.26), 288 (4.31).

2-Benzylidenedibenzoylmethane: Refluxing for 2 hr. Yield, 81%. Needles (from MeOH), mp 87—88°, lit.⁷⁾ mp 87—88°. IR ν_{max}^{KBr} cm^{-1}: 1652, 1689 (C=O), 1618 ($\rangle$C=CH–). UV λ_{max}^{MeOH} mμ (log ε): 249 (4.26), 335 (3.91). *Anal.* Calcd. for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.31; H, 4.97.

2-*m*-Nitrobenzylidenedibenzoylmethane: Refluxing for 2 hr. Yield, 49%. Pale yellow needles (from MeOH), mp 125°. IR ν_{max}^{KBr} cm^{-1}: 1642, 1663 (C=O), 1611 ($\rangle$C=CH–), 1357, 1533 (NO_2). UV λ_{max}^{MeOH} mμ (log ε): 253 (4.06). *Anal.* Calcd. for $C_{22}H_{15}O_4N$: C, 73.94; H, 4.23; N, 3.92. Found: C, 74.08; H, 4.25; N, 3.67.

2-*p*-Nitrobenzylidenedibenzoylmethane: Standing at room temperature for 3 days. At refluxing temperature, 2,2'-*p*-nitrobenzylidenebisdibenzoylmethane was mainly formed instead. Yield, 70%. Pale yellow needles (from MeOH), mp 94—97°. IR ν_{max}^{KBr} cm^{-1}: 1641, 1675 (C=O), 1618 ($\rangle$C=CH–), 1374, 1519

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5) M. Sekiya and K. Ito, *Chem. Pharm. Bull.* (Tokyo), **12**, 677 (1964).

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(NO_2). UV λ_{max}^{MeOH} mμ (log ε): 249 (4.32), 320 (3.94) (shoulder). *Anal.* Calcd. for $C_{22}H_{15}O_4N$: C, 73.94; H, 4.23; N, 3.92. Found: C, 73.57; H, 4.19; N, 4.08.

2-*p*-Methoxybenzylidenedibenzoylmethane: Refluxing for 4 hr. Yield, 75%. Pale yellow prisms (from MeOH), mp 91—93°. IR ν_{max}^{KBr} cm^{-1}: 1641, 1646 (C=O). UV λ_{max}^{MeOH} mμ (log ε): 248 (4.32), 332 (4.34). NMR (20% solution in $CDCl_3$) τ: 6.33 (3H, singlet, $-OC\underline{H}_3$), 3.35—1.89 (15H, multiplet, aromatic protons and $-C\underline{H}=C<$). *Anal.* Calcd. for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.50; H, 5.28 .

2-Cinnamylidenedibenzoylmethane: Refluxing for 0.5 hr. Yield, 56%. Yellow prisms (from MeOH–benzene), mp 130°. IR ν_{max}^{KBr} cm^{-1}: 1630, 1658 (C=O), 963 (*trans* –CH=CH–). UV λ_{max}^{MeOH} mμ (log ε): 244 (4.37), 255 (4.25) (shoulder), 341 (4.51). *Anal.* Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 84.93; H, 5.32.

2-Benzylidene-1,3-indandione: Refluxing for 0.5 hr. Yield, 90%. Yellow leaflets (from EtOH), mp 150°, lit.[8] mp 153°. IR ν_{max}^{KBr} cm^{-1}: 1690, 1713 (C=O), 1615 (>C=CH–). UV λ_{max}^{MeOH} mμ (log ε): 239 (4.32), 341 (4.58).

Reaction of α,β-Unsaturated Ketones with TEAF. General Procedure——In a flask provided with a thermometer, an inlet tube and an air condenser tube were placed 0.02 mole of α,β-unsaturated ketone and 20.8 g (0.24 mole as HCOOH) of TEAF. The mixture was heated with stirring. A stream of dry air free from CO_2 was introduced, in order to check transfer of emission of CO_2 by $Ba(OH)_2$ solution. In most cases, the temperature was maintained at 145—150° until CO_2 emission was almost ceased. Treatment of the reaction mixture and identities of the products are given in the following.

Reaction of 2-Benzylidenebenzoylacetone: The reaction mixture was concentrated under reduced pressure to remove triethylamine and excess of TEAF. The resulting residue was submitted to distillation under reduced pressure to give 2-benzylbenzoylacetone. bp 136—139° (0.02 mmHg). Yield, 3.6 g (71%). Needles (from MeOH), mp 55—56°, lit.[9] mp 55—56°. IR ν_{max}^{KBr} cm^{-1}: 1690, 1731 (C=O). UV λ_{max}^{MeOH} mμ (log ε): 294 (4.10). *Anal.* Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 81.10; H, 6.13. The foregoing TEAF distillate was diluted with H_2O and excess of KOH was added. The liberated triethylamine layer was separated and dried with $MgSO_4$. After evaporation of triethylamine, the residue was subjected to distillation under reduced pressure to give benzylacetone, which was identified as *p*-nitrophenylhydrazone by noting exact correspondence of its IR spectrum with that of authentic sample. Yield as *p*-nitrophenylhydrazone, 1.1 g (20%). Reddish leaflets (from EtOH), mp 110—112°, which decomposes gradually in air. *Anal.* Calcd. for $C_{16}H_{17}O_2N_3$: C, 67.82; H, 6.05; N, 14.83. Found: C, 67.58; H, 5.99; N, 14.70.

Reaction of 2-Benzylideneacetylacetone: The reaction mixture was processed by the same manner as in the reaction of 2-benzylidenebenzoylacetone. 2-Benzylacetylacetone was obtained as an oily distillate. bp 110° (2 mmHg), lit.[10] bp 110—112° (2 mmHg)). Yield, 2.7 g (72%). IR ν_{max} cm^{-1}: 1700, 1724 (C=O), lit.[10] IR ν_{max}^{KBr} cm^{-1}: 1700, 1725 (C=O)). UV λ_{max}^{MeOH} mμ (log ε): 289 (3.54), lit.[10] UV λ_{max} mμ (log ε): 290 (3.54)). *Anal.* Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.88; H, 7.36.

Reaction of 2-Benzylidenedesoxybenzoin: The reaction mixture was processed by the same manner as in the reaction of 2-benzylidenebenzoylacetone. 2-Benzyldesoxybenzoin was obtained as a solid distillate. bp 190—192° (0.05 mmHg). Needles (from EtOH), mp 114—116°, lit.[11] mp 120—121°. Yield, 4.8 g (84%). IR ν_{max} cm^{-1}: 1674 (C=O). UV λ_{max}^{MeOH} mμ (log ε): 248 (4.13). *Anal.* Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.36. Found: C, 88.13; H, 6.54.

Reaction of 2-*p*-Methoxybenzylidenedibenzoylmethane: The crystalline residue obtained by concentration of the reaction mixture was recrystallized from MeOH. 2-*p*-Methoxybenzyldibenzoylmethane was obtained as scales, mp 95—96°. Yield, 5.7 g (81%). IR ν_{max}^{KBr} cm^{-1}: 1664, 1682 (C=O). UV λ_{max}^{MeOH} mμ (log ε): 228 (4.27), 248 (4.37), 280 (3.65) (shoulder). NMR (20% solution in $CDCl_3$) τ: 7.70 (3H, singlet, $-OC\underline{H}_3$), 7.41 (2H, doublet, $J=7$ cps, $>CH-C\underline{H}_2-$), 5.55 (1H, triplet, $J=7$ cps, $>C\underline{H}-CH_2-$), 4.68—2.00 (14H, multiplet, aromatic protons). *Anal.* Calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.25; H, 5.81.

Reaction of 2-Cinnamylidenedibenzoylmethane: To the concentrated residue of the reaction mixture, MeOH was added for crystallization. After standing overnight, the crystals were collected by filteration and washed with MeOH. The product, 2-cinnamyldibenzoylmethane thus obtained was almost pure without further recrystallization. Yellow prisms (from MeOH–benzene), mp 88—89°. Yield, 5.1 g (74%). IR ν_{max}^{KBr} cm^{-1}: 1674, 1684 (C=O), 961 (*trans* –CH=CH–). UV λ_{max}^{MeOH} mμ (log ε): 250 (4.57), 282 (3.73), 293 (3.52). NMR (10% solution in $CDCl_3$) τ: 6.99 (2H, triplet, $J=7$ cps, $>CH-C\underline{H}_2-CH=CH-$), 4.62 (1H, triplet, $J=7$ cps, $>C\underline{H}-C\underline{H}_2-CH=CH-$), 2.95—1.89 (17H, multiplet, aromatic protons and $-C\underline{H}=C\underline{H}-$). *Anal.*

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10) H.O. House and W.F. Gunon, *J. Org. Chem.*, **23**, 879 (1958).

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Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 85.07; H, 6.04.

Reaction of 2-Benzylidenedibenzoylmethane: This product, 2-benzyldibenzoylmethane, was crystallized in the reaction mixture on cool and collected by filtration. The filtrate was concentrated under reduced pressure to remove triethylamine and excess of TEAF. By addition of MeOH to the resulting residue, additional crystals of 2-benzyldibenzoylmethane were obtained. Needles (from MeOH), mp 104—106°, lit.12) mp 103.5—104°. Yield, 3.5 g (56%). IR ν_{max}^{KBr} cm^{-1}: 1665, 1700 (C=O). UV λ_{max}^{MeOH} mμ (log ε): 248 (4.37), 321 (2.50) (shoulder). *Anal.* Calcd. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.94; H, 5.83.

Reaction of 2-Benzylidene-1,3-indandione: Most of the product, 2-benzyl-1,3-indandione, was crystallized in the reaction mixture on cool and additional crystals were obtained by concentration of the mother liquid. Yellow prisms (from EtOH), mp 97—98°, lit.8a,13) mp 95—97°. Yield, 2.6 g (55%). IR ν_{max}^{KBr} cm^{-1}: 1713, 1745 (C=O). UV λ_{max}^{MeOH} mμ (log ε): 225.5 (4.61), 247.5 (4.07). *Anal.* Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.46; H, 4.92.

Reaction of 2-*p*-Nitrobenzylidenedibenzoylmethane: 2-*p*-Nitrobenzyldibenzoylmehane was crystallized in the reaction mixture on cool, collected by filtration and washed with MeOH. Pale yellow needles (from EtOH), mp 125°. Yield, 4.3 g (59%). IR ν_{max}^{KBr} cm^{-1}: 1665, 1693 (C=O), 1345, 1513 (NO_2). UV λ_{max}^{MeOH} mμ (log ε): 253 (4.43), 279 (4.14) (shoulder). *Anal.* Calcd. for $C_{22}H_{17}O_4N$: C, 73.57; H, 4.77; N, 3.90. Found: C, 73.65; H, 4.88; N, 3.65. The foregoing TEAF filtrate was concentrated under reduced pressure to remove triethylamine and excess of TEAF. MeOH was added to the resulting residue to give crystals, which were shown to be identical with β-(*p*-nitrophenyl)propiophenone. Recrystallization from MeOH gave prisms, mp 96—97°, lit.14) mp 99—100°. Yield, 2.1 g (40%). IR ν_{max}^{KBr} cm^{-1}: 1675 (C=O), 1342, 1510 (NO_2). UV λ_{max}^{MeOH} mμ (log ε): 220 (3.98), 245 (4.20), 276 (4.11). *Anal.* Calcd. for $C_{15}H_{13}O_3N$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.34; H, 5.16; N, 5.28.

Reaction of 2-*m*-Nitrobenzylidenedibenzoylmethane: 2-*m*-Nitrobenzyldibenzoylmethane was crystallized in the reaction mixture on cool, collected by filtration and washed with MeOH. Pale yellow prisms (from MeOH), mp 132—134°. Yield, 4.2 g (58%). IR ν_{max}^{KBr} cm^{-1}: 1673, 1695 (C=O), 1352, 1527 (NO_2). UV λ_{max}^{MeOH} mμ (log ε): 251(4.45), 280 (3.69) (shoulder). *Anal.* Calcd. for $C_{22}H_{17}O_4N$: C, 73.57; H, 4.77; N, 3.90. Found: C, 73.21; H, 4.71; N, 3.75. The foregoing TEAF filtrate was concentrated under reduced pressure to remove triethylamine and excess of TEAF. MeOH was added to the resulting residue to give crystals, which were shown to be identical with β-(*m*-nitrophenyl)propiophenone. Recrystallization from MeOH gave plates, mp 82—84°. Yield, 1.7 g (33%). IR ν_{max}^{KBr} cm^{-1}: 1680 (C=O), 1345, 1529 (NO_2). UV λ_{max}^{MeOH} mμ (log ε): 244 (4.24), 268 (3.95). *Anal.* Calcd. for $C_{15}H_{13}O_3N$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.37; H, 5.23; N, 5.35.

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