Thermolysis of Hexasubstituted-4,5-dihydro-3H-pyrazoles: Synthesis of 1-Alkoxy- and 1-Acetoxy-1,2,2,3,3-pentasubstituted-cyclopropanes

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A series of 5-alkoxy- and 5-acetoxy-4,4-dimethyl-3,3,5-trisubstituted-4,5-dihydro-3H-pyrazoles **2a-f** (hexasubstituted pyrazolines) was synthesized by oxidation of the corresponding 3,4-dihydro-2H-pyrazoles with lead tetraacetate in the appropriate solvents. The 5-acetoxy compounds were produced when the oxidations were carried out in methylene chloride. Oxidation with lead tetraacetate in dry alcoholic solvents resulted in the formation of the 5-alkoxy derivatives as the major products. Thermolysis of the hexasubstituted-4,5-dihydro-3H-pyrazoles **2a-f** in cyclohexane or as the melt at high temperature yielded the 1-alkoxy- and 1-acetoxy-1,2,2,3,3-pentasubstituted cyclopropanes **3a-f** in good yields. Trace amounts of alkene products were formed in several reactions. No products attributable to cycloreversion pathways were detected. The product distributions were consistent with extrusion of nitrogen gas from **2a-f** to yield the singlet 1,3-diradical, closure of which resulted in cyclopropane formation with partial retention of stereochemistry.
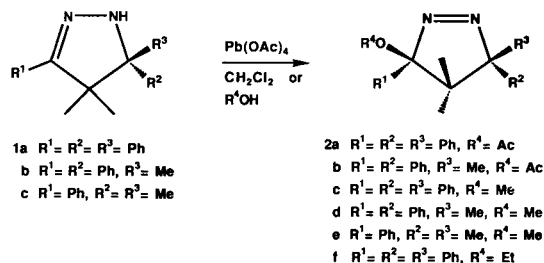
Introduction.

Alkoxy- and acetoxycyclopropanes play an important role in organic synthesis [1]. Cyclopropane synthesis has been accomplished over the years by several methods. The two most common approaches to this class of compounds have been carbene addition to olefins and 1,3-dipolar diazoalkane addition to olefins to yield pyrazolines with subsequent thermal or photochemical extrusion of molecular nitrogen [2]. The generation of carbenes from diazo compounds in the presence of various metal catalysts such as rhodium(II) carboxylates, copper(II) acetylacetonate or copper bronze has been reported, but cyclopropane formation typically does not occur with tetra-substituted olefins [3]. In a similar fashion, disubstituted diazoalkanes do not undergo 1,3-dipolar cycloaddition readily to tetrasubstituted olefins [4]. Both of these methods have been limited generally to the preparation of tetra-or less substituted cyclopropanes. The synthesis of pentaalkyl alkoxy or acetoxy cyclopropanes has been reported in a few special cases [5]. The recent report of the synthesis of hexasubstituted-4,5-dihydro-3H-pyrazoles suggested a general route for the synthesis of highly substituted cyclopropanes [6]. We report here the synthesis of a series of 5-alkoxy- and 5-acetoxy-4,4-dimethyl-3,3,5-trisubstituted-4,5-dihydro-3H-pyrazoles, thermolysis of which produced the corresponding 1-alkoxy- and 1-acetoxy-1,2,3,3-pentasubstituted-cyclopropanes in good yield.

Results.

The synthesis of a series of 5-acetoxy- and 5-alkoxy-4,4-

dimethyl-3,3,5-trisubstituted-4,5-dihydro-3H-pyrazoles **2a-f** was accomplished in 70-80% isolated yields by oxidation of the corresponding 3,4-dihydro-2H-pyrazoles **1a-c** with lead tetraacetate in the appropriate solvents (Reaction 1). The conversion of 3,4-dihydro-2H-pyrazoles **1a** and

1a R¹= R²= R³= Ph
b R¹= R²= Ph, R³= Me
c R¹= Ph, R²= R³= Me

2a R¹= R²= R³= Ph, R⁴= Ac
b R¹= R²= Ph, R³= Me, R⁴= Ac
c R¹= R²= R³= Ph, R⁴= Me
d R¹= R²= Ph, R³= Me, R⁴= Me
e R¹= Ph, R²= R³= Me, R⁴= Me
f R¹= R²= R³= Ph, R⁴= Et

1b to 5-acetoxy-4,5-dihydro-3H-pyrazoles **2a-b** was accomplished by carrying out the oxidation with lead tetraacetate in (dry) methylene chloride at 0° under inert atmosphere [8,9]. It is interesting to note that oxidation of 3,4-dihydro-2H-pyrazole **1b** only yielded product **2b** with the two phenyl groups in a *cis* relationship. The lead tetraacetate procedure was modified by switching the solvent from methylene chloride to dry methanol or absolute ethanol [8,10]. Under these conditions, 5-alkoxy-4,5-dihydro-3H-pyrazoles, **2c-f**, were obtained in good yields. 5-Methoxy-4,5-dihydro-3H-pyrazole **2d** was found to be a single stereoisomer with the phenyl groups *cis* to one another as was determined for 5-acetoxy-4,5-dihydro-3H-pyrazole **2b**. The ¹H nmr spectra of **2b** and **d** showed the signals for one of the 4,4-dimethyl groups to be upfield from that of tetramethylsilane. This indicates that the methyl group must lie between the faces of the two phenyl groups. Small
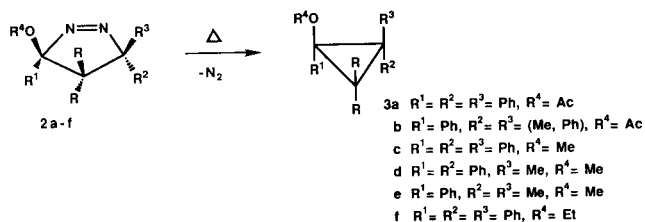
Table 1
Physical and Spectral Data for 4,5-Dihydro-3H-pyrazoles 2a-f

No.	Yield %	Mp (°C)	^{1}H NMR (ppm)	^{13}C NMR (ppm)	MS (70 ev)	IR (cm^{-1})	Analysis Calcd./Found C	H	N
2a	83	168-169	δ 0.01 (s, 3H), 1.27 (s, 3H), 6.97-8.03 (M, 15H), 1.35 (s, 3H)	19.4, 20.7, 24.9, 48.8, 100.0, 113.1, 124.7, 126.2, 126.6, 127.4, 127.9, 128.0, 128.3, 136.2, 142.1, 165.8	385 (M+1) (23% of base at 325) (CI)	1745 (C=O) KBr	76.34 76.21 $C_{25}H_{24}N_2O_2 \cdot 0.5H_2O$	6.36 6.35	
2b	81	182-183	δ-0.26 (s, 3H), 1.40 (s, 3H), 1.70 (s, 3H), 2.03 (s, 3H), 7.33 (br s, 10H)	17.2, 21.8, 24.2, 25.8, 45.5, 97.2, 114.7, 124.2, 125.2, 127.1, 128.1, 128.2, 137.1, 141.9, 166.1	323 (M+1) (28% of base at 263) (CI)	1754 (C=O) KBr	74.50 74.60 $C_{20}H_{22}N_2O_2$	6.88 6.91	8.69 8.68
2c	76	132-133	δ 0.19 (s, 3H), 1.35 (s, 3H), 3.20 (s, 3H), 7.22-8.02 (m, 15H)	19.4, 26.5, 48.3, 52.4, 101.2, 115.1, 126.3, 126.7, 127.0, 127.3, 127.5, 128.2, 128.4, 128.6, 136.7, 141.8, 142.9	357 (+1) (95% of base at 297) (CI)		80.90 80.45 $C_{24}H_{24}N_2O$	6.74 6.82	7.89 7.80
2d	73	98-100	δ-0.35 (s, 3H), 1.25 (s, 3H), 1.75 (s, 3H), 3.45 (s, 3H), 7.3-7.8 (m, 10H)	16.8, 23.7, 26.3, 45.4, 53.2, 97.5, 115.2, 125.3, 127.1, 128.2, 128.3, 137.1, 142.6, 142.9	294 (M/e) (0.1% of base at 105)		77.55 77.57 $C_{19}H_{22}N_2O$	7.48 7.58	9.52 9.46
2e	72	93-96	δ 0.14 (s, 3H), 1.05 (s, 3H), 1.36 (s, 3H), 1.41 (s, 3H), 3.30 (s, 3H), 7.38-7.48 (m, 5H)	16.6, 22.3, 24.1, 24.3, 44.2, 52.9, 92.5, 114.7, 128.1, 128.2, 137.4, 140.7	232 (M/e) (0.1% of base at 105)		72.41 72.46 $C_{14}H_{20}N_2O$	8.62 8.71	12.07 12.00
2f	79	124-125	δ 0.15 (s, 3H), 0.78 (t, J = 7 Hz, 3H), 1.40 (s, 3H), 3.55 (m, 2H), 7.07-8.02 (m, 15H)	15.2, 19.6, 26.4, 48.0, 60.2, 100.9, 114.9, 126.2, 126.6, 126.8, 127.2, 127.3, 127.5, 128.0, 128.1, 128.4, 137.3, 142.1, 143.0	371 (M+1) (49% of base of 297) (CI)		81.08 80.61 $C_{25}H_{26}N_2O$	7.03 6.95	7.57 7.42

quantities of 5-acetoxy-4,5-dihydro-3H-pyrazoles **2a**, and **b** were formed in competition with respective alkoxy derivative formation. The structures **2a-f** were proven by spectroscopic and physical methods. The data are summarized in Table 1.

The preparation of the 3,4-dihydro-2H-pyrazoles **1a-c** was accomplished by addition of organolithium reagents to 3,4,4-trimethyl-5-phenyl-4H-pyrazole and 4,4-dimethyl-3,5-diphenyl-4H-pyrazole [6,7]. The 3,4-dihydro-2H-pyrazoles **1a-c** were kept under inert atmosphere and could be converted, *in situ*, to the corresponding 4,5-dihydro-3H-pyrazoles. The 3,4-dihydro-2H-pyrazoles **1b-c** undergo rapid autoxidation in aprotic solvents to form α-azo hydroperoxides while compound **1a** is relatively oxygen stable.

The thermolysis of the hexasubstituted-4,5-dihydro-3H-pyrazoles **2a-f** under inert atmosphere produced the 1-alkoxy- and 1-acetoxy-1,2,2,3,3-pentasubstituted-cyclopropanes **3a-f** in good yield (Reaction 2). The cyclopropanes

2a-f

3a   R^1= R^2= R^3= Ph, R^4= Ac
b   R^1= Ph, R^2= R^3= (Me, Ph), R^4= Ac
c   R^1= R^2= R^3= Ph, R^4= Me
d   R^1= R^2= Ph, R^3= Me, R^4= Me
e   R^1= Ph, R^2= R^3= Me, R^4= Me
f   R^1= R^2= R^3= Ph, R^4= Et

were isolated in approximately 80% yield. Minor (>2%) quantities of terminal-olefinic products were noted in the thermolysis of **2b, d** and **e** by ^{1}H nmr spectroscopy. No products attributable to cycloreversion processes were detected. Thermolysis of 4,5-dihydro-3H-pyrazole **2b** yielded a mixture of *cis* and *trans* cyclopropanes **3b** (R^2 = Ph, R^3 = Me and R^2 = Me, R^3 = Ph) in a 3:1 ratio respectively. The *cis* relationship of the phenyl groups for the major isomer of **3b** (determined by analysis of the ^{1}H nmr data) corresponded to retention of stereochemistry. Thermolysis of the methoxy analog **2d** resulted in the isolation of a single product **3d** the stereochemistry of which corresponded to retention. The thermolysis of the 4,5-dihydro-3H-pyrazoles was carried out by heating in cyclohexane in a sealed high-pressure tube at 200-220° under inert atmosphere. Alternatively, this reaction could also be done at slightly lower temperatures when the thermolysis is done neat (at temperatures of approximately 180-200°), or toluene at 111° (heated under reflux). Despite the high temperatures involved, all three procedures gave cyclopropane formation in better than 90% yields as determined by ^{1}H nmr spectroscopy. The cyclopropanes were characterized by spectroscopic and physical methods (Experimental).

Discussion.

The present approach allows the synthesis of a wide variety of acetoxy- and alkoxy-pentasubstituted-4,5-dihy-

dro-3*H*-pyrazoles, **2** (Scheme 1). The groups, R, R¹, R² and

Scheme 1
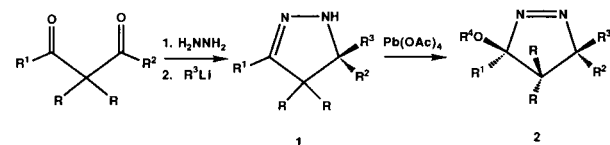
R³, can be alkyl and/or aryl. The oxidation of less-substituted 3,4-dihydro-2*H*-pyrazoles by lead tetraacetate in methylene chloride to yield acetoxy pyrazoline derivatives was well-established [9]. The oxidation of ketone arylhydrazones by lead tetraacetate in alcoholic solvent was reported to yield azoethers [10]. This modification worked well to yield the alkoxy pyrazoline examples **2c-f**. The observation of the acetoxy derivative as minor products in the present examples is consistent with the acyclic results [10].

The lead tetraacetate oxidation of **1b** yielded only compounds **2b** and **2d** in which the 3,5-phenyl groups were *cis*. No *trans* derivatives were detected. This appears to reflect a stereochemical preference and thus may provide little mechanistic insight into the mechanism of oxidation. For example, the autoxidation (free-radical) of **1b** yielded only the α-azo hydroperoxide with the 3,5-phenyl groups *cis* [6]. Similarly, the addition of electrophilic bromine to 4,4-dimethyl-3,5-diphenyl-4*H*-pyrazole in the presence of hydrogen peroxide was reported to yield exclusively the *cis*-3-bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole [11].

The oxidation of the 3,4-dihydro-2*H*-pyrazoles by lead tetraacetate yielded the acetoxy- or alkoxy pyrazoline compounds in 70-80% yields. These yields were superior to those *via* the initial route (Scheme 2) to this type of pyrazoline **2** [6]. Autoxidation of the 3,4-dihydro-2*H*-pyrazoles

Scheme 2
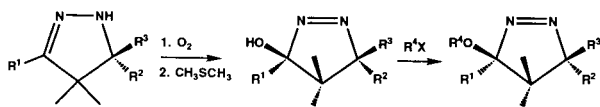
yielded the α-azo hydroperoxides in ~80% yield [6,12]. Reduction with dimethyl sulfide yielded the corresponding α-azo hydroxy compounds in quantitative yield [12]. However, the tertiary hydroxy group of the α-azo alcohols proved difficult to acetylate or alkylate.

The thermal decomposition of azo compounds to produce nitrogen gas and organic free-radicals is well established [13]. The mechanism of 3,5-disubstituted pyrazoline thermolysis has been shown to be complex [14]. The intermediate in this type of thermolysis, a singlet 1,3-diradical, is known to undergo ring closure with a high degree of retention [13,14]. In addition, no cycloreversion products

and only trace amounts of other olefinic products had been found in 3,5-disubstituted pyrazoline thermolysis [13,14]. The present data can be rationalized by a simple diradical mechanism (Scheme 3). Loss of nitrogen from the hexasubstituted pyrazolines would be expected to be rapid since both positions would yield relatively stable radicals. The resulting singlet 1,3-diradical should under-

Scheme 3
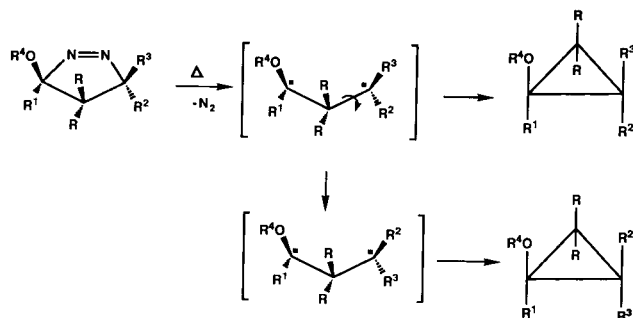
go ring closure preferentially with partial retention of stereochemistry. The formation of both *cis* and *trans* cyclopropanes **3b** during the thermolysis of **2b** is quite reasonable from a mechanistic standpoint. The singlet 1,3-diradical intermediate can undergo intramolecular coupling to the product corresponding to retention of stereochemistry or undergo a bond rotation then coupling to the *trans* product. For thermolysis of pyrazoline **2d**, only one product **3d** was isolated with the phenyl groups in a *cis* relationship. The high degree of retention observed in the present examples is consistent with the results for 3,5-disubstituted pyrazolines [14].

In conclusion, we have developed a general procedure for the preparation of 5-acetoxy- and 5-alkoxy-4,4-dimethyl-3,3,5-trisubstituted-4,5-dihydro-3*H*-pyrazoles. Thermolysis of these hexasubstituted pyrazolines proved to be an excellent method for the synthesis of 1-acetoxy and 5-alkoxy pentasubstituted cyclopropanes.

EXPERIMENTAL

All solvents were commercially available, and of (at least) reagent grade. Methylene chloride (HPLC grade-Fisher) was used without further purification. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. The synthesis of 3,4-dihydro-2*H*-pyrazoles **1a-c** has been reported [6,7]. The ¹H and ¹³C nmr spectra were recorded on a JEOL GX-270 NMR spectrometer. The ir spectra were recorded on a Bomem-Michelson 100-FTIR spectrometer. Melting points were taken in a Thomas Hoover Uni-melt apparatus and are uncorrected. Elemental analyses were performed by Atlanta Microlab, Atlanta, Georgia. All ms data were obtained at the Georgia Institute of Technology.

5-Acetoxy-4,4-dimethyl-3,3,5-trisubstituted-4,5-dihydro-3*H*-pyrazoles 2a-b.

The following procedure for the preparation of **2a** is represen-

tative for the synthesis of 4,5-dihydro-3H-pyrazoles **2a-b**. A 200 mg (0.61 mmole) sample of 3,4-dihydro-2H-pyrazole **1a** was placed in 20-25 ml of methylene chloride under nitrogen at 0°. To this stirred solution was added, all at once, 320 mg (0.72 mmole) of lead tetraacetate. This solution was stirred one hour at 0° then allowed to warm to room temperature over an additional one hour. The crude product was washed with 5% hydrochloric acid and saturated sodium bicarbonate solution. The organic layer was dried with magnesium sulfate and the solvent was removed under reduced pressure. The crude solid was recrystallized from acetone/petroleum ether and yielded 195 mg (0.51 mmole, 83%), **2a**, mp 168-169°. The spectral and physical data for **2a,b** are listed in Table 1.

5-Alkoxy-4,4-dimethyl-3,3,5-trisubstituted-3H-pyrazoles 2c-f.

The following procedure is representative. A 10 ml solution of 3,4-dihydro-2H-pyrazole **1a** (0.489 g, 1.5 mmoles) was added dropwise to 0.93 g (2.1 mmoles) of lead tetraacetate in 10 ml of dry methanol at 0° under a nitrogen atmosphere. This mixture was stirred overnight at room temperature. Methanol was removed under reduced pressure. The residue was mixed with water and extracted with ether (3 x 30 ml). The combined organic layers were washed with 5% hydrochloric acid, water and saturated sodium chloride solution. The organic layer was dried over magnesium sulfate. The solvent was removed under reduced pressure. The crude product was recrystallized from ethanol/water and yielded 0.406 g (76%, **2c**), mp 132-133°. The spectral and physical data for compounds **2c-f** are listed in Table 1.

Thermolysis of 2a-g.

The following procedure is representative. A solution of 100 mg (0.26 mmole) of 4,5-dihydro-3H-pyrazole **2a** in 5-10 ml of cyclohexane was saturated with nitrogen, sealed in a high pressure vessel and heated at approximately 210° for one hour (sand bath). The high pressure vessel was allowed to cool. The solvent was removed under pressure. The crude product was recrystallized from acetone/petroleum ether yielding 77 mg (83%, **3a**), mp 126-127°; ^{1}H nmr (perdeuterioacetone): δ 1.07 (s, 3H), 1.45 (s, 3H), 1.55 (s, 3H), 6.62-7.60 (m, 15H); ^{13}C nmr (deuteriochloroform): δ 21.1, 21.7, 24.9, 32.0, 45.0, 71.4, 125.3, 125.4, 126.8, 127.1, 127.3, 130.2, 130.3, 137.7, 141.0, 141.5, 169.6; ms: M$^+$/e 357 (2% of base at 297); ir (potassium bromide): 1725 cm^{-1}.

Anal. Calcd. for C$_{25}$H$_{24}$O$_2$: C, 84.27; H, 6.74. Found: C, 84.00; H, 6.78.

Cis-1-acetoxy-2,3,3-trimethyl-1,2-diphenylcyclopropane (3b).

The data for *cis*-1-acetoxy-2,3,3-trimethyl-1,2-diphenyl-cyclopropane **3b** are as follows: (an inseparable *cis/trans* mixture) 84% yield; ^{1}H nmr (deuteriochloroform): *cis* isomer δ 1.32 (s, 3H), 1.70 (s, 3H), 1.71 (s, 3H), 2.39 (s, 3H), 7.37-7.96 (m, 10H); ^{1}H nmr (deuteriochloroform): *trans* isomer δ 1.34 (s, 3H), 1.35 (s, 3H), 1.71 (s, 3H), 2.04 (s, 3H), 7.37-7.96 (m, 10H); ms: M$^+$/e 294 (16% of base at 105); ir (neat): 1743 cm^{-1}.

Anal. Calcd. for C$_{10}$H$_{20}$O$_2$: C, 81.63; H, 7.48. Found: C, 81.69; H, 7.55.

1-Methoxy-3,3-dimethyl-1,2,2-triphenylcyclopropane (3c).

The data for 1-methoxy-3,3-dimethyl-1,2,2-triphenylcyclopropane **3c** are as follows: 82% yield; mp 176-177°; ^{1}H nmr (deuteriochloroform): δ 1.47 (s, 3H), 1.57 (s, 3H), 2.98 (s, 3H), 6.95-7.74 (m, 15H); ^{13}C nmr (deuteriochloroform): δ 21.3, 26.3, 31.8, 46.4, 54.9, 73.8, 125.3, 125.4, 127.2, 127.6, 127.8, 127.9, 130.7, 130.9,

131.5, 138.1, 142.5, 142.7; ms: M$^+$/e 328 (64% of base at 135); ir (potassium bromide): 2926 cm^{-1}.

Anal. Calcd. for C$_{24}$H$_{24}$O: C, 87.80; H, 7.32. Found: C, 87.56; H, 7.42.

1-Methoxy-2,3,3-trimethyl-1,2-diphenylcyclopropane (3d).

The data for 1-methoxy-2,3,3-trimethyl-1,2-diphenylcyclopropane **3d** are as follows: 85% yield; ^{1}H nmr (deuteriochloroform): δ 1.01 (s, 3H), 1.42 (s, 3H), 1.54 (s, 3H), 3.23 (s, 3H), 7.15-7.35 (m, 10H); ^{13}C nmr (deuteriochloroform): δ 16.9, 22.0, 24.4, 28.5, 38.0, 55.5, 72.4, 125.5, 126.4, 127.4, 127.8, 130.5, 130.7, 138.6, 141.0, 143.7; ms: M$^+$/e 266 (base); ir (neat): 2742 cm^{-1}.

Anal. Calcd. for C$_{19}$H$_{22}$O: C, 85.71; H, 8.27. Found: C, 85.53; H, 8.34.

1-Methoxy-2,2,3,3-tetramethyl-1-phenylcyclopropane (3e).

The data for 1-methoxy-2,2,3,3-tetramethyl-1-phenylcyclopropane **3e** are as follows: 82% yield; ^{1}H nmr (deuteriochloroform): δ 1.06 (s, 6H), 1.36 (s, 6H), 3.16 (s, 3H), 7.41-7.43 (br s, 5H); ^{13}C nmr (deuteriochloroform): δ 16.8, 21.2, 25.5, 54.9, 72.3, 127.2, 127.8, 132.2, 136.1; ms: M$^+$/e 204 (base); ir (neat): 2931 cm^{-1}.

Anal. Calcd. for C$_{14}$H$_{20}$O·1/3H$_2$O: C, 79.93; H, 9.60. Found: C, 79.63; H, 9.61.

1-Ethoxy-3,3-dimethyl-1,2,2-triphenylcyclopropane (3f).

The data for 1-ethoxy-3,3-dimethyl-1,2,2-triphenylcyclopropane **3f** are as follows: 88% yield; mp 128-130°; ^{1}H nmr (deuteriochloroform): δ 0.90 (t, 3H, J = 0.02 Hz), 1.44 (s, 3H), 1.60 (s, 3H), 3.16 (m, 2H), 6.90-7.75 (m, 15H); ^{13}C nmr (deuteriochloroform): δ 15.1, 21.5, 26.3, 31.9, 46.1, 62.5, 73.0, 125.1, 125.2, 127.0, 127.5, 127.6, 130.9, 131.1, 131.4, 138.8, 142.6, 142.8; ms: M$^+$/e 342 (38% of base at 105); ir (potassium bromide): 2929 cm^{-1}.

Anal. Calcd. for C$_{25}$H$_{26}$O: C, 87.72; H, 7.60. Found: C, 87.67; H, 7.66.

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