Thermal Decomposition of 3,3,5-Trisubstituted-4,4-dimethyl-4,5-dihydro-5-hydroperoxy-3*H*-pyrazoles: Route to β,γ-Unsaturated Ketones

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The thermal decomposition of a series of cyclic α-azo hydroperoxides (3,3,5-R_1, R_2, R_3-4,4-dimethyl-4,5-dihydro-5-hydroperoxy-3*H*-pyrazoles; **2a** $R_1 = R_2 = R_3$ = Ph; **2b** $R_1 = R_3$ = Ph, R_2 = Me; **2c** $R_1 = R_3$ = *p*-Anisyl, R_2 = Me; **2d** $R_1 = R_2$ = Me, R_3 = Ph; **2e** $R_1 = R_3$ = Me, R_2 = Ph), synthesized by oxidation of the corresponding 3,4-dihydro-2*H*-pyrazoles, proceeded smoothly with evolution of nitrogen. The relative stability series was found to be **2a** > **2c** ≈ **2b** > **2d** > **2e**. For **2a**, the products were 1,4,4-triphenyl-2,2-dimethyl-1-propanone and 1,1-dimethyl-2,2-diphenylethylene. For **2b-e**, β,γ-unsaturated ketones [R_1-C(=CH_2)-CMe_2-C(=O)R_3, **5a-d**] were obtained as the major products in ~60% yield from the thermolyses. The products are consistent with a free-radical mechanism involving initial homolysis of the O-O bond followed by loss of nitrogen to yield a free-radical *beta* to the carbonyl group. For **2a**, β-scission and hydrogen-atom abstraction of the hydroperoxy proton by the β-keto radical (induced decomposition) are the major pathways leading to products. For **2b-c**, abstraction of a γ-hydrogen atom of the β-keto radicals by hydroxy radical accounts for the formation of the β,γ-unsaturated compounds as the major product.

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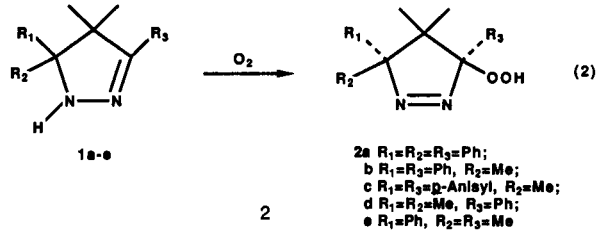
α-Azo hydroperoxides are an extremely reactive class of organic hydroperoxides in electrophilic oxygen-atom transfer chemistry [1] (reaction 1). In addition, α-azo hydroperoxides undergo homolytic cleavage [2] of the peroxy bond readily. For example, the thermal decomposition of acyclic α-azo hydroperoxides has been shown to be an

$$R_2C(OOH)\text{-}N{=}N\text{-}R + :X \longrightarrow R_2C(OH)\text{-}N{=}N\text{-}R + O{=}X \qquad (1)$$

excellent method for the formation of hydroxy radicals [2,3]. Although many acyclic α-azo hydroperoxides have been reported [2,3,4], only three cyclic [5] examples are known. While cyclic compounds have been shown to be approximately two orders of magnitude more reactive [1,5b] than acyclic analogs [4,6] in electrophilic oxygen-atom transfer reactions, no studies of their thermolytic properties have been carried out. We report here the results of the thermal decomposition of a series of cyclic α-azo hydroperoxides which show that the reaction proceeds *via* generation of β-keto radical intermediates.

Results.

Cyclic α-azo hydroperoxides **2a-e**, 3,3,5-trisubstituted-4,4-dimethyl-4,5-dihydro-5-hydroperoxy-3*H*-pyrazoles, were synthesized by autoxidation or photooxidation (at low temperature) of the corresponding 3,4-dihydro-2*H*-pyrazoles **1a-e** in good yield (reaction 2). α-Azo hydroperoxide **2a** was synthesized in good yield by photooxidation



(2)

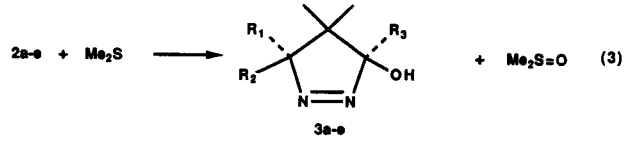
1a-e

2a R_1=R_2=R_3=Ph;
b R_1=R_3=Ph, R_2=Me;
c R_1=R_3=*p*-Anisyl, R_2=Me;
d R_1=R_2=Me, R_3=Ph;
e R_1=Ph, R_2=R_3=Me

2

of **1a** since **1a** proved to be inert to oxygen under free-radical conditions. Compounds **2b-c** were prepared readily by autoxidation of **1b-c** in acetone at 0° in the dark. Compounds **2a-c** were isolated by crystallization (**Caution!**) from acetone in good yield (~80%). Autoxidation of **1d-e** was rapid in acetone at −20°. However, compounds **2d-e** could not be isolated without decomposition. At −20°, **2d-e** were stable, in solution (acetone), for approximately 30 to 60 minutes after which degradation was rapid. Since α-azo hydroperoxides are explosive, the structures were proven by spectroscopic methods for **2a-c** and/or by conversion (for **2a-e**) to the thermal, stable reduction products **3a-e**.

α-Azo hydroxides **3a-e** (reaction 3), obtained by reduction of **2a-e** with dimethyl sulfide with concomitant formation of dimethyl sulfoxide, were isolated in moderate yields



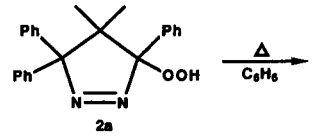
(3)

3a-e

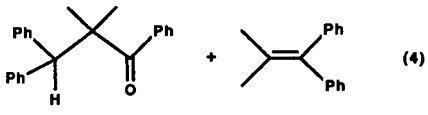
and characterized completely by physical and spectroscopic methods. The stereochemical relationship of R_1 and R_3 in **3b-c** was found to be *cis*, showing that the aryl groups in **2b-c** (see reaction 2) are *cis*, exclusively. The reduction of **2e** yielded **3e** with R_1 and R_3 *cis* in ~80% yield (60% isolated) as well as ~20% of the corresponding *trans* isomer; indicating that **2e** is a 80/20 mixture of the *cis* and *trans* α-azo hydroperoxides.

α-Azo hydroperoxide **2a** proved to be the most stable compound of the series. Thermal decomposition of **2a** in benzene was sluggish, requiring prolonged heating and yielded 1,4,4-triphenyl-2,2-dimethyl-1-propanone **4** in 85% yield as well as a minor amount of 1,1-dimethyl-2,2-diphen-

ylethylene (10%) (reaction 4). Benzoic acid (9%) was identified as an additional, minor product of this reaction. Trace amounts of 2,2-dimethyl-3,3-diphenyl-1-indanone were produced in reaction 4. The thermolysis of **2b-e**



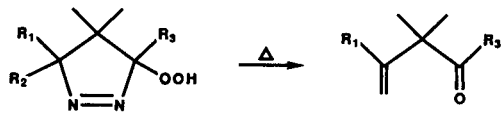
2a



(4)

4

proceeded smoothly under milder conditions (ambient temperature) with noticeable evolution of a gas (nitrogen). The major products produced by the thermal decomposition of **2b-e** were the corresponding β,γ-unsaturated ketones **5a-d** (reaction 5). Compounds **5a-d** were isolated in



(5)

2b-e

5a R_1=R_3=Ph
b R_1=R_3=p-Anisyl
c R_1=Me, R_3=Ph
d R_1=Ph, R_3=Me

approximately 60% yields when the thermolysis were carried out under "inert" conditions and at elevated temperature. Thermolysis, carried out in the presence of oxygen, produced the β,γ-unsaturated ketones in substantially lower yields (35-40%) as well as additional side products. The physical and spectral data for **5a-d** are summarized in Table 1.

The thermolysis of **2b-e** produced a number of minor (side) products, the yields of which were dependent on the conditions. For **2b,d**, the corresponding 2,2,3-trimethyl-3-R_1-1-indanones (**6a** R_1 = Ph and **6b** R_1 = Me) were the major side products and were isolated in 15-7% yields. Minor quantities of saturated ketones [R_1R_2CH-CMe_2-COR_3] were noted in several of the thermolyses. For the decomposition of **2d**, a β-hydroxyketone [1-phenyl-2,3,3-trimethyl-3-hydroxy-1-butanone] was isolated as a minor thermolysis product.

Discussion.

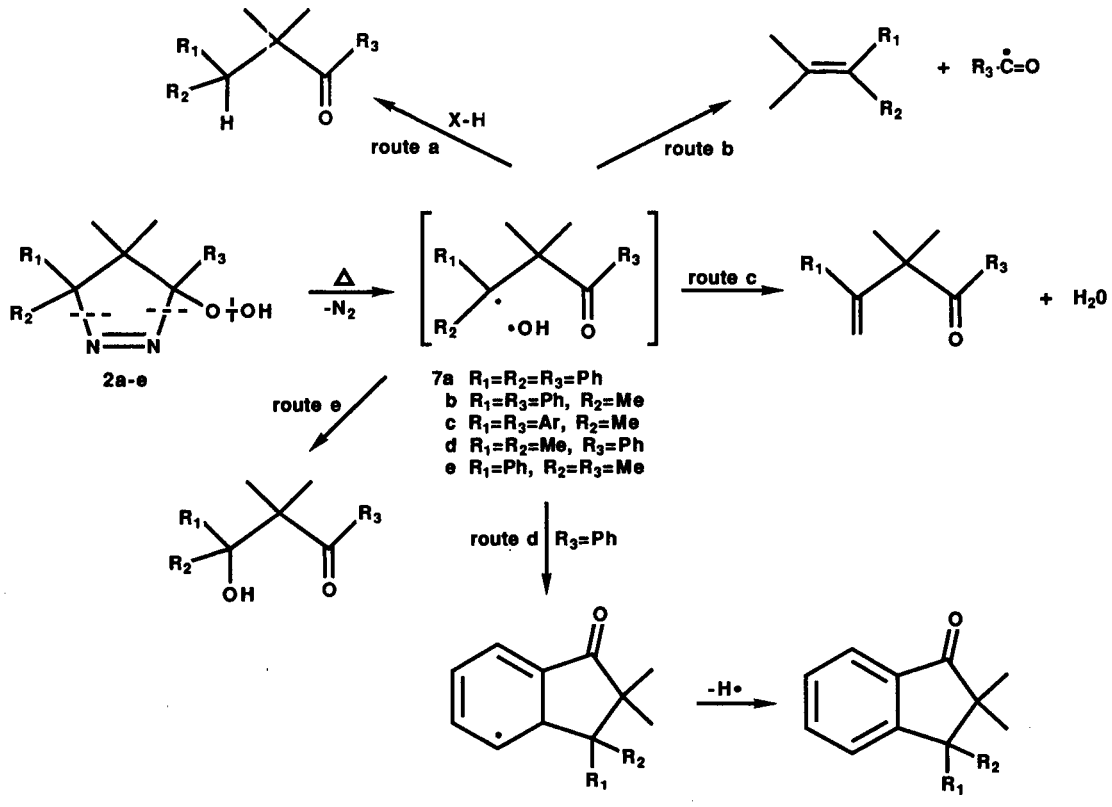
Acyclic α-azo hydroperoxides could be considered [2] to undergo thermolysis to generate hydroxy and α-azo alkoxy radicals (reaction 6). Subsequent fragmentation of the α-azo alkoxy radicals would yield nitrogen, carbonyl fragments and additional radicals (reaction 7). However, since three bonds in the α-azo hydroperoxides are labile (peroxy bond and two azo carbon-nitrogen bonds), the homolytic

Table 1. Physical Data for β, γ-Unsaturated Ketones **4a-d** [$R_1C(=CH_2)$-CMe_2COR_3]

#	R_1	R_3	% Yield	mp° C	^{1}H NMR (ppm)[a]	^{13}C NMR (ppm)[a]	MS(70eV)	IR (cm^{-1})	Analysis Calcd.	Found
4a	Ph	Ph	65	oil	1.48 (s, 6H), 5.33 (s, 1H), 5.45 (s, 1H),7.20-7.60 (m, 8H), 7.95-8.20 (m, 2H)	27.6, 52.9, 115.4, 127.4, 128.1, 129.5, 129.7, 132.0, 137.1, 141.3, 154.6, 203.4	250 (m^+/e) 5.0% of base at 105	1677 (C=0) neat	C: 86.36 H: 7.25 $C_{18}H_{18}O$	C: 86.46 H: 7.30
4b	p-Anisyl	p-Anisyl	63	105.5 -107	1.49 (s, 6H), 3.74 (s, 3H), 3.82 (s, 3H), 5.29 (s, 1H), 5.41 (s, 1H) 6.72-6.84 (m, 4H), 7.09-7.13 (m, 2H), 8.07-8.11 (m, 2H)	28.0, 52.8, 55.3, 55.5, 113.3, 113.5, 113.8, 129.1, 129.7, 132.1, 133.8, 154.6, 158.9, 162.7, 201.7	310 (m^+/e) 4.8% of base at 135	1659 (C=0) KBr	C: 75.20 H: 6.94 $C_{20}H_{22}O_3 \cdot \frac{1}{2} H_2O$	C: 75.22 H: 6.91
4c	Me	Ph	61	oil	1.39 (s, 6H), 1.73 (m, 3H), 5.00 (m, 1H), 5.10 (m, 1H), 7.33 (m, 2H), 7.41 (m, 1H), 7.98 (m, 2H)	20.4, 26.0, 52.9, 100.7, 128.1, 128.4, 132.0, 136.9, 149.7, 203.8	188 (m^+/e) 4.2% of base at 105	1679 (C=0) neat	C: 82.93 H: 8.57 $C_{13}H_{16}O$	C: 82.74 H: 8.52
4d	Ph	Me	59	oil	1.29 (s, 6H), 2.18 (s, 3H), 5.31 (s, 1H), 5.36 (s, 1H), 7.12 (m, 2H), 7.26 (m, 3H)	24.9, 25.3, 53.8, 115.7, 127.3, 127.5, 128.0, 141.3, 153.3, 211.5	188 (m^+/e) 1.3% of base at 145	1708 (C=0) neat	C: 82.93 H: 8.57 $C_{13}H_{16}O$	C: 82.81 H: 8.61

[a] $CDCl_3$

Scheme 1



decomposition could proceed *via* one-bond (reaction 6), two-bond or three-bond cleavage routes as rate-determining steps. Kinetic data [7] have been interpreted [2] to suggest simultaneous cleavage of, at least, the peroxy bond and one carbon-nitrogen bond for acyclic cases. Thus the rate-determining step for acyclic α-azo hydroperoxide thermolysis might be considered to be a composite of reactions 6 and 7. The same basic processes are involved in thermolysis of the cyclic α-azo hydroperoxides, **2a-e**.

$$R_2C(OOH)\text{-}N{=}N\text{-}R' \xrightarrow{\Delta} R_2C(O\bullet)\text{-}N{=}N\text{-}R' + \bullet OH \quad (6)$$

$$R_2C(O\bullet)\text{-}N{=}N\text{-}R' \longrightarrow R_2CO + N_2 + \bullet R' \quad (7)$$

However, in the cyclic cases, formal fragmentation of the "α-azo alkoxy radicals" by loss of nitrogen will yield β-keto radicals **7a-e** as intermediates. The fate of the β-keto radicals should depend on their relative reactivity and stability. Five major reaction pathways [a) hydrogen-atom abstraction; b) β-scission; c) abstraction (loss) of a γ-hydrogen atom; d) ring-closure; and e) radical recombination], available to intermediates **7a-e** are shown in Scheme 1.

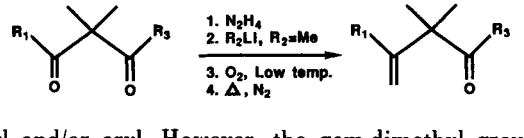
The product distribution for each thermolysis can be rationalized by considering the reactivity and stability of the β-keto radical. α-Azo hydroperoxide **2a**, the most stable compound of the series, is of reasonable thermal stability. The β-keto radical **7a** should also be the most stable intermediate of the series since the radical is stabilized by two phenyl groups. The isolation of **4** as the major product for thermolysis of **2a** shows that the major reaction of **7a** is hydrogen-atom abstraction (route a, Scheme 1). Since the reaction was carried out in benzene, the major hydrogen-atom source appears to be the α-azo hydroperoxide starting material. This will yield the saturated ketone **4** and the peroxy radical of **2a** as products. This process is equivalent to induced decomposition of **2a** since combination of two peroxy radicals would result in the formation of oxygen and two resultant α-azo alkoxy radicals which will regenerate **7a** by loss of nitrogen. β-Scission of **7a** (route b) would account for the formation of the alkene found in reaction 4. The $R_3\dot{C}{=}O$ fragment should eventually lead to the formation of benzoic acid under the reaction conditions, in agreement with the observed results. Apparently, ring-closure of radical **7a** (route c, Scheme 1) is slow since only minor amounts of α-indanone-type product were observed.

For α-azo hydroperoxides **2b-e**, the resultant β-keto radicals **7b-e** are much less stable than **7a** since one or two methyl groups formally replace the phenyl groups attached to the radical. The formation of β,γ-unsaturated ketones **5a-d** (reaction 5) shows that abstraction of a γ-hydrogen (route c, Scheme 1) from **7b-e** (presumably by the hydroxy radical to yield water) is the dominant process. Ring

closure (route d, Scheme 1) by intramolecular attack on R_3 = Ph by reactive radical **7b-d** would account for the presence of the α-indanone products. In addition, for the least stable radical, **7e**, of the series, a radical combination product (route e, Scheme 1) was observed. No β-scission products were observed in reactions in which **7b-e** were generated. This (presumably) is due to the greater reactivity of these radicals as well as the lower stability of the alkenes that would have been generated.

The relative stability series for α-azo hydroperoxides was found to be: **2a** > **2c** ≈ **2b** > **2d** > **2e**. The least stable cyclic α-azo hydroperoxide was that with an α-methyl group (R_3). This is consistent with results for acyclic compounds [6,8]. Acyclic α-aryl α-azo hydroperoxides are more stable than the alkyl analogs. The relative stability series shows that additional phenyl groups (*vs* methyl groups) increase the stability of the compound. This seems to suggest that one-bond scisson may be the rate-determining step for the cyclic cases.

Synthetic routes to β,γ-unsaturated ketones are limited. Compounds with R_3 = Me have been made by Friedal-Crafts acylation of alkenes [9]. Compound **4c** has been reported previously [10] as a product of a photochemical reaction of benzoic acid and 2,3-dimethyl-2-butene. The α-azo hydroperoxide route compares favorably with these processes. Since the precursors to the cyclic α-azo hydroperoxides are 1,3-diketones, the thermolysis of compounds with R_2 = Me is equivalent formally to a Wittig reaction on a 1,3-diketone (reaction 8). R_1 and R_3 groups may be



alkyl and/or aryl. However, the gem-dimethyl groups or the equivalent are necessary for the synthesis of the α-azo hydroperoxide. The overall yield of this process from the 1,3-diketones is 40% (isolated). Although of limited scope, this sequence is a good general route to this type of β,γ-unsaturated ketone.

In conclusion, the thermal decomposition of cyclic α-azo hydroperoxides proceeds *via* a free-radical mechanism. β-Keto radicals are produced as intermediates in this process. The relative product distribution depends on the structure and relative stability of the β-keto radical intermediates.

EXPERIMENTAL

All solvents were of reagent grade. Acetone (HPLC grade-Fisher) was used without further purification. Benzene was distilled, from over calcium hydride, before use. The synthesis of the 3,4-dihydro-2*H*-pyrazoles **1a-e** has been reported [11]. The synthetic route to cyclic α-azo hydroperoxides **2b-c** has been published [5b]. The ^1H and ^{13}C nmr spectra were recorded on a JEOL GX-270 NMR spectrometer. IR spectra were recorded on a Bomem-Michelson 100-FT-IR spectrometer. Melting points were taken in a Thomas Hoover Uni-melt apparatus and are uncorrected. Combustion analyses were performed by Atlanta Microlabs, Atlanta, Georgia. The ms data were obtained at the Georgia Institute of Technology.

3,3,5-Triphenyl-4,4-dimethyl-4,5-dihydro-5-hydroperoxy-3*H*-pyrazole **2a**.

Photooxygenation of 1.0 g (3.1 mmoles) 3,4-dihydro-2*H*-pyrazole **1a** in 15 ml of acetone with polymer-bound Rose Bengal (Polysciences, Inc.) at low temperature (ice bath) was complete within 2-3 hours. The solution was filtered to remove the sensitizer, concentrated and cooled to −78° to afford the α-azo hydroperoxide as a crystalline solid. Recrystallization from acetone at −78° yielded 0.80 g (2.2 mmoles, 73% yield) of **2a**, mp 91-93° dec with detonation; ^1H nmr (acetone-d_6): δ 0.25 (s, 3H), 1.32 (s, 3H), 7.17-7.67 (m, 13H), 8.05-8.20 (m, 2H); ^{13}C nmr (acetone-d_6): δ 19.3, 27.3, 48.8, 101.65, 118.9, 127.0, 127.2, 127.4, 127.9, 128.2, 128.5, 128.6, 128.7, 128.9, 137.8, 141.6, 143.2. Due to the explosive properties of α-azo hydroperoxides, the final structure proof was carried out on the reduction product **3a**.

3,3,5-Trisubstituted-4,4-dimethyl-5-hydroxy-3*H*-pyrazoles **3a-e**.

The following procedure for reduction of α-azo hydroperoxide **2a** is representative for the synthesis of **3a-e**. An excess (100 μl) of dimethyl sulfide was added to 0.100 g (~0.3 mmole) of **2a** in 5 ml of acetone (ice bath, −78° for **2b-e**). After several minutes, the volatile components were removed under reduced pressure. An ^1H nmr spectrum was taken after addition of an internal standard to determine the yield of dimethylsulfoxide. The sulfoxide yield was within experimental error of that of the α-azo hydroxide (in all cases). The α-azo hydroxide was recrystallized from acetone at −30° to yield 0.089 g (0.26 mmole, 93% **3a**), mp 156.5-158°; ^1H nmr (acetone-d_6): δ 0.23 (s, 3H), 1.41 (s, 3H), 5.76 (s, 1H), 7.13-7.54 (m, 13H), 8.06 (d, J = 7 Hz, 2H); ^{13}C nmr (acetone-d_6): δ 19.8, 26.9, 46.8, 100.2, 112.2, 125.7, 126.5, 126.7, 127.0, 127.4, 127.7, 127.8, 127.9, 128.4, 139.2, 141.1, 142.1; ms: M^+/e = 342 (0.36% of base at 167), Cl 343 (M^+ + 1, 100%).

Anal. Calcd. for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.48; N, 8.18. Found: C, 80.58; H, 6.51; N, 8.13.

The data for **3b-c** have been reported [5b]. The data for **3d** are, mp 140-142°; ^1H nmr (deuteriochloroform): δ 0.23 (s, 3H), 1.10 (s, 3H), 1.31 (s, 3H), 1.38 (s, 3H), 3.35 (br s, 1H), 7.37 (m, 3H), 747 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 16.8, 21.3, 24.3, 24.5, 43.1, 92.2, 111.6, 125.8, 128.1, 128.5, 140.8: ms: Cl-219 (M^+ + 1).

Anal Calcd. for $C_{13}H_{16}N_2O$: C, 71.53; H, 8.31; N, 12.83. Found: C, 71.46; H, 8.34; N, 12.79.

The data for **3e** are, mp 143-145° dec; ^1H nmr (deuteriochloroform): δ 0.24 (s, 3H), 1.20 (s, 3H), 1.62 (s, 3H), 1.66 (s, 3H), 3.86 (br s, 1H), 7.33 (m, 5H); ^{13}C nmr (deuteriochloroform): δ 17.7, 22.5, 24.2, 24.7, 43.1, 96.9, 111.9, 125.6, 127.2, 128.3, 142.9; ms: M^+/e = 218 (105 base), Cl-219 (M^+ + 1).

Anal. Calcd. for $C_{13}H_{16}N_2O$; C, 71.53; H, 8.31; N, 12.83. Found: C, 71.40; H, 8.31; N, 12.92.

Thermolysis of **2a-e**.

The following procedure is representative: a solution of 250 mg of α-azo hydroperoxide in 5 ml of acetone or benzene (benzene for **2a**) at room temperature (in the dark, inert atmosphere) was allowed to decompose until evolution of nitrogen ceased (~1

hour or less for **2b-e**, 17 hours at 60° for **2a**). The solvent was removed under reduced pressure. The ^{1}H nmr spectrum was recorded to confirm complete loss of α-azo hydroperoxide and the presence of the "reaction products" before isolation. The residue was passed through a chromatotron (silica gel, petroleum ether/diethyl ether as eluent) and fractions collected. The solvent was removed under reduced pressure. Fractions that contained the major product(s) were characterized by spectroscopic and physical methods. The data for **2a** are: major product, 1,4,4-triphenyl-2,2-dimethyl-1-propanone **4** oil, 85%; ^{1}H nmr (deuteriochloroform): δ 1.41 (s, 6H), 4.73 (s, 1H), 7.26 (m, 13H), 7.46-7.79 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 25.6, 52.1, 58.6, 126.4, 127.1, 127.8, 128.1, 128.3, 130.2, 132.4, 141.6, 210.5; ms: M$^+$/e = 314; ir (neat): 1670 cm^{-1}.

Anal. Calcd. for $C_{23}H_{22}O$: C, 87.90; H, 7.01. Found: C, 87.86; H, 7.05.

The minor product was 1,1-dimethyl-2,2-diphenylethylene, oil; 10%; ^{1}H nmr (deuteriochloroform): δ 1.80 (s, 6H), 7.20 (m, 8H), 7.45-7.65 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 22.5, 126.1, 127.9, 128.8, 129.9, 131.1, 143.4; ms: M$^+$/e = 208 (100%), Cl-209 (M$^+$ + 1)].

For **2b-e** the data of β,γ-unsaturated ketones **5a-d** are listed in Table 1. Maximum yields of **5a-d** were obtained when **1a-e** underwent autoxidation in benzene heated under reflux [11].

Minor products, 1-indanones **6a-b**, were isolated from the thermolysis of **2b,d**, respectively. The spectra data are: for **6a** ^{1}H nmr (deuteriochloroform): δ 0.62 (s, 3H), 1.24 (s, 3H), 1.66 (s, 3H), 7.12 (m, 2H), 7.26 (m, 3H), 7.45 (m, 2H), 7.64 (m, 1H), 7.84 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.0, 25.0, 26.4, 53.4, 54.6, 124.0, 126.0, 126.6, 127.6, 127.8, 128.0, 134.5, 134.7, 144.1, 159.7, 210.7; ir (neat) 1705 cm^{-1} (C = O); ms: M$^+$/e = 250 (51% of base at 235); for **6b** [12]; ^{1}H nmr (deuteriochloroform): δ 1.10 (s, 6H), 1.25 (s, 6H), 7.22-7.82 (m, 4H); ^{13}C nmr (deuteriochloroform): δ 21.8, 26.4, 44.8, 53.6, 124.0, 127.4, 134.8, 161.8, 211.3; ir (neat) 1714 cm^{-1} (C=O).

Acknowledgements.

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