Preparation and N.M.R. Spectra of 2,5-Diaryl-2,5-di-t-butyl- Δ^3 -1,3,4-thiadiazoline 1,1-Dioxides

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Abstract

The reaction of 1-(4-methoxyphenyl)-2,2-dimethyldiazopropane with sulphur dioxide in benzene at 5° gave a 54% yield of 2,5-di-t-butyl-2,5-bis(4-methoxyphenyl)- Δ^3 -1,3,4-thiadiazoline 1,1-dioxide (4a). The n.m.r. spectra of this and the analogous compounds from 1-(4-chlorophenyl)-, and 1-(3,4,5-trimethoxyphenyl)-diazopropane, showed temperature dependence due to restricted rotation of the aryl groups. The energy barriers associated with this process were determined.

Structural factors profoundly influence the course of the reaction of 1-aryldiazoalkanes with sulphur dioxide. For example, 1-adamantyl-1-(4-methoxyphenyl)diazomethane gave no detectable amount of the thiadiazoline derivative, but an almost quantitative yield of 1-(4-methoxybenzoyl)-adamantane.

Introduction

The reaction of 1-aryldiazoalkanes (2) with sulphur dioxide has been used to prepare α, α' -dialkylstilbenes (8) via the corresponding episulphones (5).^{1,2} Attempts to use this reaction to prepare α, α' -di-t-butyl-4,4'-dimethoxystilbene (8a), which was required for another project, resulted instead in the formation of 2,5-di-t-butyl-2,5bis(4-methoxyphenyl)- Δ^3 -1,3,4-thiadiazoline 1,1-dioxide (4a) in about 54% yield. The only 2,2,5,5-tetrasubstituted Δ^3 -1,3,4-thiadiazoline 1,1-dioxides previously reported to have been formed under similar conditions were from 1-(cycloalkyl)diazoalkanes.^{3,4} This paper is concerned with the mode of formation, and with features of the n.m.r. spectra of (4a) and of related compounds. Only one stereoisomer of each of (4a), (4b) and (4c) was isolated, and the stereochemistry of these has not yet been determined. The depiction of the *cis* isomer in structural formulae throughout this paper is not meant to imply that this assignment has been made to the compounds described.

Results and Discussion

(a) Reaction of Diazoalkanes with Sulphur Dioxide

There are at least three possible pathways, summarized in Scheme 1, for the reaction of diazoalkanes with sulphur dioxide. Each is believed³⁻⁷ to involve inter-

² Nagai, Y., Juki Gosei Kagaku Kyokai Shi., 1961, 19, 464, 470 (Chem. Abstr., 1961, 55, 18662).

³ Hesse, G., and Reichold, E., Chem. Ber., 1957, 90, 2101.

⁵ Hesse, G., Reichold, E., and Majmudar, S., Chem. Ber., 1957, 90, 2106.

⁷ King, J. F., de Mayo, P., Morkved, E., Sattar, A. B. M. A., and Stoessel, A., *Can. J. Chem.*, 1963, **41**, 100.

¹ Vargha, L. v., and Kovacs, E., Ber. Deut. Chem. Ges., 1942, 75, 794.

⁴ Inhoffen, H. H., Jonas, R., Krosche, H., and Eder, U., Justus Liebigs Ann. Chem., 1966, 694, 19.

⁶ Staudinger, H., and Pfenninger, F., Ber. Deut. Chem. Ges., 1916, 49, 1941.

mediate formation of the sulphene (3), which may then undergo (a) 1,3-dipolar addition⁴ of the diazoalkane to give the thiadiazoline (4), (b) 'carbene-like' addition of the diazoalkane with elimination of nitrogen to give the episulphone (5), or (c) reaction with a molecule of sulphur dioxide to give the ketone $(9)^{3,6,7}$ with elimination of sulphur monoxide and sulphur dioxide. A possible mechanism for the last reaction involves formation of the cyclic intermediate (6) which might fragment as shown. Evidence for the involvement of the sulphenes (3) in the formation of the episulphones (5) derives from the fact that dehydrochlorination of primary alkanesulphonyl chlorides with triethylamine in the presence of diazoalkanes at 0° gives good yields of episulphones.^{8,9}



It is not clear what factors affect the relative rates of formation of the Δ^3 -1,3,4thiadiazoline 1,1-dioxides (path *a*), episulphones (path *b*), or the ketones (path *c*). In addition to differences in the reactivity of the diazoalkanes (2) and the sulphenes (3), there is a marked solvent effect. Only in benzene at 5–10° was 1-(4-methoxyphenyl)-2,2-dimethyldiazopropane (2a) converted into an isolable amount of (4a). In light petroleum, methylene chloride or toluene, at -50° , the main product was 4'-methoxy-2,2-dimethylpropiophenone (9a). None of the episulphone (5a) or the

⁸ Opitz, G., and Fischer, K., Z. Naturforsch. B, 1963, 18, 775.

⁹ Opitz, G., and Fischer, K., Angew. Chem., Int. Ed. Engl., 1965, 4, 70.

stilbene (8a) was detected in any of the reactions of (2a) with sulphur dioxide. The azine (7a) which was isolated from some initial reactions in benzene is presumed to have arisen by loss of sulphur dioxide from (4a). The latter is very sensitive to visible light; irradiation of (4a) in benzene with light of wavelength > 350 nm gave an almost quantitative yield of the azine (7a) within 30 min. The preparation of (4a) was therefore carried out in subdued light, and the solution was evaporated as soon as the reaction was complete. Conceivably, the azine might arise by the reaction of two molecules of the diazoalkane (2a) with elimination of nitrogen, or via the isomeric azirine, but these explanations fail to take account of the involvement of sulphur dioxide.

The main competing reaction in the preparation of (4a) is the formation of the ketone (9a). Even with the slow passage of sulphur dioxide through the rapidly stirred solution the percentage of ketone formed was high. Indirect evidence for the reaction of sulphur dioxide with the sulphene (path c) was the presence of a small amount of sulphur in the crude product, and a strong smell of hydrogen sulphide, probably formed from reactions of sulphur monoxide with the solvent and solutes. Sulphur monoxide has been shown to oxidize hydrocarbons with the formation of sulphur dioxide and hydrogen sulphide,¹⁰ and in some cases, of sulphur.¹¹

The synthesis of a few analogues of (4a) was attempted to get some indication of the degree to which the relatively high yield and the stability of (4a) depends upon the special properties of the 4-methoxyphenyl and/or t-butyl groups. Also, we required an analogue of (4a) with 3,4,5-trisubstitution in the aryl groups in order to simplify the n.m.r. signal pattern for the *ortho* aromatic protons, for the purpose of determining the barrier to restricted rotation (see below). 4'-Chloro-2,2-dimethylpropiophenone (9b), prepared by Jones oxidation¹² of 1-(4-chlorophenyl)-2,2dimethylpropan-1-ol,¹³ was converted into its hydrazone (1b), which was then subjected to the lead dioxide–sulphur dioxide reaction sequence under the conditions used for the preparation of (4a), to give 18% yield of (4b). The major product was 4'-chloro-2,2-dimethylpropiophenone (9b); none of the episulphone (5b) or the stilbene (8b) was detected. In the first experiment with (1b), careful chromatography of the mother liquors from the product (4b) yielded small amounts of α -t-butyl-4,4'dichlorostilbene (10), 4'-t-butyl-2,2-dimethylpropiophenone azine (11a) and the



¹⁰ Rao, B. S., and Rao, M. R. A., Curr. Sci., 1935, 4, 406.

¹¹ Schenk, P. W., Thoma, F., and Bohm, E., Monatsh. Chem., 1950, 81, 907.

- ¹² Bowden, K., Heilbron, I. M., Jones, E. R. H., and Weedon, B. C. L., J. Chem. Soc., 1946, 39.
- ¹³ Skerrett, E. J., and Woodcock, D., J. Chem. Soc., 1950, 2718.

mixed azine (11b), each of which was characterized by microanalysis, mass, n.m.r., infrared and ultraviolet spectroscopic data. Compounds (10), (11a) and (11b) were formed by cross reactions of the diazo compounds and sulphenes obtained from 4'-chloro-2.2-dimethylpropiophenone, 4-chlorobenzaldehyde and 4'-t-butyl-2.2-dimethylpropiophenone, the last two compounds being impurities in the original sample of 4'-chloro-2,2'-dimethylpropiophenone (9b) which was prepared by oxidation of the carbinol from the reaction of t-butylmagnesium chloride with 4-chlorobenzaldehyde at $-30^{\circ.13}$ Presumably, the crude carbinol contained some 1-(4-t-butylphenyl)-2,2-dimethylpropan-1-ol produced by reaction of the 1-(4-chlorophenyl)-2,2dimethylpropan-1-ol magnesium complex with more of the Grignard reagent. The hydrazone of pure (9b) was used in subsequent reactions, but the point of interest here is the formation of the stilbene (10), probably via the corresponding episulphone (12). Apparently path (b) is competitive with paths (a) and (c) (Scheme 1) when there is only one t-butyl group in the episulphone produced; but it is not known whether the asymmetric episulphone (12) was formed by one or by both possible combinations of sulphene and diazoalkane. The azines (11a) and (11b) are presumed to have been formed via the corresponding thiadiazolines.

2,5-Di-t-butyl-2,5-bis(3,4,5-trimethoxyphenyl)- Δ^3 -1,3,4-thiadiazoline 1,1-dioxide (4c), required for the n.m.r. study, was synthesized in low yield (6 %) by the sulphur dioxide reduction of the diazo compound (2c), prepared from 3',4',5'-trimethoxy-2,2dimethylpropiophenone hydrazone. The ketone (9c) was prepared by Jones oxidation of 1-(3,4,5-trimethoxyphenyl)-2,2-dimethylpropan-1-ol, obtained from the reaction of t-butylmagnesium chloride with ethyl 3,4,5-trimethoxybenzoate. The major product from the sulphur dioxide reduction of (2c) was the ketone (9c), formed by path (c). It is not clear to what extent the low yield of (4c) is due to electronic or steric effects on the reactivity of (2c) and/or (3c). The steric effect of the alkyl group R in (2) and (3) certainly has a profound effect on the course of the reaction. The diisopropyl, diethyl and dimethyl thiadiazolines (4e), (4f) and (4g) were not obtainable by the procedure used to prepare (4a). It has been reported¹⁴ that the reaction of 1-(4-methoxyphenyl)diazoethane (2g) with sulphur dioxide in light petroleum at room temperature gave low yields of 4,4'-dimethoxy- α, α' -dimethylstilbene (8g), and 4'methoxyacetophenone azine (7g). In benzene at about 5° we found that the reaction of (2g) with sulphur dioxide gave a yellow solution which yielded 32% of 4'-methoxyacetophenone azine (7g), 19% of a mixture of (E)- and (Z)-4,4'-dimethoxy- α,α' dimethylstilbenes, and 15% of 4'-methoxyacetophenone. The azine was probably formed by elimination of sulphur dioxide from the unstable thiadiazoline 1,1dioxide (4g).

In the case of 4'-methoxy-2-methylpropiophenone hydrazone (1e), the lead dioxide-sulphur dioxide reaction sequence gave an oil from which none of the thiadiazoline (4e), the episulphone (5e) or the stilbene (8e) could be isolated. G.l.c. analysis showed that the product contained 54% of the ketone (9e). These results indicate that the t-butyl groups confer relatively high stability on (4a), (4b) and (4c), and/or facilitate the reaction of (3) by path (a) relative to paths (b) and (c).

Attempts to prepare the 2,5-bis(1-adamantyl)-2,5-bis(4-methoxyphenyl)- Δ^3 -1,3,4-thiadiazoline 1,1-dioxide (4d) by sulphur dioxide reduction of (2d) in benzene at 5° or in toluene at -50° failed; the ketone (9d) was obtained in high yield. Presum-

¹⁴ Bennett, J. G., and Bunce, S. C., J. Org. Chem., 1960, 25, 73.

ably, steric effects mitigate against approaches to transition states leading to (4d) and (5d), and the sulphene (3d) reacts almost exclusively with sulphur dioxide.

(b) N.M.R. Studies

The 100 MHz n.m.r. spectrum of (4a) (CDCl₃, 10% w/v) showed singlets of expected relative intensities at 1.06 p.p.m. (t-butyl) and 3.83 p.p.m. (methoxyl), but the signals assigned to the aromatic protons, while of the expected relative intensity, gave a complex pattern (Fig. 1) instead of the expected symmetrical AA'BB' multiplet. The analysis of this spectrum by means of the iterative computer program LAOCN3¹⁵ gave the parameters listed in Table 1 which, by arguments detailed elsewhere,^{16,17}



Fig. 1. Portion of 100-MHz n.m.r. spectrum of (4a) in CDCl₃ (10% w/v) at 29°. The computed spectrum¹⁵ corresponds to the parameters listed in Table 1.

Table 1. N.m.r. parameters (at 100 MHz) for the aromatic protons of (4a)

The probable error quoted is taken from the computer output. The actual uncertainty of the parameters is probably better represented by the experimental accuracy of the measurement of the position of the individual lines (here ± 0.05 Hz). The stereochemistry of (4a) and related compounds is unknown. The structural formula shown here and those shown above do not imply *cis* stereochemistry at C2 and C5

MeO.	Chem. shift (Hz)	Co	Coupling constants (Hz)		
$ \begin{array}{c} 3 \\ 5 \\ 6 \\ Bu^{t} \\ O_{2} \\ Bu^{t} \\ O_{2} \\ Bu^{t} \\ (4a) \end{array} $	H 2 763 · 22 ^A H 3 689 · 13 ^A H 5 698 · 04 ^A H 6 748 · 25 ^A	$J_{2,3}\ J_{2,5}\ J_{2,6}$	8 · 82 ^B 0 · 23 ^B 2 · 49 ^A	$J_{3,5} \ J_{3,6} \ J_{5,6}$	2·93 ^A 0·30 ^B 8·88 ^B
	$A \pm 0.02 B \pm 0.03$				

show conclusively that the spectrum corresponds to a *p*-substituted benzene nucleus and that the assignments are as shown in Table 1. It must be noted that the relative assignments within the pairs H2/H6 and H3/H5 cannot be deduced at this stage.

¹⁵ Bothner-By, A. A., and Castellano, S. M., in 'Computer Programs for Chemistry' (Ed. D. F. DeTar) Vol. 1, Ch. 3 (Benjamin: New York 1968).

¹⁶ Gall, R. E., Landman, D., Newsoroff, G. P., and Sternhell, S., Aust. J. Chem., 1972, 25, 109.
 ¹⁷ Gerteisen, T. J., Kleinfelter, D. C., Brophy, G. C., and Sternhell, S., Tetrahedron, 1971, 27, 3013.

SO2

н'n

By analogy with previous work¹⁶⁻¹⁸ it was proposed that the complexity of the aromatic region of the n.m.r. spectrum of (4a) is due to slow (on the n.m.r. time-scale) rotation about the sp²-sp³ carbon-carbon single bonds indicated by arrows in the structural formula shown in Table 1 with the pairs H 2/H 6 and H 3/H 5 exchanging environments. This was confirmed by the examination of the n.m.r. spectrum of (4a) at various temperatures in diethylene glycol dimethyl ether. The complex multiplet assigned to the aromatic protons in the spectrum taken at 28° collapsed to a symmetrical multiplet expected for an AA'BB' system at 120°. The same effect was observed in dimethyl sulphoxide.

Fig. 2. Coordinate system used to describe the conformation of (4a).

The preferred conformation of (4a) can be described in terms of the dihedral angle ϕ (Fig. 2) and the dynamic phenomenon reflected in the n.m.r. spectra must correspond to a rotation of 180°, i.e. interchange between H2 and H6. Examination of models and data from the cyclohexane system¹⁹ suggest that the steric requirements of the t-butyl group are greater than those of the sulphone group but that both are bulky. The effective size of the nitrogen atom is almost certainly very much smaller. If the above assumptions are correct, the most stable conformation of (4a) corresponds to the angle ϕ assuming some value between 0 and 30°, or between 330 and 360° depending on the relative steric requirements of the t-butyl group and the sulphone group, in this particular environment.

Irradiation of the resonance assigned to the t-butyl group in the n.m.r. spectrum of (4a) in CDCl₃ caused an enhancement²⁰ of 16% for the signal at 7.48 p.p.m., of c. 3% for the signal at 7.63 p.p.m. and a negative n.O.e. effect of c. 5% for the complex multiplet corresponding to H3 and H5 (cf. Table 1). Given the fact that the dynamic process tends to equalize²⁰ the n.O.e. enhancement between H2 and H6, the above result suggests strongly that the highly populated conformation of (4a) corresponds to values of ϕ other than 30° where the t-butyl group would be equidistant from H2 and H6. Further, it is now possible to give the relative assignments of the resonances assigned to H2 and H6 which are made as shown in Fig. 2 and Table 1, i.e. H6 closer to the t-butyl group. The relative assignments of H3 and H5 follow in a trivial fashion from the magnitudes of the coupling constants listed in Table 1.

¹⁸ Sternhell, S., in 'Dynamic Nuclear Magnetic Resonance Spectroscopy' (Eds. L. M. Jackman and F. A. Cotton) Ch. 5 (Academic Press: New York, in press).

¹⁹ Hirsch, J. A., in 'Topics in Stereochemistry' (Eds. N. L. Allinger and E. L. Eliel) Vol. 1 (John Wiley: New York 1967).

²⁰ Noggle, J. H., and Schirmer, R. E., 'The Nuclear Overhauser Effect' (Academic Press: New York 1971).

The kinetics of the process corresponding to the interchange between H2 and H 6 in (4a) could be more conveniently studied from the variable temperature n.m.r. spectra of a more highly substituted derivative, conveniently, the hexamethoxy analogue (4c). The 100-MHz n.m.r. spectrum of (4c) (CDCl₃, 8% w/v) showed a singlet of relative intensity 9H at 1.14 p.p.m. (t-butyl); a singlet of relative intensity 3H at 3.84 p.p.m. and a singlet of relative intensity 6H at 3.91 p.p.m. (methoxyl groups), and an AB quartet of relative intensity 2H at 6.72 and 6.93 p.p.m. (aromatic protons, J_{AB} 2·1 Hz). The difference between the chemical shifts of the aromatic resonances (0.21 p.p.m.) compares reasonably well with the difference between the chemical shifts of H2 and H6 in (4a) (0.15 p.p.m., cf. Table 1) and the average upfield shift (0.72 p.p.m.) of the AB quartet in (4c) with respect to the average chemical shift of the protons assigned to H 2 and H 6 in (4a) is in reasonable agreement with that expected from the introduction of the two additional methoxyl groups per benzene ring $(0.92 \text{ p.p.m.})^{21}$ It is therefore attractive to assign the signal at 6.72 to H6 and that at 6.93 to H2 in the sense defined in Fig. 2. In confirmation of this assignment, irradiation of the resonance assigned to the t-butyl group gave an n.O.e. enhancement²⁰ of 15% for the signal at 6.72 p.p.m. and of c. 7% for the signal at 6.93 p.p.m. Variable-temperature 100-MHz n.m.r. spectra of (4c) in dimethyl $[D_6]$ sulphoxide (10%, w/v) (Fig. 3) were analysed by means of the Rogers-Woodbrey



Fig. 3. Portions of 100-MHz n.m.r. spectra of (4c) in $(CD_3)_2SO$ (10% w/v) at various probe temperatures. The instrumental gain control is not constant throughout the series.

approximation^{16,22} to yield the data presented in Table 2. The Arrhenius plot (Fig. 4) gave a satisfactory straight line and a standard least-squares computer $program^{23}$ gave the following kinetic parameters:

²¹ Beeby, J., Sternhell, S., Hoffmann-Ostenhof, T., Pretsch, E., and Simon, W., Anal. Chem., 1973, 45, 1571.

²² Rogers, M. T., and Woodbrey, J. C., J. Phys. Chem., 1962, 66, 540.

²³ Roberts, J. D., personal communication.

In spite of the apparently satisfactory confidence limits, we consider the parameters other than ΔG° to be only semiquantitative indications, because of the narrow range of temperatures accessible to our method. The free energies of activation in (4c) are very similar to those found by us in related systems.^{16,17}

Table 2. Kinetic data for (4c)										
Probe temp. (°C)	79.5	80.5	81 . 5	82.5	83.5	84.5				
r ^A	$5\cdot4\pm0\cdot2$	$3\cdot9\pm0\cdot2$	$3 \cdot 2 \pm 0 \cdot 1$	$2 \cdot 3 \pm 0 \cdot 1$	$1 \cdot 9 \pm 0 \cdot 1$	$1 \cdot 5 \pm 0 \cdot 1$				
$k (s^{-1})$	16.5 ± 0.7	19.7 ± 0.8	$21 \cdot 9 \pm 0 \cdot 5$	$26 \cdot 6 \pm 0 \cdot 7$	30.0 ± 0.6	$33 \cdot 9 \pm 0 \cdot 7$				
$\Delta G^{\circ} (\text{kJ/mol})^{B}$	$76 \cdot 5 \pm 0 \cdot 4$	$76 \cdot 5 \pm 0 \cdot 4$	$76 \cdot 1 \pm 0 \cdot 4$	$75 \cdot 7 \pm 0 \cdot 4$	$75 \cdot 7 \pm 0 \cdot 4$	$75 \cdot 7 \pm 0 \cdot 4$				

^A Experimental intensity ratios in the temperature region below the coalescence point.^{16,22} The error limits refer to reproducibility among 6–8 scans.

^B Part of the output of standard computer program.²³





The 100-MHz n.m.r. spectrum of (4b) in CDCl_3 (8%, w/v) showed a singlet of relative intensity 9H at 1.06 p.p.m. (t-butyl) and a complex multiplet of relative intensity 4H between 7.3 and 7.75 p.p.m. (aromatic protons). N.m.r. spectra taken at various temperatures in dimethyl[D_6] sulphoxide exhibited reversible phenomena, but also irreversible changes indicating decomposition. The compound was not further investigated by n.m.r.

Experimental

Melting points are uncorrected. Infrared spectra were recorded with a Perkin–Elmer 137 Infracord spectrophotometer, and ultraviolet spectra with a Perkin–Elmer 402 spectrophotometer. Mass spectra were run in an A.E.I. MS-9 spectrometer. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne.

Gas chromatograms were run with an F&M 810 chromatograph fitted with dual flame ionization detectors, and 4 ft by 1/4 in. stainless steel columns packed with $3 \cdot 2\%$ neopentylglycol succinate on Gaschrom Q (80–100 mesh); oven temperature 200°; carrier gas helium, 60 ml/min.

N.m.r. spectra were obtained with Varian A60 and HA100 spectrometers and refer to 5-10% (w/v) solutions in CDCl₃ unless otherwise stated. All data are considered significant to ± 1 of the last significant place quoted, unless otherwise stated. Details of measurements of probe temperatures

have been given elsewhere.¹⁶ The n.O.e. experiments were performed on degassed samples, signals due to chloroform or impurity being used as internal standard.

(a) 4'-Methoxy-2,2-dimethylpropiophenone and Derivatives

To an ice-cold suspension of powdered anhydrous aluminium chloride (46.2 g) in dry light petroleum (250 ml) was added a solution of anisole (49.7 g) in light petroleum (50 ml). This mixture was then treated at 0–5° with a solution of pivaloyl chloride (27.7 g) in light petroleum (50 ml). The mixture was stirred with cooling for 1 h, warmed at 40° for 1 h, then poured onto ice (300 g) and concentrated hydrochloric acid (80 ml). Ether-benzene was added, and the organic layer was washed with 1N hydrochloric acid, water, 5% sodium bicarbonate, water, dried and evaporated. Fractional distillation gave 4'-methoxy-2,2-dimethylpropiophenone (25 g), b.p. 100–104°/0.2 mm (lit.²⁴ 138–140°/8 mm). ν_{max} (film) 1660 cm⁻¹ (C=O). The semicarbazone crystallized from ethanol as needles, m.p. 153–154° (lit.²⁴ 150–151°) (Found: C, 62.5; H, 7.5; N, 16.8. Calc. for C₁₃H₁₉N₃O₂: C, 62.6; H, 7.7; N, 16.9%).

Hydrazone (1a)

A solution of the ketone (16 g) in ethanol (100 ml) was added during 15 min to a stirred, boiling solution of hydrazine hydrate (25 ml, 98%) in ethanol (25 ml). The solution was stirred and heated under reflux for a further 5 h. After removal of the ethanol in vacuum, water was added, and the product extracted with ether-benzene. Crystallization from light petroleum gave the *hydrazone* as needles, m.p. 64–67° (9·5 g). The pure sample had m.p. 67–69° (Found: C, 69·7; H, 8·7; N, 13·9. C₁₂H₁₈N₂O requires C, 69·9; H, 8·8; N, 13·6%). ν_{max} (Nujol) 3356 cm⁻¹ (NH₂); λ_{max} (ethanol) 225 (12430), 274 (1770), 281 (1270); λ_{min} 208 (9790), 262 (1270), 279 nm (1220).

Azine (7a)

To a solution of the ketone $(25 \cdot 6 \text{ g})$ in ethanol (30 ml) was added hydrazine hydrate (3 $\cdot 6 \text{ ml}$, 98%) and glacial acetic acid (5 $\cdot 6 \text{ ml}$). The mixture was heated under reflux for 7 h, allowed to cool, and the crystalline product was collected and washed with cold ethanol. Several crystallizations from methanol gave the pure colourless azine, m.p. 125–125 $\cdot 5^{\circ}$ (lit.²⁴ 123–125 \cdot) (Found: C, 75 $\cdot 8$; H, 8 $\cdot 4$; N, 7 $\cdot 5$. Calc. for C₂₄H₃₂N₂O₂: C, 75 $\cdot 8$; H, 8 $\cdot 5$; N, 7 $\cdot 4^{\circ}$ %). v_{max} (Nujol) 1605 (C=N). The u.v. spectrum showed no maxima above 210 nm, but shoulders at 226 (17620), 245 (11310), 276 (4990) and 282 nm (3990). P.m.r. (60 MHz): $\delta 6 \cdot 88$, s, 8H (aromatic), 3 $\cdot 70$, s, 6H (2OCH₃), 0 $\cdot 92$, 18H (2Bu¹). Mass spectrum: m/e 380 (M), 323 (base peak), m* 274 $\cdot 6$ (380 \rightarrow 323).

(b) 2,5-Di-t-butyl-2,5-bis(4-methoxyphenyl)- Δ^3 -1,3,4-thiadiazoline 1,1-Dioxide (4a)

Lead dioxide (250 g) was added to a solution of 4'-methoxy-2,2-dimethylpropiophenone hydrazone (25 0 g) in dry benzene (600 ml), and the suspension was stirred at room temperature for 4 h. The mixture was filtered and the lead dioxide cake was washed with benzene. Sulphur dioxide was passed slowly through the cooled (5–10°) filtrate and washings until the deep red colour of the diazo compound had faded. The solution was boiled to remove the excess of sulphur dioxide, and the solvent evaporated. Crystallization from benzene-methanol gave 2,5-di-t-butyl-2,5-bis(4-methoxy-phenyl)- Δ^3 -1,3,4-thiadiazoline 1,1-dioxide (12 g), m.p. 195–197°. A further 2.54 g of this material was obtained from the mother liquors; total yield of crude material, 14 5 g (54%). The pure sample melted at 197–198° (Found: C, 65 3; H, 7·2; N, 6·7; S, 7·2. C₂₄H₃₂N₂O₄S requires C, 64·8; H, 7·3; N, 6·3; S, 7·2%). ν_{max} (Nujol) 1605s, 1577m, 1504s, 1475m, 1453s, 1433s, 1406w, 1389m, 1368m, 1357s, 1294s, 1241s, 1211m, 1196m, 1172s, 1135s, 1116m, 1029s, 1006m, 987w, 953w, 936m, 927m, 908m, 882w, 830s, 815w, 810w, 804m, 792m, 786m, 726w, 720w. λ_{max} (cyclohexane) 234 (12530), 282 (2390), 380 (147); λ_{min} 215 (1915), 279 (2378), 330 (1440); λ_{inf1} 258 (2976), 269 (2942), 275 nm (2839). Mass spectrum: no parent ion, essentially the same as that of the azine (7a). For n.m.r. data, see discussion.

Chromatography on Florisil of the oily residue (c. 10 g) from the mother liquor gave sulphur (300 mg), and 4'-methoxy-2,2-dimethylpropiophenone (2.5 g), identified by its i.r. spectrum. No other pure compounds were obtained.

²⁴ Rothstein, E., and Saville, R. W., J. Chem. Soc., 1949, 1950.

When the diazo compound was prepared in light petroleum and sulphur dioxide passed at -50° , no crystalline thiadiazoline was obtained. Reactions carried out under similar conditions in methylene chloride or in toluene also failed to yield appreciable amounts of the thiadiazoline.

(c) Photolysis of 2,5-Di-t-butyl-2,5-bis(4-methoxyphenyl)- Δ^3 -1,3,4-thiadiazoline 1,1-Dioxide (4a)

A solution of the thiadiazoline $(1 \cdot 11 \text{ g})$ in dry benzene (500 ml) was irradiated with light of wavelength > 350 nm (through a 5% aqueous copper sulphate filter) with passage of nitrogen. Within 30 min the absorption at 380 nm had disappeared, and evaporation, and crystallization of the product from methanol gave 4'-methoxy-2,2-dimethylpropiophenone azine (0.84 g), m.p. 125–126°, undepressed on admixture with authentic material. Identity was confirmed by the i.r. spectrum.

(d) Treatment of 4'-Methoxy-2,2-dimethylpropiophenone Azine with Sulphur Dioxide

Sulphur dioxide was bubbled through a solution of the azine (100 mg) in dry benzene (10 ml) at about 5° for 1 h. The solution was kept at room temperature for 1 h, then evaporated at $< 30^{\circ}$. Crystallization of the residue from methanol gave starting material (82 mg), m.p. and mixed m.p. 132–133°; the i.r. spectrum confirmed its identity.

(e) 4'-Chloro-2,2-dimethylpropiophenone (9b) and Derivatives

A solution of 1-(4-chlorophenyl)-2,2-dimethylpropan-1-ol¹³ (5 4 g) in acetone (200 ml) was oxidized at 0° with Jones reagent to give the ketone (4 6 g), b.p. $80-85^{\circ}/0.2$ mm (lit.¹³ 84-86°/0.7 mm). ν_{max} (film) 1672 cm⁻¹.

(i) *Hydrazone* (1*b*).—A solution of the crude ketone ($4 \cdot 6$ g) in ethanol (24 ml) containing hydrazine hydrate (7 \cdot 5 ml, 98%) was heated under reflux for 4 h. Recrystallization of the product from light petroleum gave the pure *hydrazone*, m.p. 109–111° (Found: C, 62 \cdot 8; H, 7 \cdot 0; N, 13 \cdot 4. C₁₀H₁₅ClN₂ requires C, 62 \cdot 7; H, 7 \cdot 2; N, 13 \cdot 3%). v_{max} (Nujol): 3356, 3205 (NH₂ free, and H-bonded). λ_{max} (ethanol) 219 nm (13460).

(ii) Azine (7b).—A solution of the ketone (2 \cdot 0 g) in ethanol (3 ml) containing hydrazine hydrate (0 \cdot 25 ml) and glacial acetic acid (0 \cdot 4 ml) was heated on the steam bath for 11 h. The product (2 \cdot 5 g), m.p. 143–144°, was recrystallized from methanol to give the pure *azine*, m.p. 144–145° (Found: C, 68 \cdot 1; H, 6 \cdot 9; Cl, 18 \cdot 4; N, 7 \cdot 2. C₂₂H₂₆Cl₂N₂ requires C, 67 \cdot 8; H, 6 \cdot 7; Cl, 18 \cdot 2; N, 7 \cdot 2%). The i.r. spectrum showed absence of N–H absorption. λ_{max} (ethanol): 205 (31870), 297 (1305), 309 (1450); λ_{min} 291 (1255), 302 (1298); λ_{inf1} 223 (20260), 330 (1313), 343 (703). The n.m.r. spectrum (60 MHz) showed δ 6 \cdot 78–7 \cdot 44, m, 8H (aromatic); 0 \cdot 93, s, 18H (2CMe₃). The mass spectrum showed the parent ion at m/e 389.

(f) 2,5-Di-t-butyl-2,5-bis(4-chlorophenyl)- Δ^3 -1,3,4-thiadiazoline 1,1-Dioxide (4b)

A solution of 4'-chloro-2,2-dimethylpropiophenone hydrazone (8 \cdot 0 g) in dry benzene (250 ml) was stirred with lead dioxide (75 g) at room temperature for 4 h and filtered. Sulphur dioxide was bubbled slowly through the filtrate at 5–10°. Evaporation of the solution at <40°, and addition of methanol (40 ml) gave a yellow solution which deposited a crystalline solid (1 \cdot 58 g, 18%). Recrystallization from benzene–light petroleum gave pure 2,5-di-t-butyl-2,5-bis(4-chlorophenyl)- Δ^3 -1,3,4-thiadiazoline 1,1-dioxide, m.p. 200–201° (dec.) (Found: C, 58 \cdot 3; H, 6 \cdot 0; Cl, 16 \cdot 2; N, 5 \cdot 9; S, 7 \cdot 0. C₂₂H₂₆Cl₂N₂O₂S requires C, 58 \cdot 3; H, 5 \cdot 8; Cl, 15 \cdot 6; N, 6 \cdot 2; S, 7 \cdot 1%). ν_{max} (Nujol): 1587m, 1565w, 1543w, 1477s, 1456s, 1391s, 1361s, 1304s, 1285s, 1263m, 1211m, 1195s, 1138s, 1109m, 1094s, 1038m, 1010s, 989w, 969w, 953m, 945m, 929s, 907m, 887w, 835s, 828s, 804m, 729s, 717m cm⁻¹. The mass spectrum showed no parent ion, and was virtually identical with that of the corresponding azine (7b). For n.m.r. data, see discussion.

Evaporation of the methanol mother liquor at $<40^{\circ}$ gave an oil (6.43 g), the i.r. spectrum of which showed it to be mainly 4'-chloro-2,2-dimethylpropiophenone (9b).

In the first experiment using the hydrazone prepared from crude 4'-chloro-2,2-dimethylpropiophenone, chromatography of the mother liquors yielded small amounts of the following compounds:

 α -t-Butyl-4,4'-dichlorostilbene (10), m.p. 123–126° (Found: C, 70·9; H, 5·9; Cl, 23·5. C₁₈H₁₈Cl₂ requires C, 70·8; H, 5·9; Cl, 23·5 %). ν_{max} (Nujol): 1629m, 1590m, 1486s, 1456s, 1403m, 1374s, 1355s, 1299w, 1238m, 1215w, 1196w, 1167m, 1105s, 1099s, 1089s, 973s, 963m, 950w, 895s, 854s, 836s, 824s, 818s, 793m, 763s, 720m, 710, 689m, 685m cm⁻¹. λ_{max} (ethanol): 206 (28550), 263 (14510),

293 (12200), 303 (12540), 318 (12230); λ_{\min} 246 (9632), 285 (11870), 298 (12070), 312 (11410); $\lambda_{\inf I}$ 218 (15950), 227 (14520), 231 (14040), 238 (12590), 273 (13810), 331 nm (7891). The n.m.r. spectrum (60 MHz) showed $\delta 6 \cdot 50-7 \cdot 53$, m, 9H (8 aromatic and 1 olefinic); $1 \cdot 15$, $1 \cdot 32$, 2s, in a ratio of 9 : 1, 9H (CMe₃ groups of *cis* and *trans* isomers; the higher field resonance is tentatively assigned to the *trans* isomer). The mass spectrum showed the parent ion at m/e 305.

I-(4-Chlorophenyl)-*I*-(α,4'-di-t-butylbenzylidenehydrazone)-2,2-dimethylpropane (11b), m.p. 110–111° (Found: C, 75·7; H, 8·6; Cl, 8·6; N, 6·6. $C_{26}H_{35}ClN_2$ requires C, 76·0; H, 8·6; Cl, 8·6; N, 6·8 %). v_{max} (Nujol): 1603m, 1590m, 1506w, 1486s, 1471s, 1456s, 1414w, 1383s, 1370s, 1353s, 1335w, 1290w, 1261m, 1215m, 1206m, 1198s, 1172w, 1116m, 1107m, 1098m, 1086s, 1035w, 1012m, 997s, 950m, 932w, 835s, 820s, 807w, 773w, 760s, 731m, 722m, 713m cm⁻¹. λ_{max} (ethanol): 205 (32380), 298 (1099), 310 (1191); λ_{min} 292 (1071), 302 (1091); λ_{inf1} 225 (17850), 319 (1079), 334 nm (583). The n.m.r. spectrum (60 MHz) showed δ 6·82–7·45, m, 8H (aromatic); 1·33, s, 9H (C₆H₄CMe₃); 0·95, s, 9H (CMe₃); 0·88, s, 9H (CMe₃). The mass spectrum showed the parent molecular ion at *m/e* 411.

4'-t-Butyl-2,2-dimethylpropiophenone azine (11a), m.p. 159–161° (lit.²⁵ 160–162°) (Found: C, 83·0; H, 10·0; N, 6·9. Calc. for $C_{30}H_{44}N_2$: C, 83·3; H, 10·3; N, 6·5%). v_{max} (Nujol): 1603s, 1595s, 1506m, 1473s, 1456s, 1385s, 1368s, 1353s, 1290m, 1261s, 1215m, 1202s, 1188m, 1166w, 1116s, 1107s, 1086m, 1035m, 1015m, 996s, 951s, 932m, 861w, 838s, 820s, 807m, 762m, 756w, 733m, 720m, 715m cm⁻¹. λ_{max} (ethanol): 206 (30260), 297 (1272), 309 (1407); λ_{min} 291 (1219), 301 (1264); λ_{inf1} 236 (11860), 320 (1292), 333 nm (711). The n.m.r. spectrum (60 MHz) showed δ 6·82–7·45, m, 8H (aromatic); 1·32, s, 9H (CMe₃); 0·90, s, 9H (CMe₃). The mass spectrum showed the parent ion at m/e 432.

4'-Chloro-2,2-dimethylpropiophenone azine, m.p. 144–145° (identical, i.r. and mixed m.p., with material prepared in (e)(ii)).

(g) 3', 4', 5'-Trimethoxy-2,2-dimethylpropiophenone Hydrazone (1c)

To an ice-cold solution of t-butylmagnesium chloride, prepared from magnesium $(12 \cdot 7 \text{ g})$ and freshly distilled t-butyl chloride $(50 \cdot 2 \text{ g})$ in dry ether (330 ml), was added under nitrogen a solution of ethyl 3,4,5-trimethoxybenzoate $(31 \cdot 1 \text{ g})$ in dry ether (150 ml). The mixture was stirred at room temperature for 2 h and heated under reflux with stirring for 5 h, then dry 1,2-dimethoxyethane (150 ml) was added and the mixture heated under reflux for a further 6 h. The cold mixture was treated with saturated ammonium chloride solution, benzene was added, and the product isolated from the washed, dried organic extract. Crystallizations from light petroleum gave 2,2-dimethyl-1-(3,4,5-trimethoxyphenyl)propan-1-ol $(12 \cdot 8 \text{ g})$, m.p. $113-114^\circ$. The pure carbinol had m.p. $114-115^\circ$. N.m.r. spectrum (60 MHz): $6 \cdot 53$, s, 2H (aromatic); $4 \cdot 30$, s, 1H (CHOH); $3 \cdot 86$, s, 9H (3OCH₃); $2 \cdot 06$, s, 1H (OH, exch.); $0 \cdot 94$, s, 9H (CMe₃).

A solution of the carbinol (5 g) in acetone (35 ml) containing manganous sulphate (5 g), was treated at room temperature with Jones reagent (8N chromic acid, 7 5 ml). The usual workup gave an oil which crystallized upon trituration with light petroleum. The crude ketone was chromatographed on alumina (Merck grade II, basic). Elution with light petroleum containing benzene (20 %), and with benzene, and recrystallization of the product from light petroleum gave pure 3',4',5'-trimethoxy-2,2-dimethylpropiophenone (2 · 5 g), m.p. 66–68° (Found: C, 66 · 6; H, 8 · 1. C₁₄H₂₀O₄ requires C, 66 · 6; H, 8 · 0%). v_{max} (Nujol): 1656 cm⁻¹ (C=O).

A solution of the ketone $(3 \cdot 5 \text{ g})$ in ethanol (30 ml) containing hydrazine hydrate (5 ml, 98%) was heated under reflux for 14 h. Crystallization of the product from light petroleum gave the hydrazone (1c) (2 \cdot 9 g), m.p. 85–86° (Found: C, 63 \cdot 0; H, 8 \cdot 2; N, 10 \cdot 4. C₁₄H₂₂N₂O₄ requires C, 63 \cdot 1; H, 8 \cdot 3; N, 10 \cdot 5%). v_{max} (Nujol): 3356, 3195 cm⁻¹. λ_{max} (ethanol): 243 (6997), 249 (5868), 254 (4965), 261 (3611); λ_{min} 242 (6884), 248 (4965), 253 (3386), 259 (2488); λ_{inf1} 268 nm (1309).

(h) Reaction of 3',4',5'-Trimethoxy-2,2-dimethylpropiophenone Hydrazone with Lead Dioxide Followed by Sulphur Dioxide

A solution of the hydrazone $(2 \cdot 0 \text{ g})$ in dry benzene (120 ml) was stirred with lead dioxide (20 g) under nitrogen for 5 h. The lead dioxide was removed by filtration and sulphur dioxide passed slowly through the red solution of the diazo compound at $5-10^{\circ}$ until the colour was discharged

²⁵ Elquero, J., Jacquier, R., and Marzin, C., Bull. Soc. Chim. Fr., 1968, 713.

Removal of the solvent and trituration with methanol gave a solid (120 mg). Crystallization from benzene-methanol gave 2,5-di-t-butyl-2,5-bis(3,4,5-trimethoxyphenyl)- Δ^3 -1,3,4-thiadiazoline 1,1-dioxide, m.p. 216° (dec.) (Found: C, 59 9; H, 7 1; N, 5 1; S, 5 4. C₂₈H₄₀N₂O₈S requires C, 59 6; H, 7 1; N, 5 0; S, 5 7%). v_{max} (Nujol): 1582s, 1560m, 1546m, 1511s, 1458s, 1445s, 1439s, 1408s, 1370m, 1361m, 1316s, 1302s, 1247s, 1182m, 1138s, 1124s, 1036w, 1008s, 971w, 935m, 909w, 840m, 809w, 794w, 756w, 729m, 696w cm⁻¹. For n.m.r. data, see discussion.

The i.r. spectrum of the residue from the original mother liquor showed it to be mainly 3',4',5'-trimethoxy-2,2-dimethylpropiophenone. Crystallization from a small volume of methanol afforded 3',4',5'-trimethoxy-2,2-dimethylpropiophenone (670 mg), m.p. 66–68°, identified by mixed m.p. and its i.r. spectrum.

(i) Reaction of 4'-Methoxyacetophenone Hydrazone with Lead Dioxide and Sulphur Dioxide

A solution of *p*-methoxyacetophenone hydrazone $(10 \cdot 0 \text{ g})$ in benzene (500 ml) was stirred with lead dioxide (100 g) at room temperature for 5 h. Sulphur dioxide was passed through the red filtrate at 5–10° for 30 min to give a light yellow solution. The concentrated solution deposited a yellow solid which was crystallized from ethanol to give crude 4'-methoxyacetophenone azine (2·5 g, 32%), m.p. 192°. The i.r. spectrum was virtually identical with that of a pure authentic sample, m.p. 200–201° (lit.²⁶ 200–200·5°).

The residual oil (6.4 g) from the benzene mother liquor was chromatographed on Florisil (200 g). Elution with light petroleum containing benzene (5–20%) gave a mixture of (*E*)- and (*Z*)-4,4'-dimethoxy- α , α' -dimethylstilbene (1.5 g). Elution with light petroleum containing benzene (20–50%) gave an oil (1.4 g) which was shown by the i.r. spectrum to be 4'-methoxyacetophenone. No other pure products were isolated.

(j) 4'-Methoxy-2-methylpropiophenone Hydrazone

A mixture of the ketone²⁷ (5 · 1 g) and hydrazine hydrate (7 · 5 ml, 98%) in ethanol (30 ml) was heated under reflux for 50 h. Most of the ethanol was removed in vacuum, ether-benzene added, and the solution washed with saturated sodium chloride solution and then water, dried and evaporated. The i.r. spectrum showed absence of carbonyl absorption. Distillation gave the pure *hydrazone*, b.p. 116-117°/0·2 mm (Found: C, 69·1; H, 8·4; N, 14·8. C₁₁H₁₆N₂O requires C, 68·7; H, 8·4; N, 14·6%). v_{max} (film): 3356, 3165 (free and H-bonded NH₂).

(k) Reaction of 4'-Methoxy-2-methylpropiophenone Hydrazone with Lead Dioxide and Sulphur Dioxide

A solution of the diazo compound prepared in the usual way from the hydrazone $(1 \cdot 0 \text{ g})$ in toluene (25 ml) at -50° was treated with a slow stream of sulphur dioxide until the red colour had discharged. The excess of sulphur dioxide was removed by passage of nitrogen at -40° . Addition of ethanol (25 ml) gave an amorphous solid (130 mg) which was filtered off. Evaporation of the filtrate gave an orange oil (860 mg), t.l.c. of which revealed 4'-methoxy-2-methylpropiophenone as the main component, and three more polar unidentified compounds. G.l.c. showed the oil to contain 54% of the ketone; the polar materials were not identified.

(l) 1-(4-Methoxybenzoyl)adamantane and Derivatives

To a suspension of powdered anhydrous aluminium chloride (8 g) in dry light petroleum (50 ml) at 0° was added a solution of anisole (8 g) in the same solvent (50 ml). To the stirred solution at 0° was then added a solution of adamantane-1-carbonyl chloride (from $6 \cdot 0$ g of the acid) in light petroleum (50 ml) during 30 min. After a further 1 h at 0°, the mixture was heated under reflux for 2 h, cooled and then treated with crushed ice and 4N hydrochloric acid. The product was extracted with ether-benzene, washed with water, 5% sodium carbonate (0·31 g of adamantane-1-carboxylic acid was recovered), water, then dried and evaporated. Distillation gave fraction 1, 176 mg, b.p. <180°/3 mm, fraction 2, 3·68 g, b.p. 180-210°/3 mm, and fraction 3, 3·9 g, b.p. 210-230°/3 mm.

²⁶ Zanden, J. M. van der, and Vries, G. de, *Rec. Trav. Chim. Pays-Bas*, 1956, 75, 1159.
 ²⁷ Dominguez, X. A., Gomez, B., Slim, J., Giesecke, D., and Ureta, E., *J. Amer. Chem. Soc.*, 1954, 76, 5150.

Trituration of fraction 2 with methanol gave a solid, m.p. $61-64^{\circ}$ (1 · 9 g). Several recrystallizations from methanol gave pure 1-(4-methoxybenzoyl)adamantane (1 · 74 g), m.p. $66-68^{\circ}$ (lit.²⁸ 66-67°) (Found: C, 80 · 1; H, 8 · 6. C₁₈H₂₂O₂ requires C, 80 · 0; H, 8 · 2%). ν_{max} (Nujol): 1664 (C=O).

Trituration of fraction 1 with methanol yielded crystalline *1-(4-methoxyphenyl)adamantane* (ref.²⁹; these authors quote n.m.r. data for this compound, but no other physical constant or microanalysis), m.p. 81–82°, which upon recrystallization showed m.p. 82·5–84° (Found: C, 83·9; H, 9·1. $C_{17}H_{22}O$ requires C, 84·3; H, 9·2%). This was identical with material prepared in (*m*).

The hydrazone crystallized from methanol, m.p. 151–152° (2·2 g) (Found: C, 76·4; H, 8·6; N, 9·6. C₁₈H₂₄N₂O requires C, 76·0; H, 8·5; N, 9·9%). ν_{max} 3371, 3215 (free and H-bonded NH₂); λ_{max} (ethanol): 202 (15300), 224 (13300), 275 (1470), 281 (1200); λ_{min} 215 (11740), 263 (1220), 279 nm (1150).

The azine was obtained from methanol as colourless prisms, m.p. 250–251° (Found: C, 80.5; H, 8.3; N, 5.1. $C_{36}H_{44}N_2O_4$ requires C, 80.6; H, 8.3; N, 5.2%). λ_{max} (ethanol): 203 (33000); λ_{infl} 214 (25800), 225 (19900), 245 (11440), 275 (4980), 282 nm (3980).

(m) 1-(4-Methoxyphenyl)adamantane

A solution of 1-bromoadamantane $(2 \cdot 0 \text{ g})$ in dry anisole (10 ml) was added dropwise with stirring to a mixture of powdered anhydrous aluminium chloride in anisole (10 ml). The mixture was heated on the steam bath with stirring for 3 h, then kept overnight at room temperature. The mixture was treated with 4N hydrochloric acid (100 ml) containing crushed ice, and the product extracted with ether. Several recrystallizations from methanol gave 1-(4-methoxyphenyl)adamantane, m.p. $82 \cdot 5-84^\circ$, undepressed on admixture with material described in (*l*).

(n) Reaction of 1-(4-methoxybenzoyl)adamantane Hydrazone with Lead Dioxide and Sulphur Dioxide

(i) A solution of the hydrazone (0.5 g) in benzene (50 ml) was stirred with lead dioxide (7.0 g) for 4 h at room temperature. The filtered, deep red solution was cooled in an ice bath, and sulphur dioxide was bubbled through slowly with stirring until the red colour was discharged. Evaporation at room temperature gave an oil which smelled strongly of H₂S. Chromatography on silica gel (20 g) and elution with benzene–light petroleum (4–20%), and with benzene, afforded 1-(4-methoxy-benzoyl)adamantane (350 mg), m.p. 64°. No other pure compound was isolated.

(ii) A solution of the hydrazone (0.5 g) in toluene (25 ml) was treated with lead dioxide (5 g) in the usual way. The deep red filtrate was cooled to -50° and sulphur dioxide bubbled through until the red colour had discharged. Evaporation at $< 20^{\circ}$ in vacuum gave a yellow oil, t.l.c. of which showed a single spot, and quantitative gas chromatography of an aliquot indicated an almost quantitative yield of 1-(4-methoxybenzoyl)adamantane.

Acknowledgments

This work was supported by a grant from the Ford Foundation to Professor C. W. Emmens whom we thank for his interest, and by grant number C65/15567 from the Australian Research Grants Committee to one of us (S.S.).

Manuscript received 28 June 1974

²⁸ Pratt, D. G., and Rothstein, E., J. Chem. Soc., 1968, 2548.
 ²⁹ Fort, R. C., Jr, and Schleyer, P. von R., J. Org. Chem., 1965, 30, 789.