

PREPARATION AND REACTIONS OF 5,7-DITERT-BUTYL-1,2-DIPHENYLSPIRO[2,5]OCTA-1,4,7-TRIEN-6-ONE:
A REVISION OF THE LITERATURE*

Libuše PAVLÍČKOVÁ and Milan SOUČEK

*Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6*

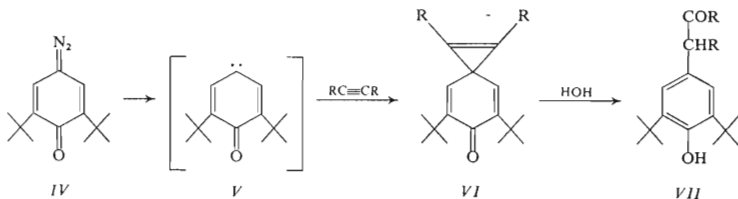
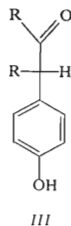
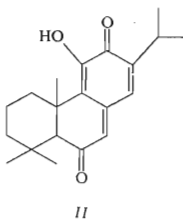
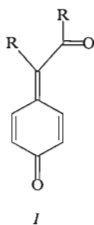
Received September 27th, 1978

The structure *Vib*, suggested previously on the basis of physico-chemical data for the compound reported to be the sole product of thermolysis of 2,6-ditert-butyl-4-diazo-2,5-cyclohexadien-1-one (*IV*) in the presence of diphenylacetylene, is incorrect. We have now shown that the main product is in fact 4-(3',5'-ditert-butyl-4'-hydroxybiphenyl)phenylacetylene (*VIII*). Other, minor, products of this reaction are the isomeric ketones *VIIb* and *IX*, the diphenoquinone *XI* and the cyclic azo compound *XII*. A small quantity of the spirotrienone *Vib* was isolated only when the reaction had been performed with a large excess of diphenylacetylene. The structure of *Vib* was determined unequivocally by physico-chemical methods and chemical transformations to compounds, prepared by independent syntheses. Air-oxidation of the ketone *VIIb* in an alkaline medium afforded the quinone methide *X*.

In the course of our investigations on quinone methides we intended to study compounds with a carbonyl group attached to the methide carbon. We supposed that such a system of double bonds and carbonyl groups should exhibit properties of both a quinone methide and an extended vinylogous quinone. Moreover, compounds of the structure *I* could possibly show cytostatic activity, similarly as in the case of taxodione (*II*), isolated¹ from the seeds of *Taxodium distichum*.

Compounds *I* or *III*, from which quinone methides are accessible by oxidation, can be synthesized by several methods. The oldest synthesis² consists in the acid-catalysed alkylation of phenol with deoxybenzoin but the desired phenol *III* ($R = \text{phenyl}$) is formed in a low yield and the complicated reaction mixture is separable only with difficulty. Another method, the photoaddition of diphenylacetylene to 1,4-benzoquinone^{3,4}, leads directly to the quinone methide *I* ($R = \text{phenyl}$); however, in the case of 2,6-disubstituted quinones this reaction fails. The reaction sequence (Scheme 1), described for $R = \text{CH}_3$ (ref.⁵) and $R = \text{phenyl}$ (ref.⁶), seemed to be of general applicability.

* Part XIV in the series Quinone Methides and Fuchsones; Part XIII: This Journal 44, 110 (1979).



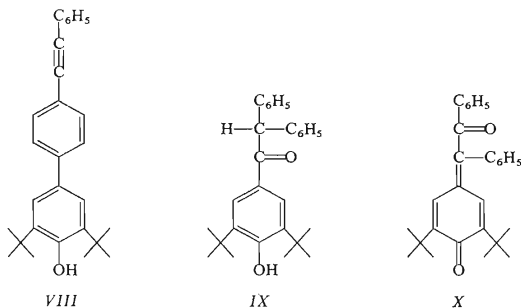
In formulae *VI* and *VII*: *a*, R = CH₃, *b*, R = C₆H₅

SCHEME 1

The starting diazo oxides *IV* are easily available and their decomposition to the reactive substituted cyclohexadienonylidenes *V* can be performed either photochemically⁵ or thermally^{6,7}. Addition of the carbene *V* to acetylenes gives the spirotrienones *VI* which are hydrolysed with trifluoroacetic⁵ or trichloroacetic⁶ acids to give the desired phenols *VIIa* or *VIIb*.

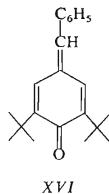
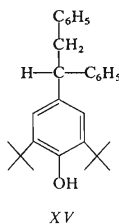
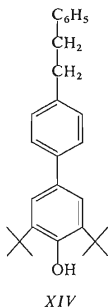
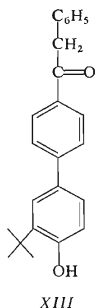
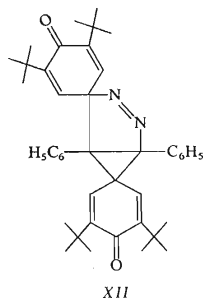
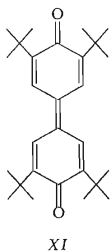
Reproducing the described⁶ experiments, we found that heating the diazo oxide *IV* with diphenylacetylene led to a complicated mixture of at least six compounds. In addition to the starting diphenylacetylene we isolated as the major product a compound whose composition, C₂₈H₃₀O (mol.w. 382.2284), corresponded to the originally described 5,7-ditert-butyl-1,2-diphenylspiro[2,5]octa-1,4,7-trien-6-one (*VIb*). Its infrared spectrum, however, did not correspond to this structure, since it exhibited no bands in the carbonyl and cyclopropene regions⁸. On the other hand, it contained a strong and sharp absorption band at 3645 cm⁻¹ indicating the presence of a phenolic hydroxyl, flanked on both sides by tert-butyl groups, and a band at 2220 cm⁻¹ which we ascribed to stretching vibration of a disubstituted triple bond. The ¹H-NMR spectrum which displayed a singlet due to eighteen protons of the two tert-butyl groups, a hydroxyl proton singlet and a multiplet of eleven aromatic protons, indicat-

ed unequivocally a symmetric molecule. All this evidence suggested the structure *VIII* for this compound. From the reaction mixture we isolated small amounts of two ketones to which we ascribed structures *VIIb* and *IX* on the basis of their mass and $^1\text{H-NMR}$ spectra. These structures were confirmed by independent syntheses: the ketone *IX* was prepared by Friedel-Crafts acylation of 2,6-ditert-butylphenol with diphenylacetyl chloride in dichloroethane, whereas the ketone *VIIb* was synthesized by alkylation of sodium 2,6-ditert-butylphenoxide with 2-chloro-1,2-diphenylethanone in dimethyl sulfoxide. The ketone *VIIb* was very easily oxidised



with atmospheric oxygen in an alkaline medium to 7-benzoyl-3,5-ditert-butyl-7-phenylquinone methide (*X*). Further compounds, isolated after the thermolysis of *IV*, were the diphenoquinone *XI* and an orange-coloured, nitrogen-containing compound of the composition $\text{C}_{42}\text{H}_{50}\text{N}_2\text{O}_2$ the spectral data of which suggested the structure *XII*.

Our repeated experiments afforded reproducibly the acetylene *VIII* in yields identical with those described⁶ for the spirotrienone *VIb*; also some physical constants of the acetylene *VIII* agreed fairly well with those reported⁶ for *VIb*. We therefore suspected that the compound prepared by Sviridov and coworkers⁶ was in fact the impure acetylene *VIII*. In order to prove this assumption, we subjected the acetylene *VIII* to several reactions, described⁶ for the spirotrienone *VIb*. Heating the acetylene *VIII* with trichloroacetic acid afforded a ketone whose melting point and UV spectrum fairly agreed with those of the ketone, to which Sviridov and coworkers assigned the formula *VIIb*. This structure, however, was not in accord with the published phenolic hydroxyl band occurring at a wavenumber typical for an intermolecular hydrogen bond (3486 cm^{-1}). Our ketone exhibited also a band in this region (3435 cm^{-1}), together with a free phenolic hydroxyl band at 3594 cm^{-1} . Its mass

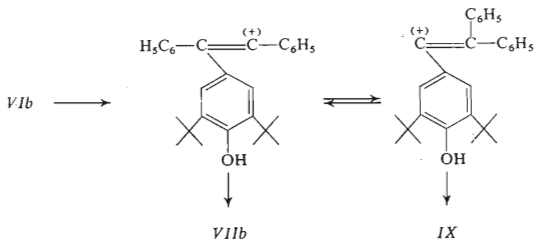


spectrum showed a loss of one of the tert-butyl groups during the hydrolysis, and since the spectrum contained a fragment $M^+ - C_6H_5CH_2$, this ketone was assigned the structure XIII. Hydrogenation of the acetylene VIII led to the tetrahydro derivative XIV which melted higher than, but had identical spectra with, the Sviridov's product believed to be XV. The published chemical shift of the benzylic protons, however, casts doubt on the correctness of the Sviridov's conclusions. The singlet of $\delta = 2.88$ ppm indicates the structure XIV rather than XV for which we would expect a doublet for the CH_2 and a triplet of the CH group. In order to explain this discrepancy, we prepared the phenol XV from 3,5-ditert-butyl-7-phenylquinone methide (XVI) and benzylmagnesium chloride. The 1H -NMR spectrum of the obtained product exhibited all the signals with the expected multiplicity. Also the mass

spectrum, containing the fragments $C_7H_7^+$ and $C_{21}H_{27}O^+$, was in accord with the structure *XV*. We can thus conclude that the compound, prepared by Sviridov and coworkers from the carbene *V*, was not the spirotrienone *Vib*.

In all the attempted preparations of the spirotrienone the molar ratio of the diazoxide *IV* to diphenylacetylene was 1 : 2.5. However, when diphenylacetylene was used in a ten-fold molar excess, the reaction mixture contained, in addition to the already found compounds *VIIb–XII*, also a minor amount of another compound with a mass spectrum corresponding to the spirotrienone *Vib*. The IR spectrum of this colourless substance displayed strong carbonyl and cyclopropene ring absorption bands, besides the bands of a monosubstituted benzene nucleus and tert-butyl groups. Its 1H -NMR spectrum exhibited a typical singlet of two vinylic protons of the cyclohexadiene ring. All these values were in good accord with the data, published⁵ for the spirotrienone *VIa*. The final proof that our compound has indeed the structure *Vib* was given by its unequivocal chemical transformations to known products. Hydrogenation of the trienone *Vib* over palladium in acetic acid proceeded with hydrogenolysis of the cyclopropene ring giving rise to a product the physical properties of which were identical with those of the phenol *XV*. The trienone *Vib* was hydrolysed with trifluoroacetic acid and methanol to two ketones, identical with the authentic compounds *VIIb* and *IX*.

These ketones were formed also from the pure spirotrienone *Vib* by repeated chromatography on silica gel or deactivated alumina. Such an opening of the cyclopropene ring on alumina was also observed with 1,2-dioctylcyclopropene^{9,10}. It is thus probable that the spirotrienone *Vib* was formed in small amount also in our experiments using a 2.5 fold excess of diphenylacetylene but during the isolation the cyclopropene ring was opened in a carbonyl-forming hydrolysis. This reaction obviously proceeds *via* a stilbene carbocation^{11,12} which undergoes a rearrangement and nucleophilic addition of water (Scheme 2). The addition of dichloro- or dibromocarbenes to diphenylacetylene is known to be a versatile method for preparing di-



SCHEME 2

phenylcyclopropenes⁸, and dimethylacetylene⁵ and phenylacetylene⁶ afford the corresponding spirotrienones; therefore the fact that the reaction failed for the combination carbene *V* – diphenylacetylene is somewhat unexpected. If we assume that the carbene *V* reacts in the singlet state^{13,14} the preference of the insertion reaction at the periphery of diphenylacetylene over the addition reaction can be plausibly explained by a steric hindrance to the formation of a CT-complex between the bonding π MO of the triple bond and the vacant π MO of the carbene.

EXPERIMENTAL

The melting points were determined on a Kofler block and are uncorrected. The analytical samples were dried at room temperature and 0.1 Torr for 7 h. The IR spectra were measured on an IR-20 spectrophotometer and the wavenumbers (in cm^{-1}) of the most important bands are given. UV spectra were taken on a Specord-UV-VIS instrument (λ_{max} given in nm). Mass spectra (MS) were measured on an AEI MS 902 mass spectrometer (70 eV; source temperature 110–230°C), the accuracy of high resolution measurements being 2 ppm. ¹H-NMR spectra were taken in CDCl_3 on a Varian HA-100 instrument (tetramethylsilane as internal standard; δ in ppm, *J* in Hz).

Thermolysis of the Diazo Oxide *IV* in the Presence of Diphenylacetylene

A. A mixture of the diazo oxide¹⁵ *IV* (750 mg) and diphenylacetylene (1.50 g) was heated in an argon atmosphere at the rate 5°C/min. Between 80–90°C a vigorous evolution of nitrogen occurred. The mixture was then kept at 90°C until the UV spectrum showed complete disappearance of *IV* (hexane, 353 nm). After cooling, the product was taken up in light petroleum and the extract (1.48 g) chromatographed on alumina (Brockmann, activity II–III, 100 g). Gradient elution with ether–light petroleum (1 : 9 to 1 : 1) afforded the following compounds:

2,2',6,6'-Tetratert-butylidiphenoquinone (*XI*, 31 mg; 5%), m.p. 245–246°C (ethanol), no depression on admixture with an authentic sample¹⁶.

4-(3',5'-Ditert-butyl-4'-hydroxybiphenyl)phenylacetylene (*VIII*, 506 mg; 41%), m.p. 184°C (hexane–ether). For $\text{C}_{28}\text{H}_{30}\text{O}$ (382.5) calculated: 87.91% C, 7.90% H; found: 87.71% C, 8.10% H. UV(CH_2Cl_2): 310. IR(CCl_4): 3645 (free OH), 2220 (C=C). ¹H-NMR: 1.48 (s, 18 H, 2 C(CH₃)₃), 5.24 (s, 1 H, OH), 7.15 to 7.65 (m, 11 H, arom. H). MS: 382.2284 (for $\text{C}_{28}\text{H}_{30}\text{O}$ calculated: 382.2296).

Diphenylacetylene (516 mg), m.p. 63–64°C (ethanol, no depression on admixture with an authentic sample).

Compound *XII* (98 mg, 10%), m.p. 213–218°C (capillary, hexane). For $\text{C}_{42}\text{H}_{50}\text{N}_2\text{O}_2$ (614.8) calculated: 82.04% C, 8.19% H, 4.56% N; found: 81.83% C, 8.32% H, 4.30% N. UV(CH_2Cl_2): 347, 413 (sh). IR(CCl_4): 1612 (conjugated C=O). MS: 614 (M^+), 586 ($\text{M}^+ - \text{N}_2$).

Benzhydryl-(3,5-ditert-butyl-4-hydroxyphenyl) ketone (*IX*, 38 mg; 3%), m.p. 191°C (hexane). For $\text{C}_{28}\text{H}_{32}\text{O}_2$ (400.6) calculated: 83.95% C, 8.05% H; found: 84.10% C, 7.95% H. UV(CH_2Cl_2): 286. IR(CCl_4): 3634 (free OH), 1680 (conjugated C=O), 1401 (COCH), 1391, 1361 (C(CH₃)₃). ¹H-NMR: 1.38 (s, 18 H, 2 C(CH₃)₃), 5.66 (s, 1 H, OH), 5.96 (s, 1 H, HC–CO), 7.28 (centre of m, 10 H, 2 C₆H₅), 7.89 (s, 2 H, 2 arom. H). MS: 400 (M^+), 233 (3,5-(tert-C₄H₉)₂-4-OH-C₆H₂C≡O⁺), 167 ((C₆H₅)₂CH⁺).

Benzoyl-(3,5-ditert-butyl-4-hydroxyphenyl)phenylmethane (VIIb, 43 mg; 3%), m.p. 117–118°C (hexane). For $C_{28}H_{32}O_2$ (400.6) calculated: 83.95% C, 8.05% H; found: 83.84% C, 8.20% H. UV(CH_2Cl_2): 244, 283 (sh). IR(CCl_4): 3645 (free OH), 1685 (C=O). 1H -NMR: 1.87 (s, 18 H, 2 $C(CH_3)_3$), 5.11 (s, 1 H, OH), 5.95 (s, 1 H, HCC_6H_5), 7.07 (s, 2 H, arom. H), 7.15–7.55 (m, 8 H, arom. H), 8.00 (m, 2 H, arom. H). MS: 400 (M^+), 295 ($(C_6H_5)_2(3,5\text{-tert-C}_4H_9)_2\text{-4-OH-C}_6H_2CH^+$), 105 ($C_6H_5C=O^+$).

B. A mixture of the diazo oxide *IV* (750 mg) and diphenylacetylene (7.50 g) was thermolysed and worked up as described under *A*. The compounds *XI*, *VIII*, *IX*, *VIIb* and *XII* were obtained in 3%, 35%, 3%, 2% and 10% yield, respectively. The acetylene *VIII* was preceded by 5,7-ditert-butyl-1,2-diphenylspiro[2,5]octa-1,4,7-trien-6-one (*VIb*, 39 mg; 3%), m.p. 190–192°C (hexane). For $C_{28}H_{30}O$ (382.5) calculated: 87.91% C, 7.90% H; found: 87.56% C, 8.05% H. UV(CH_2Cl_2): 238, 296, 313, 330. IR(KBr): 1870 (cyclopropene)⁸, 1621, 1608 (conjugated C=O), 754, 689 (C_6H_5). 1H -NMR: 1.29 (s, 18 H, 2 $C(CH_3)_3$), 6.52 (s, 2 H, quinoid H), 7.475 (centre of m, 10 H, arom. H). MS: 382 (M^+).

Benzoyl-(3,5-ditert-butyl-4-hydroxyphenyl)phenylmethane (*VIIb*)

A stirred mixture of sodium hydride (0.72 g; 30 mmol) and dimethyl sulfoxide (3 ml) was heated to 70–75°C for 45 min under nitrogen. After cooling to 5°C tetrahydrofuran (5 ml), followed by a solution of 2,6-ditert-butylphenol (6.18 g; 30 mmol) was added dropwise under stirring. After 45 min at 10°C a concentrated solution of 2-chloro-1,2-diphenylethanone (2.31 g; 10 mmol) in dimethyl sulfoxide was added dropwise during 1 h. After another hour the yellow mixture was poured in water (100 ml), acidified with citric acid and extracted with light petroleum (10 × 50 ml). Gradient elution on silica gel (500 g; ether–light petroleum 1 : 9–1 : 1) afforded the ketone *VIIb* (1.61 g; 40%), m.p. 117–118°C (hexane). The spectral properties of this product were identical with those of the ketone obtained from the diazo oxide *IV* and diphenylacetylene. Further fraction, eluted from the column, was yellow and contained 7-benzoyl-3,5-ditert-butyl-7-phenylquinone methide (*X*, 755 mg; 19%), m.p. 148–150°C (hexane). MS: 398.2230 (for $C_{28}H_{30}O_2$ calculated: 398.2246). UV (CH_2Cl_2): 247, 300 (sh), 342. IR (CCl_4): 1668 ($C_6H_5C=O$), 1625 (quinoid C=O), 1390, 1365 ($C(CH_3)_3$). 1H -NMR: 1.14 (s, 9 H, $C(CH_3)_3$); 1.25 (s, 9 H, $C(CH_3)_3$), 6.9 (d, 1 H, quinoid H, $J = 2.5$), 7.27 (d, 1 H, quinoid H, $J = 2.5$), 7.15–7.65 (m, 8 H, arom. H), 7.94 (m, 2 H, arom. H).

Benzhydryl 3,5-Ditert-butyl-4-hydroxyphenyl Ketone (*IX*)

A solution of diphenylacetyl chloride (1.12 g; 5 mmol) in dichloroethane (2 ml) was added to a stirred suspension of aluminium chloride (0.66 g; 5 mmol) in dichloroethane (2 ml) under cooling with ice and the stirring was continued for 15 min. Then, a solution of 2,6-ditert-butylphenol (1.03 g; 5 mmol) in dichloroethane (2 ml) was added in one portion. After 1 h the reaction mixture was warmed to room temperature, stirred for 2 h and poured into ice-cold water (20 ml). The organic layer was worked up and the product chromatographed on silica gel (60 g; ether–light petroleum 1 : 4), affording the ketone *IX* (0.78 g; 39%), m.p. 191°C (hexane).

1-(3,5-Ditert-butyl-4-hydroxyphenyl)-1,2-diphenylethane (*XV*)

A solution of 3,5-ditert-butyl-7-phenylquinone methide (*XVI*; 500 mg) in ether (5 ml) was added at room temperature to a stirred solution of benzylmagnesium chloride (prepared from 150 mg of magnesium, 0.3 ml of dibromoethane and 750 mg of benzyl chloride in 5 ml of ether). After stirring for 1 h the mixture was decomposed by addition of ammonium chloride solution (10 ml).

The usual work-up of the ethereal layer afforded the triarylethane *XV* (420 mg; 64%), m.p. 118–119°C (hexane). For $C_{28}H_{34}O$ (386.5) calculated: 86.99% C, 8.86% H; found: 87.25% C, 8.63% H. IR(CCl_4): 3645 (free OH), 1391, 1360 ($C(CH_3)_3$). 1H -NMR: 1.35 (s, 18 H, 2 $C(CH_3)_3$), 3.26 (d, 2 H, CH_2), 4.1 (t, 1 H, CH), 4.98 (s, 1 H, OH), 6.90–7.35 (m, 12 H, arom. H). MS: 386 (M^+), 295 (386 – $C_6H_5CH_2$), 91 ($C_6H_5CH_2^+$).

Acid-Catalysed Hydration of the Ethyne *VIII*

A mixture of the ethyne *VIII* (382 mg) and trichloroacetic acid (2.00 g) was heated on a steam bath for 4 h. After cooling and dilution with ice-cold water (50 ml), the trichloroacetic acid was neutralized with solid sodium hydrogen carbonate, the precipitate extracted with ether and worked up. Chromatography on silica gel (30 g, ether–light petroleum 1 : 4) afforded *benzyl 4-(3'-tert-butyl-4'-hydroxybiphenyl) ketone* (*XIII*; 194 mg, 56%), m.p. 173–175°C (ether–light petroleum). For $C_{24}H_{24}O_2$ (344.4) calculated: 83.68% C, 7.02% H; found: 83.39% C, 7.34% H. UV(CH_2Cl_2): 310. IR($CHCl_3$): 3594 (free OH), 3435 (bonded OH), 1765 ($C=O$), 1392, 1363 ($C(CH_3)_3$). MS: 344 (M^+), 253 (344 – $C_6H_5CH_2$), 91 ($C_6H_5CH_2^+$).

Hydrogenation of the Acetylene *VIII*

A solution of the acetylene *VIII* (19 mg; 0.055 mmol) in ethyl acetate (5 ml) was hydrogenated over palladium (7 mg). The consumption of hydrogen (2.6 ml, 744 Torr, 23°C) corresponded to a complete reduction of the triple bond. Filtration and evaporation afforded 18 mg (95%) of 1-[4-(3',5'-ditert-butyl-4'-hydroxybiphenyl)]-2-phenylethane (*XIV*), m.p. 149–150°C (methanol). For $C_{28}H_{34}O$ (386.5) calculated: 86.99% C, 8.86% H; found: 86.70% C, 8.81% H. UV(CH_2Cl_2): 270. IR(CCl_4): 3650 (free OH). 1H -NMR: 1.46 (s, 18 H, 2 $C(CH_3)_3$), 2.91 (s, 4 H, CH_2CH_2), 5.17 (s, 1 H, OH), 7.13–7.53 (m, 11 H, arom. H). MS: 386 (M^+), 295 (386 – $C_6H_5CH_2$), 91 ($C_6H_5CH_2^+$).

Acid-Catalysed Hydrolysis of the Spirotrienone (*Vib*)

A solution of the spirotrienone *Vib* (50 mg) in trifluoroacetic acid (0.5 ml) was set aside for 24 h at room temperature, the mixture diluted with methanol (2 ml), poured into ice-cold water (20 ml), neutralized with solid sodium hydrogen carbonate and extracted with ether (5 . 10 ml). The ethereal extract was subjected to preparative thin layer chromatography on silica gel (Woelm GF; ether–light petroleum 1 : 4; detection by UV light at 254 nm), affording the ketones *VIIb* (18 mg; 34%) and *IX* (21 mg; 42%). Physical constants of these products were identical with those of authentic samples.

Hydrogenation of the Spirotrienone *Vib*

A solution of the spirotrienone *Vib* (11.6 mg; 0.03 mmol) in ethanol (5 ml) was hydrogenated over Adams catalyst (9 mg). The hydrogen consumption (1.5 ml, 742 Torr, 24°C) corresponded to the addition of 0.06 mmol H_2 . After filtration and evaporation the product (9 mg) was crystallised from hexane; m.p. 118–119°C, no depression on admixture with an authentic sample of *XV*.

Chromatography of the Spirotrienone (*Vib*)

The compound *Vib* (75 mg) was chromatographed on an alumina column (10 g, Brockmann, activity II–III). Gradient elution with ether–light petroleum (1 : 9 to 2 : 3) afforded the starting spirotrienone *Vib* (24 mg, 32%) and the ketones *IX* (25 mg, 31%) and *VIIb* (19 mg, 24%).

Quinone Methide *X* by Air-Oxidation of the Ketone *VIIb*

A solution of the ketone *VIIb* (100 mg) in a mixture of acetonitrile (13 ml) and 0.1M sodium hydroxide was vigorously stirred at room temperature in an open flask till disappearance of the starting ketone (checked by thin layer chromatography on silica gel GF Woelm; ether-light petroleum 1 : 4). The yellow solution was neutralised with citric acid, the acetonitrile removed on a rotatory evaporator (bath temperature lower than 15°C) and the residue extracted with light petroleum. The extract, after evaporation of the solvent, afforded the pure quinone methide *X* (93 mg; 92%), m.p. 148–150°C (hexane).

Thanks are due to Dr S. Vašíčková for recording the infrared spectra, to Dr M. Buděšinský for measurement and interpretation of NMR spectra, to Dr L. Dolejš for measurement of mass spectra, and to the Analytical Department (Dr J. Horáček, Head) for elemental analyses.

REFERENCES

1. Kupchan M. S., Karim A., Mercks C.: *J. Org. Chem.* **34**, 3912 (1969).
2. Japp T. R., Meldrum A. N.: *J. Chem. Soc.* **75**, 1035 (1899).
3. Zimmerman H. E., Craft K.: *Tetrahedron Lett.* **1964**, 2131.
4. Bryce-Smith D., Frey G. I., Gilbert A.: *Tetrahedron Lett.* **1964**, 2137.
5. Pirkle W. H., Chamot D., Day W. A.: *J. Org. Chem.* **33**, 2152 (1968).
6. Sviridov B. D., Nikiforov G. A., Ershov V. V.: *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 2388.
7. Dewar M. J. S., Narayanaswami K.: *J. Amer. Chem. Soc.* **86**, 2422 (1964).
8. Closs G. L.: *Advan. Alicycl. Chem.* **1**, 60 (1966).
9. Breslow R., Winter R., Batiste M.: *J. Org. Chem.* **24**, 415 (1959).
10. Shimadate T., Kircher H. W., Berry J. W., Deutschman A. J.: *J. Org. Chem.* **29**, 485 (1964).
11. Curtin D. Y., Kampmeier J. A., O'Connor B. R.: *J. Amer. Chem. Soc.* **87**, 863 (1965).
12. Curtin D. Y., Kampmeier J. A., Farmer M. L.: *J. Amer. Chem. Soc.* **87**, 874 (1965).
13. Pirkle W. H., Koser G. F.: *Tetrahedron Lett.* **1968**, 3959.
14. Nikiforov G. A., Markaryan Sh. A., Plekhanova L. G., Sviridov B. D., Pekhh T. I., Rykov S. V., Lipmaa E. T., Ershov V. V., Buchachenko A. L.: *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 93.
15. Koser G. F., Pirkle W. H.: *J. Org. Chem.* **32**, 1992 (1967).
16. Cook C. D., English E. S., Wilson B. J.: *J. Org. Chem.* **23**, 755 (1958).

Translated by M. Tichý.