Tetrahedron. Vol. 34, pp. 1267 to 1270. Pergamon Press 1978. Printed in Great Britain

DIISOPHORONE AND RELATED COMPOUNDS—IV[1]

2,7-EPOXYDIISOPHORANES: SYNTHESIS AND REACTIONS OF 3,4-DIKETO-2,7-EPOXYDIISOPHORAN-1-OL

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(*Received in the UK 6 October 1977; Accepted for publication 15 November 1977*)

Abstract—Selenium dioxide oxidises 2,7 - epoxydiisophoran - 1 - ol - 3 - one to the corresponding yellow 3,4-diketone. This is reduced to diisophor - 2(7) - en - 1 - ol - 3 - one ("diisophorone") by Zn in acetic acid or on catalytic hydrogenation, or to 2,7 - epoxydiisophorane - 1,3,4 - triol by LAH or $NaBH_4$. Alkaline H_2O_2 cleaves ring A of the 3,4-diketone, providing a degradation of the diisophorane- to the bicyclo[3.3.1]nonane-system. The resulting 3 - (2' - carboxy - 2',2' - dimethyl)ethyl - 2,3 - epoxy - 1 - hydroxy - 5,7,7 - trimethylbicyclo[3.3.1]nonane - 2-carboxylic acid is convertible into its dimethyl ester by the action of diazomethane.

The degradation of the diisophorone structure by the scission of one of its cyclohexane rings is one of the principal aims of the present work. Our initial efforts towards this objective have centred on cleaving ring A. The attraction of this approach, amongst others, was the possible direct relation of the diisophorane and bicyclo[3.3.1]nonane ring system, by the conversion of members of the former into those of the latter series.

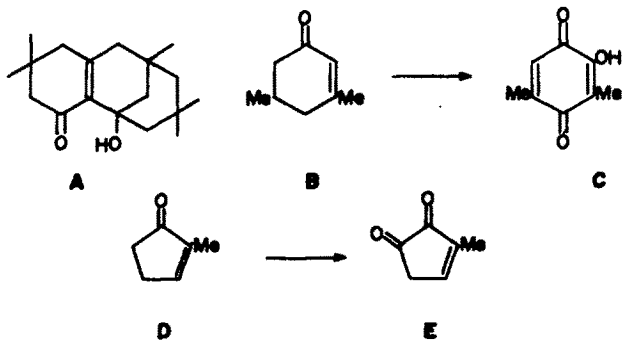
Although there is no lack of methods of opening oxygenated cyclohexane rings (the route having proved particularly useful in classical structural studies in the sterol field[2,3]), it seemed desirable to modify ring A of diisophorone to form an α-diketone or glycol structure, to which specific oxidative ring cleavage reactions are applicable. We now report the results of some work in this direction, involving the preparation and oxidation of 3,4 - diketo - 2,7 - epoxydiisophoran - 1 - ol (2).

The oxidation of reactive methylene- to carbonyl-groups by selenium dioxide[4] is a general reaction[5] that has proved particularly suitable for converting ketones into 1,2-diketones. The prototype relevant to the present work is the conversion of cyclohexanone into cyclohexane - 1,2 - dione[4,6] but numerous applications in terpene,[5,7] sterol[5,8] and triterpene[9,10] syntheses are on record. An attempt was therefore made to extend this reaction to suitable diisophorone derivatives.

The availability of 2,7 - epoxydiisophoran - 3 - on - 1 - ol was an essential factor in the success of the scheme: diisophorone (A), the parent compound of the series was of doubtful suitability, because its 2(7)-double bond was liable to divert the oxidation to the allyl-positions (C-6 or C-8). Thus, selenium dioxide converts 3,5 - dimethylcyclohex - 2 - enone into 3 - hydroxy - 2,6 - dimethylquinone (B→C),[11] showing that oxidation first affects the methylene group adjacent to the double bond; in 2 - methylcyclopent - 2 - enone (D),[12] on the other hand, the carbonyl group retains the predominating activating influence and promotes the formation of the 1,2-diketone (E). In the event, the action of selenium dioxide on diidophor - 2(7) - en - 1 - ol - 3 - one (A) resulted in multiple oxidation, producing yellow mixtures (tlc) (see Ref. 13), from which no uniform product could be separated. This difficulty was circumvented by the use of the epoxide (1).

Selenium dioxide in glacial acetic acid at 100° slowly converted 2,7 - epoxydiisophoran - 1 - ol - 3 - one (1) into a yellow crystalline product (60%), the properties of which are consistent with its formulation as 3,4 - diketo - 2,7 - epoxydiisophoran - 1 - ol (2). The stability of the epoxide-ring under the severe acidic oxidising conditions is noteworthy. The IR spectrum of 2 included, apart from the usual alkane bands,[14] a peak at 3525 cm^{-1} due to OH absorption, and a very intense peak at 1720 cm^{-1}, within the usual range of 1,2-diketones. The effect of the epoxide ring vibration could not be allocated with confidence, since many bands appeared in the 1000–840 cm^{-1} range. The compound did not absorb significantly in the UV region; the absence of a maximum near 270 nm is in accord with its inability to enolise to an α-hydroxy-ketone,[15] both carbon atoms (C-2, C-5) adjoining the 1,2-dione system being fully substituted.

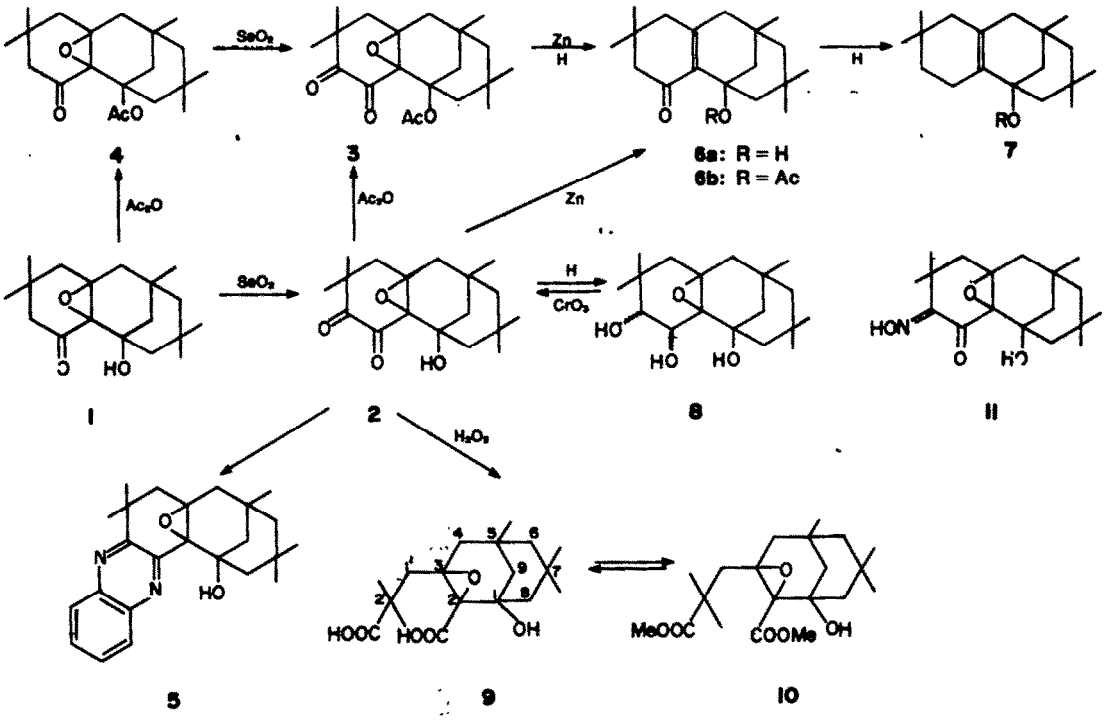
Perchloric acid-catalysed acetylation of 2 gave good



yields of the 1 - acetyl - derivative 3, which was also accessible by the action of selenium dioxide on 1 - acetoxy - 2,7 - epoxydiisophoran - 3 - one (4). With 1,2-diaminobenzene, the dione (2) readily formed a quinoxaline (5); the presence of the α-diketone system, and hence the formulation of 2 is thus confirmed.

preserved. However, the configuration of the 3- and 4-OH-groups in 8 remains undecided.

Ring-opening of cyclic 1,2-diketones by various oxidising agents provides a general route to the appropriate dicarboxylic acids. 4 - Methyl - *o* - benzoquinone[17] and β-naphtoquinone,[18] for example, are cleaved by peroxy-



The reduction of 2 (and 3) by several methods provided further structural support. Zinc in boiling acetic acid converted the 3,4-diketone 2 rapidly in good yield into diisophorone (6a), and the corresponding 1 - acetoxy-compound underwent the same reduction (3→6b). The reaction presents several points of interest: the 2(7)-double bond is thought to arise (in 6a, 6b) by reductive scission of the oxirane ring, followed by dehydration (see Part III[1]). The contrasting response to the reducing agent of the reactive 4 - keto-group and the unaffected 3-keto-function (in 2, 3) is noteworthy. Finally, the striking difference in the high rates of the reduction of 2 and 3 to 6a and 6b, compared with the low rates of the incomplete reduction of 1 and 4 to the same products by the same technique[1] must ultimately be ascribed to the enhanced activating effect of the 3,4-diketo-system in the former examples (2, 3). Catalytic hydrogenation of 3 also reduced the 4-keto-group preferentially, giving again 6b as the principal product; small amounts of 1 - acetoxydiisophor - 2(7) - ene (7) were formed as by-product by the subsequent slow hydrogenation of the 3-keto-group.[16]

The reduction of 2 by LAH or $NaBH_4$ gave moderate yields of a product formulated, on the basis of its origin, composition, molecular weight and properties, as the 1,3,4-triol 8. Its IR spectrum lacked CO-absorption and resembled very closely that of the comparable 2,7 - epoxydiidophorane - 1,3 - diol.[1] Reoxidation of the 1,3,4-triol (8) to the original 3,4-diketone (2) by chromic acid in good yield showed that the oxirane-ring, and the configuration of the structure as a whole have been

acids, phenanthrenequinone[19] is split by hydrogen peroxide in acetic acid to diphenic acid, while 1,2,3-triketocyclohexane[20] is oxidised quantitatively by periodate to glutaric acid. The oxidative scission of ring C in steroids[10] by this method served as model in the present work. Alkaline hydrogen peroxide in methanol decolourised the yellow 3,4-diketone 2 very rapidly, giving excellent yields of a product, formulated in accordance with its properties, as the substituted bicyclo[3.3.1]nonane dicarboxylic acid 9. 1 - Acetoxy - 2,7 - epoxydiisophorane - 3,4 - dione (3) gave the same diacid (9), the alkaline conditions at slightly raised temperatures causing simultaneous hydrolysis of the 1-acetoxy-grouping. The diacid 9 was invariably isolated as a monohydrate forming prismatic massive needles remarkable for an internal refraction appearing as a dark "spine" along the axis of each crystal. Treatment with boiling toluene converted the lustrous monohydrate into the white opaque anhydrous product, and recrystallisation from aqueous ethanol reversed the process. The IR spectra of the two forms differed in some respects: in addition to slight displacements of the principal absorption peaks of the functional groups (Experimental), the hydrate displayed additional prominent peaks at 1250, 1230 and 850 cm^{-1} as well as a strong broad band at 3160–3120 cm^{-1}; the last may reasonably be attributed to HO-absorption of the water of crystallisation.

On treatment with diazomethane, 9 gave excellent yields of the dimethyl ester 10, which was reconvertible into 9 by alkaline hydrolysis. Its IR spectrum included the expected carboxylic keto- (1725 cm^{-1}) and ester

peaks (1280, 1145 cm^{-1}). The frequency of its HO-band (3520 cm^{-1}) had hardly altered from that of the parent dicarboxylic acid (9), suggesting the absence in 9 of hydrogen bonding involving its carboxyl groups.

In conclusion, we briefly report another approach towards the functionalisation of the activated C-4 methylene group of diisophorone, based on the conversion of ketones into α-oximinoketones by the action of isoamyl nitrite.[21,22] The experimental procedure adopted was that developed for the production of steroid α-oximinoketones.[21] Diisophor - 2(7) - en - 1 - ol - 3 - one (6a) gave again intractable oils, from which no uniform product was isolable. The epoxide (1) was convertible into 2,7 - epoxy - 4 - oximinodiisophoran - 1 - ol - 3 - one (11), but yields were poor (maximum 20%, with 50% recovery of the reactant) even at the relatively high temperatures employed. In view of these difficulties, and the success of the direct synthesis of the α-diketones (2, 3), this route has for the present not been further explored.

EXPERIMENTAL

General information is given in Part I[14] concerning standard procedures, apparatus, reagents, solvents and abbreviations. Light petroleum had b.p. 60–80° unless otherwise specified. Catalytic hydrogenations were performed at room temp and atmospheric pressure.

3,4-Diketo-2,7-epoxydiisophoran-1-ol 2

A stirred soln of 1[1] (5.84 g, 0.02 mole) in glacial AcOH (30 ml), treated with selenium dioxide (2.45 g, 0.022 mole), was kept at 100° for 6–8 hr. The black deposit of Se was filtered off, the filtrate kept at 100° for another 10–30 min to coagulate the remaining (colloidal) oxidant and filtered again. The lemon-yellow liquid was stirred into hot H_2O (80–90°, 200 ml), and the finely divided ppt collected. Crystallisation from light petroleum (*ca.* 80 ml per g, recovery 80%) or preferably EtOH (*ca.* 8 ml per g, recovery 70%) gave light yellow prisms (3.4–4.15 g, 56–68%) of 2, m.p. 159–161° (Found: C, 71.1; H, 8.7. M, mass spectrometrically, 306. $C_{18}H_{26}O_4$ requires: C, 70.6; H, 8.5%. M 306). IR: 3525s (OH); 2970s, 2930s, 2875s, 1470m, 1460–1455m br (CH_3, CH_2); 1395m, 1365s (·CMe_2); 1720vs (CO), 1050s (C–O of OH); 1340m, 1260m, 1157m, 1000m, 927m, 860m, 790s cm^{-1}. UV: λ_{max} 215 nm (shallow) (log ϵ 3.3).

Action of selenium dioxide on diisophor-2(7)-en-1-ol-3-one (6, R=H)

The reactant (2.76 g, 0.01 mole) was treated with selenium dioxide (1.66 g, 0.015 mole) in boiling 1,4-dioxan or AcOH or Ac_2O (*ca.* 30 ml) for 2–3 hr. Removal of most of the solvent under reduced pressure, and addition of the filtered liquid to H_2O gave deep yellow to orange soft sticky resins which gave no crystalline solids on various purification attempts.

3,4-Diketo-2,7-epoxydiisophoran-1-ol Reactions

(a) *Quinoxaline derivative* 5. A soln of 2 (0.31 g, 0.001 mole) and 1,2-diaminobenzene (0.16 g, 0.0015 mole) in EtOH (10 ml) was boiled under reflux for 2 hr, evaporated (vacuum) to half volume, and added to H_2O (80 ml). The ppt gave prisms (0.23 g, 62%) of 5, m.p. 175–177° (from light petroleum) (Found: C, 76.3; H, 7.8; N, 7.3. $C_{24}H_{30}N_2O_2$ requires: C, 76.2; H, 7.9; N, 7.4%). IR: 3465s (OH); 3070w, 3015w, 770vs (CH, arom.); 2935vs, 2885s, 2865s, 1470s (CH_3, CH_2); 1390w, 1370s (·CMe_2); 1495m (C=C, arom); 1045s (C–O of OH); 920s (C–O–C epoxide); 1570w, 1420–1410s br, 1090s, 1000m cm^{-1}.

(b) 1 - *Acetoxy* - 3,4 - *diketo* - 2,7 - *epoxydiisophorane* (3). (i) A soln of 2 (0.62 g, 0.002 mole) in glacial AcOH (8 ml)–Ac_2O (0.8 ml) was treated with 60% perchloric acid (6 drops) with cooling, the liquid kept at room temp. for 1 hr, then poured on ice. The yellow ppt gave pale yellow flat needles (0.53 g, 75%) of 3, m.p. 154–156° (Found: C, 69.3; H, 8.05. $C_{20}H_{28}O_5$ requires: C, 69.0; H, 8.0%). IR: 2965s, 2950s, 2885ms, 1475s, 1457m (CH_3, CH_2); 1390w, 1367s (·CMe_2); 1720vs (CO, acetyl and diketone, superimposed), 1255s, 1240vs (C–O of acetate); 1270m, 870m (C–O–C epoxide); 1405w, 1050ms, 1025ms, 990m, 790m cm^{-1}.

(ii) Compound 4[1] (0.67 g, 0.002 mole) and selenium dioxide (0.24 g, 0.0024 mole) in glacial AcOH (15 ml) were stirred at 100° for 4 hr and the product isolated as described above. Compound 3 was obtained (58%) as needles, m.p. and m.m.p. 154–156°.

(c) *Reduction.* A soln of 2 (0.31 g, 0.001 mole) in boiling glacial AcOH (15 ml) was treated with Zn dust (2.0 g) in portions, and refluxed for 2.5 hr. The colourless liquid was decanted into ice water; the mixture slowly deposited white solid (0.18 g, 64%), identified as 6 (R = H) by its IR, UV spectra, and m.m.p. 84–85°.

1(Acetoxy-3,4-diketo-2,7-epoxydiisophorane Reduction

(a) *Action of zinc.* A boiling soln of 3 (0.35 g, 0.001 mole) in glacial AcOH (15 ml) containing a little H_2O (0.5 ml) was treated with portions of Zn dust (total, 2 g). After 30 min boiling under reflux, the colourless liquid was decanted, stirred into H_2O (150 ml) and treated with 3 N NaOH (10 ml). The resulting ppt (0.26 g, 80%) was 6b, identified by its IR spectrum and m.m.p. (124–125°).[23]

(b) *Catalytic hydrogenation.* A soln of 3 (0.35 g, 0.001 mole) in glacial AcOH (8 ml) was hydrogenated over Adam's catalyst[24] (0.12 g). Hydrogen uptake was rapid during 30 min, and continued very slowly thereafter (2 hr) (total, 105 cc; calc: 22 cc for catalyst, 67 cc for the first stage 3→6b; all at NTP). The usual work-up of the colourless liquid gave a soft low-melting solid consisting, according to tlc and IR spectra, mainly of 6b together with some 7 (R = CH_3CO).[23] Very small quantities of the former (identified by m.m.p. 124–126°, and IR spectrum)[23] were isolable therefrom by crystallisation from light petroleum.

2,7-Epoxydiisophorane-1,3,4-triol 8

(a) To a stirred turbid soln of LAH (0.19 g, 0.005 mole) in dry ether (25 ml) was added dropwise 2 (0.31 g, 0.001 mole) in the same solvent (30 ml) (gentle ebullition and effervescence), the liquid boiled under reflux for 1 hr, then set aside at room temp for 12 hr. The usual work-up[1] produced a colourless oil, which gave opaque prismatic platelets (0.09–0.125 g, 30–40%) of 8, m.p. 132–136° (but occasionally as low as 124–126°) (from light petroleum) (Found: C, 70.2; H, 9.7; M, mass-spectrometrically, 310. $C_{18}H_{30}O_4$ requires: C, 69.7; H, 9.7%. M 310). IR: 3460s vbr (OH); 2980, 2920s br d, 1470s, 1420ms (CH_3, CH_2); 1395ms, 1370s (·CMe_2); 1255m br, 865ms (C–O–C epoxide); 1345m, 1320m, 1170m, 1080s d, 1045s, 995m, 960s, 825m, 775–760ms d, 665m cm^{-1}. The spectrum closely resembles that of 2,7 - epoxy-diisophorane-1,3 - diol.[1]

(b) A soln of 2 (0.61 g, 0.002 mole) in EtOH (10 ml)–MeOH (2 ml) was treated with $NaBH_4$ (0.19 g, 0.005 mole). The colour of the mixture faded from orange to colourless; when all the reagent had been consumed, the liquid was added to H_2O. The ppt (0.18 g, 30%) was the 1,3,4-triol 8, identical (m.m.p., IR spectrum) with material obtained in (a).

(c) Reoxidation of 8 to its precursor 2. The 1,3,4-triol (8) (0.31 g, 0.001 mole) in acetone (12 ml) was treated with Kiliani's 10% chromic acid[25] (3 ml). The dark green soln was set aside at room temp. for 30 min, then diluted with H_2O. The pale yellow ppt (50%) was 2 (identified by m.m.p. and IR spectrum).

3 - (2' - Carboxy - 2',2' - dimethyl)ethyl - 2,3 - epoxy - 1 - hydroxy - 5,7,7 - trimethylbicyclo[3.3.1]nonane - 2 - carboxylic acid 9

A soln of 2 (1.53 g, 0.005 mole) in MeOH (20 mole) in MeOH (20 ml) was treated at 0° with 30% H_2O_2 (4.5 ml, 0.04 mole), followed by 3 N NaOH (3.3 ml, 0.01 mole) (slight temp rise). The liquid, the yellow colour of which was discharged (1–2 min), was set aside at room temp for 2 hr, diluted with H_2O (350 ml) and acidified with 3 N HCl. The resulting slightly cloudy liquid slowly deposited (12 hr) massive prismatic flat needles (1.35–1.52 g, 75–85%) of the *hydrated dicarboxylic acid* 9, m.p. 204–206° (decomp), forming prisms (from aqueous EtOH, 1:3) (Found: C, 60.3; H, 8.6. $C_{18}H_{32}O_6 \cdot H_2O$ requires: C, 60.3; H, 8.4%). IR: 3490vs (OH, alcohol); 3125m br (OH, H-bonded); 2955s, 2920ms–

2890m br, 1470m, 1445m (CH_3, CH_2); 1390m, 1370m (·CMe_2); 2580–2540w mult, 1420m, 915m (OH of COOH); 1720vs (CO of COOH); 1690–1685ms, 1635m (shoulders of CO peak); 1340m, 1320m, 1250s br, 1230s, 1160m, 1050m, 985m, 960ms, 850s, 705ms cm^{-1}.

The use of EtOH as solvent gave the same product **9** in 65% yield, as did the use of 2 M $NaHCO_3$ (0.025 mole) as the base (1 hr, 64%).

Compound **3** gave, in the above procedure (but allowing the reaction mixture to warm up spontaneously) the same product **9** (identified by m.m.p. and IR spectrum) in 85% yield.

On being kept at 110°/6 mm for 4 hr, or refluxed in anhyd toluene (25 ml per g, forming a suspension) for 3 hr, the foregoing hydrate gave (95%) the *anhydrous dicarboxylic acid* **9** as dull white needles, m.p. 202–204° (Found: C, 63.15, 63.6; H, 8.15, 8.0; M, mass-spectrometrically, 336, 340 [lower intensity]. $C_{18}H_{28}O_6$ requires: C, 63.5; H, 8.2%. M, 340.) IR: 3535m (OH, alcohol); 2965s, 2920–2900s br; 1480–1445m mult, 1425m (CH_3, CH_2); 1390w, 1365ms (·CMe_2); 2730–2565w mult; 920m (OH of COOH); 1700vs (CO of COOH); 1320m, 1300s, 1150m, 1120m, 1060ms, 960ms, 860m, 740m cm^{-1}. The anhyd acid was reconverted into the solvated form on crystallisation as above.

Dimethyl ester **10**

To an ethereal soln of diazomethane (from 0.02 mole of toluene - *p* - sulphonylmethylnitrosamide[26]) was added dropwise the foregoing **9** (0.68 g, 0.002 mole) dissolved in EtOH–(Na dried) ether (1:1, 15 ml), N_2 being evolved gently. The pale-yellow liquid was stored at room temp for 30 min, and the excess of diazomethane destroyed by the addition of glacial AcOH. The solvents were removed in a vacuum, and the residual pale yellow oil treated with H_2O. The solidified material gave, on crystallisation from light petroleum, needles (0.62 g, 85%) of the *dimethyl ester* **10**, m.p. 121–124° (Found: C, 65.2; H, 8.6. M, mass-spectrometrically, 367. $C_{20}H_{32}O_6$ requires: C, 65.2; H, 8.7%. M, 368). IR: 3520s (OH); 2965s, 1475m, 1455m (CH_3, CH_2); 1390w, 1365m (·CMe_2); 1725vs (CO); 1280s, 1145m (CO of ester); 1437m, 1060m, 1040m, 920w, 810w, 740m cm^{-1}.

A soln of **10** (0.37 g, 0.001 mole) in EtOH (10 ml)–3 N NaOH (1 ml) was boiled under reflux for 2 hr, diluted with H_2O (50 ml) and acidified with 3 N HCl (5 ml). The lustrous refractive needles (80%), which separated slowly on storage, were the hydrated dicarboxylic acid **9** (identified by m.m.p. and IR spectrum).

2,7-*Epoxy-4-oximinodiisophoran-1-ol-3-one* **11**

Potassium (0.47 g, 0.012 g atom) was dissolved in t-BuOH (25 ml) at 35–40° under N_2, followed by **1** (0.29 g, 0.001 mole). The liquid was kept at 60° under N_2 for 4 hr, then treated with isoamyl nitrite (0.30 g, 0.0025 mole) (colour change from deep yellow to dark bluish-green). After storage (12 hr) the liquid was added to ice-water, ether-extracted (extracts: E), and acidified with glacial acetic acid (*ca.* 6 ml). The solid, which separated slowly at 0°, gave **11** as a white opaque microcrystalline powder (0.065 g, 20%), m.p. 191–194° (after shrinking at 185°) (from aqueous 1:2 EtOH) (Found: C, 66.7; H, 8.5; N, 5.0. $C_{18}H_{27}NO_4$ requires: C, 67.3; H, 8.4; N, 4.4%). IR: 3420m br, 3275ms, 3190m (OH); 2960s, 2920vs, 2880s, 1475s, 1460s (CH_3, CH_2); 1390w, 1360m (·CMe_2); 1703vs (CO); 865s (C–O–C, epoxide); 1305m, 1170w, 1045m, 1030s, 995m, 940m, 820m, 805m, 780m cm^{-1}. On evaporation of extracts E, unchanged **1** (up to 50%) was recovered.

Applied to **6** (R = H), the foregoing method gave rise to the same colour changes, but the products were resinous and could not be successfully purified.

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