An Improved Two-step Route for the Preparation of β-Diketones from Aldehydes and its Application to the Synthesis of β-Damascone

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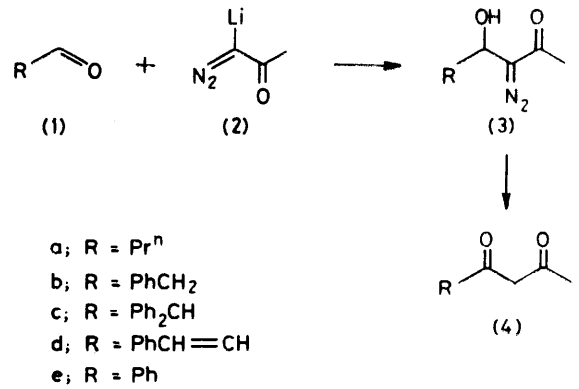
α-Diazo-β-hydroxyketones, obtained by condensation of aldehydes with 1-diazo-1-lithioacetone, are efficiently transformed into the corresponding β-diketones by exposure to rhodium(II) acetate. The sequence is applied to a new synthesis of β-damascone (10).

SEVERE experimental limitations have until recently limited the use of the long-known, synthetically appealing reactions of diazoacylmethanes with aldehydes.[1] Indeed, while the diazomethyl carbon atom of diazomethyl ketones is not nucleophilic enough to attack carbonyl groups at moderate temperatures, the thermolysis of these compounds in the presence of aldehydes leads to the formation of a variety of products, with serious difficulties being encountered in attempts to direct the reaction towards the formation of particular products.[2]

The report of Schöllkopf,[3] in 1970, of the successful preparation of ethyl diazo(lithio)acetate and the subsequent report of its non-destructive aldol-type condensation with ketones [4] and aldehydes to give the corresponding α-diazo-β-hydroxy-esters, has given new importance to these reactions as synthetic tools. Thus, a two-step procedure for the useful conversion of aldehydes into β-diketones, consisting in the condensation of an aldehyde (1) with 1-diazo-1-lithioacetone (2) followed by the acid-induced transformation of the α-diazo-β-hydroxy-keto-derivative (3) thus formed into the corresponding β-diketone (4) (Scheme 1), has recently been described.[5a-c]



SCHEME 1

The acid treatment required for the transformation (3) ⟶ (4), however, is again a serious limitation to the generality of the method. It has been reported, indeed, that in this medium compounds (3) partially undergo a retro-aldol reaction leading to the presence of variable amounts of the starting aldehyde (1) and diazoketone (2) in the reaction mixture. The method is unsuitable, moreover, for the preparation of β-diketones from α-diazo-β-hydroxy-keto-derivatives (3) which have acid-sensitive groups or a double bond vicinal to the hydroxy-group; in the latter case in particular, the acid treatment gives rise to highly complex reaction mixtures.

We now report that the transformation (3) ⟶ (4) occurs rapidly upon addition of a catalytic amount of rhodium(II) acetate [6,†] to a solution of (3) in 1,2-dimethoxyethane; by this technique the aforementioned acid-induced side reactions are suppressed and higher yields of cleaner products are obtained.

The results of the reactions of a number of representative aldehydes (1) with 1-diazo-1-lithioacetone (2) followed by the rhodium dicarbonyl-dimer-catalysed conversion of the resulting α-diazo-β-hydroxy-keto-derivatives (3) into the corresponding β-diketones (4) are shown in the Table.

	Step 1		Step 2		
Starting aldehyde	Product	Yield (%) [a]	Time/min	Yield (%) [b]	Final product
(1a)	(3a)	60 [c]	5	81 (85)	(4a)
(1b)	(3b)	61 [c]	2	77 (80)	(4b)
(1c)	(3c)	50 [c]	10	68 (86)	(4c)
(1d)	(3d) [d]	92	60	79 (82)	(4d)
(1e)	(3e) [e]	68	10	(90) [f]	(4e)

[a] The yields quoted refer to isolated samples of at least 98% purity. [b] Numbers in parentheses refer to yields obtained by g.l.c. standard method. [c] Isolated yields are not optimized. [d] Prepared according to ref. 5b. [e] Prepared according to ref. 5a. [f] Analytical data in agreement with an authentic sample.

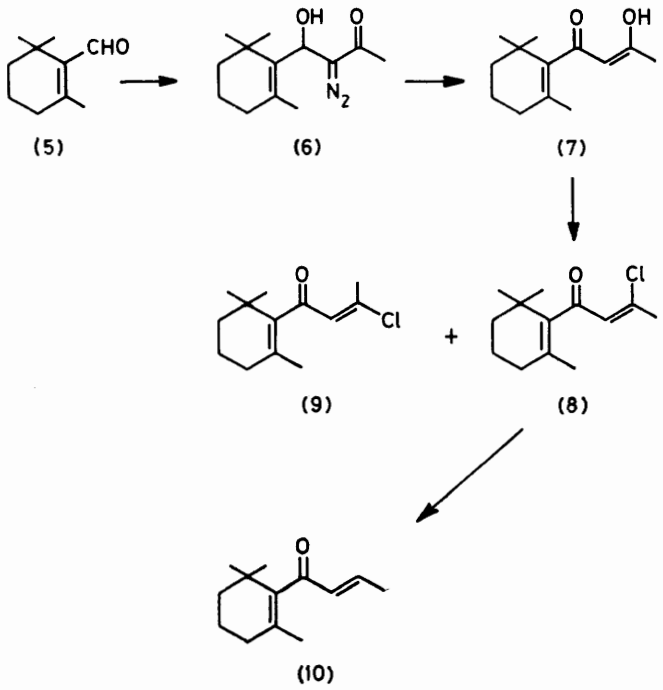
The first entry in the Table provides an example of the efficiency of the method for the preparation of aliphatic β-diketones such as (4a), which had previously been prepared in very low yield by Claisen condensation [8a,b] followed by copper(II) salt purification and preparative g.l.c.[8a] Earlier methods for the preparation of the γ-phenyl-β-diketone (4b) were based on Claisen condensations [9] or on the benzyne method; [10] an improvement of the latter, the phenylation of pentane-2,4-dione with diphenyliodonium chloride has been reported by Hampton *et al.*[11,‡] The only method for the preparation

† $Rh_2(OAc)_4$ has been successfully employed for the conversion of α-diazo-β-hydroxy-esters into the corresponding β-keto-esters (see ref. 7).

‡ There are a number of older, less advantageous methods for the preparation of (4b); see ref. 12.

of the γ-diphenyl-β-diketone (4c), which involves the unravelling of a cyclobutanonic precursor has been reported by Huisgen *et al.*,[13] while cinnamoylacetone (4d) can be obtained in low yield from ethyl cinnamate, acetone, and sodamide.[14] Benzoylacetone (4e), finally, can be prepared by a variety of methods such as condensation of ethyl acetate with acetophenone or of ethyl benzoate with acetone, or by treatment of benzene with keten dimer and hydrogen chloride in the presence of aluminium chloride.[15,*] Our procedure compares favourably with the methods quoted above in such aspects as number of steps, purity of the final products, and overall yield.

β-Diketones can be usefully employed in the synthesis of natural products. Scheme 2 outlines the application of the reaction sequence (1) ⟶ (3) to a short synthesis



SCHEME 2

of β-damascone (10), an important norisoprenoid constituent of the Burley,[16] Greek,[17] Virginia,[18] and Oriental [19] brands of tobacco as well as tea [20] and rose oils.[21]

β-Damascone (10) has been synthesized by a number of methods,[22] the interest in this compound, as well as in the other members of the small damascone family, being motivated by their high value for the flavour and fragrancy industry.[23] Aldol-type condensation of 1-diazo-1-lithioacetone with β-cyclocitral (5) [24] afforded the corresponding α-diazo-β-hydroxy-keto-derivative (6) in 83% yield. Exposure of (6) to a catalytic amount of rhodium(II) acetate in warm 1,2-dimethoxyethane for 3 h led to the formation of the corresponding β-diketone (7) (86%), which is a crucial intermediate *en route* to β-damascone (10) and as such has already been employed by Schulte-Elte *et al.*[22f] We have developed an alternate method for the preparation of (10) from (7). Treatment of (7) with oxalyl chloride in chloroform led to a reaction mixture consisting of the β-chloroenone isomers (8) and (9) in the ratio *ca.* 4 : 1. The required isomer (8) was easily separated by column chromatography and, finally, dehalogenated with silver–zinc couple [25] to give β-damascone (10) having analytical and spectroscopic properties identical with those reported for the natural product.[16a]

* (4e) is an important synthetic intermediate and several patented processes for its preparation are reported. See, *e.g.* I. Yoshinori, Jap. P. 7,015,723 (*Chem. Abstr.*, 1970, **73**, 45135w).

EXPERIMENTAL

All reactions involving organometallic reagents were performed in dry apparatus under nitrogen. Ether, 1,2-dimethoxyethane (DME), and tetrahydrofuran (THF) were distilled from $LiAlH_4$ immediately prior to use. Diisopropylamine was distilled from calcium hydride and stored over 4 Å molecular sieves. M.p.s were determined on a Kofler micro-hotstage. I.r. spectra were determined with a Beckman Acculab 5 spectrophotometer. ^1H N.m.r. spectra were recorded with a JEOL INM-C-60 HL and Varian EM-360 spectrometers. G.l.c. was performed with a Hewlett–Packard 5830 A gas chromatograph. All aldehydes were obtained commercially and were distilled from nitrogen prior to use. Diazoacetone was prepared by the reaction of acetyl chloride with an excess of diazomethane. Column chromatography was performed with Merck silica gel (0.063—0.200 mm), Florisil (Merck, 60—100 mesh), and aluminium oxide (Merck, neutral, activity IV).

3-Diazo-4-hydroxy-ketones (3).—A cold (−10 °C) solution of lithium di-isopropylamide [from addition of n-butyllithium in hexane (2 ml of a 2M solution) to a solution of di-isopropylamine (4.5 ml) in tetrahydrofuran (10 ml)] was added over 40 min to a stirred solution of butyraldehyde (1a) (0.25 g, 3.47 mmol) and diazoacetone (0.3 g, 3.57 mmol) at −78 °C. After being stirred at −78 °C for 30 min acetic acid (0.3 g) in diethyl ether (3 ml) was added during 5 min and the mixture was allowed to warm to room temperature. Water (100 ml) was then added, and the organic layer was separated, washed with saturated aqueous sodium hydrogencarbonate and brine, dried, and evaporated under vacuum to give a yellow oil (0.6 g). Chromatography on Florisil and elution with 7 : 3 (v/v) light petroleum–ether gave *3-diazo-4-hydroxyheptan-2-one* (3a) as a yellow oil (0.32 g, 60%); $\nu_{max.}$ 3 610 (OH), 2 090 (C=N_2), and 1 640 (C=O) cm^{-1}; δ(CCl_4) 2.2 (3 H, s, CH_3CO), 4.65 (1 H, m, C*H*OH), and 5.40br (1 H, s, OH) (Found: C, 53.7; H, 7.7; N, 18.0. $C_7H_{12}N_2O_2$ requires C, 53.8; H, 7.7; N, 17.9%).

Treatment of phenylacetaldehyde (1b) (0.29 g) by the above procedure, followed by chromatography of the crude product on Florisil with light petroleum–ether as eluant, gave 0.3 g (60%) of *3-diazo-4-hydroxy-5-phenylpentan-2-one* (3b), $\nu_{max.}$ 2 100 (C=N_2) cm^{-1}; δ(CCl_4) 1.98 (3 H, s, CH_3CO), 3.45 (2 H, benzylic H), 6.8 (1 H, t, C*H*OH), and 7.0—7.3 (5 H, m, ArH) (Found: C, 64.7; H, 6.0; N, 13.8. $C_{11}H_{12}N_2O_2$ requires C, 64.7; H, 5.9; N, 13.7%).

Treatment of diphenylacetaldehyde (1c) (0.2 g) as for (1a) above, followed by chromatography of the crude pro-

duct on Florisil with 7 : 3 (v/v) light petroleum–ethyl acetate as eluant yielded *3-diazo-4-hydroxy-5,5-diphenylpentan-2-one* (3c) (0.34 g, 50%), $\nu_{max.}$ 2 095 (C=N_2) cm^{-1}; δ(CCl_4) 1.9 (3 H, s, CH_3CO), 3.2br (1 H, s, OH), 4.05 (1 H, d, $CHPh_2$), 5.22 (1 H, d, C*H*OH), and 7.2—7.4 (10 H, m, ArH) (Found: C, 72.8; H, 5.8; N, 10.0. $C_{17}H_{16}N_2O_2$ requires C, 72.8; H, 5.8; N, 10.0%).

β-Diketones (4).—To a stirred solution of 3-diazo-4-hydroxyheptan-2-one (3a) (0.18 g) in DME (4 ml) was added rhodium(II) acetate (*ca.* 1 mg) and the mixture was stirred at room temperature for 5 min. The mixture was then filtered through a Celite pad, the filtrate was evaporated under vacuum, and the residue was chromatographed on Florisil. Elution with 4 : 1 (v/v) light petroleum–ether gave *heptane-2,4-dione* (4a) (0.12 g, 81%) as an oil (Found: C, 65.8; H, 9.3. $C_7H_{12}O_2$ requires C, 65.6; H, 9.4%); $\nu_{max.}$ 1 606 and 1 700 cm^{-1}; δ(CCl_4) 0.93 (3 H, t, CH_3CH$_2$), 1.5 (2 H, m, CH_3CH_2), 1.95 (3 H, s, CH_3CO), 2.15 (2 H, t, $CH_3CH_2CH_2$), 5.18 (1 H, s, CH=C), and 15.6br (1 H, s, enolic OH).

Treatment of 3-diazo-4-hydroxy-5-phenylpentan-2-one (3b) (0.3 g) by above procedure for 2 min gave a residue which was purified by chromatography on Florisil with 1 : 1 (v/v) light petroleum–ether to give 1-phenylpentane-2,4-dione (4b) (0.2 g, 80%), m.p. 50—53 °C, b.p. 150—155 °C at 6 mmHg) (lit.,[11] 133—136 °C at 10 mmHg); $\nu_{max.}$ ($CHCl_3$) 1 605 and 1 705 cm^{-1}; δ(CCl_4) 1.15 (3 H, s, CH_3CO), 3.45 (2 H, s, CH_2), 5.2 (1 H, s, CH=C), and 7.1—7.4 (5 H, m, ArH).

3-Diazo-4-hydroxy-5,5-diphenylpentan-2-one (3c), treated as above for 10 min, gave a residue (0.15 g) which was chromatographed on silica gel with chloroform as eluant to give *1,1-diphenylpentane-2,4-dione* (4c) (68%), m.p. 45—47 °C (from pentane) (Found: C, 80.8; H, 6.5. $C_{17}H_{16}O_2$ requires C, 80.8; H, 6.5%); $\nu_{max.}$ (CCl_4) 1 598 cm^{-1}; δ(CCl_4) 1.92 (3 H, s, CH_3CO), 4.77 (1 H, s, $CHPh_2$), 5.3 (1 H, s, CH=C), and 7.1—7.3 (10 H, m, ArH).

Treatment of 3-diazo-4-hydroxy-6-phenylhex-5-en-2-one (3d) [5b] for 1 h as above and chromatography of the residue (0.32 g) on silica gel with hexane as eluant yielded 6-phenylhex-5-ene-2,4-dione (4d) (0.22 g, 78%), m.p. 82—84 °C (lit.,[14] 83—84 °C], $\nu_{max.}$ (CCl_4) 1 640 (C=O) and 1 590 (C=C) cm^{-1}; δ(CCl_4) 2.07 (CH_3CO), 5.47 (1 H, s, C=CH–CO), 6.28 (1 H, d, *J* 16.5 Hz, 5-H), 7.29 (5 H, m, ArH), and 7.46 (1 H, d, *J* 16.5 Hz, 6-H).

Treatment of 3-diazo-4-hydroxy-4-phenylbutan-2-one (3e) [5a] for 10 min as above, filtration of the reaction mixture over Celite, and evaporation of the filtrate under vacuum gave a residue consisting 90% (g.l.c.) of benzoylacetone (4e) identical (n.m.r. and i.r. spectra, mixed m.p.) with an authentic sample.

3-Diazo-4-hydroxy-4-(2,6,6-trimethylcyclohex-1-enyl)butan-2-one (6).—A cold (−10 °C) solution of lithium di-isopropylamide [from addition of n-butyl-lithium in hexane (11.2 ml of a 2M solution) to a solution of di-isopropylamine in tetrahydrofuran (2 ml)] was added over 45 min to a stirred solution of β-cyclocitral (5) (3.1 g) and diazoacetone (1.7 g) at −78 °C. After the mixture had been stirred at −78 °C for 30 min a solution of acetic acid (3 ml) in ether (15 ml) was added during 5 min and the reaction mixture was allowed to warm to room temperature. Water (200 ml) was then added and the organic layer was separated, washed with saturated aqueous sodium hydrogencarbonate and brine, dried, and evaporated under vacuum to give a yellow oil (4.6 g). Chromatography on Florisil with 9 : 1 (v/v) hexane–ether as eluant gave the pure α-diazo-β-hydroxyketone (6) as a yellow oil (4 g, 83%); $\nu_{max.}$ 3 400 (OH), 2 090 (C=N_2), and 1 630 cm^{-1} (C=O); δ 1.09 (6 H, d, CMe_2), 1.82 (3 H, s, 2′-Me), 3.75br (1 H d, *J* 3.75 Hz, OH), and 5.45 (1 H, d, *J* 3.75 Hz, OCH) (Found: C, 66.15; H, 8.55; N, 11.85. $C_{13}H_{20}O_2N_2$ requires C, 66.07; H, 8.50; N, 11.79%).

3-Hydroxy-1-(2,6,6-trimethylcyclohex-1-enyl)but-2-en-1-one (*9-Hydroxy-β-damascone*) (7).—A solution of the α-diazo-β-hydroxyketone (6) and (2.1 g) rhodium(II) acetate [15] (80 mg) in DME (35 ml) was stirred at 45 °C for 3 h and the solvent was then evaporated off. G.l.c. of the residue (1.75 g) revealed the presence of only one product (93% yield). The residue was chromatographed on Florisil with 97 : 3 (v/v) light petroleum–ether as eluant to give the ketone (7) (1.68 g, 86%) as an oil, b.p. 93—96 °C at 10^{-1} Torr [lit.,[22b] 65—68 °C at 10^{-2} Torr]; $\nu_{max.}$ 3 350 (OH) and 1 600 cm^{-1} (C=O); δ 1.07 (6 H, s, CMe_2), 1.65 (3 H, s, 2′-Me), 1.4—1.9 (6 H, m, 3 × CH_2), 2.02 (3 H, s, Me), 5.38 (1 H, s, olefinic H), and 16 (1 H, s, enolic OH).

(Z)- and (E)-3-Chloro-1-(2,6,6-trimethylcyclohex-1-enyl)but-2-en-1-ones (8) *and* (9).—To a solution of the ketone (7) (1.1 g) in chloroform (7 ml) was added slowly oxalyl chloride (1.33 g). The mixture was stirred under nitrogen at room temperature for 10 min and then refluxed for 3 h. The solution was then evaporated to give an oily residue (1.5 g). Chromatography on Florisil with light petroleum as eluant yielded the pure (Z)-*β-chloroenone* (8) (0.89 g, 67%) (Found: C, 68.7; H, 8.5. $C_{13}H_{19}ClO$ requires C, 69.0; H, 8.4%); $\nu_{max.}$ 1 670 (C=O) and 1 595 cm^{-1} (C=C); δ 1.01 (6 H, s, CMe_2) 1.2—2.0 (6 H, m, methylenes), 1.6 (3 H, s, 2-Me), 2.58 (3 H, s, 1-Me), and 6.4br (1 H, s, olefinic H). Further elution with light petroleum–ether (97 : 3 v/v) gave the (E)-*β-chloroenone* (9) (0.2 g, 16.6%) (Found: C, 68.7; H, 8.6); $\nu_{max.}$ 1 670 (C=O) and 1 595 cm^{-1} (C=C); δ 1.01 (6 H, s, CMe_2), 1.2—2.0 (6 H, m, 3 × CH_2), 1.6 (3 H, s, 2-Me), 2.28 (3 H, s, Me), and 6.23br (1 H, s, olefinic H).

4-(2,6,6-Trimethylcyclohex-1-enyl)but-2-en-1-one (trans-β-*Damascone*) (10).—Aqueous HCl (10%) (8 ml) was added to zinc dust (1 g) (previously treated with H_2SO_3–HNO_3 (3 : 1 v/v), then washed with water and acetone) and the resulting suspension was mechanically stirred. After 1 h, the supernatant liquid was decanted and the zinc washed several times with acetone and then ether. A suspension of silver acetate (40 mg) in boiling acetic acid (60 ml) was then added and after the mixture had been stirred for 2 min, the supernatant was decanted and the zinc–silver couple washed with acetic acid (3 ml), ether (3 × 3 ml), and methanol (5 ml). A solution of the β-chloroenone (8) (0.6 g) in methanol (5 ml) was added to the zinc–silver couple and the resulting suspension was vigorously stirred at room temperature for 21 h. The mixture was then filtered, the residue was washed with methanol, and the filtrate was evaporated under vacuum to give an oily residue (0.5 g). Chromatography on silica gel with light petroleum as eluant gave pure *trans*-β-damascone (10) (0.31 g, 60%), $\nu_{max.}$ (EtOH) 225 nm; $\nu_{max.}$ 980 (CH=CH-*trans*) and 1 615, 1 650, and 1 680 (C=C–C=O) (no trace of the CH=CH-*cis* band at 750—780 cm^{-1}); δ($CDCl_3$) 1.0 (6 H, s), 1.50 (3 H, s), 1.91 (3 H, dd, *J* 6.5 and 1 Hz), 6.0 (1 H, dq, *J* = 16 and 1 Hz), and 6.6 (1 H, dq, *J* 16 and 6.5 Hz); *m/e* 192 (M^+). The above spectroscopic data and analytical properties are identical with those of natural *trans*-β-damascone.[16a]

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REFERENCES

[1] E. Buchner and T. Curtius, *Ber.*, 1885, **18**, 2371; F. Schlotterbeck, *ibid.*, 1907, **40**, 3000; F. Schlotterbeck, *ibid.*, 1909, **42**, 2565; W. Diekmann, *ibid.*, 1910, **43**, 1024; C. D. Gutsche and M. Hillman, *J. Amer. Chem. Soc.*, 1945, **76**, 2236; A. S. Wasfi, *J. Indian Chem. Soc.*, 1970, **47**, 341.

[2] *Cf.* M. E. Alonso and P. Jano, *J. Heterocycl. Chem.*, 1980, **17**, 721.

[3] U. Schöllkopf and H. Frasnelli, *Angew. Chem.*, 1970, **82**, 291.

[4] R. Pellicciari, B. Natalini, M. Taddei, A. Ricci, G. A. Bistocchi, and G. De Meo, *J. Chem. Res.* (*S*), 1979, 143 and references cited therein.

[5] (*a*) E. Wenkert and C. A. McPherson, *J. Am. Chem. Soc.*, 1972, **94**, 8084; (*b*) U. Schollkopf, B. Banhidai, H. Frasnelli, R. Meyer, and H. Beckhaus, *Liebigs Ann. Chem.*, 1974, 1767; (*c*) R. Pellicciari, E. Castagnino, and S. Corsano, *J. Chem. Res.* (*S*), 1979, 76.

[6] P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. A*, 1970, 3322.

[7] R. Pellicciari, R. Fringuelli, P. Ceccherelli, and E. Sisani, *J. Chem. Soc., Chem. Commun.*, 1979, 959.

[8] (*a*) N. Thoai, N. Ngochien, and C. Beautè, *Bull. Soc. Chim. Fr.*, 1970, **10**, 3656; (*b*) F. Vlacil, B. M. Saych, and J. Koncky, *Coll. Czech. Chem. Commun.*, 1975, **40**, 1345.

[9] G. T. Morgan and C. R. Porter, *J. Chem. Soc.*, 1924, **125**, 1269; C. R. Hauser and J. Manyik, *J. Org. Chem.*, 1953, **18**, 588; F. Castelli and P. Canonne, *Bull. Soc. Chim. Fr.*, 1974, 317.

[10] K. G. Hampton, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, 1964, **29**, 3511; C. R. Hauser and T. Harris, *J. Am. Chem. Soc.*, 1958, **80**, 6360.

[11] K. G. Hampton, T. M. Harris, and C. R. Hauser, *Org. Synth.*, 1971, **51**, 132.

[12] E. Fischer and C. Bulow, *Chem. Ber.*, 1885, **18**, 2131; L. I. Smith and J. S. Showell, *J. Org. Chem.*, 1952, **17**, 836.

[13] R. Huisgen, L. Feiler, and P. Otto, *Chem. Ber.*, 1969, **102**, 3405.

[14] R. Levine, J. A. Conroy, J. T. Adams, and C. R. Hauser, *J. Am. Chem. Soc.*, 1945, **67**, 1510.

[15] C. D. Hurd and C. D. Kelso, *J. Am. Chem. Soc.*, 1940, **62**, 1548.

[16] E. Demole and D. Berthet, *Helv. Chim. Acta*, 1971, **54**, 681; 1972, **55**, 1866.

[17] B. Kimland, A. J. Aasen, and C. R. Enzell, *Acta Chem. Scand.*, 1972, **26**, 2177.

[18] I. Wahlberg, K. Karlsson, D. J. Austin, N. Junker, J. Roeraade, C. R. Enzell, and W. H. Johnson, *Phytochemistry*, 1977, **16**, 1217.

[19] E. Demole and P. Enggist, *Helv. Chim. Acta*, 1978, **61**, 2318.

[20] W. Renold, R. Naf-Muller, U. Keller, B. Willhalm, and G. Ohloff, *Helv. Chim. Acta*, 1974, **57**, 1301.

[21] E. Demole, personal communication, quoted by G. Ohloff in ref. 22, p. 488.

[22] Synthesis of β-damascone (i) from β-cyclocitral: (*a*) E. Demole, P. Enggist, U. Sauberli, M. Stoll, and E. sz. Kovats. *Helv. Chim. Acta*, 1970, **53**, 541; (*b*) E. Kovats, E. Demole, G. Ohloff, and M. Stoll, Ger. Offen. 1,807,568 (*Chem. Abstr.*, 1969, **71**, 80,798); (*c*) M. Kasano and Y. Matsubara, *Kinki Daigaku Rikogakubu HenkyuHokuku*, 1978, **13**, 37 (*Chem. Abstr.*, 1978, **89**, 163 794); (ii) from cyclogeranic acid methyl ester: (*d*) K. H. Schulte-Elte, Ger. Offen. 2,305,140/1973 (*Chem. Abstr.*, 1973, **79**, 115,743); (iii) from β-ionone: (*e*) G. Buchi and J. C. Vederas, *J. Am. Chem. Soc.*, 1972, **94**, 9128; (*f*) K. H. Schulte-Elte, B. L. Muller, and G. Ohloff, *Helv. Chim. Acta*, 1973, **56**, 310; (iv) from β-ionol: (*g*) S. Isoe, S. Katsumura, and T. Sakan, *Helv. Chim. Acta*, 1973, **56**, 1514; (v) from 2,2,6-trimethylcyclohexanone: (*h*) G. Ohloff, V. Rautenstrauch, and K. H. Schulte-Elte, *Helv. Chim. Acta*, 1973, **56**, 1503; (*i*) V. Rautenstrauch and F. Naf, Ger. Offen, 2,242,751/1973 (*Chem. Abstr.*, 1973, **79**, 5053); (*j*) K. H. Schulte-Elte, Ger. Offen, 2,646,322/1977.

[23] For a review on damascones and related products, see G. Ohloff, ' Recent Developments in the Field of Naturally Occurring Aroma Components,' in ' Progress in the Chemistry of Organic Natural Products,' Springer–Verlag, Wien and New York, 1978, vol. 38, p. 483.

[24] L. Colombi, A. Bosshard, H. Schinz, and C. F. Seidel, *Helv. Chim. Acta*, 1951, **34**, 265.

[25] R. D. Clark and C. H. Heatcock, *J. Org. Chem.*, 1976, **41**, 636.