Intramolecular Hetero-Diels-Alder Reaction of 3-Benzylidene-1,2-dicarbonyl Compounds[1]

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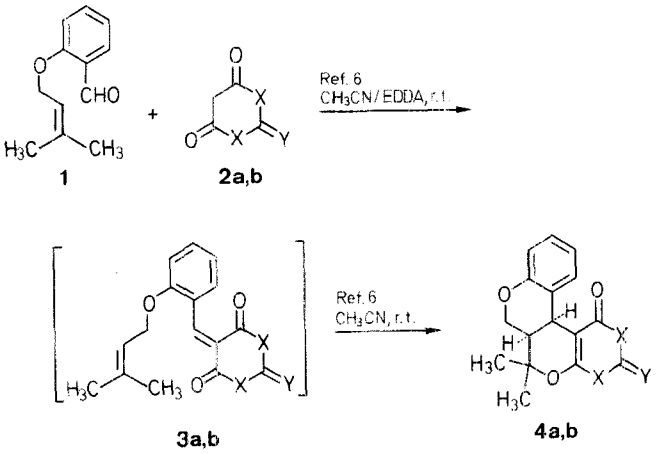
The intramolecular hetero-Diels-Alder reaction of benzylidene 2-oxocarboxylic acid esters **7** is described, and the diastereoselectivity of the reaction determined. Condensation of the aldehyde **1** with 2-oxocarboxylic acids **5a, b** followed by esterification gives **7a, b** which cyclize in refluxing xylene to **8a, b** and **9a, b** in better than 95% yield.

The intramolecular hetero-Diels-Alder reaction of α,β-unsaturated carbonyl compounds is an efficient method for the construction of annulated dihydropyrans.[2-4] In order to obtain acceptable reaction rates, the heterodiene has to be activated by an electron acceptor substituent in the 3-position.[5] The necessary heterodienes **3** are easily synthesized by Knoevenagel condensation of suitable aldehydes like **1** with 1,3-dicarbonyl compounds like **2a, b**. They are usually formed *in situ* only and undergo highly selective Diels-Alder reactions to the corresponding dihydropyrans **4**. Thus only *cis*-annulated cycloadducts are found in this reaction.[6]

It has been shown by calculations,[7] that an activation of oxadienes by electron acceptors should also be feasible from other positions, thus giving access to dihydropyrans with different substitution patterns. Of special interest is the 2-position, since easily accessible 1,2-dicarbonyl compounds can be used as starting materials. In this paper we describe the intramolecular hetero-Diels-Alder reaction of heterodienes, which were obtained by condensation of the unsaturated aldehyde **1** with 2-oxoacids **5**.

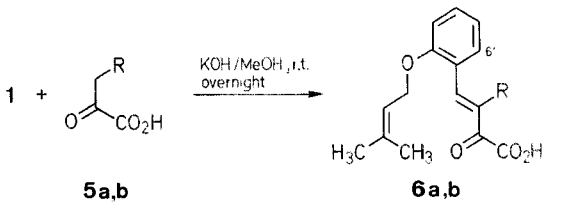


1 **2a,b** **3a,b** **4a,b**

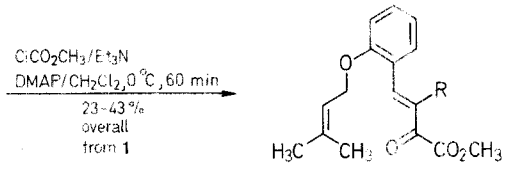
EDDA = ethylenediammonium diacetate

2,3,4	X	Y
a	O	$(CH_3)_2$
b	NCH_3	O

The condensation of **1** with **5a, b** followed a published procedure.[8,9] The acids **6a, b** were converted without isolation to the corresponding methyl esters **7a, b**. The overall yield of analytically pure esters was 43% (**7a**) and 23% (**7b**). The synthesis was not optimized, since the aim of this work is to demonstrate the feasibility of the cycloaddition.



5a,b **6a,b**

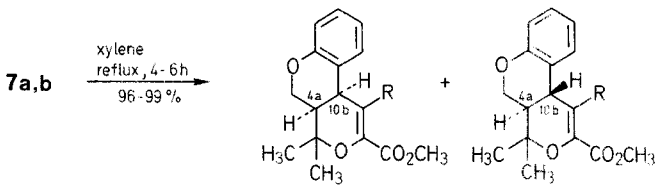


7a,b

5,6,7	R
a	H
b	CH_3

DMAP = 4-dimethylaminopyridine

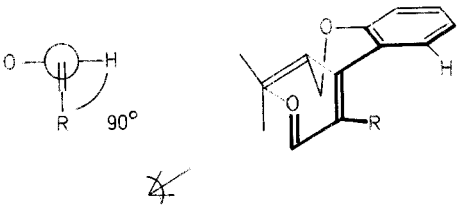
The E-configuration of **7a** is evident from the ^{1}H-NMR-spectrum, where the absorption for 4-H is found with a coupling constant of $J_{3,4}$ = 16 Hz. In the case of **7b**, the determination of the configuration proved difficult. Neither the ^{13}C-chemical shifts nor the determination of the ^{13}C,^{1}H-coupling constants[10,11] gave an unambiguous assignment. However an NOE of 12% was observed at 6'-H on irradiation of the absorption of the methyl group at C-3. No enhancement was seen for the signal of 4-H, which finally demonstrated the E-configuration of **7b**.



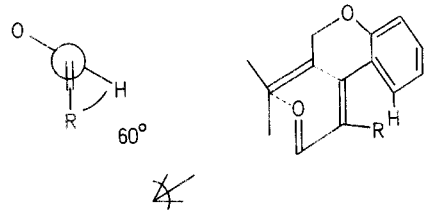
8a,b **9a,b**

7,8,9	R
a	H
b	CH_3

The Diels-Alder reaction was conducted in refluxing xylene. After 4 and 6 h, respectively, the mixture of diastereomeric cycloadducts **8a/9a** and **8b/9b** were isolated in 96% and 99% yield. The *cis/trans* ratio was determined from ^{13}C-NMR spectra of the reaction mixtures. The unsubstituted **7a** gave *trans*-annulated **9a** preferably (ni-de[12] = 38%), whereas the reaction of the methyl derivative **7b** was *cis*-selective (ni-de = 67%). The diastereomers **8** and **9** were separated by chromatography on silica gel. The stereochemistry of the cycloadducts was determined from ^{1}H-NMR spectra. The signals of the four protons at C-4a, C-5 and C-10b are well resolved. The coupling constant $J_{4a,10b}$ was 11.5 Hz for the *trans*- compounds **9a** and **9b**; values of 6.1 and 5.0 Hz were observed for the *cis*-annulated **8a** and **8b**, respectively. In the *cis*-fused adducts an additional coupling between the equatorial proton at C-5 and H-10b was seen, thus indicating the pseudoequatorial position of the latter.



endo-E-syn



exo-E-anti

Since both dienes possess the *E*-configuration, it seems reasonable to take only the two transition states with the *E*-configuration into consideration, assuming that, even if an isomerization takes place during the reaction, the *E*-diene reacts preferentially.[13] In the *exo-E-anti*-transition state leading to **9**, the angle between the heterodiene and the aromatic ring in the chain in the transition state should be about 60°. Thus the proton at C-6' of the aromatic nucleus and the substituent at C-3 are close to each other. In **7a** the interaction is not severe, since R is hydrogen; thus the reaction is *trans*-selective. Introduction of a methyl group at C-3 increases the interaction of the two substituents at 6' and 3 and the *exo*-transition state is destabilized. However, in the *endo-Z-syn*-transition state leading to **8** the above mentioned angle should be about 90°. This gives the minimum interaction possible. Therefore the *endo*-transition state is not destabilized by any substituent R. In accord with these considerations, **7b** gives predominantly **8b**. Thus a control of selectivity can by achieved by choice of the substituents at C-3 and C-6' in **7**. This is in accord with our investigation on benzylidene pyrazolones,[13] where a substituent in an equivalent position strongly influenced the stereochemical result of the cycloaddition reaction.

Synthesis of the Heterodienes 7a, b; General Procedure:

A third of a solution of KOH (8.40 g, 0.15 mol) in MeOH (25 mL) is added dropwise to a mixture of 2-(3-methyl-2-butenyloxy)benzaldehyde (**1**; 19.0 g, 0.10 mol) and pyruvic acid (**5a**; 8.8 g, 0.10 mol) or 2-oxobutyric acid (**5b**; 10.2 g, 0.10 mol) in MeOH (10 mL). The remainder of the alkaline solution is added quickly, which causes the temperature to rise to ca. 40°C. After the reaction mixture has stirred overnight, H_2O (50 mL) is added, and the organic layer separated. After extraction with *t*-butyl methyl ether (80 mL) the aqueous phase is acidified with conc. HCl to pH 1 and then thoroughly extracted with *t*-butyl methyl ether (3 × 80 mL). The combined organic phase of this extraction is washed with saturated aq. NaCl and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the product is dried *in vacuo*. The yield of crude acid **6** is ≈ 100%.

To a solution of the crude product 4-[2-(3-methyl-2-butenyloxy)phenyl]-2-oxo-3-butenoic acid (**6a**; 2.00 g, 7.70 mmol) or 3-methyl-4-[2-(3-methyl-2-butenyloxy)phenyl]-2-oxo-3-butenoic acid (**6b**; 2.00 g, 7.30 mmol) in CH_2Cl_2 (100 mL) is added methyl chloroformate (3.90 mL, 50.0 mmol) and triethylamine (7.60 mL, 55.0 mmol). The resulting mixture is cooled to 0°C and the reaction is started by addition of 4-dimethylaminopyridine (600 mg, 4.90 mmol). After stirring at this temperature for 60 min, CH_2Cl_2 (200 mL) is added and the solution washed with saturated aq. NH_4Cl. The organic phase is dried (Na_2SO_4), the solvent removed *in vacuo*, and the crude ester purified by flash-chromatography with the eluent given below. Yields refer to analytically pure crystalline products.

Methyl 4-[2-(3-Methyl-2-butenyloxy)phenyl]-2-oxo-3-butenoate (**7a**): R_f 0.26 (ether/petroleum ether, 1:3); yield: 860 mg (43%); m.p. 38–40°C (hexane).

$C_{16}H_{18}O_4$ (274.3) calc. C 70.06 H 6.61 found 70.02 6.63

MS (70 eV): *m/e* (rel. int. %) = 274 (5), 215 (29), 206 (39), 147 (100), 103 (55), 69 (100), 41 (100).

IR (KBr): ν = 1745, 1685, 1595, 1260, 750 cm^{-1}.

UV (CH_3CN): λ_{max} (log ε) = 228 (sh.), 238 (sh.), 303 (4.05), 355 nm (4.04).

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.76 (d, 3H, J = 1.0 Hz, CH_3); 1.81 (d, 3H, J = 1.0 Hz, CH_3); 3.94 (s, 3H, OCH_3); 4.63 (br d, 2H, J = 7 Hz, CH_2); 5.54 (mc, 1H, =C–H); 6.90–7.06 (m, 2H, 3'-H, 5'-H); 7.41 (ddd, 1H, J = 8.5 Hz, 7.5 Hz, 2.0 Hz, 4'-H); 7.49 (d, 1H, J = 16 Hz, 3-H); 7.65 (dd, 1H, J = 8.0 Hz, 2.0 Hz, 6'-H); 8.23 (d, 1H, J = 16 Hz, 4-H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 18.29 (CH_3 *cis*); 25.76 (CH_3 *trans*); 52.82 (OCH_3); 65.43 (CH_2); 112.64 (C-3'); 119.21 (C-2''); 120.72, 120.80 (C-5', C-3); 123.22 (C-1'); 129.73 (C-6'); 133.02 (C-4'); 138.39 (C-3''); 144.37 (C-4); 158.70 (C-2'); 162.92 (C-1); 183.01 (C-2).

Methyl 3-Methyl-4-[2-(3-methyl-2-butenyloxy)phenyl]-2-oxo-3-butenoate

(**7b**): R_f 0.25 (ether/petroleum ether, 1:4); yield: 460 mg (23%); m.p. 38–39°C (ether/hexan).

$C_{17}H_{20}O_4$ (288.4) calc. C 70.81 H 6.99 found 70.78 6.98

MS (70 eV): *m/e* (rel. int. %) = 288 (1), 229 (2), 220 (3), 161 (100), 69 (48).

IR (KBr): ν = 1740, 1665, 1615, 1595, 1255, 1045, 750 cm^{-1}.

UV (CH_3CN): λ_{max} (log ε) = 220 (4.05), 240 (sh.), 287 (4.13), 333 nm (4.00).

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.73 (br s, 3H, CH_3 *cis*); 1.79 (br s, 3H, CH_3 *trans*); 2.08 (d; 3H, J = 1.5 Hz, 3-CH_3); 3.93 (s, 3H, OCH_3); 4.56 (br d, 2H, J = 7 Hz, CH_2); 5.48 (mc, 1H, =C–H); 6.90–7.06 (m, 2H, 3'-H, 5'-H); 7.32–7.50 (m, 2H, 4'-H, 6'-H); 7.78 (br s, 1H, 4-H).

NOE-experiment: Irradiation at δ = 2.08 (3-CH_3). Significant enhancements in the difference spectrum: δ = 3.93 (OCH_3, 13%), 7.46 (6'-H, 12%).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 12.10 (3-CH_3); 18.25 (CH_3 *cis*); 25.74 (CH_3 *trans*); 52.28 (O–CH_3); 65.40 (CH_2); 112.19 (C-3'); 119.38 (C-2''); 120.34 (C-5'); 124.02 (C-1'); 130.28 (C-6'*); 131.40 (C-4'*); 132.64 (C-3); 138.13 (C-3''); 143.14 (C-4); 157.33 (C-2'); 165.89 (C-1); 190.15 (C-2).

Cyclization of the Heterodienes 7a, b; General Procedure:

A solution of methyl benzylidene-2-oxo-carboxylates **7a** (400 mg, 1.46 mmol) or **7b** (400 mg, 1.39 mmol) and hydroquinone (5 mg, 0.05 mmol) in dry xylene is refluxed under argon for 4 h (**7a**) or 6 h (**7b**). The solvent is removed *in vacuo*, and the residue flash chromatographed (eluent, ether/petroleum ether, 1:2). The sample is analyzed by ^{13}C-NMR, the diastereomers then separated by column chromatography on silica gel, using the eluents given below. Yields refer to the mixture of diastereomers.

In the reaction of **7a**; diastereomers **8a/9a** are produced in a ratio of 1:2.2 (0.2); yield: 384 mg (96%); separation (eluent, EtOAc/petroleum ether, 1:6) and subsequent crystallization (hexane).

Fraction 1: *Methyl (4a RS, 10b SR)-4,4-Dimethyl-4a,10b-dihydro-4H,6H-[1]benzopyrano[4,3-d]pyran-2-carboxylate* **8a** (*cis*); m.p. 84–88°C (hexane)

$C_{16}H_{18}O_4$ (274.3) calc. C 70.06 H 6.61 found 70.19 6.77

MS (70 eV): *m/e* (rel. int. %) = 274 (41), 259 (4), 241 (5), 231 (24), 215 (100).

IR (KBr): ν = 1750, 1640, 1590, 1495, 750 cm^{-1}.

UV (CH_3CN): λ_{max} (log ε) = 221 (4.00), 241 (3.95), 246 (sh.), 276 (3.64), 283 nm (3.58).

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.37 (s, 3H, 4-CH_3 ax); 1.51 (s, 3H, 4-CH_3 eq); 2.12 (dddd, 1H, J = 11.5 Hz, 6.1 Hz, 3.8 Hz, 1.5 Hz, 4a-H); 3.56 (dd, 1H, J = 11.5 Hz, 11.0 Hz, 5-H ax); 3.54–3.61 (m, 1H, 10b-H); 3.66 (s, 3H, OCH_3); 4.39 (ddd, 1H, J = 11.0 Hz, 3.8 Hz, 1.6 Hz, 5-H eq); 6.12 (dd, 1H, J = 2.5 Hz, 1.5 Hz, 1-H); 6.85 (dd, 1H, J = 8.5 Hz, 1.2 Hz, 7-H); 6.97 (td, 1H, J = 7.5 Hz, 1.3 Hz, 9-H); 7.12–7.24 (m, 1H, 8-H); 7.25–7.34 (m, 1H, 10-H).

^{13}C-NMR (50 MHz), $CDCl_3$): δ = 24.98, 25.81 (4-CH_3); 31.22 (C-10b); 37.32 (C-4a); 52.23 (OCH_3); 63.47 (C-5); 76.02 (C-4); 112.72 (C-1), 116.80 (C-7), 121.08 (C-9), 122.46 (C-10a), 127.98 (C-8), 129.61 (C-10), 139.98 (C-2), 154.24 (C-6a), 163.27 (CO_2Me).

Fraction 2: *Methyl (4a RS, 10b RS)-4,4-dimethyl-4a,10b-dihydro-4H,6H-[1]benzopyrano[4,3-d]pyran-2-carboxylate* **9a** (*trans*); m.p. 121–123.5°C (hexane).

$C_{16}H_{18}O_4$ (274.3) calc. C 70.06 H 6.61 found 69.82 6.47

MS (70 eV): *m/e* (rel. int. %) = 274 (33), 259 (8), 243 (6), 231 (35), 215 (100).

IR (KBr): ν = 1715, 1645, 1580, 1490, 750 cm^{-1}.

UV (CH_3CN): λ_{max} (log ε) = 220 (sh.), 238 (3.97), 267 (sh.), 275 (3.57), 283 nm (3.50).

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.22 (s, 3H, 4-CH_3 ax), 1.54 (s, 3H, 4-CH_3 eq); 2.03 (td, 1H, J = 11.5 Hz, 3.5 Hz, 4a-H); 3.54 (br d, 1H, J = 11.5 Hz, 10b-H); 3.84 (s, 3H, OCH_3); 3.93 (dd, 1H, J = 11.5 Hz, 10.0 Hz, 5-H ax); 4.42 (ddd, 1H, J = 10.0 Hz, 3.5 Hz, 1.0 Hz, 5-H-eq); 6.54 (br d, 1H, J = 1.9 Hz, 1-H); 6.84 (dd, 1H, J = 8.1 Hz, 1.4 Hz, 7-H); 6.94 (td, 1H, J = 7.5 Hz, 1.4 Hz, 9-H); 7.11–7.24 (m, 1H, 8-H); 7.34–7.42 (m, 1H, 10-H).

^{13}C-NMR (50 MHz, $CDCl_3$9: δ = 20.48 (4-CH_3 ax); 27.40 (4-CH_3 eq); 31.53 (C-4a); 42.00 (C-10b); 52.32 (OCH_3); 67.44 (C-5); 76.98 (C-4); 108.05 (C-1); 116.79 (C-7); 120.49 (C-9); 122.53 (C-10a), 125.59 (C-8); 127.95 (C-10); 143.01 (C-2); 153.41 (C-6a); 163.56 (CO_2CH_3).

In the reaction of **7b**, diastereomers **8b/9b** are produced in a ratio of 5.0 (0.3): 1; yield: 396 mg (99%); separation (eluent, ether/petroleum ether, 1:3) and subsequent crystallization (hexane).

Fraction 1: *Methyl (4a RS, 10b RS)-1,4,4-Trimethyl-4a,10b-dihydro-4H,6H-[1]benzopyrano[4,3-d]pyran-2-carboxylate* **8b** (*cis*); m.p. 84–86°C (hexane).

$C_{17}H_{20}O_4$ (288.4) calc. C 70.81 H 6.99 found 70.75 7.03

MS (70 eV): *m/e* (rel. int. %) = 288 (100), 273 (3), 257 (7), 245 (4), 229 (45), 161 (78).

IR (KBr): ν = 1720, 1585, 1495, 770, 765 cm^{-1}.

UV (CH_3CN): λ_{max} (log ε) = 216 (3.96), 251 (3.83), 275 (3.69), 283.5 nm (3.60).

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.35 (s, 3H, 4-CH_3 ax); 1.45 (s, 3H, 4-CH_3 eq); 1.98 (d, 3H, J = 1.3 Hz, 1-CH_3); 2.07 (ddd, 1H, J = 11.5 Hz, 5.0 Hz, 4.0 Hz, 4a-H); 3.52 (br d, 1H, J = 5.0 Hz, 10b-H); 3.79 (s, 3H, OCH_3); 3.90 (t, 1H, J = 11.5 Hz, 5-Hax); 4.43 (ddd, 1H, J = 11.5 Hz, 4.0 Hz, 2.0 Hz, 5-H eq); 6.80–6.96 (m, 2H, 7-H, 9-H); 7.14–7.27 (m, 2H, 8-H, 10-H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 16.22 (1-CH_3); 25.11, 25.89 (4-CH_3 ax and eq); 36.48, 37.47 (C-10b, C-4a); 51.99 (OCH_3); 63.79 (C-5); 74.39 (C-4); 116.59 (C-7); 117.64 (C-1); 119.42 (C-9); 120.37 (C-10a); 128.46 (C-8); 132.72 (C-10); 136.31 (C-2); 154.25 (C-6a); 163.50 (CO_2Me).

Fraction 2: *Methyl (4a RS, 10b SR)-1,4,4-Trimethyl-4a,10b-dihydro-4H,6H-[1]benzopyrano[4,3-d]pyran-2-carboxylate* **9b** (*trans*); m.p. 150–151°C (hexane).

$C_{17}H_{20}O_4$ (288.4) calc. C 70.81 H 6.99 found 70.66 7.08

MS (70 eV): *m/e* (rel. int. %) = 288 (25), 273 (4), 257 (3), 245 (4), 229 (39), 161 (100).

High resolution MS of *m/e* = 245:

$C_{14}H_{13}O_4$ calc. 245.0813 found 245.0813
$C_{15}H_{17}O_3$ calc. 245.1177 found 245.1177 ratio ca. 2:1

High resolution MS of *m/e* = 161:

$C_{10}H_9O_2$ calc. 161.0600 found 161.0610

IR (KBr): ν = 1710, 1620, 1585, 1495, 760 cm^{-1}.

UV (CH_3CN): λ_{max} (log ε) = 220 (3.94), 251.5 (3.93), 272 (sh.), 280 nm (sh.).

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.23 (s, 3H, 4-CH_3 ax); 1.58 (s, 3H, 4-CH_3 eq); 2.00 (td, 1H, J = 12.0 Hz, 5.3 Hz, 4a-H); 2.22 (d, 3H, J = 1.3 Hz, 1-CH_3); 3.32 (br d, 1H, J = 12 Hz, 10b-H); 3.82 (s, 3H, OCH_3); 3.90 (dd, 1H, J = 12.0 Hz, 10.0 Hz, 5-H ax); 4.27 (dd, 1H, J = 10.0 Hz, 5.3 Hz, 5-H eq); 6.88–7.02 (m, 2H, 7-H, 9-H); 7.14–7.28 (m, 2H, 8-H, 10H)

^{13}C-NMR (50 MHz, $CDCl_3$): δ = 17.51 (1-CH_3); 20.10 (4-CH_3 ax); 27.90 (4-CH_3 eq); 39.07 (C-10b); 47.51 (C-4a); 51.87 (OCH_3); 67.97 (C-6); 76.58 (C-4); 117.40 (C-7); 120.81 (C-9); 125.79; 126.50 (C-10a, C-1); 127.37; 127.69 (C-8, C-10); 139.88 (C-2); 155.21 (C-6a); 164.44 (CO_2Me).

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(1) Intra- und Intermolecular Hetero-Diels-Alder Reactions. 18. Part 17: see (13). In part from the Ph.D. Thesis of Thomas Brumby (Göttingen, 1987).
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(12) For the introduction of the terms induced/non induced diastereoselectivity (i-de, ni-de) see Tietze, L.F., Beifuß, U. *Angew. Chem.* **1985**, *97*, 1067; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1042.
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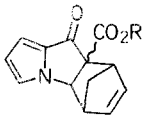
Errata and Addenda 1987

Hall, G., Sugden, J.K., Waghela, M.B.
Page 10. Line 3 of the Abstract should read: dropyrolizines ...
Page 14. The first word of Section 3.11. should be: Benzo[*b*]pyrrolizines.
Page 15. Formula **27** should be:



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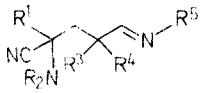
Page 15. The product referred to in Section 4.6., lines 4–5, should be: 10*H*-pyrrolizino[1,2-*b*]quinoline
Page 17. In Section 7., line 4 of the second paragraph should read: **34**.[182] ...

Ahlbrecht, H., von Daacke, A.
Page 24. Formula **8** should be:



8

Costisella, B., Keitel, I.
Page 45. In the heading of the experimental procedure, **6** should read **3** and **8** should read **7**.

Stoss, P., Merrath, P., Schlüter, G.
Page 174. Numbers 1 and 3 should be exhanged in formula **2a–f**.

Singh, G., Deb, B., Ila, H., Junjappa, H.
Page 286. Compounds **1** are 2-aroyl-2-arylthioketene dithioacetals.

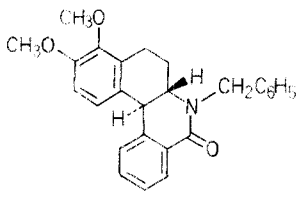
Asaad, F.M., Becher, J., Møller, J., Varma, K.S.
Page 301. Under the reaction scheme, the X group in compounds **3b,d** and **4b,d** should be $CO_2C_2H_5$.

Legrel, P., Baudy-Floc'h, M., Robert, A.
Page 306. The title should read: A One-Pot Synthesis of α-Halohydrazides from 2,2-Dicyanooxiranes.
Page 306. In the table under the reaction scheme, the second heading R^1 should be R^2.

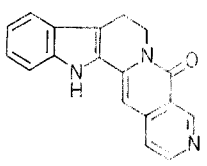
van der Goorbergh, J.A.M., van der Steeg, M., van der Gen, A.
Pages 314–317. The systematic names for the heterocycles involved are: 4,5-dioxo-3,4-dihydro-2*H*,5*H*-thiopyrano[3,2-*c*][1]benzopyrans **4** (RF 24756), 4,5-dioxo-2*H*,5*H*-thiopyrano[3,2-*c*][1]benzopyrans **7** (RF 24756), and 4,5-dioxo-1,3,4,4a,5,10b-hexahydro-2*H*-[1]benzopyrano[4,3-*b*]pyridines **8** (RF 24539).

Attanasi, O.A., Filippone, P., Santensanio, S., Serra-Zanetti, F.
Page 382. In the table under the reaction scheme, R^3 for **1b** should be $CO_2C_2H_5$ and R^3 for **1c** should be CO_2CH_3.

Campbell, A.L., Lenz, G.R.
Pages 428 and 446. Formulae **95** and **298** should be:



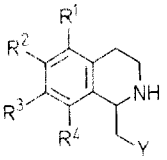
95



298

Page 437. The heading for Table 3 should be: Intermolecular ...

Pelletier, J.C., Cava, M.P.
Page 476. Formula **1a–m** should be:



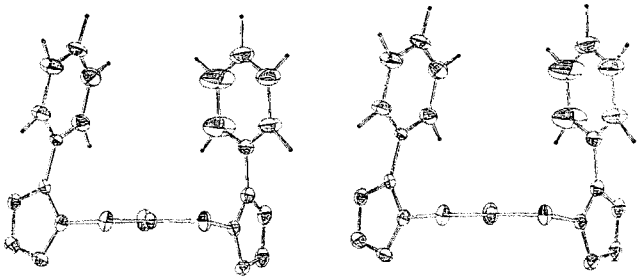
1a-m

L'abbé, G.
Page 528. Compound **45** should be named: 3-(2-pyridyl)-2,4-dithioxo-3,4-dihydro-2*H*-pyrido[1,2-*a*][1,3,5]triazine (RF 9177).

Evans, R.D., Schauble, J.H.
Page 551. Compounds **10** and **11** are tricyclo[2.2.1.0^{2,6}]heptane derivatives.

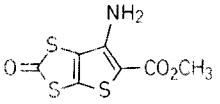
Takeda, K., Tsuboyama, K., Hoshino, M., Kishino, M., Ogura, H.
Page 559. The Y-group for **2g** and **2j** should be furfuryloxy.

Takeda, K., Tsuboyama, K., Takayanagi, H., Ogura, H.
Page 560. The following figure should appear after the 4th paragraph:



Eicher, T., Stapperfenne, U.
Page 625. Compounds **13a,b** are 6,7-dihydrofuro[2,3-*b*]pyridines (RF 7431), and compounds **15a,b** are 1,4-dihydrocyclopentimidazoles (RF 5892).

Dölling, W., Augustin, M., Ihrke, R.
Page 655. Formula **6** should be:



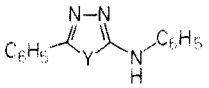
6

Mikołajczyk, M., Bałczewski, P.
Page 661. The second paragraph of ref. 21 should be ref. 22; refs. 22 and 23 should be 23 and 24, respectively.

Rösch, W., Regitz, M.
Page 692. Compounds **21a,b** are 2*H*-1,2,3-diazaphospholes.

Tietze, L.-F., Brumby, T., Pretor, M.
Page 702. Compounds **8** and **9** are 4a,10b-dihydro-4*H*,5*H*-pyrano[3,4-*c*][1]benzopyran-2-carboxylic esters.

Wamhoff, H., Zahran, M.
Page 877. Formula **18a,b** should be:



18a,b

Castaldi, G., Giordano, C.
Page 1039. The target compounds **3** are 1-bromoalkyl aryl ketones.