present two different approaches of the diene and the dienophile which could result in two different tricyclic products: *cis–syn–cis* (CSC) and *trans–syn–trans* (TST) configurations. In the transition state the CSC conformation experiences two 1–3 diaxial interactions between the newly formed double bond and the axial methyl esters at C(5) and C(12) (see scheme above). The TST conformation does not have these interactions, resulting in a sterically and energetically favorable chair–boat–chair transition-state conformation. This intramolecular Diels–Alder reaction from non-activated dienophile and diene is realized at low temperature (353 K). The reaction of triene (I) (TTC) to form compound (III) is relatively fast. This can be explained because it is possible for the *trans–trans* diene easily to adopt the *cisoid* configuration since there are no important steric interactions inside the macrocycle. Another important reason is that the two entities are facing each other in the starting material (Lamothe, 1989). This result demonstrates the tremendous reactivity enhancement caused by the transannular arrangement although neither the diene nor the dienophile are activated by polar substituents. Interestingly, the competition for the formation of (II) and (IV) is important: 23% of (IV) was isolated. This compound was simply the result of an S_N2' reaction of the malonate anion on the allylic chloride favoured by the proximity of the two centers *a* and *b* in the starting material (I).

No abnormally short contacts were observed in either structure.

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Structure of 2,3-Dihydro-1-methylquinolin-2-spiro-2′-indan-3′-spiro-2″-(1″,3″-dithiane)-4,1′-dione

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Abstract. $C_{21}H_{19}NO_2S_2$, $M_r = 381.51$, monoclinic, $C2/c$, $a = 24.911\ (4)$, $b = 10.028\ (2)$, $c = 17.042\ (2)$ Å, $\beta = 121.367\ (8)°$, $V = 3634.8\ (9)$ Å^3, $Z = 8$, $D_x = 1.394$ g cm^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1.54178$ Å, $\mu = 27.25$ cm^{-1}, $F(000) = 1600$, $T = 295$ K, $R = 0.036$ for 2385 observed $[I/\sigma(I) \geq 3]$ reflexions. The dithiane

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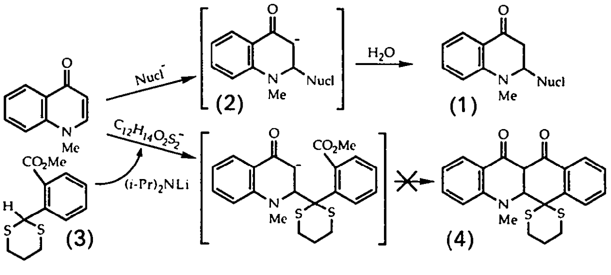
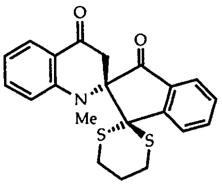
ring adopts a flattened chair conformation; in the dihydroquinolone ring both the *N*-methyl and the carbonyl group are essentially coplanar with the benzene ring; the spiro junction is made with the indanone carbonyl pseudo equatorial and the spiro-dithiane linked pseudo axially. The structure shows the novel result of attempted tandem addition (nucleophile then electrophile; at 2-C then 3-C positions in a quinolin-4-one) of methyl 2-formylbenzoate dithiane anion to 1-methylquinolin-4-one. A mechanistic explanation is suggested.

Introduction. We have shown (Griera, Rigat, Alvarez & Joule, 1992) that treatment of 1-methylquinolin-4-one with nucleophiles effects Michael-type addition with formation of 2-substituted-2,3-dihydroquinolin-4-ones, (1). We reasoned that it ought to be possible to trap the initial enolate (2) with an added electrophile, or, even more interestingly, intramolecularly with an electrophilic centre already present in the added nucleophile [*cf.* Baldwin & Dupont (1980), Mpango, Mahalanabis, Mahdavi-Damghani & Sniekus (1980), Tamaru, Harada, Iwamoto & Yoshida (1978) and Tamaru, Harada & Yoshida (1979)]. Accordingly, the dithiane (3) was prepared from methyl 2-formylbenzoate and the quinolone treated with the anion of (3) in the expectation that we would obtain (4). Such structures would ultimately allow syntheses of several of the recently described quinoline-containing sea alkaloids (Salas, Alvarez & Joule, 1991).



Experimental. Methyl 2-formylbenzoate (Brown & Sargent, 1969) was converted into the dithiane (3), b.p. 403 K (0.5 mm Hg), m.p. 357–359 K, by reaction with 1,3-propanedithiol/toluene-4-sulfonic acid (cat.) in refluxing benzene with removal of water. 1-Methyl-4-quinolone (Griera, Alvarez & Joule, 1992) was reacted with the lithio derivative of (3), generated using lithium diisopropylamide (1.5 mol equiv.), at 195 K in tetrahydrofuran in the presence of hexamethylphosphoramide, which produced spiro-ketone (5), m.p. 422–424 K, crystallized from methylene chloride. The ^{1}H NMR spectrum of the product, which had the molecular formula $C_{21}H_{19}NO_2S_2$ corresponding to anticipated product (4), did not, however, have signals for vicinal protons at a ring junction, but instead had an *AB* quartet at δ 2.85 and 3.15, J 15 Hz. It also showed two IR stretches for carbonyl groups, 1600 and 1720 cm^{-1}, the latter characteristic of a five-ring aromatic ketone. These data led to the proposal of structure (5), but in view of the novelty an X-ray crystal analysis was undertaken to verify this hypothesis.



(5)

A pale-yellow prismatic crystal of (5), of approximate dimensions 0.350 × 0.450 × 0.600 mm, was mounted on a glass fibre and used for data collection on a Rigaku AFC-5*R* diffractometer with graphite-monochromated Cu *Kα* radiation and a 12 kW rotating-anode generator. Cell constants and an orientation matrix for data collection were determined by least-squares refinement using the setting angles of 20 carefully centred reflexions in the range $78.78 < 2\theta < 79.88°$. Data were collected at 295 (1) K using the $\omega/2\theta$ scanning technique to a maximum 2θ value of 120.1°. ω scans of several intense reflexions, made prior to data collection, had an average width at half-height of 0.24° with a take-off angle of 6.0°. Scans of $(1.42 + 0.30\tan\theta)°$ were made at a speed of 32.0° min^{-1} (in ω). The weak reflexions $[I < 10.0\sigma(I)]$ were rescanned and the counts accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflexion. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident-beam collimator was 0.5 mm and the crystal was 400.0 mm from the detector. Of the 2959 reflexions, 2881 were unique ($R_{\rm int} = 0.041$). Intensities of three representative reflexions, measured after every 150 reflexions, declined by −0.50%, so a linear correction factor was applied. The linear absorption coefficient for Cu *Kα* is 27.25 cm^{-1}. An empirical absorption correction using the program *DIFABS* (Walker & Stuart, 1983) was applied which resulted in transmission factors ranging from 0.88 to 1.09. The range of *hkl* was: h −6 to 27, k −4 to 11, l −19 to 17.

The structure was solved by direct methods (Sheldrick, 1985). Non-H atoms were refined anisotropically. H atoms were located by difference Fourier syntheses and their positions and isotropic temperature factors then refined. The final cycle of full-matrix least-squares refinement was based on 2385 observed reflexions $[I > 3.00\sigma(I)]$ and 311 variable parameters and converged (largest parameter shift

Table 1. *Positional parameters and equivalent isotropic thermal parameters* (Å^2) *for the non*-H *atoms*

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S1	0.19479 (3)	0.09867 (6)	0.49867 (4)	2.80 (2)
S2	0.05653 (3)	0.08685 (6)	0.43326 (4)	2.75 (2)
O1	0.18222 (9)	0.5321 (2)	0.5197 (1)	4.04 (8)
O2	−0.01575 (8)	0.3183 (2)	0.5181 (1)	3.74 (7)
N1	0.17434 (9)	0.3052 (2)	0.6219 (1)	2.73 (7)
C1	0.1229 (1)	0.1949 (2)	0.4612 (1)	2.30 (8)
C2	0.0851 (1)	−0.0279 (2)	0.5292 (2)	3.2 (1)
C3	0.1429 (1)	−0.1062 (3)	0.5493 (2)	3.5 (1)
C4	0.1999 (1)	−0.0176 (3)	0.5839 (2)	3.5 (1)
C5	0.1120 (1)	0.2585 (2)	0.3729 (2)	2.52 (8)
C6	0.0876 (1)	0.2002 (3)	0.2870 (2)	3.0 (1)
C7	0.0865 (1)	0.2749 (3)	0.2181 (2)	3.6 (1)
C8	0.1080 (1)	0.4044 (3)	0.2323 (2)	4.0 (1)
C9	0.1317 (1)	0.4638 (3)	0.3170 (2)	3.5 (1)
C10	0.1340 (1)	0.3891 (2)	0.3878 (2)	2.72 (9)
C11	0.1558 (1)	0.4300 (2)	0.4819 (2)	2.84 (9)
C12	0.1330 (1)	0.3219 (2)	0.5234 (2)	2.46 (8)
C13	0.0697 (1)	0.3810 (2)	0.5020 (2)	2.72 (9)
C14	0.0411 (1)	0.3156 (2)	0.5502 (2)	2.9 (1)
C15	0.0854 (1)	0.2598 (2)	0.6410 (2)	2.81 (9)
C16	0.0631 (1)	0.2124 (3)	0.6960 (2)	3.8 (1)
C17	0.1030 (2)	0.1639 (3)	0.7824 (2)	4.4 (1)
C18	0.1674 (2)	0.1638 (3)	0.8162 (2)	4.3 (1)
C19	0.1908 (1)	0.2110 (3)	0.7641 (2)	3.4 (1)
C20	0.1506 (1)	0.2599 (2)	0.6745 (2)	2.67 (8)
C21	0.2421 (1)	0.3188 (3)	0.6643 (2)	3.6 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for the non*-H *atoms*

S1—C1	1.832 (2)	C6—C7	1.381 (4)
S1—C4	1.814 (3)	C7—C8	1.377 (4)
S2—C1	1.820 (2)	C8—C9	1.378 (4)
S2—C2	1.815 (3)	C9—C10	1.396 (3)
O1—C11	1.206 (3)	C10—C11	1.459 (3)
O2—C14	1.224 (3)	C11—C12	1.557 (3)
N1—C12	1.450 (3)	C12—C13	1.540 (3)
N1—C20	1.383 (3)	C13—C14	1.491 (3)
N1—C21	1.457 (3)	C14—C15	1.465 (3)
C1—C5	1.523 (3)	C15—C16	1.397 (4)
C1—C12	1.592 (3)	C15—C20	1.414 (3)
C2—C3	1.515 (4)	C16—C17	1.366 (4)
C3—C4	1.510 (4)	C17—C18	1.393 (4)
C5—C6	1.390 (3)	C18—C19	1.376 (4)
C5—C10	1.391 (3)	C19—C20	1.409 (3)

C1—S1—C4	105.4 (1)	O1—C11—C10	127.9 (2)
C1—S2—C2	105.4 (1)	O1—C11—C12	125.1 (2)
C12—N1—C20	120.1 (2)	C10—C11—C12	106.8 (2)
C12—N1—C21	120.4 (2)	N1—C12—C1	116.7 (2)
C20—N1—C21	119.1 (2)	N1—C12—C11	113.5 (2)
S1—C1—S2	111.6 (1)	N1—C12—C13	110.0 (2)
S1—C1—C5	101.8 (1)	C1—C12—C11	102.9 (2)
S1—C1—C12	113.7 (1)	C1—C12—C13	111.3 (2)
S2—C1—C5	108.7 (1)	C11—C12—C13	101.3 (2)
S2—C1—C12	117.2 (1)	C12—C13—C14	115.1 (2)
C5—C1—C12	102.0 (2)	O2—C14—C13	121.1 (2)
S2—C2—C3	114.4 (2)	O2—C14—C15	122.8 (2)
C2—C3—C4	111.9 (2)	C13—C14—C15	115.9 (2)
S1—C4—C3	113.9 (2)	C14—C15—C16	119.7 (2)
C1—C5—C6	128.3 (2)	C14—C15—C20	120.1 (2)
C1—C5—C10	111.4 (2)	C16—C15—C20	120.2 (2)
C6—C5—C10	120.2 (2)	C15—C16—C17	121.6 (3)
C5—C6—C7	118.2 (3)	C16—C17—C18	118.8 (3)
C6—C7—C8	121.8 (3)	C17—C18—C19	121.1 (3)
C7—C8—C9	120.5 (3)	C18—C19—C20	121.2 (3)
C8—C9—C10	118.4 (3)	N1—C20—C15	121.9 (2)
C5—C10—C9	120.9 (2)	N1—C20—C19	120.9 (2)
C5—C10—C11	110.6 (2)	C15—C20—C19	117.2 (2)
C9—C10—C11	128.6 (2)		

was 0.01 times its e.s.d.) with unweighted and weighted factors of $R = 0.036$ and $wR = 0.049$. The standard deviation, S, of an observation of unit weight was 1.98. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflexions. Plots of $\sum w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflexion order in data collection, $\sin\theta/\lambda$, and various classes of indices, showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.22 and −0.19 e Å^{-3}, respectively.

All calculations were performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985). Neutral-atom scattering factors were taken from Cromer & Waber (1974), anomalous-dispersion effects were included in F_{calc} (Ibers & Hamilton, 1964), and the values of f' and f'' were those of Cromer (1974).*

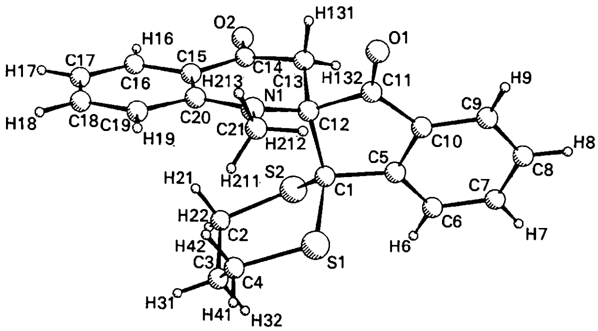


Fig. 1. *PLUTO* (Motherwell & Clegg, 1985) drawing of spiro-ketone (5) showing the numbering scheme used in Tables 1 and 2.

Discussion. The atomic parameters for the title compound, (5), are listed in Table 1; Table 2 lists bond lengths and bond angles; Fig. 1 shows a *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule and the numbering system used in the tables. The dithiane ring adopts a flattened chair conformation. In the dihydroquinolone ring both the N-methyl and the carbonyl group are essentially coplanar with the benzene ring. The spiro junction to the dihydroquinolone is made with the indanone carbonyl in a pseudo equatorial position and with the spirodithiane being linked pseudo axially.

The formation of (5) can be rationalized by assuming 2-lithiation of the quinolone by the lithiated dithiane, followed by acylation to generate ketone (6) (which was also isolated from the reaction mixture)

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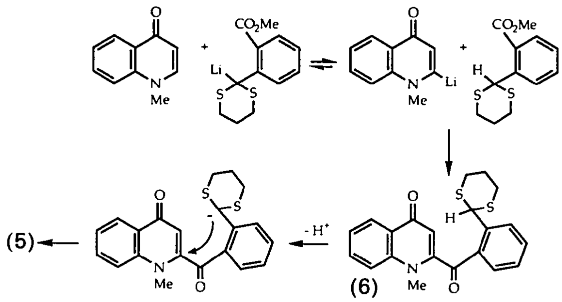
* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55251 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0048]

then finally intramolecular dithiane anion addition at the 2-C position.



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Structure du 2-Nitro-2′-diacétamidobiphényle

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Abstract. 2-Diacetylamino-2′-nitrobiphenyl, $C_{16}H_{14}N_2O_4$, $M_r = 298.3$, monoclinic, $P2_1/a$, $a = 8.442\ (3)$, $b = 23.706\ (7)$, $c = 8.090\ (2)$ Å, $\beta = 115.05\ (4)°$, $V = 1466.7\ (7)$ Å^3, $Z = 4$, $D_m = 1.34\ (2)$, $D_x = 1.351$ g cm^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1.5418$ Å, $\mu = 8.32$ cm^{-1}, $F(000) = 624$, $T = 293$ K, $R = 0.047$ for 1102 independent reflections. The torsion angle between the benzene rings is 67.1 (6)°. Conformational

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