Photorearrangement of Dimethyl 9,10-Cyclopropano-9,10-dihydroanthracene-11,12-dicarboxylate

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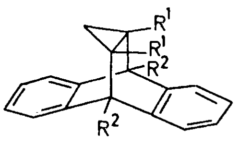
Summary Dimethyl 9,10-cyclopropano-9,10-dihydroanthracene-11,12-dicarboxylate (**1b**) has been prepared and found to rearrange photochemically by direct or sensitized irradiation with participation of the cyclopropyl ring to the isomers (**4a**) and (**5a**).

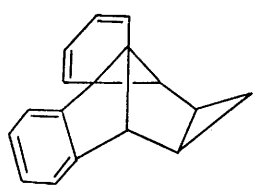
IRRADIATION of triptycenes[1] and dibenzonorbornadienes[2] with u.v. light led to products by a route which involved the intermediate formation of a carbene and not a di-π-methane rearrangement. Direct irradiation of compound (**1a**) in tetrahydrofuran or cyclohexane, however, proceeded at least partially by the di-π-methane route, and a semibullvalene derivative (**2**) was formed together with 3-(9-fluorenyl)cyclobutene (**3**), while sensitized irradiation was ineffective.[3]

We now report that irradiation of the cyclopropanodihydroanthracene (**1b**) with u.v. light in acetone gives, in contrast, tricyclo[3.3.1.0^{2,8}]nona-3,6,diene (**4**) and 9,10-propeno-9,10-dihydroanthracene (**5**) derivatives.

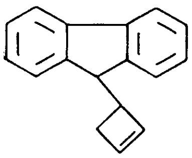


(1)

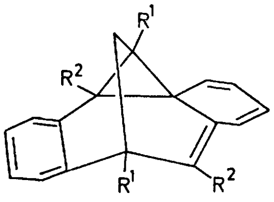
a, R^1 = R^2 = H
b, R^1 = CO$_2$Me, R^2 = H
c, R^1 = CO$_2$Me, R^2 = D



(2)

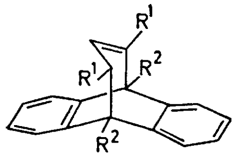


(3)



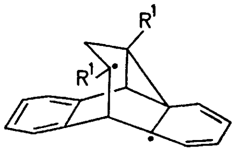
(4)

a, R^1 = CO$_2$Me, R^2 = H
b, R^1 = CO$_2$Me, R^2 = D



(5)

a, R^1 = CO$_2$Me, R^2 = H
b, R^1 = CO$_2$Me, R^2 = D



(6)

a, R^1 = CO$_2$Me
b, R^1 = H

Compound (**1b**) was synthesized by addition of diazomethane to dimethyl 9,10-etheno-9,10-dihydroanthracene-11,12-dicarboxylate[4] giving a pyrazoline compound in 96% yield which underwent photolytic conversion in acetone at 310 nm to give (**1b**) in 93% yield, m.p. 149—150 °C; ^{1}H n.m.r. (60 MHz, CCl$_4$): δ 0·6 and 1·9 (each 1H, d, *J* 6 Hz, CH$_2$), 3·5 (6H, s, MeO) 4·6 (2H, s, CH), and 6·9—7·4 (8H, m, ArH); M^+ 334; ν_{max} 1720 cm^{-1}. The deuteriated material (**1c**) was obtained from 9,10-dideuterioanthracene by addition of dimethyl acetylenedicarboxylate, followed by the procedures described above, and was deuteriated (68·2%) in the benzylic bridgehead positions.

A solution of (**1b**) (2 g) in acetone (1 l) was irradiated with sunlight phosphore lamps in a Rayonet RPR 100 reaction vessel under N$_2$ at 20 °C to a conversion of 25%. After removal of the acetone *in vacuo* 1·35 g of unchanged (**1b**) was crystallized out by addition of methanol and filtered off; purification of the filtrate by column chromatography on silica gel with benzene as eluent and recrystallization from methanol gave compound (**4a**) (210 mg), m.p. 117—118 °C; ^{1}H n.m.r. (90 MHz, CCl$_4$): δ 1·1 (1H, dd, CH$_2$), 3·55 (1H, s, cyclopropyl), 3·65 (3H, s, OMe), 3·7 (3H, s, OMe), 3·75 (1H, d, *J* 17·5 Hz, CH$_2$), 5·4—6·3 (4H, m, olefinic), and 7·0—7·5 (5H, m, 1 olefinic and 4 aromatic protons); ^{13}C n.m.r. (CDCl$_3$): δ 21·68 (t, *J* 140 Hz, CH$_2$), 43·87 (s), 46·98 (d, *J* 185 Hz), and 47·04 (s) (all cyclopropyl), 51·51 (s, benzylic-C), 51·67 and 52·35 (two q, *J* 154 Hz, MeO), 8 d and 3 s in the olefinic–aromatic range 121·46—145·92, and 2 s at 165·66 and 170·25 p.p.m. (C=O); ν_{max} (CCl$_4$) 1640 (C=C) and 1720 cm^{-1} (C=O); λ_{max} (cyclohexane) 282 and 274 nm (ϵ_{max} 2764 and 2769 mol^{-1} cm^{-1}).

Compound (**5a**) was obtained from the filtrates after removal of (**4a**) by high pressure liquid chromatography on Lichrosorb-C 21 with methanol–H$_2$O (70:30), m.p. 128·5—129 °C; ^{1}H n.m.r. (90 MHz, CCl$_4$): δ 3·46 (1H, t, *J* 3·5 Hz), 3·60 (3H, s, OMe), 3·70 (3H, s, OMe), 4·54 (1H, m, benzylic), 5·06 (1H, s, benzylic), 6·44 (1H, m, HC=C), and 6·95—7·45 (8H, m, ArH); M^+ 334; λ_{max} 273·5 and 266·5 nm (ϵ_{max} 1470 and 1540 mol^{-1} cm^{-1}).

Irradiation of the deuteriated material (**1c**) led to (**4b**) and (**5b**) with the deuterium distribution shown.

The photoisomerization of (**1b**) at 254 nm in cyclohexane in presence of cyclohexadiene was efficiently quenched. Stern–Volmer plots of ϕ°/ϕ for the formation of (**4a**) and (**5a**) against quencher concentration in the range 0·481—1·925 × 10^{-3}M gave straight lines with identical slopes. This implies that (**4a**) and (**5a**) are formed from the same electronic excited state. Irradiation of the photoproducts in cyclohexane at 254 nm under conditions identical to those in the quenching experiments revealed that (**4a**) reacted efficiently forming unidentified polymeric materials, whereas (**5a**) showed only an insignificant reactivity. In contrast, irradiation of (**4a**) and (**5a**) in acetone at 300 nm showed that (**4a**) was stable and (**5a**) reacted only modestly.

The results show that both (**4a**) and (**5a**) are primary photoproducts and arise from a triplet state of (**1b**) in the direct and sensitized irradiation. The different photochemical behaviour of (**1a**) and (**1b**) can be attributed to the greater stability of the biradical (**6a**) over (**6b**), likely intermediates leading to the tricyclo[3.3.1.0^{2,8}]nona-3,6-diene derivatives (**4**); also benzo–benzo bridging, which leads either to a carbene intermediate or a di-π-methane rearrangement in the direct irradiation is an energetically unfavourable route because of the loss of the aromaticity in the two benzene rings.

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