purification of the products are as follows: (A) UCON-550X-20%-50LB, 12 ft × 0.75 in. (o.d.); (B) 10% Carbowax 20M, 6 ft × 0.75 in. (o.d.); (C) 10% Carbowax 20M, 6 ft × 0.75 in. (o.d.); (D) SE-30, 12 ft × 0.75 in. (o.d.).

General Photoaddition Procedure. A solution of the aromatic ether and olefin in cyclohexane (2 M in each solute) was introduced into a cylindrical quartz irradiation tube. The tube was placed in a Rayonet RPR-208 reactor equipped with four 253.7-nm lamps (Hg), and sealed with a rubber serum cap to allow removal of samples with a syringe. The part of the tube void of solution was covered with Al foil to prevent reactions in the gas phase.

After irradiation, the solution was transferred to a round-bottom flask and the volatile materials removed at reduced pressure while heating on a water bath (<80 °C). The residue was distilled bulb-to-bulb using a liquid N_2 trap to separate the adducts from polymeric materials. The neat products were stored in a freezer to avoid polymerization. The mixture of products appeared as a very viscous yellow oil and was further separated and purified by GLC.

General Rearrangement Procedure. The procedure has been described elsewhere.[10] To a solution of the adduct mixture described above in 80% acetone was added a small amount of concentrated HCl (1–2 mL) and the mixture was refluxed for a period of approximately 6 h. After reflux, an equal amount of H_2O was added and the reactants allowed to cool. The mixture was extracted with CH_2Cl_2 and the organic layer washed with 10% HCl, saturated $NaHCO_3$, and water and allowed to dry over anhydrous $MgSO_4$. On a scale of 0.1–1.0 g, the mixture was distilled via a short-path column. The ketone(s) appeared as viscous yellow oil(s). The latter were further isolated and purified by GLC for spectroscopic analysis.

The spectroscopic features of some of the partially deuterated adducts and ketones that were prepared are given here:

***d*$_5$-1-Methoxy-4(6)-methyltetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene (14).** GLC purified (A), ^{1}H NMR spectrum (60 MHz) δ 3.25 (3 H), 3.0–2.8 (2 H), 2.1–1.1 (5 H), 1.0–0.8 (3 H).

***d*$_5$-1-Methoxytetracyclo[8.3.0.0^{2,13}0.^{3,9}]tridec-11-ene (11).** Purification by GLC (C); IR spectrum (film) 2950, 2900, 1560, 1450, 1370, 1350, 1220, 1165, 1087, 1030, 1015, 1000, 785, 715, 680 cm^{-1}; ^{1}H NMR spectrum (60 MHz) δ 3.25 (3 H), 3.0–2.2 (2 H), 2.0–0.6 (10 H).

***d*$_5$-Tricyclo[7.3.1.0^{2,8}]tridecen-10-one (13).** Purification was effected by GLC (C); IR spectrum (film) 2940, 2860, 1750, 1450, 1205, cm^{-1}; ^{1}H NMR spectrum (60 MHz) δ 2.6 (1 H), 2.25 (2 H), 2.1–0.7 (10 H); mass spectrum, parent peak (base) *m/e* 195, other major peaks, 167, 91, 84.

***d*$_5$-Methoxypentacyclo[9.3.0.0^{3,10}.0^{2,14}.0^{5,9}]tetradec-12-ene (16).** Purification by GLC (C); IR spectrum (film) 2950, 2850, 1610, 1475, 1450, 1225, 1180, 1070, 700 cm^{-1}; ^{1}H NMR spectrum (60 MHz) δ 3.21 (3 H), 2.5 (2 H), 2.2–1.8 (2 H), 1.4 (8 H).

Registry No.—1, 55265-10-6; **2**, 55306-29-1; **5**, 61394-01-2; **9**, 61394-02-3; **10**, 61394-03-4; **11**, 61394-04-5; **12**, 61394-05-6; **13**, 61394-06-7; **14a**, 61394-07-8; **14a**-*d*$_5$, 61394-09-0; **14b**, 61394-08-9; **14b**-*d*$_5$, 61394-10-3; **15a**, 61394-11-4; **15b**, 61394-12-5; **16a**, 61394-13-6; **16a**-*d*$_5$, 61394-14-7; **16b**, 61394-15-8; **16b**-*d*$_5$, 61436-68-8; **17**, 61394-16-9; **18**, 61394-17-0; **20**, 61394-18-1; **21**, 61394-19-2; **22**, 61394-20-5; **23**, 61394-21-6; **24**, 61394-22-7; **25**, 61394-23-8; **26**, 61394-24-9; **27**, 61394-25-0; **28**, 61394-26-1; anisole, 100-66-3; 2-butene, 590-18-1; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; bicyclo[3.3.0]octene, 5549-09-7; norbornene, 498-66-8; 3-methylcyclopentene, 1120-62-3; *cis*-3,5-dimethylcyclopentene, 30213-29-7; *trans*-3,5-dimethylcyclopentene, 61394-27-2; 1-methylcyclopentene, 693-89-0; 1,2,2a,2b,4a,4b-hexahydro-4b-methoxy-1,2-dimethylcyclopenta[*cd*]pentalene, 61394-28-3; *p*-methylanisole, 104-93-8; *m*-methylanisole, 100-84-5; anisole-*d*$_5$, 50629-14-6.

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Formation of 3-Cyclopentene-1-acetaldehydes on Photolysis of Substituted Norcamphors

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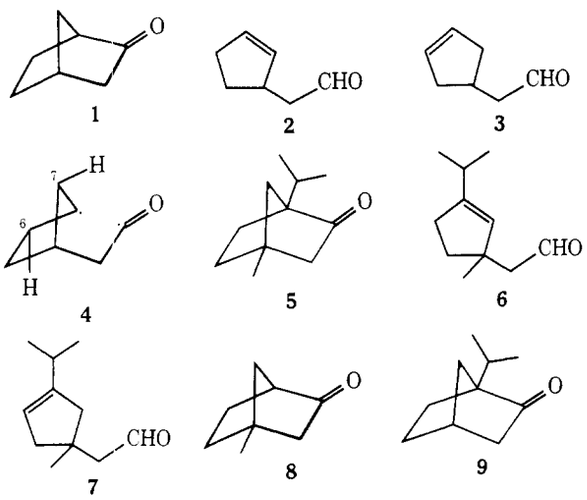
In contrast to the behavior of norcamphor (1) and various of its derivatives previously investigated, photolysis of 1-isopropyl-4-methylnorcamphor (5), 4-methylnorcamphor (8), and 1-isopropylnorcamphor (9) leads in each case to both 2- and 3-cyclopentene-1-acetaldehydes. Quantum yields for these isomerizations are reported, and the results are explained in terms of conformational and stereochemical effects in the biradical intermediates.

A recent review has called attention to the fact that photolysis of norcamphor (1) leads specifically to the Δ^2 aldehyde **2** and not to the Δ^3 isomer **3**, although in principle the presumed intermediate biradical **4** could disproportionate to both **2** and **3**.[1] Various 1- and/or 3-substituted norcamphors also have been examined in the past and found to behave similarly.[1] These facts have been available for some time, and with them in mind we took particular notice of the photochemical behavior of 1-isopropyl-4-methylnorcamphor (**5**), a new ketone which had arisen unexpectedly in a rearrangement reaction.[2] In the course of securing the structure of this compound we investigated its photochemistry and found that photolysis furnished both the Δ^2 and the Δ^3 aldehydes, **6** and **7**, respectively, in the ratio 62:38.[2] This result suggested more careful study of **5**, along with examination of the two simpler ketones 4-methylnorcamphor (**8**) and 1-isopropylnorcamphor (**9**). An additional reason for our interest was that this problem appeared related to our earlier investigation of the photochemical behavior of various substituted bicyclo[3.2.1]-octan-6-ones (**10**). In this latter series we had demonstrated

Table I. Quantum Yields for Products from Norcamphors

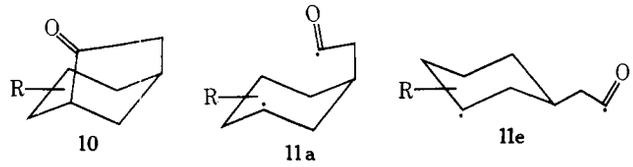
Norcamphor	Quantum yield[a] Δ^2 aldehyde	Δ^3 aldehyde	Total
1	2, 0.28[b]	0	0.28
5	6, 0.16	7, 0.10	0.26
8	12, 0.19	13, 0.13	0.32
9	14, 0.29	15, 0.04	0.33

[a] Estimated error ±~10%. [b] From ref 6.



1 2 3 4 5 6 7 8 9

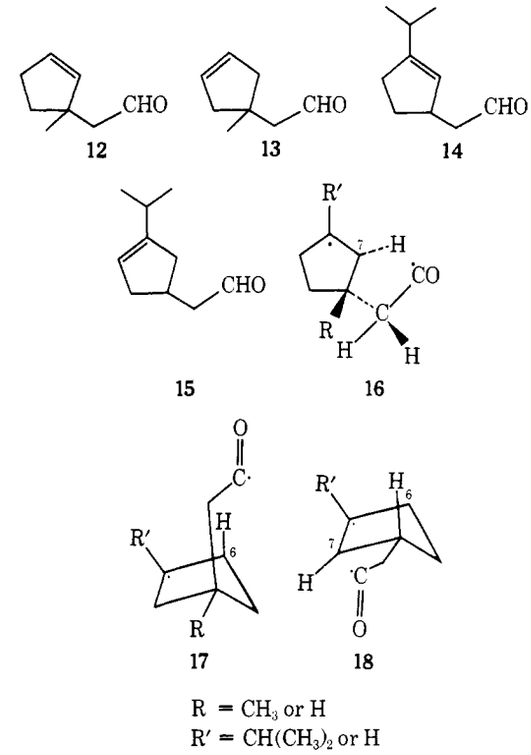
that the lifetime and energy content of the biradical **11** formed on photolysis permit this species to undergo conformational relaxation of the six-membered ring before disproportionation, so that the photoproducts arise specifically from the stable conformer **11a** or **11e**.[3] From the results described below similar behavior appears to play a role in the photochemistry of norcamphor and its derivatives.



10 11a 11e

Irradiation of 8[4] in benzene through Pyrex as previously described for 5[2] gave both the Δ^2 and Δ^3 aldehydes **12** and **13** in the ratio of 59:41. Similar photolysis of 9[2] also yielded both products **14** and **15**, but now in the ratio of 88:12.[5] No other products were found in significant amount. Structures of these new aldehydes were assigned from IR and NMR spectroscopic and vapor phase chromatographic (VPC) properties and comparison of these data with those previously found for **6** and **7**.[2] In particular the difference in double bond position in the Δ^2 and Δ^3 aldehydes leads to two fewer allylic hydrogens in the Δ^2 compounds **6**, **12**, and **14** than in their respective Δ^3 isomers **7**, **13**, and **15**. As a result the ^{1}H NMR spectra (220 MHz) of **6**, **12**, and **14** all show an upfield signal for these two protons ($\delta \sim 1.6$ ppm) that is absent in the spectra of the three Δ^3 aldehydes. Also in all three cases the Δ^2 aldehyde has a shorter retention time than its Δ^3 isomer under standardized VPC conditions. Quantum yields for these products were determined in benzene solution at low conversion (4–5%) by calibrated VPC analysis and using a merry-go-round apparatus. Norcamphor (**1**), for which the quantum yield for formation of **2** under these conditions is known,[6] served as a convenient actinometer. The results are collected in Table I.

From these data it is apparent that alkyl substitution affects the distribution of products with only minor changes in overall quantum yield. While there is a small, as yet unexplained, effect due to the isopropyl substitutent, it is clear from the chemical and quantum yield data that the presence or absence of the methyl group at C(4) largely controls product distribution in these four isomerizations. Examination of molecular models suggests two ways in which this can occur. The geometry of the biradical (see **16**) leading to abstraction from C(7) and formation of Δ^2 aldehyde involves an unavoidable eclipsing nonbonded interaction between the C(4) substituent and hydrogen of the adjacent side chain methylene group. This is true regardless of the specific conformation adopted by the five-membered ring (see below). Substitution of methyl for hydrogen at C(4) will disfavor **16** and should then decrease



12 13 14 15 16 17 18

R = CH_3 or H
R′ = $CH(CH_3)_2$ or H

abstraction at C(7). Steric effects of this sort have been recognized as important in ketone photochemistry for some years.[7] A second effect of the methyl group is to favor the geometry (see **17**) leading to abstraction from C(6) with formation of Δ^3 aldehyde, which requires an axial-like orientation of both the acyl side chain and the C(6) hydrogen atom. This conformation will be favored by substitution of methyl for hydrogen at C(4), since in this case either this methyl group or the acyl side chain must adopt an axial-like position. With hydrogen at C(4) the preferred conformation (such as **18**) is expected to have the acyl side chain in an equatorial-like position, from which abstraction at C(7) but not C(6) is possible. This second effect appears directly analogous to the conformational relaxation of biradical **11** referred to above. The failure of the bulky isopropyl group to exert an important conformational effect is understandable, since it is directly attached to the effectively planar radical center in the biradical intermediate. A close analogy exists in the bicyclo[3.2.1]-octan-6-ones, where replacement of hydrogen by methyl at the cyclohexyl radical center of **11** has little effect.[3]

From these results we conclude that the regiospecific photochemical conversion of norcamphor (**1**) into the Δ^2 aldehyde **2** is satisfactorily explained by a combination of stereochemical and conformational factors which are already recognized as significant determinants of the course of related transformations. The unusual product specificity observed on photolysis of **1** and its previously examined derivatives led several years ago to the proposal that the particular geometry of

norcamphor favored concerted transfer of the syn C(7) hydrogen to the carbonyl carbon as α-cleavage occurred, and that this process was faster than the common biradical disproportionation pathway.[8] This suggestion would be difficult to reconcile with our present findings, which would require that remote alkyl substitution on the rigid norbornane skeleton strongly influence the rate of the proposed concerted transfer of hydrogen. While further studies with various stereospecifically substituted norcamphors are certainly desirable to support this conclusion, it seems clear from our results that no special mechanism is necessary to account for the product specificity observed with norcamphor.

Experimental Section

Materials and Equipment. Unless noted otherwise below, these were the same as we have described previously.[3] NMR spectra were obtained at 60 MHz unless otherwise indicated.

Photolysis of 4-Methylnorcamphor (8). A 120-mg sample of 8[4] in 40 mL of benzene containing 1.2 mL of methanol was degassed for 15 min with N_2 and then irradiated through Pyrex for 8 h. Most of the solvent was removed by distillation through a Vigreux column and the products were isolated by preparative VPC on a 25 ft × 0.25 in. 25% DEGS column to give, in order of elution, 1-methylcyclopent-2-en-1-acetaldehyde (**12**) and 1-methylcyclopent-3-en-1-acetaldehyde (**13**) in the ratio 3:1.

Characterization data for **12:** IR 3040 (w), 2940 (s), 2850 (m), 2720 (m), 1725 (s), 1450 cm^{-1} (m); NMR δ 1.17 (s, 3 H), 1.48–1.97 (m, 2 H), 2.10–2.60 with d, J = 3 Hz, at 2.37 (m, 4 H), 5.63 (s, 2 H), 9.70 (t, J = 3 Hz, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.62; H, 9.73.

Characterization data for **13:** IR 3045 (m), 2945 (s), 2830 (s), 2720 (m), 1725 (s), 1615 (w), 1435 (w), 1375 (w), 670 cm^{-1} (m); NMR δ 1.12 (s, 3 H), 2.1–2.5 with s at 2.30 and d, J = 3 Hz, at 2.38 (m, 6 H), 5.60 (s, 2 H), 9.72 (t, J = 3 Hz, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.39; H, 9.66.

Photolysis of 1-Isopropylnorcamphor (9). Irradiation of 77 mg of 9[2] for 7 h and workup under conditions described above for photolysis of 8 gave these products, isolated by preparative VPC on an 9 ft × 0.25 in. 15% DEGS column, in order of elution: 3-isopropylcyclopent-2-en-1-acetaldehyde (**14**) and 3-isopropylcyclopent-3-en-1-acetaldehyde (**15**) in the ratio 13:1.

Characterization data for **14:** IR 3035 (w), 2955 (s), 2860 (m), 2700 (m), 1725 (s), 1640 (w), 1470 (m), 1380 (m), 1365 cm^{-1} (m); NMR δ 1.03 (d, J = 7 Hz, 6 H), 1.18–2.58 (m, 7 H), 3.05 (m, 1 H), 5.22 (m, 1 H), 9.67 (t, J = 2 Hz, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.08; H, 10.67.

Characterization data for **15:** IR 3035 (w), 2955 (s), 2700 (m), 1725 (s), 1650 (w), 1470 (m), 1380 (m), 1375 cm^{-1} (m); NMR (220 MHz) δ 1.00 (d, J = 7 Hz, 6 H), 1.80–2.82 (m, 8 H), 5.18 (m, 1 H), 9.64 (t, J = 3 Hz, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.11; H, 10.48.

Determination of Quantum Yields. Benzene solutions of the VPC purified norcamphor derivatives were prepared to give an absorbance at 313 nm of 0.502–0.553 (0.035–0.037 M). Aliquots (4 mL) of these solutions were degassed in three freeze–thaw cycles, sealed in identical Pyrex tubes, and irradiated with a Hanovia Model L 450-W mercury lamp in a merry-go-round apparatus for 15 min (4–5% conversion). The product yields were determined by calibrated VPC on an 8 ft × 0.25 in. 3% DEGS column.

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Registry No.—**8,** 49664-72-4; **9,** 59247-60-8; **12,** 61436-67-7; **13,** 61394-30-7; **14,** 61394-31-8; **15,** 61394-32-9.

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Synthesis of Isocoumarins, Dihydroisocoumarins, and Isoquinolones via π-Allylnickel Halide and π-Olefin–Palladium Complexes

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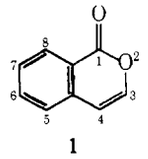
2-Bromobenzoic esters were treated with π-(2-methoxyallyl)nickel bromide to produce 2-acetonylbenzoic esters. These were cyclized to isocoumarins by treatment with NaH/*tert*-butyl alcohol, or to dihydroisocoumarins by treatment with $NaBH_4$. The sodium salts of 2-bromobenzoic acids were reacted with a variety of π-allylnickel halide complexes to produce 2-allylbenzoic acids. These were cyclized to isocoumarins by treatment with palladium chloride. In a similar fashion isoquinolones were prepared from 2-allylbenzamides. This cyclization is thought to proceed by a palladium-assisted nucleophilic attack on the olefin of the allyl group.

Isocoumarins[1] (1*H*-2-benzopyran-1-one, **1**) are a class of naturally occurring lactones which display a wide range of biological activity.[2] They have been prepared by cyclization of homophthalic acid derivatives,[3] 2-vinylbenzoic acid derivatives,[4] 2-carboxybenzyl ketones[5] (available primarily from the Hurtley reaction),[6] by the ortholithiation of *N*-methyl-



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