then removed via syringe to the conductance cell. The reaction tube was washed with 3 × 10 mL of $ClCH_2CH_2Cl$, followed each time by centrifugation, with the supernatant added to the conductance cell.

1-Iodo-1-methylarsenanium Tetrafluoroborate. The procedure paralleled the method given above for the bromine compound.

1-Methylphosphorinane Cl_2 (1:1 adduct), 1-methylphosphorinane Br_2 (1:1 adduct), 1-methylphosphorinane $2Br_2$ (1:2 adduct), 1-methylphosphorinane I_2 (1:1 adduct), and 1-methylphosphorinane $2I_2$ (1:2 adduct) were prepared from 1-methylphosphorinane (**5**) in the same fashion as the corresponding arsenic adducts described above.

Registry No.—Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; 1-methylarsenane I_2, 61395-02-6; 1-methylarsenane $2I_2$, 61395-03-7; 1-methylphosphorinane Cl_2, 61395-04-8; 1-methylphosphorinane Br_2, 61395-05-9; 1-methylphosphorinane I_2, 61395-06-0.

Supplementary Material Available. Figures 4–7, 10, and 11 (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This work was supported by the National Science Foundation, Grant CHE-75-05006.

(2) (a) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964); (b) E. E. Smissman, H. N. Alkaysi, and M. W. Creese, *J. Org. Chem.*, **40**, 1640 (1975).

(3) G. O. Doak and L. D. Freedman, "Organometallic Compounds of Arsenic, Antimony, and Bismuth", Wiley-Interscience, New York, N.Y., 1970, pp 201–209.

(4) J. B. Lambert, *Acc. Chem. Res.*, **4**, 87 (1971).

(5) J. B. Lambert, D. H. Johnson, R. G. Keske, and C. E. Mixan, *J. Am. Chem. Soc.*, **94**, 8172 (1972).

(6) A. D. Beveridge and G. S. Harris, *J. Chem. Soc.*, 6076 (1964).

(7) Figures 4–7, 10, and 11 appear only in the microfilm edition of this journal. See paragraph at end of paper regarding supplementary material.

(8) J. B. Lambert and H.-n. Sun, *J. Organomet. Chem.*, **117**, 17 (1976); actually, the variant **8b** is AA′BC by accidental equivalence.

(9) J. B. Lambert, S. A. Khan, and H.-n. Sun, *J. Chem. Educ.*, in press.

(10) H.-n. Sun, Ph.D. Dissertation, Northwestern University, 1975.

(11) Some of the ^{13}C shifts have already been reported by us: J. B. Lambert, D. A. Netzel, H.-n. Sun, and K. K. Lilianstrom, *J. Am. Chem. Soc.*, **98**, 3778 (1976).

(12) S. I. Featherman and L. D. Quin, *J. Am. Chem. Soc.*, **97**, 4349 (1975).

(13) J. B. Lambert, *Top. Stereochem.*, **6**, 19 (1971).

(14) Deceptively simple AA′XX′ spectra of this type can be analyzed either by observation of the low intensity antisymmetric transitions that must be in a mirror image relationship in the AA′ and XX′ portions (as is possible with **6a**-Br_2) or by examining the ratio of the width of the inner peak to the outer peaks of the triplet (as is possible with **6a**-Br_4). Once a value of ΔJ_{gem} is settled on, the other parameters fall into place rapidly. A second possible solution for **6a**-Br_4 ($\Delta J_{gem} = 0$) was discarded because a large ΔJ_{gem} is expected on the basis of electronegativity differences between the 1 and 4 atoms. It was not, however, eliminated on experimental grounds.

(15) G. Grüttner and M. Wiernik, *Chem. Ber.*, **48**, 1473 (1915).

(16) K. Sommer, *Z. Anorg. Chem.*, **377**, 278 (1970).

(17) F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony and Bismuth", 2nd ed, Wiley-Interscience, New York, N.Y., 1970.

(18) E. V. Zappi and H. Degiorgi, *Bull. Soc. Chim. Fr.*, **49**, 366 (1931).

Photochemical 1,3-Addition of Anisole to Olefins. Synthetic Aspects

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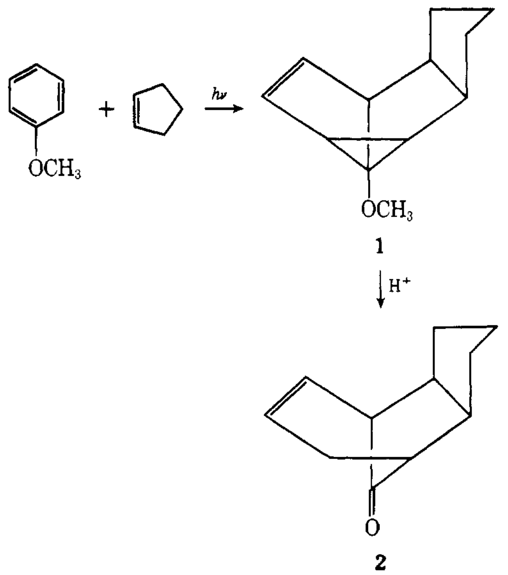
Anisole undergoes photochemical 1,3-addition to a variety of olefins with about the quantum efficiency of benzene but in considerably greater chemical yield. The latter feature may result from the stability of the adducts to continued irradiation. A 1,3 photoadduct of an aromatic compound (anisole) to cyclohexene has been isolated for the first time. All of the 1,3 adducts rearrange readily on treatment with acid to derivatives of bicyclo[3.2.1]oct-2-en-8-one.

The photochemical 1,3-addition of benzene to olefins has been the subject of numerous investigations over the past 10 years.[1] Although both 1,2- and 1,4-additions occur concurrently to various extents, 1,3-addition is usually the dominant process when olefins lacking powerful substituent groups are used. The synthetic potential of this reaction has been limited by the difficulty in the isolation of the products and the susceptibility of the photoadducts to secondary photolysis.

It has been shown[2] that the 1,3-addition of anisole to cyclopentene under the influence of light proceeds in high chemical yield and that the reaction shows a great degree of locospecificity. Since the product **1** underwent rearrangement readily with acid (often even without a preliminary separation) to a bicyclo[3.2.1]octen-8-one, the synthetic potential of this reaction merited further investigation. These results are reported here. A few data on the mechanistic aspects of this reaction are also included but the bulk of the studies on the mechanism are published elsewhere.[3]



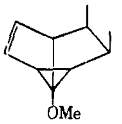
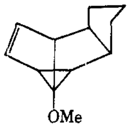
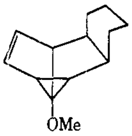
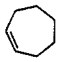
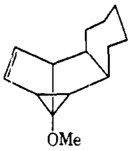
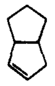
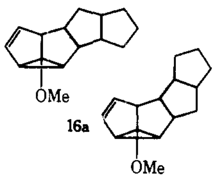
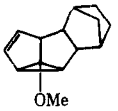
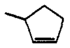
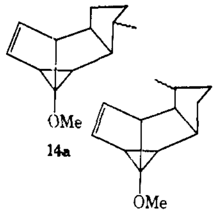
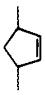
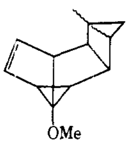
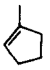
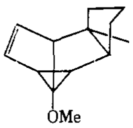
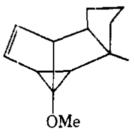
(1)

(2)

Results

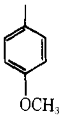
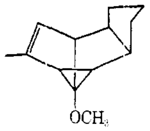
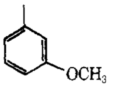
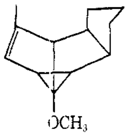
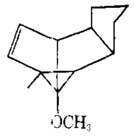
Exactly the same procedure was followed in all of the photoaddition reactions. A solution of the olefin (2 M) and anisole (2 M) in cyclohexane was irradiated at 254 nm without degassing the solution until product formation (as monitored by GLC) slowed down to a negligible rate. The isolated yields of the products, product composition, and the quantum yields in the initial stages of the reaction are given in Table IA and IB. The former lists the addition of anisole to various olefins and the latter the addition of alkyl-substituted anisoles to cyclopentene. *o*-Methylanisole did not undergo addition under these conditions. The structures of the 1,3 adducts have been established by (1) elemental analyses and/or high-resolution mass spectrometry which showed that they were 1:1

Table IA. Addition of Anisole to Olefins

Olefin	Products	Chem yield	Quantum yield[d]	Mass spectrum, *m/e*	Infrared spectrum,[a] cm^{-1}	Ultraviolet[b] spectrum, nm (log ϵ)	NMR spectrum, δ (H)
		22	0.09	164 (P) 108 (base)	3010, 2950 2850, 1640 1450, 1370 1220, 1140 1050, 785, 700	220 (3.34)	5.65 (2); 3.75 (3); 3.0 (1); 2.8–1.2 (4); 1.0–0.7 (6)
 [c]	 1	85	0.17	176 (P) 144, 129, 116 108 (base)	3050, 2950 2875, 1600 1450, 1390 1240, 1210, 1145 1090, 1030, 880	220 (3.40)	6.64 (2); 3.30 (3); 3.1–3.0 (3); 2.08 (2); 1.56 (6)
	 5	20	0.02	190 (P) 158, 143, 129, 115 108 (base), 91, 78 65, 32, 28	3005, 2950 2850, 1630 1450, 1400, 1150 1100, 1020, 830 775	220 (3.42)	5.57 (2); 3.25 (3); 2.95 (2); 2.60 (1); 2.39 (1); 2.10 (1); *J* = 7; 1.96 (1), *J* = 8; 1.59–1.39 (8)
	 10	62	0.21	204 (P) 172, 129, 108 (base), 28	3005, 2950 2890, 1600 1450, 1390 1150, 1130 1100, 1020 805, 690	221 (3.47)	3.0 (1), 2.7–2.3 (2); 5.6 (2), 3.3 (3), 2.15 (2); 1.9–0.8 (10)
	 16a 16b	64	0.08	216 (P) 184, 169, 155 141, 128, 115 108 (base), 91 79, 28	3005, 2950 2900, 1650 1440, 1390 1230, 1130 1100, 790 770	218 (3.4)	5.65 (2); 3.25 (3); 3.05 (1); 2.6 (2); 2.3–1.8 (2); 1.4 (10)
	 18	59	0.05	202 (P) 188, 170, 159 129, 108 (base) 91	3005, 2950 2900, 1600 1460, 1400 1150, 1030 715, 680	220 (3.35)	5.5 (2); 3.25 (3); 2.95 (1); 1.9–2.3 (5); 1.8–2.8 (7)
	 14a 14b	60	0.11	190 (P) 158, 129 108 (base), 91 78, 41, 40, 39 32, 28	3050, 2950 2880, 1600 1455, 1400 1240, 1220 1150, 1100, 1030	220 (3.52)	5.64 (2); 3.25 (3); 3.1 (1); 3.0–2.6 (2); 1.90 (2); 1.9–1.2 (5); 1.0–0.8 (3) (pattern indicative of mixture of isomers).
 cis:trans 3:2	 20	24	0.08	204 (P) 108 (base)	3005, 2950, 2900 1600, 1450, 1400 1380, 1240, 1225, 1150, 1100, 1040 855, 820, 725	220 (3.38)	5.64 (2); 3.25 (3); 3.1 (1); 2.95–2.20 (2); 0.9 (6); 1.9 (2); 1.7 (4)
	 21	35	0.02	190 (P) 176, 133, 108 (base) 105, 98, 97, 96 94	3050, 2950, 2880 1740, 1600, 1450 1400, 1250, 1225 1140, 1125, 1100, 1010, 745		5.67 (2); 3.26 (3); 3.1–2.8 (2); 2.2–1.6 (8); 1.18 (3)
	 22	30			3050, 2950, 2875 1590, 1450, 1395 1250, 1200, 1130 1100, 755		5.64 (2); 3.23 (3); 2.75 (1); 2.6–1.4 (9); 1.26 (3)

[a] Liquid film. [b] Solvent: cyclohexane. [c] From ref 2. [d] Quantum yield values reported based on olefin 1 M.

Table IB. Addition of Methylanisoles to Cyclopentene

Anisole	Products	Chem yield	Quantum yield	Mass spectrum, m/e	Infrared spectrum, cm^{-1}	Ultraviolet spectrum, nm ($\log \epsilon$)	NMR spectrum, δ (H)
	 27	45	0.01	190 (P), 175, 158 147, 143, 130, 128 122, (base), 115, 91 79, 77, 65, 63, 39 32, 28	3050, 2950 2850, 1650 1450, 1400 1250, 1205 1140, 1130 1090, 1030 890, 820	Solvent: cyclohexane 220 (3.48)	5.2 (1); 3.25 (3); 3.2–2.2 (3); 1.8 (3); 1.8–0.8 (8)
	 24	26	<0.01	190 (P), 150 122 (base), 92 81, 79	3100, 3000, 2900 1640, 1600, 1490 1470, 1460, 1400 1390, 1360, 1260 1210, 1130, 1035 920, 790, 760		5.6 (2); 3.27 (3); 3.2–2.6 (3); 2.0–1.4 (7); 1.22 (3)
	 25	33			3005, 2950, 2900 1720, 1630, 1460 1450, 1390, 1240 1210, 1125, 1090 1035, 875, 840 820, 780		5.23 (1); 3.23 (3); 3.2–2.2 (3); 1.8 (3); 2.0–0.1 (8)

[a] Liquid film. [b] Solvent CCl_4, Me_4Si as internal reference.

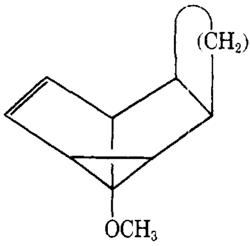
adducts; (2) infrared spectra which indicated the presence of a cyclopentenyl double bond at ca. 1600–1640 cm^{-1} (weak); (3) ultraviolet spectra which showed an absorption maximum or shoulder at 220–241 nm (ϵ_{max} ~2000) indicating a vinylcyclopropane chromophore; (4) proton magnetic resonance spectra which are highly characteristic of these adducts.[4] These NMR spectra will be discussed in detail for individual cases.

In many instances, partially deuterated 1,3 adducts were synthesized from anisole-d_5 and appropriate olefins in order to corroborate the assignments in the NMR spectrum.

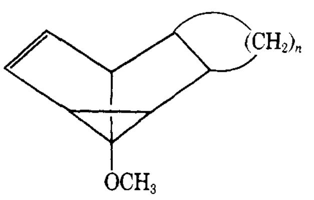
1,4 and 1,2 adducts, if formed, were no more than a small fraction of the yield of 1,3 adducts in all of these instances. 1,2-Dimethylcyclopentene did not undergo addition under the experimental conditions. Dimerization of the olefin which was presumably photosensitized by anisole was observed to take place in a few instances.

The acid-catalyzed rearrangements of these adducts was a facile process in nearly all of the instances, the isolated yields of the ketones ranging from 50 to 80%. The spectral properties of these products are listed in Table II.

The orientation of the olefinic moiety with respect to the anisole part of the adduct can be as in 3 (endo) or 4 (exo).



3

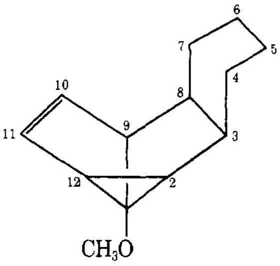


4

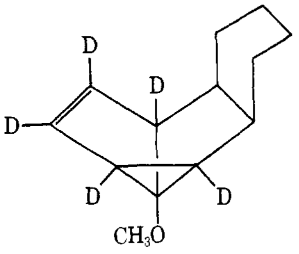
Earlier studies[1] on the 1,3-addition of benzene have shown that benzene itself gives varying mixtures of endo and exo adducts depending on the olefin that is used. With a small-ring olefin, such as cyclobutene, the endo isomer was the major product.[5] When alkyl-substituted benzenes were used endo adducts were formed exclusively.[4] A model which would explain this has been proposed[4] and will be discussed in the context of anisole addition in the next section.

In the case of anisole, with simple olefins such as cyclopentene, only one adduct was realized.[2] That this was the endo isomer was rigorously established by x-ray analysis of a derivative in the case in which the olefin was 3,4-dichlorocyclobutene.[6,7] Indirect evidence has been presented to show that the anisole:cyclopentene adduct (1) is also endo oriented.[2] In the present work, the adducts of anisole to various monocyclic olefins are represented as endo fused by extrapolation of the above results. It is emphasized that this is based on a model (see Discussion) and therefore tentative. NMR data cannot be used to assign the stereochemistry at the points of addition.

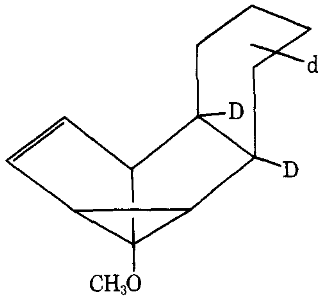
Cyclohexene. The addition of anisole to this olefin is the first reported instance of 1,3-addition of a benzene derivative to cyclohexene. A comparison of the NMR spectra (220 MHz) of the partially deuterated derivatives 6 and 7 to 5 showed that



5



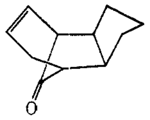
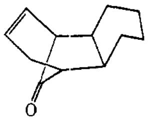
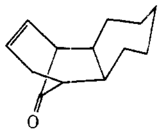
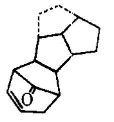
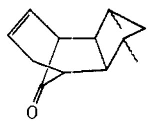
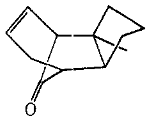
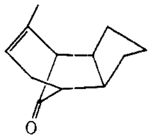
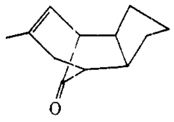
6



7

the chemical shifts of protons which belonged originally to anisole were at δ 5.55 (H_{10}, H_{11}), 3.23 ($-OCH_3$), 2.94 (H_9), 2.08 (H_{12}), and 1.93 (H_2). The chemical shifts for the ring protons agree very well with the assignments made for the 1,3 adducts

Table II. Ketones Obtained from Acid Cleavage of 1,3 Photoadducts

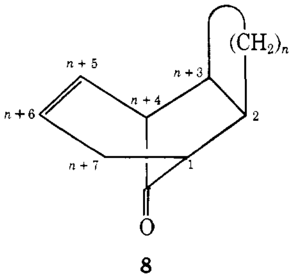
Precursor	Ketone product	Yield, %, from 1,3 adduct	Mass spectrum	Infrared[b] spectrum, cm^{-1}	NMR spectrum, δ(H)[c]	Remarks
1[a]	 2	80	See ref 2	3050, 2950, 2900 1760, 1650, 1460 1445, 1335, 1200 1110, 1010, 790, 720 685	5.62 (2); 2.65 (2); 2.4 (4); 1.7 (6)	Ultraviolet absorption: λ_{max} (pentane) 294 nm (ε 42)
5	 9	50	176 (parent) 148, 147, 105 92, 91, 81, 80 79, 40	3005, 2950, 2900 1770, 1640, 1450 1115, 805, 715, 685	5.64 (2); 2.7 (2); 2.3 (4); 2.0–1.2 (8)	2,4-DNP mp 161–163 °C
10	 12	86	190 (parent) 162, 161, 116 105, 91, 78, 41	3005, 2950, 2900 1770, 1450, 1120 780, 690	5.6 (2); 2.65 (2); 2.3 (3); 2.0 (1); 1.9–0.8 (10)	Product homogenous by GLC
16	 17a,b	47	202 (base) 162, 161, 116	3005, 2950, 2900 1760, 1450, 1190 1110, 790, 690	5.63 (2); 2.68 (2); 2.1–2.6 (4); 1.6 (10)	Two isomers; not easily separated by GLC
14 (a+b)	 15a,b	83	176 (p, base) 148, 134 93, 81, 79 77	3050, 3000, 2950 2900, 1760, 1620 1455, 1400, 1380 1225, 1110, 1010, 685	5.6 (2); 2.6 (2); 2.36 (4); 1.7 (5); 1.0 (3)	Product consisted of two isomers in the ratio 1:1.5 with retention times 28.1 and 27.0 min
22	 23	68	decomposed mass spect	2960, 2900, 1750 1450, 1370, 780 690	5.6 (2); 2.6 (2); 2.4 (1) 1.7 (8); 1.0 (3)	
24 + 25	 26	60	176 (P) decomposed mass spect sample	3005, 2950, 2900 1755, 1605, 1510 1440, 1250, 1160	5.3–5.8 (1); 2.6 (7); 2.3 (3); 1.65 (3); 1.6 (6)	
27	 28	80	176 (p, base) 133, 119 104, 93, 78 68, 44, 42	3005, 2940, 2900 1760, 1450, 1380 1195, 1150, 1135 810	5.3 (1); 2.55 (3); 2.28 (3), 1.65 (d, 3); 1.60 (6)	

[a] From ref 2. [b] Liquid film. [c] CCl_4 solution with Me_4Si as internal reference.

derived from benzene and alkylbenzenes.[4] The large coupling between H_{12} and H_2 (7–8 Hz) and the absence of any other strong coupling (since C_1 is substituted by the $-OCH_3$ group) confirm this observation. In contrast to both cyclopentene[5] and cycloheptene (see below), the addition to cyclohexene was inefficient in terms of both the chemical yield (20%) and rate.[3]

Ketones derived by the acid cleavage of the photoadducts had the general structure 8.[2,7]

The stereochemistry has been assigned in two cases[6,7] as mentioned already. In all of the ketones that were isolated both in this study and in earlier ones, the characteristic chemical shifts of protons on the bicyclo[3.2.1]octen-8-one system were δ 2.2–2.5 (H_2, H_{n+3}), 2.6–2.7 (H_{n+2}, two protons), 5.6–5.7 (H_{n+5}, H_{n+6}). The ketone 9 derived from 5 fully conformed to this pattern.



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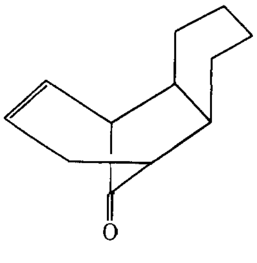
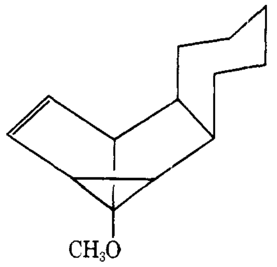


9

Cycloheptene. The evidence on which the structures 10 for adduct and 11 for its partially deuterated derivative were based was unexceptional. Ketones 12 and 13 were prepared from these adducts. In quantitative terms cycloheptene gave a high yield of product and, most surprisingly, the maximum



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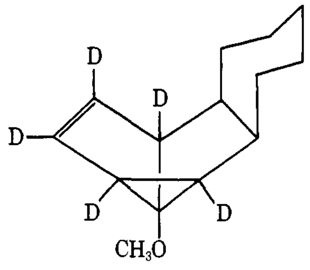

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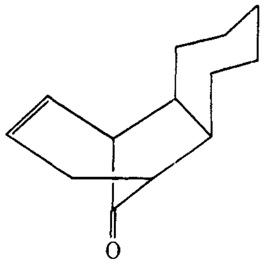

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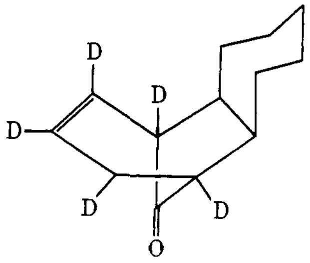
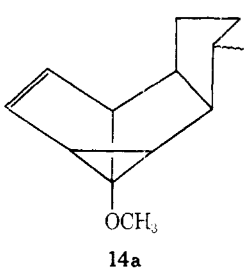


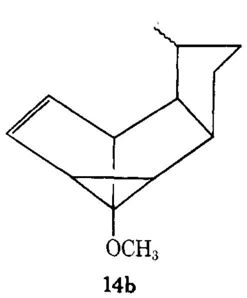
13

rate of addition[3] of any olefin.

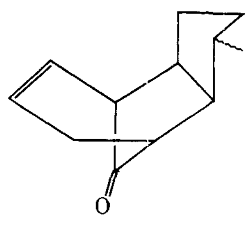
Substituted Cyclopentenes. 3-Methylcyclopentene. Gas chromatographic analysis of the product mixture showed the presence of two major products in approximately equal amounts and constituting ~80% of the products that were formed. However, they could not be isolated separately in quantity. Spectroscopic data indicated that both major products were 1,3 adducts. The NMR spectra of these adducts (as well as their partially deuterated analogues derived from anisole-d_5), when analyzed as a mixture, showed an absorption pattern for the $-CH_3$ group that consisted of two superimposed doublets which, as in the parent olefin, had a coupling of 6 Hz to the vicinal proton. The two doublets were 2–3 Hz apart and had the same chemical shift as the methyl group in the olefin. It is very likely that the cyclopentane ring was fused endo to the rest of the molecule as this was consistently true in the addition of cyclopentenes to all of the benzene and alkylbenzenes that have been studied.[4,5,8] Even so, there are four isomers possible depending on the location and orientation of the methyl group (**14a** and **14b**). The identification of only two products (according to the NMR patterns) suggest that only two of the isomers are favored. The ketones **15a** and **15b** derived from these adducts also seemed to consist of only two isomeric products.



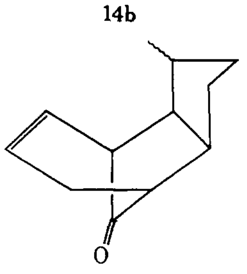
14a



14b

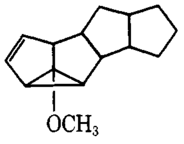


15a

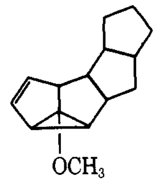


15b

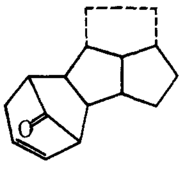
Bicyclo[3.3.0]octene. As in the preceding case, gas chromatographic analysis showed the presence of two isomeric adducts in the ratio 3:2 which together represented approximately 70% of all products formed. Comparison of the NMR spectra of the normal vs. deuterated (**16**-d_5) adduct mixture and conversion to **17** showed the typical features of the 1,3-addition products. The proposed structures **16a** and **16b** make no attempt at stereochemical assignment. Separating the isomeric products proved unsuccessful.



16a

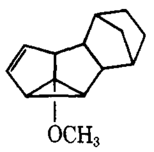


16b

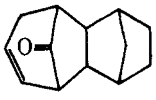


17a, b

Norbornene. Formation of the desired 1,3 adduct of norbornene with anisole was accompanied by dimerization of the olefin to produce the exo-trans-endo dimer exactly as in the photocycloaddition reaction with benzene.[9] Dimer formation decreased at high olefin concentration again as observed in the benzene:norbornene system.[9] Gas chromatographic analysis of the adduct showed the presence of only one 1:1 adduct (**18**) in 60% yield and other unidentified products in less than 10% yield. The spectroscopic characteristics of the major product (Table IA) paralleled the main features of the 1,3 adducts. Treatment with acid yielded a ketone of formula $C_{13}H_{16}O$ as the sole product (85%) whose NMR spectrum exhibited a very complex olefinic (2 H) pattern (two distinct groups: 1 H, δ 5.9 consisting of a complex triplet and 1 H, δ 5.4 consisting of two coupled triplets). The appearance of the spectrum suggested that it was not the expected ketone **19.** A deep-seated rearrangement must have occurred. The structure of the product is under investigation.



18



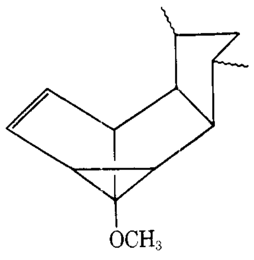
19

3,5-Dimethylcyclopentene. This reaction was carried out on a 60:40 mixture of the cis:trans isomers of this olefin (composition according to manufacturer). Separation of the product mixture showed that dimeric products as well as a 1:1 adduct were formed. Spectral data indicated the characteristic features of the 1,3 adduct (**20**). The broad peak in the GLC trace may be indicative of isomeric products being present, but attempts to resolve the peak were unsuccessful. No attempt was made to determine the stereochemistry of the products.

1-Methylcyclopentene. Addition of this olefin to anisole yielded (GLC analysis) four isomeric addition products of which three were isolated as pure materials. Two that were identified spectroscopically to be the 1,3 adducts are shown in Table IA. Their yields were **21** (35%), **22** (30%). Of these, one showed a more complex structure for H_8 and it was therefore identified as **22** in which H_7 provides an additional coupling. The ketone **23** was formed from **22** in the usual manner.

Addition of Methylanisoles to Olefins. The addition of *o*-methylanisole to cyclopentene was too slow to be detected.

The addition of *m*-methylanisole to cyclopentene gave two adducts in good yield. The quantum yield was one of the lowest observed. In both adducts, orientational specificity was evident in the location of the $-OCH_3$ group (and not the methyl) at the 1 position. The structures of the compounds could be readily distinguished by the absence of one olefinic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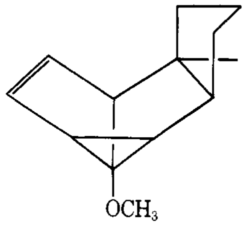
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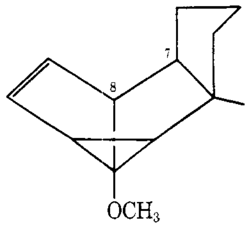
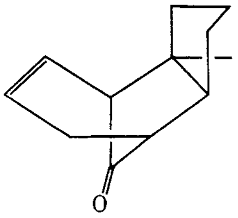
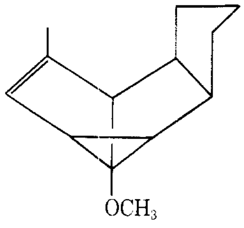


22


23

proton and the presence of an allylic methyl group in **24** but not in **25**. The formation of both products in nearly equal amounts parallels the observation made earlier[4] on the addition of *m*-xylene to olefins. Both adducts **24** and **25** were treated with acid as a mixture. Only one ketone was isolated from this solution in good yield. It was assigned the structure **26** since its NMR spectrum indicated the presence of only a single olefinic proton at δ 5.3 and the position of the methyl group at δ 1.65 (doublet, $J \sim 2$ Hz) suggested an allylic position. The addition of *p*-methylanisole to cyclopentene was slow and the yield of the adduct **27** was only 45%. It was converted to the ketone **28** efficiently.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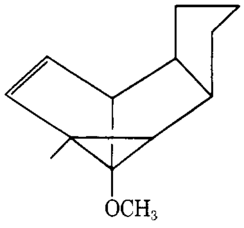
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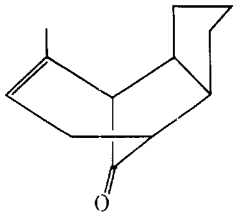
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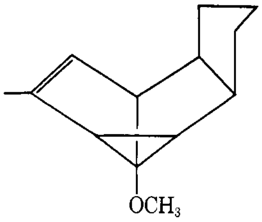
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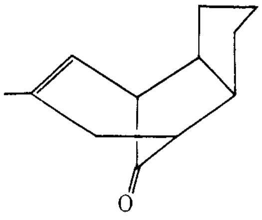
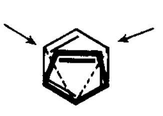

28

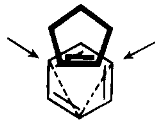
Solvent Effects. The photocycloaddition reaction between anisole and cyclopentene was carried out in a variety of solvents. Results showed no significant change in the types of products formed. The solvents used were cyclohexane, diethyl ether, tetrahydrofuran, and methanol. In none of the cases was the solvent found to be incorporated in the addition product. The same results were obtained when mixed solvents were used, i.e., cyclohexane–methanol.

Effect of Conversion. The substantially larger yields that were obtained in the reaction of anisole with a small-ring olefin such as cyclopentene in contrast to the addition of benzene to the same olefin suggested that the effect may be due to increased photostability of the product in the first instance. The 1,3 adducts of both anisole to cyclopentene (**1**) and benzene to cyclopentene were separately dissolved in cyclohexane, benzene was added as a sensitizer, and the solutions were irradiated at 254 nm. The benzene adduct (as monitored by VPC) disappeared completed within 14 h leaving only a deep-yellow, high molecular weight material. The anisole adduct was diminished by less than 10% in the same time duration.

Discussion

It is best to discuss the present results in terms of the model which has been proposed earlier[4] to explain the photochemical 1,3-addition of benzene and alkylbenzenes to olefins. This model has considerable predictive value particularly in regard to the stereochemistry of the reaction. It is suggested that benzene in its B_{2u} state (which has the hexagonal symmetry of its ground state) reversibly forms an open sandwich-type exciplex (**29a** or **b**) which first adds 1,3 to the double bond at the points indicated by the arrows. The last bond to close is the cyclopropane ring which seems to form in either way as indicated by the dotted lines. The chief point of interest in this model for the 1,3-addition of anisole to olefins is that a substituent on the ring plays a major part in determining the stereochemistry. For reasons which are not clear, the exciplex seems to prefer the structure **a** (which leads to endo addition) over **b** in the case of benzene and small rings. When a substituent is present, this preference is augmented by the steric hindrance to the alternative configuration (**29c**) that is needed for exo addition. The anisole adducts to cyclobutene and to cyclopentene have been shown to be endo oriented. Similar reasoning would serve to explain the failure of *o*-methylanisole to add to cyclopentene and the greatly decreased rate of addition of anisole to cyclopentenes with an alkyl group at the doube bond or to bicyclic cyclopentenes. It has been acknowledged elsewhere[3] that these explanations are strictly qualitative. In particular, the reasons for the wide variations in the rates of addition of cyclopentene, cyclohexene, and cylcoheptene to anisole are obscure at present.


29a


29b


29c

The scope of the 1,3-addition as a synthetic reaction has been amply demonstrated here. The presence of the methoxy group on the adduct which causes it to rearrange to the keto system **8** lends additional merit to this reaction in synthesis. We have described elsewhere[2] one method to cleave the ketone **8** further to a bicyclic derivative. Other chemistry of the ketones has also been investigated.[11,12]

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 137B spectrometer. NMR spectra were obtained at 60 MHz on a Varian T60-1 A machine or at 220 MHz on a Varian HR-220 spectrometer. The latter was operated by the consortium at Rockefeller University, New York, N.Y. Samples were dissolved in CCl_4 with Me_4Si as internal reference. Mass spectra were determined on a J.M.S. Model D-100 high-resolution mass spectrometer.

Olefins were obtained from Chemical Samples Co. Columbus, Ohio, and used as obtained. Anisole-d_5 was synthesized by Miss Laura Garwin from benzene-d_6. The solvents used were of spectroquality. Gas chromatographic separations were carried out on a Hewlett-Packard Model 5750. The GLC columns used during the isolation and 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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References and Notes

(1) D. Bryce-Smith, *Photochemistry*, **4**, 641 (1973), and references cited therein.
(2) R. Srinivasan, V. Y. Merritt, and G. Subrahmanyam, *Tetrahedron Lett.*, 2715 (1975).
(3) R. Srinivasan and J. A. Ors, *Chem. Phys. Lett.*, **42**, 506 (1976).
(4) J. Cornelisse, V. Y. Merritt, and R. Srinivasan, *J. Am. Chem. Soc.*, **95**, 6197 (1973).
(5) V. Y. Merritt, J. Cornelisse, and R. Srinivasan *J. Am. Chem. Soc.*, **95**, 8250 (1973).
(6) G. Subrahmanyam, R. Srinivasan, S. J. LaPlaca, and J. E. Wiedenborner, *J. Chem. Soc., Chem. Commun.*, 231 (1975).
(7) G. Subrahmanyam and R. Srinivasan, *Tetrahedron*, **31**, 1797 (1975).
(8) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **93**, 2073 (1971).
(9) R. Srinivasan, *J. Phys. Chem.*, **76**, 15 (1972).
(10) G. Subrahmanyam, "Organic Photochemical Syntheses", Vol. II., R. Srinivasan, T. D. Roberts, and J. Cornelisse, Ed., 1976, p 99.
(11) G. Subrahmanyam and R. Srinivasan, *Indian J. Chem.*, **14**, 462 (1976).
(12) G. Subrahmanyam, *Indian J. Chem.*, **14**, 365 (1976).

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