2,3,4,5-Tetrahydro-5,5-diphenyl-1-benzoxepin (9).—Polyphosphoric acid (100 g) was placed in a 500-ml indented (Morton) flask equipped with an efficient cone drive stirrer (Teflon paddle). The acid was preheated to 100 ± 1° and stirred very vigorously at this temperature while 10.0 g (31.4 mmol) of finely powdered **12** was added in small portions over a period of 15 min. Rapid stirring at 100 ± 1° was continued for an additional 110 min. The hot, brownish yellow mixture was then poured into 700 ml of ice water, made strongly basic (pH 10) with excess 50% sodium hydroxide solution, and extracted twice with benzene. Evaporation of the dried extracts gave 8.48 g of pale yellow solid, which was mixed well with a minimum amount of petroleum ether (bp 30–60°), cooled to −10°, and filtered to recover 5.24 g of solid. (Work-up of the filtrate yielded none of the desired product.) The solid was boiled and stirred for 3 hr with approximately 2 l. of methanol; and after filtering to remove a small amount of insoluble material, the solution was concentrated to the cloud point and cooled. Small white crystals of **9** precipitated (2.50 g, mp 180–182°); a second crop melting at 179–182° (0.31 g, total yield 30%) was obtained in the usual way. Recrystallization of the first crop from methanol gave tiny, snow-white needles: mp 182.0–182.3°; ir (CS_2) 1220 cm^{-1} (strong, =CO–), no OH or C=O; nmr (CCl_4), δ 6.6–7.3 (m, 13, two C_6H_5 and 7, 8, and 9 H of C_6H_4), 6.28 (dd, 1, J_{ortho} = 8 Hz, J_{meta} = 2 Hz, 6 H of C_6H_4),[26] 3.83 (t, 2, J = 6 Hz, CH_2O), 2.66 (distorted t, 2, $J \approx 6$ Hz, CH_2CPh_2), and 1.87 ppm (distorted qn, 2, $J \approx 6$ Hz, CH_2CH_2O); mass spectrum (70 eV) *m/e* 300.1541 (strong; calcd for $C_{22}H_{20}O$, 300.1514), 223.1122 (medium; calcd for $C_{16}H_{15}O$, 223.1123), and 181.0650 (weak; calcd for $C_{13}H_9O$, 181.0653).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 88.06; H, 6.75.

4,4-Diphenyl-3-butenyl Phenyl Ether (13).—Treatment of benzene solutions of alcohol **12** with dry HCl or phosphorus pentoxide produced **13** in essentially quantitative yield. Very high yields of **13** also resulted from reactions of **12** with polyphosphoric acid (see above) which were performed with inefficient stirring. In an experiment typifying the most convenient method of synthesis, a solution of **12** (0.50 g, 1.57 mmol) in benzene (10 ml) was placed over Drierite (0.5 g), saturated with dry hydrogen chloride, allowed to stand at room temperature in a stoppered flask for 6 hr, filtered, and evaporated, The nmr spectrum of the crude liquid residue (0.47 g, 100%) was identical with the spectrum of an analytical sample of **13** prepared by distillation of the crude product through a short spinning-band column. The pure material was obtained as a straw-colored oil: bp 179° (0.7 mm); ir (neat) 1243 cm^{-1} (strong, =CO–), no OH; nmr (CCl_4), δ 7.0–7.4 (m, 12, two C_6H_5C and *m*-H of C_6H_5O), 6.68–6.89 (m, 3, *o*- and *p*-H of C_6H_5O), 6.14 (t, 1, J = 7 Hz, $CH_2CH{=}C$), 3.91 (t, 2, J = 7 Hz, CH_2O), and 2.54 ppm (qr, 2, J = 7 Hz, $CH_2CH{=}C$); mass spectrum (70 ev) *m/e* 300.1491 (weak; calcd for $C_{22}H_{20}O$, 300.1514), 207.1174 (medium; calcd for $C_{16}H_{15}$, 207.1174), and 193.1017 (medium; calcd for $C_{15}H_{13}$, 193.1017).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.94; H, 6.77.

Registry No.—**1**, 16778-07-7; **2**, 15070-88-9; **3**, 16778-09-9; **4**, 16778-10-2; **5**, 16778-11-3; **6**, 16778-12-4; **8**, 16778-13-5; **9**, 16778-14-6; **11**, 2364-59-2; **12**, 16778-16-8; **13**, 16778-17-9; **18**, 16778-18-0; **27**, 16778-19-1; lead tetraacetate, 546-67-8.

Acknowledgment.—The author is indebted to Mr. H. J. Tarski for excellent technical assistance, and to numerous colleagues in the Analytical Research Section of this laboratory for stimulating discussions.

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[26] This assignment is based on (a) an examination of a molecular model, which indicates that the proton in question lies near the periphery of the shielding cone of one of the phenyl groups, and (b) a comparison with the nmr spectrum reported for 2,3,4,5-tetrahydro-5,5-dimethyl-1-benzoxepin [H. Hart, J. L. Corbin, C. R. Wagner, and C. Wu, *J. Amer. Chem. Soc.*, **85**, 3269 (1963)], which exhibits no aromatic peaks at δ <6.8.

Mechanisms of Photochemical Reactions in Solution. LIII.[1] Cycloaddition of Carbonyl Compounds to Allenes

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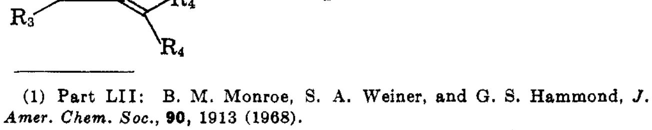
Adlehydes and ketones undergo photochemical cycloaddition reactions to allenes to form oxetanes. The latter will in turn react with the carbonyl compounds forming 1,5- and 2,5-dioxaspiro[3.3]heptane derivatives. In some cases the oxetanes undergo photoisomerization to cyclobutanones. The quantum yield for disappearance of acetophenone in the presence of tetramethylallene was found to be 0.59. A mechanism is proposed involving the addition of carbonyl triplets to the allenes.

Preliminary reports of studies of photochemical cycloaddition of ketones to allenes have recently been reported by Arnold and Glick[2] and by ourselves.[3] The principal products formed in the reactions are shown in Table I along with analytical data and key spectroscopic characteristics. In some instances pinacols derived from the ketones were also isolated. The structures of the addition compounds are indicated by their spectra and by hydrolysis in aqueous acid.



Hydrolytic cleavage of monoadducts (**1**, **4**, **7**, **9**, **11**, **12**, and **17**) gives the original ketone and the ketone that is formally derived by addition of the elements of water to the allene.

The spiro ketal, **8**, is easily cleaved to acetophenone and diisopropyl ketone.

$$8 \xrightarrow{H^+,\ H_2O} 2C_6H_5COCH_3 + (CH_3)_2CHCOCH(CH_3)_2$$

The 2,5-dioxaspiro[3.3]heptanes (**5**, **13**, **14**, and **15**) are not cleaved to ketones by aqueous acid at room temperature.

All of the monoadducts have strong infrared absorption bands at or close to 1735 cm^{-1}. We believe that the band is analogous to absorption of enol ethers found between 1633 and 1712 cm^{-1}.[4] The very high frequency of the absorption is reminiscent of the

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[1] Part LII: B. M. Monroe, S. A. Weiner, and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 1913 (1968).

[2] D. A. Arnold and A. H. Glick, *Chem. Commun.*, 813 (1966).

[3] H. Gotthardt, R. Steinmetz, and G. S. Hammond, *ibid.*, 480 (1967).

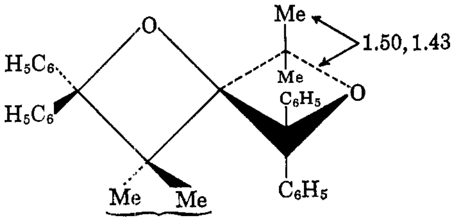
[4] S. M. McElvain and R. E. Starn, *J. Amer. Chem. Soc.*, **77**, 4571, 5601 (1955).

high carbonyl stretching frequencies in cyclobutanones,[5] and to the high frequency band assigned to the double stretch in β-isopropylidene-β-butyrolactone.[6]

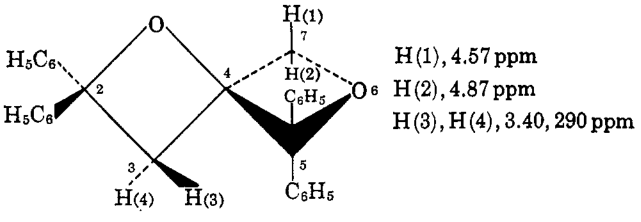
A troublesome discrepancy between our work and that of Arnold and Glick[2] appeared in the study of the reaction of benzophenone with tetramethylallene. A single, noncrystalline monoadduct has been isolated in both laboratories and we agree in assigning structure **4** to the compound. The carbide group have isolated two bis adducts melting at 150.5–152.5° and at 152–154°. Structure **5** was assigned to the former material and the latter was believed to be the spiro ketal, **6**.

The melting point of an isolated material having the composition of a bis adduct was surprisingly low, 87–89°. After the discrepancy came to our attention we investigated the matter further and accomplished partial isolation of the ambiguities. Irradiation of benzophenone and tetramethylallene in benzene solution, as was done by Arnold and Glick, led to production of a mixture from which compounds **5** and **6** could be isolated. By thin layer chromatography, the original, low melting product was separated into three fractions. The principal component melted at 147° after recrystallization and gave no melting point depression on admixture with a sample of **5** from Arnold's laboratory. The minor components were not obtained in sufficient quantity to crystallize but infrared spectra showed that neither material was identical with **6**. It is possible that **6** was present in the low melting material but that it underwent rearrangement in the course of the chromatographic separation. Crystal seeding experiments showed that the low melting material is not merely a polymorphic form of **5**.

The nmr spectrum of **5** shows four sharp resonances in the methyl proton region. The signals are tentatively assigned as follows. When **5** was treated with aqueous sulfuric acid under the same conditions that led to facile hydrolytic cleavage of spiro ketals, no cleavage products could be detected. The nmr spectrum of **6** shows sharp singlets at 1.29 and 1.03 ppm. Chemical evidence for the spiro ketal structure was obtained by Arnold and Glick.[2]



Compounds **13** and **14** are assigned the indicated structures mainly on the basis of the proton resonances of the methylene groups. Those in **13** should occur at lower field than those in **14** because the former are attached to a carbon atom which is also bonded to an oxygen atom. We believe that the resonance at 3.18 ppm in the spectrum of **13** should be attributed to the proton that is *cis* to the oxygen atom of the other ring. The basis for assignment is rather intuitive, and therefore far from compelling. However, one might expect the *cis* proton to be subject to a small, but significant, paramagnetic deshielding related to the paramagnetic deshielding of directly bound protons inferred to exist in water.[7] Similar reasoning leads to the following assignments of the resonances due to the methylene protons in **15**.



15

Two generalizations have been advanced concerning photochemical cycloaddition reactions of carbonyl compounds and alkenes.[8] First, only carbonyl compounds having the n,π* configuration in their lowest triplet states show high reactivity and, second, cycloaddition occurs only if transfer of triplet excitation from the carbonyl compound to olefinic compound is inefficient because the vertical excitation energy of the acceptor is higher than that available in the carbonyl triplet. The singlet–singlet absorption spectra of allenes have been discussed by Murrell.[9] There should be low intensity transitions having lower excitation energies than the lowest transitions of simple olefins. Such transitions may have been observed[10] in the vicinity of 2500 Å. No spectroscopic information is available concerning allenic triplets. However, one would expect the splitting between triplets and singlets to be smaller than in alkenes since the excitation effectively transfers an electron from one plane to another perpendicular to the first. In such an excited state, the electron–electron repulsion should not be decreased greatly by the singlet → triplet transition. The situation would be roughly similar to the familiar case of the n,π* states of carbonyl compounds. Consequently, the triplet states of allene might be expected to lie between those of alkenes (~82 kcal/mol) and conjugated dienes (~59 kcal/mol).[11] Acetophenone, which has an excitation energy of 74 kcal/mol,[12] adds smoothly to tetramethylallene with a quantum yield for disappearance of the ketone of 0.59. Consequently, we infer that the triplet excitation energy of the allene is significantly greater than 74 kcal/mol. Traces of materials that appear to be dimers of the allenes were noted in the vapor chromatograms in some experiments indicating that energy transfer may have occurred, but with very low efficiency.

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(5) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 62.

(6) R. H. Hasek, R. D. Clark, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1962).

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 180.

(8) D. A. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, No. 22, 1425 (1964); N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964); J. Saltiel, R. M. Coates, and W. G. Dauben, *J. Amer. Chem. Soc.*, **88**, 2745 (1966).

(9) J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, p 79.

(10) E. P. Carr and H. Stücklen, Proceedings of the Seventh Summer Conference on Spectroscopy and its Applications, John Wiley and Sons, Inc., New York, N. Y., 1940, p 128.

(11) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(12) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

TABLE I.—PHOTOADDITION OF KETONES TO ALLENES[a]

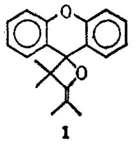
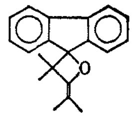
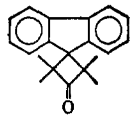
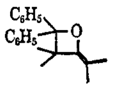
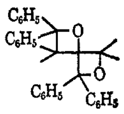
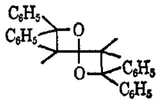
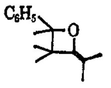
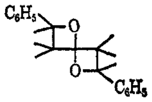
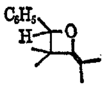
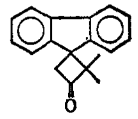
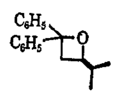
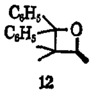
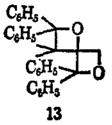
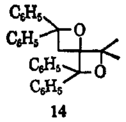
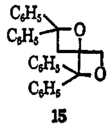
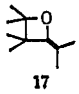
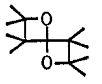
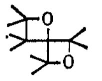
Ketone	Substrate	Products	
Xanthone	Tetramethylallene	 1	*Anal.* Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.23; H, 7.00 Ir, 1735 cm^{-1} Nmr, 7.38, 1.74, 1.53, 0.84 ppm Isolated yield, 60%
Fluorenone	Tetramethylallene	 2	*Anal.* Not obtained in pure form Ir, 1735 cm^{-1} Nmr, 7.2, 1.63, 1.59, 1.25 ppm
		 3	*Anal.* Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 87.04, H, 7.34 Ir, 1775 cm^{-1} Nmr, 7.2, 1.27 ppm Isolated yield, up to 73%
Benzophenone	Tetramethylallene	 4	*Anal.* Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.23; H, 8.14 Ir, 1735 cm^{-1} Nmr, 7.5, 1.76, 1.53, 1.15 ppm Isolated yield, 37%
		 5	*Anal.* Calcd for $C_{33}H_{32}O_2$: C, 86.05; H, 7.00. Found: C, 85.95; H, 6.87 Nmr, 7.2, 1.50, 1.43, 1.29, 0.57 ppm Isolated yield, 28%
		 6	*Anal.* See ref 2 Nmr, 7.37, 1.29, 1.03 ppm Isolated yield, 15%
Acetophenone	Tetramethylallene	 7	*Anal.* Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.44; H, 9.37 Ir, 1735 cm^{-1} Nmr, 7.39 (5), 1.66 (3), 1.63 (3), 1.53 (3), 1.42 (3), 0.82 (3) ppm Isolated yield, 25%
		 8	*Anal.* Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 82.03; H, 8.39 Nmr, 7.39 (10), 1.82 (6), 1.37 (6), 0.72 (6) ppm Isolated yield, 38%
Benzaldehyde	Tetramethylallene	 9	*Anal.* Calcd for $C_{14}H_{18}O$: C, 83.13; H, 8.97. Found: C, 83.12; H, 8.97 Ir, 1736 cm^{-1} Nmr, 7.19 (5), 5.23 (1), 1.58 (3), 1.15 (3), 1.13 (3) ppm Isolated yield, 51%
Fluorenone	1,1-Dimethylallene	 10	*Anal.* Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.95; H, 6.43 Ir, 1783 cm^{-1} Nmr, 7.3, 3.52, 1.10 ppm Yield (by nmr), 48%
Benzophenone	1,1-Dimethylallene	 11	*Anal.* Calcd for $C_{18}H_{18}O$: C, 86.34; H, 7.25. Found: C, 86.30; H, 7.15 Ir, 1744 cm^{-1} Nmr, 7.1, 3.49, 1.61, 1.38 ppm
		 12	Not isolated in pure form. Nmr, resonances overlapping those of 11 plus an AB pattern centered at 3.76 ppm with J = 3.6 cps
		 13	*Anal.* Calcd for $C_{31}H_{28}O_2$: C, 86.08; H, 6.53. Found: C, 85.89; H, 6.62 Nmr, 7.32, 3.26, 3.18, 0.92, 0.86 ppm Yield (by nmr), 42%
		 14	Not obtained in analytical purity Nmr, 7.3, 3.06, 2.98, 1.28; 1.19 ppm Yield (by nmr), 20%

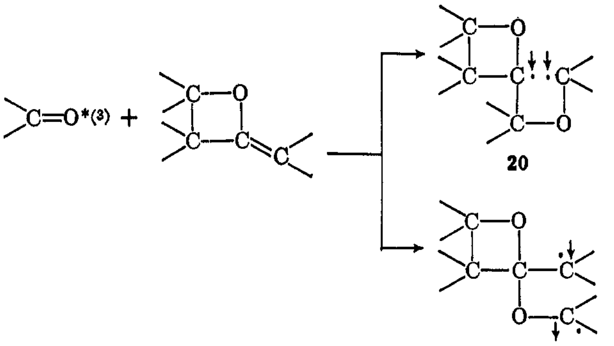
TABLE I (*Continued*)

Ketone	Substrate	Products	
Benzophenone	Allene	 **15**	*Anal.* Calcd for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found, C, 86.19; H, 6.08 Ir, none in region of interest Nmr, 7.36, AB group centered at 4.72 ppm, ($\Delta\nu$ = 18.0 cps, J_{12} = 7.2 cps) AB group centered at 3.15 ppm ($\Delta\nu$ = 22.9 cps, $J_{3,4}$ = 12.4 cps)
Acetone	Tetramethylallene	 **16**	*Anal.* Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.07, H, 11.88 Ir, none in region of interest Nmr, singlets at 1.59 and 1.43 ppm; ratio 1:2
		 **17**	*Anal.* Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.98; H, 11.94 Ir, 1732 cm^{-1} Nmr, four singlets at 1.35, 1.28, 1.19, and 1.13 ppm; ratio 1:1:2:2
		 **18**	*Anal.* Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.65; H, 11.34 Nmr, four singlets at 1.22, 1.10, 1.06 and 0.93 ppm; ratio 1:1:1:1
		 **19**	*Anal.* Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.64; H, 11.28 Nmr, three singlets at 1.38, 1.16, and 1.12 ppm (in CCl_4); ratio 1:2:1. In fluorobenzene four sharp singlets are resolved.

[a] In cases in which the relative areas are not ambiguously indicated by the structural formulas and ordinary chemical shifts, the relative areas of the nmr signals are included in parentheses after the chemical shifts.

The first step of addition seems to be highly selective and is easily rationalized if an intermediate biradical having an allylic part structure is formed in preference to alternate vinylic radical structures. The only exception to the apparently preferred direction of addition was the isolation of a small amount of **16** from the reaction of acetone with tetramethylallene.

The course of the second addition step is not nearly so obvious, since two kinds of products are formed. The usual mechanism would lead to the following formulations.



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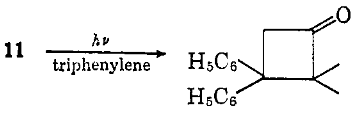
That the second step should take two courses is interesting but not astounding. One would expect that the double bonds in the enol ethers should be highly reactive because of the strain energy in the exocyclic double bonds. The high reactivity is indicated by the fact that formation of diadducts is competitive with addition to the parent allenes even though the latter are used as the reaction media. Since the reactions are very rapid one might expect that normal selectivity would not be observed. Stabilization of intermediate **20** may not be so large as would normally be expected. Three-electron bonding between the cyclic spin center and the adjacent oxygen atom may be decreased relative to that in acyclic α-oxy radicals because of decrease in the π interaction in the small-ring system. However, the factors that control competition between the two possible courses of reaction are not at all obvious. On a totally emperical basis one might expect acetophenone to show behavior intermediate between that of benzophenone and acetone. Only the spiro ketal, **8**, was isolated from acetophenone whereas with acetone both the spiro ketal, **18** and the diaoxaspiroheptane, **19**, were isolated although the former was apparently produced in the higher yield. Since the material balance was imperfect in all experiments, we now consider it unwise to attack any significance to the absence of the second bis adduct having the 2,5-dioxaspiroheptane structure from the reaction with acetophenone.

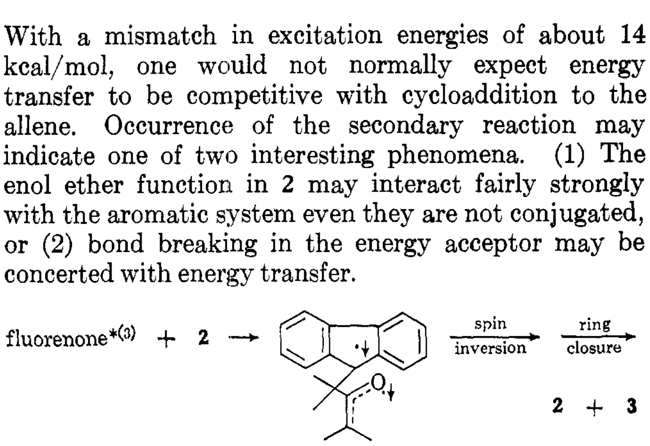
The failure of fluorenone and xanthone to form diadducts is interesting. In the former case the second addition step seems to be replaced by photoisomerization of the oxetanes to cyclobutanones, a reaction that may have some synthetic merit. The latter is almost certainly a photochemical process, although it has been studied explicitly only with **11**, one of the adducts formed from benzphenone and 1,1-dimethylallene. The rearrangement to **22** is sensitized by triphenylene.



22

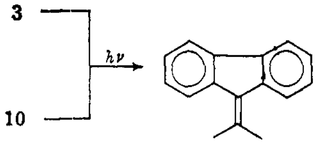
Isomerization of **2** was not studied in separate experiments because the compound could never be obtained free from the isomeric ketone, **3**. Probably cyclobutanones are formed in the course of preparative experiments by reactions in which the parent ketones serve as sensitizers. Such a mechanism deserves special comment. Consider the case of the fluorenone–tetramethylallene system. The monoadduct, **2**, would be expected to have a triplet excitation energy similar to that of fluorene (67.6 kcal/mol) whereas the excitation energy of fluorenone is only 53.3 kcal/mol.[12]

With a mismatch in excitation energies of about 14 kcal/mol, one would not normally expect energy transfer to be competitive with cycloaddition to the allene. Occurrence of the secondary reaction may indicate one of two interesting phenomena. (1) The enol ether function in 2 may interact fairly strongly with the aromatic system even they are not conjugated, or (2) bond breaking in the energy acceptor may be concerted with energy transfer.



23

Another product isolated from the reactions of fluorenone with tetramethylallene and 1,1-dimethylallene is isopropenylfluorene. This product could well have been formed by fragmentation of 23 with the concommitant formation of dimethylketene. We have observed that 3 and 10 the cyclobutanones formed from reaction of fluorenone with tetramethylallene and dimethylallene undergo photolysis to isopropylidenefluorene when excited by direct irradiation.



Experimental Section

Materials.—Tetramethylallene, Aldrich Chemical Co., was used directly for preparative runs. For use in quantum yield determinations the compound was purified by preparative vapor chromatography. 1,1-Dimethylallene was prepared from 3-methylbut-1-yn-3-ol by the method of Bailey and Pfeifer.[13] Allene, from Matheson Co., was used without further purification. The ketones were all reagent grade of the best purity available commercially and were further purified by distillation or recrystallization.

Procedures.—Solutions were prepared by dissolution of the appropriate ketone in the hydrocarbon, which was used in excess. Solutions were placed in constricted Pyrex ampoules (100 × 13 mm), degassed through three freeze–thaw cycles, and sealed under vacuum. The tubes were placed in the well surrounding a medium-pressure mercury lamp (Hanovia 450-W) and irradiated for periods of 5–28 days. Infrared spectra were taken with a Beckman spectrophotometer, Model IR-7, in carbon tetrachloride solutions. Microanalyses were carried out by the Spang Analytical Laboratory, Ann Arbor, Mich. Nuclear magnetic resonance spectra were determined using a Varian A-60 spectrometer. Carbon tetrachloride solutions were used except where indicated otherwise. All melting points are uncorrected.

Xanthone–Tetramethylallene.—A tube containing 900 mg of xanthone in tetramethylallene was irradiated 115 hr. The colorless crystals of xanthone slowly disappeared and a small amount of a new precipitate was formed; 71 mg of the product was collected by filtration and found to be the pinacol derived by photoreduction of xanthone, mp 160–163°. The filtrate was concentrated by evaporation and the residual oil was distilled at 0.1 torr with a bath temperature of 125–160°. The light yellow distillate (804 mg) solidified and was recrystallized from hexane, mp 114–115°. Structure 1 was assigned to the compound. A mixture of 100 mg of the product and 3 cc of 20% aqueous sulfuric acid was allowed to stand for 3 days at room temperature. The light yellow reaction mixture was extracted with 2 cc of carbon tetrachloride and the extract was dried and distilled at atmospheric pressure. The distillate had an infrared spectrum identical with that of authentic diisopropyl ketone. The residue was recrystallized from methanol and identified as xanthone by mixture melting point (173–174°).

Fluorenone–Tetramethylallene.—Two tubes, each containing 500 mg of fluorenone and 3 cc of tetramethylallene, were irradiated for 12 days. The precipitated crystals were collected by filtration and identified as 2-keto-1,1,3,3-tetramethylspiro-(cyclobutane-4,9′-fluorene), 3, colorless needles, mp 205–206° recrystsllized from ethyl acetate. The filtrate was concentrated by evaporation under vacuum at room temperature. The residual, light yellow oil was separated into three fractions by chromatography on 30 g of Florisil. The first fraction, eluted with 210 cc of pentane plus 90 cc of benzene, was identified as 9-isopropylidenefluorene:[14] mp 112–114°; yield, 82 mg, 7.4%. The second fraction (0.126 g), eluted with 150 cc of pentane and 350 cc of benzene, was a mixture of 2 and 3 and the third fraction, eluted with 280 cc of benzene and 120 cc of ether, was pure 3. The amount of 2 in the second fraction was estimated by nmr analysis; the over-all yield of 3 was 1.12 g (73%). In two other runs yields of 66 and 72% were obtained. Compound 2 was not obtained in pure form because of the ease with which it undergoes rearrangement to 3.

Benzophenone–Tetramethylallene.—A solution of benzophenone (1.0 g) and tetramethylallene (3 cc) was irradiated for 27 days in a degassed, sealed Pyrex tube. Benzopinacol, identical with an authentic sample, precipitated and was removed by filtration (0.137 g, 13.6%), mp 167–170°. The excess tetramethylallene was removed by distillation and the residual oil was distilled at 1–2 torr with a bath temperature of 130–160°. The colorless oil (0.56 g, 36.6%) was identified as 2,2-diphenyl-3,3-dimethyl-4-isopropylideneoxetane, 4. The residue from distillation (0.660 g) was chromatographed on Florisil (30 g). Elution with a mixture of pentane (400 cc) and benzene (100 cc) gave an unidentified oil (0.210 g). Further elution with a mixture of 170 cc of pentane and 170 cc of benzene gave colorless crystals (0.350 g, 27.6%), mp 87–89°, identified as 3,3,7,7-tetramethyl-1,1,6,6-tetraphenyl-2,5-dioxaspiro[3.3]heptane, 5.

A sample of the above material was separated by thin layer chromatography using benzene as a developer. Examination under ultraviolet light showed three bands. The intermediate band, which moved at the same rate as Arnold's sample of 5, was eluted with ethyl ether and recrystallized from aqueous ethanol, mp 147°. The other fractions were obtained in very samll quantities and could not be crystallized. The infrared spectra of thin films showed that neither material was identical with 6.

Compound 4 was hydrolyzed by allowing a 0.170-g sample to stand with 2 cc of 20% aqueous sulfuric acid for 2 days at room temperature. The reaction mixture was extracted with 2 cc of carbon tetrachloride, dried, and distilled at atmospheric pressure. The infrared spectrum of the distillate was identical with that of diisopropyl ketone. The residue was identified as benzophenone by its infrared spectrum.

A mixture of benzophenone (5.5 g) and tetramethylallene (3.0 g) in 300 cc of benzene was irradiated 9.5 hr in the immersion well of a high-pressure mercury lamp (Hanau Q 700). Purified nitrogen was bubbled through the solution. The solution was concentrated and distilled at 0.001 torr with a bath temperature of 120°. An oily, colorless distillate (0.61 g, 7.3%) was collected and identified as 4. The distillation residue (5.25 g of light yellow solid) was chromatographed on 400 g of neutral alumina (activity grade III). Elution with benzene gave some benzpinacol and 3.5 g of a noncrystalline product which was rechromatographed on alumina (400 g, activity grade II). Elution with a mixture of petroleum ether and benzene (9:1) gave 0.1 g of an unidentified oil and 1.02 g (15%) of a white, crystalline material which melted 150–152° after recrystallization from methanol. Comparison of the nmr spectra indicated that the material is identical with compound 6 isolated by Arnold and Glick; however, the remaining sample of the latter was insufficient to permit comparison by mixture melting point. Further elution with benzene yielded 1.90 g (27%) of 5, mp 149–151°.

Acetophenone–Tetramethylallene.—A mixture of acetophenone (4 cc) and tetramethylallene (12 cc) was irradiated for 24 days in four ampoules. Vapor chromatographic analysis indicated complete disappearance of acetophenone and the ap-

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(13) W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 95 (1955).

(14) P. Maitland and S. H. Tucker, *J. Chem. Soc.*, 2559 (1929).

pearance of no dimers from tetramethylallene. The combined solutions were concentrated and distilled at 1 torr. The first fraction (80–110° bath temperature) was a colorless oil (2.136 g, 29%) identified as 2-phenyl-2,3,3-trimethyl-4-isopropylideneoxetane, **7**. The second fraction (140–170° bath temperature) was a colorless glass (3.867 g). Recrystallization from methanol gave 1.375 g (10%) of white crystals identified as 2,6-diphenyl-2,3,3,6,7,7-hexamethyl-1,5-dioxaspiro[3.3]heptane, **8**, mp 133–134.5°. In another run a 38% yield of **8** isolated by chromatography on silica gel using benzene as the elution solvent. An 8% yield of 2,3-diphenylbutane-2,3-diol was also isolated.

A mixture of **7** (280 mg) and 20% sulfuric acid (5 cc) was allowed to stand for 2 days at room temperature and then heated under reflux for 1 hr. The product was extracted with carbon tetrachloride and distilled at atmospheric pressure. The distillate contained diisopropyl ketone and the residue was acetophenone. Vapor chromatography showed that the two ketones were present in equimolar amounts.

Compound **8** (300 mg) was allowed to stand with 40% sulfuric acid (2.5 cc) for 24 hr at room temperature. The mixture was extracted with carbon tetrachloride and vpc analysis of the extract showed the presence of diisopropyl ketone and acetophenone in the ratio 1:2.02.

Benzaldehyde–Tetramethylallene.—A mixture of benzaldehyde (3 cc) and tetramethylallene was irradiated for 27 days in two ampoules. Vapor chromatography showed the presence of 4.4% unreacted benzaldehyde and 68% **9**. After concentration, the products were distilled at 8–10 torr (100–180° bath temperature) giving 4.24 g of light yellow oil which was purified by preparative vapor chromatography. The product was identified as 2-phenyl-3,3-dimethyl-4-isopropylideneoxetane, **9**.

A 50-mg sample of **9** was hydrolyzed by treatment with 20% sulfuric acid (1 cc) for 1 day at room temperature. The reaction mixture was extracted with carbon tetrachloride, washed, dried, and distilled at atmospheric pressure. The distillate and residue were identified respectively as diisopropyl ketone and benzaldehyde by vapor chromatography and infrared spectra.

Acetone–Tetramethylallene.—A mixture of acetone (3 cc) and tetramethylallene (6 cc) was irradiated for 20 days in two degassed, sealed Pyrex test tubes and irradiated for 20 days. Unreacted materials were removed by distillation and the residue was distilled at 17 torr. At 110–170° bath temperature a colorless oil (440 mg) was collected. Analysis by vapor chromatography of the distillate showed a major product (85%) and two unidentified minor products. The main product was separated by preparative gas chromatography and identified as 2,2,3,3-tetramethyl-4-isopropylideneoxetane, **17**.

In another experiment a solution of tetramethylallene (20 g) and acetone (400 cc) was irradiated in two portions using a 450-W mercury resonance lamp for 18 hr. During irradiation dry nitrowas bubbled through the solutions. The combined solutions were concentrated and distilled under vacuum. At 70–110° and 17 torr a liquid which deposited some crystals was obtained; at 105–115° and 1 torr 2.3 g of a yellow oil (shown by vpc to contain at least four compounds) was obtained. The crystalline material (5.60 g) was removed from the first fraction by filtration, purified by sublimation at 70° (1 torr), and identified as 1,1,3,3,-6,6,7,7-octamethyl-2,5-dioxaspiro[3.3]heptane (**19**), mp 81–82°. The filtrate was separated by preparative vapor chromatography (9-ft UCON polar, 20%, 90°) into six fractions. The first was 0.3 g of colorless oil, identified as 3-isopropylidene-2,2,4,4-tetramethyloxetane, **16**. The second fraction was 0.5 g of colorless oil identified as **17**. This material was hydrolyzed to acetone and diisopropyl ketone when treated with 20% sulfuric acid. Fractions 3 and 4 contained samll amounts of unidentified materials. Fraction 5 was 3.5 g 2,2,3,3,6,6,7,7-octamethyl-1,5-dioxaspiro[3.3]heptane, **18**. Hydrolysis with 20% sulfuric acid gave acetone and diisopropyl ketone. The sixth fraction was 2.60 g of **19**.

Fluorenone–1,1-Dimethylallene.—Three tubes, each containing fluorenone (0.5 g) and 1,1-dimethylallene (3 cc), were irradiated for 212 hr. The contents of two tubes were combined and the excess dimethylallene was removed by distillation and the residue was distilled at 1–2 torr with a bath temperature of 145–170°. The product was a yellow oil (845 mg) and was found by nmr analysis to be a mixture of **10** and 9-isopropylidenefluorene. The material was separated by chromatography on 30 g of Florisil with pentane–benzene (80:20) as the eluent. The first fraction (176 mg) was isopropylidenefluorene, mp 112–114° after recrystallization from methanol. Further elution with increasing amounts of benzene yielded colorless needles (0.572 g), mp 89–90° after recrystallization from methanol. The material was identified as **10** by elementary analysis and infrared and nmr spectroscopy (see Table I). The most significant spectral features were the strong carbonyl absorption at 1783 cm^{-1} in the infrared spectrum and the occurrence of a sharp singlet due to six methyl protons at 1.10 ppm downfield from the tetramethylsilane resonance. The yield of **10** in the distillate was measured at 48% by integration of the nmr spectrum of the crude distillate.

The contents of the thrid tube were concentrated *in vacuo* and the spectra of the residue was determined. The infrared spectrum showed no absorption in the region of the enol ether bands (~1735 cm^{-1}) and the nmr spectrum indicated the presence of only the two compounds isolated.

Benzophenone–1,1-Dimethylallene.—Six tubes, each containing benzophenone (1 g) and 1,1-dimethylallene (3 cc), were degassed, sealed under vacuum, and irradiated for 11 days. The combined contents of five tubes were concentrated and then distilled at a pressure of 2.5–4 torr with a bath temperature of 135–160°. The distillate yielded 2.56 g of brownish red oil and the residue was 3.86 g of light yellow solid. The distillate was separated into five fractions after passages through a Florisil column using pentane and 1:1 pentane–benzene as elution solvents. The first fraction was 40 mg of unidentified oil. The second was 80 mg of oil identified as a mixture of **11** and **12**. The third fraction (200 mg) was identified as 2,2-diphenyl-4-isopropylideneoxetane (**11**). The fourth fraction was 153 mg of unidentified material. The last fraction was 1.36 g of colorless oil identified as 2,2-dimethyl-3,3-diphenylcyclobutan-1-one, believed to be an artifact formed by rearrangement of **11** and **12**.

The residue was separated into two principal fractions by chromatography on Florisil using pentane containing 20% benzene as the eluent. The first fraction was recrystallized from hexane giving colorless crystals, mp 117–119°, and was identified as 7,7-dimethyl-1,1,6,6-tetraphenyl-2,5-dioxaspiro-[3.3]heptane, **13**. The second fraction contained an oil identified as 3,3-dimethyl-1,1,6,6-tetraphenyl-2,5-dioxaspiro[3.3]heptane, **14**. Integration of the nmr spectrum of the unseparated distillation residue gave the yields of **13** and **14** shown in Table I.

The vacuum distillate (0.1 g) containing **11**, **12**, and **22** was treated with 20% aqueous sulfuric acid (5 cc) at room temperature for 24 hr. The reaction mixture was extracted with carbon tetrachloride and the extract was analyzed by vapor chromatography. Equal amounts of benzophenone and methyl isopropyl ketone were found. None of the latter product was formed when the distillation residue was treated with aqueous acid under similar conditions.

The reaction mixture of the sixth irradiated tube was concentrated at room temperature under vacuum. Both the infrared and nmr spectrum of the residue showed absence of **22**. This indicates that **22** was formed during distillation by a thermal rearrangement of **11** and **12**.

Benzophenone–Allene.—Two tubes, each containing benzophenone (4 g) and liquid allene (about 10 cc) were degassed, sealed under vacuum, and irradiated for 26 days. The excess allene was removed by evaporation and the residue was crystallized from methanol. After four recrystallizations, colorless crystals, mp 127–127.5°, were isolated and identified as 1,1,6,6-tetraphenyl-2,5-dioxaspiro[3.3]heptane, **15**. Treatment of the compound with 20% aqueous sulfuric acid at room temperature for 24 hr did not lead to production of either acetone or benzophenone.

Photolysis of 3.—A solution of **3** (0.150 g) in 4 cc of benzene was irradiated for 24 hr. The resulting light yellow solution was concentrated by evaporation under vacuum. The solid residue was treated with carbon tetrachloride (1 cc) and filtered. Comparison of nmr and infrared spectra with those of authentic material showed the product to be 9-isopropylidenefluorene.

Photolysis of 10.—A solution of **10** (0.1 g) in 3 cc of benzene was irradiated for 48 hr. Examination as in the above experiment sowed that the starting material was converted quantitatively into 9-isopropylidenefluorene.

Sensitized Photolysis of 11.—A solution of **11** (0.042 g) in 5 cc of benzene saturated with triphenylene was irradiated for 24 hr. The solvent was removed by distillation under vacuum. The residue was dissolved in 2 cc of carbon tetrachloride for determination of the infrared spectrum which showed the presence of 2,2-dimethyl-3,3-diphenylcyclobutanone, **22**, in addition to residual **11**.

Quantum Yield Determination.—A solution was prepared by dissolution of 0.130 g of acetophenone and 0.062 g of chlorobenzene[15] in enough tetramethylallene to make the total volume 10 cc. Two tubes, each containing 3.4 cc of the solution, were irradiated in a merry-go-round apparatus for periods of 4 and 6 hr using solution filters containing $NiSO_4$–$CoSO_4$ and potassium acid phthalate to isolate the 3130-Å group of lines. Samples containing 3.4 cc of a mixture of 1,3-cyclohexadiene (1.312 g), benzophenone (0.916 g), and hexadecane[15] (0.1395 g) in 50.0 cc of benzene were irradiated in parallel with the reaction samples. The product mixtures were analyzed by vapor chromatography and the quantum yield for disappearance of acetophenone was calculated on the assumption that the quantum yield for dimerization of cyclohexadiene is 0.88 under the specified conditions.[16] The measured value of the quantum yield was 0.58 after 4 hr and 0.60 after 6 hr.

Registry No.—**1**, 16717-87-6; **2**, 16717-86-5; **3**, 16717-88-7; **4**, 14315-05-0; **5**, 14315-03-8; **6**, 14315-04-9; **7**, 16717-92-3; **8**, 16717-93-4; **9**, 16717-94-5; **10**, 16717-95-6; **11**, 16717-96-7; **12**, 16717-97-8; **13**, 16717-98-9; **14**, 16718-04-0; **15**, 14315-02-7; **16**, 16718-00-6; **17**, 2570-82-3; **18**, 14315-08-3; **19**, 14315-07-2.

Acknowledgment.—This work was supported by a grant from the National Science Foundation. We are indebted to Drs. Chin-Hua Wu and Robert Ning who carried out the thin layer chromatographic separation.

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[15] Internal standard for vapor chromatographic analysis.

[16] G. F. Vesley, unpublished study.

Sesquiterpene Lactones of *Helenium alternifolium* (Spreng.) Cabrera. Structures of Brevilin A, Linifolin A, and Alternilin[1,2]

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Helenium alternifolium (Spreng.) Cabrera from near Tucuman, Argentina, furnished primarily tenulin and smaller amounts of brevilin A, previously isolated from *H. brevifolium* (Nutt.) A. Wood, linifolin A, previously isolated from *H. linifolium* Rybd., and 6,3′-dimethoxy-5,7,4′-flavone. A collection of *H. alternifolium* from near La Plata, Argentina, afforded the new sesquiterpene lactone alternilin as the sole crystallizable constituent. Structures of brevilin A, linifolin A, and alternilin have been established.

Since our last summary[4] of work on constituents of *Helenium* species, the complete stereochemistry of mexicanin A,[5] thurberilin,[6] and tetrahydrobigelovin[6] has been established and the relative configuration of bromomexicanin E[7] has been determined. A new guaianolide, virginolide, has been extracted from *H. virginicum* Blake,[1] a structure has been deduced for mexicanin H[8] and previously known lactones have been isolated from *H. plantagineum* (DC.) MacBride.[9] In the present paper we wish to report our work on the Argentinian species *H. alternifolium* (Spreng.) Cabrera which allowed us to determine the structure of two previously isolated pseudoguaianolides, brevilin A[10] and linifolin A,[11] and that of a new congener, alternilin.

Examination of *H. alternifolium* collections from near Tucuman, Argentina, furnished 6,3′-dimethoxy-5,7,4′-trihydroxyflavone[12] and tenulin[13] as the principal sesquiterpene lactone constituent. Smaller quantities of other lactones were also isolated. One of the minor lactones was identified as linifolin A, $C_{17}H_{20}O_5$, mp 201–203°,[11,14] previously isolated from *H. linifolium* Rydb., to which we had assigned[11] a gross structure stereoisomeric with that of acetylhelenalin (**2**) (Chart I),[13b,15] balduilin (**3**),[13b,16] and bigelovin (**4**).[17,18] Because hydrogenation of linifolin A afforded, in our hands,[11] a tetrahydro derivative of mp 149–150° which differed from acetyltetrahydrohelenalin (**6**), acetyldihydromexicanin C (11-epiacetyltetrahydrohelenalin), tetrahydrobalduilin (**7**), 11-epitetrahydrobalduilin, tetrahydrobigelovin (**8**), and dihydroisotenulin (**9**) and, because of a subsequent report[19] that hydrogenation of the fourth possible *trans*-fused isomer acetylmexicanin I (**5b**) afforded a substance of mp 109° which was presumably 11-epidihydroisotenulin (**10**), we were forced to conclude[11] that linifolin A differed from compounds **2**–**5** in configuration at one or more of the asymmetric centers at C-1, C-5, C-7, and C-10 and suggested[5] that, because of the inversion of the Cotton effect during hydrogenation, linifolin A might belong to the 1-*epi* series.

The physical constants of the freshly isolated linifolin A from *H. alternifolium*, however, coincided so closely with those reported for acetylmexicanin I (**5b**)[9,19] that a direct comparison was called for. Acetylation of samples of mexicanin I supplied by Dr. Romo de Vivar or isolated from *Helenium autumnale* L.[20] gave material

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[1] Constituents of Helenium Species. XXI. Previous paper: W. Herz and P. S. Santhanam, *J. Org. Chem.*, **32**, 507 (1967).

[2] Supported in part by a grant from the U. S. Public Health Service (GM-05814).

[3] National Science Foundation Undergraduate Research Participant, 1966–1967.

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[14] The melting point was slightly higher than that reported earlier,[11] but the compound was identical in all respects (nmr and ir spectra, tlc) with the sample from *H. linifolium*.

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[20] P. S. Subramaniam, unpublished work.