Methyl Vinyl Ketone.—Methyl vinyl ketone (K & K Laboratories) (redistilled, b.p. 79°, $n^{24}\text{D}$ 1.4089, pure by g.l.p.c.) (10.0 g.) was stirred vigorously with copper(II) chloride hydrate (48.8 g.) and lithium chloride (6.1 g.) in dimethylformamide for 40 min. at 75–85°. Continuous extraction by pentane (91 hr., followed by optical density at 3300 Å.) yielded 3 g. of oil. Multifold extraction with pentane of a similar reaction mixture gave 2.2 g. of oil. The latter material (15% chloro ketone by g.l.p.c.) was fractionated through a Teflon spinning band column to yield 0.4 g. of distillate in three fractions (the pot contained a viscous black liquid). Pure chloro ketone, b.p. 50–60°/75 mm., was isolated from the third fraction (100 mg.) by g.l.p.c. on 7.5% polyethylene glycol 600 distearate at 135°. The ketone became a black viscous mass on standing in the refrigerator for 1 month. $\tilde{\nu}_{C=O}$ 1705 cm.$^{-1}$., λ_{max} (isoöctane) 3160 Å., 2295 Å. (ϵ 9000). The corresponding figures for methyl vinyl ketone are $\tilde{\nu}_{C=O}$ 1680 cm.$^{-1}$, λ_{max} (isoöctane) 3304 Å. (ϵ 20), 2040 Å. (ϵ 8500). The properties of the chloro ketone were identical to those of 3-chloro-3-butenone which was synthesized in 4% yield by the method of Petrov and Leporskaya[6] and quite different from those of 1-chloro-3-buten-2-one prepared by the reaction of ethylene, aluminum chloride, and chloroacetyl chloride.[7] Although the yield of 3-chloro-3-butenone isolated as above was quite low, g.l.p.c. analysis of the crude product indicated that 30–40% of chloro ketone was present.

Mesityl Oxide.—Redistilled ketone (3.5% isomer by g.l.p.c.) was chlorinated at 90–95°. The color lightened appreciably after 15 min., then became dark black. After 20 min. reaction, oil was isolated in the usual way with pentane (14 g. from 24 g. of starting ketone.) G.l.p.c. analysis of the crude product is illustrated in Fig. 1, using 20% polyethylene glycol 600 distearate on firebrick. Fractional distillation of the oil under reduced pressure gave mixtures which could be resolved into reasonably pure components by g.l.p.c.

Isomesityl oxide (69% pure by g.l.p.c.)[28] was chlorinated to give a yellow oil. Comparison of the g.l.p.c. analysis of the oil with that of the mesityl oxide product revealed that components **A**, **B′**, and **C′** increased and components **B**, **C**, and **D** decreased in yield.

From a fraction containing **B** and **C** (b.p. 80–92°/30 mm.), chloro ketones **B** and **C** were separated by g.l.p.c., 20 λ at a time, to give small quantities of the pure ketones.

Ketone B: *Anal.* Calcd. for C_6H_9OCl: C, 54.35; H, 6.84; Cl, 26.74. Found: C, 54.15; H, 6.78; Cl, 26.35, 26.49.

N.m.r. spectrum (capillary benzene reference = 0, internal hexamethyldisiloxane (HMD) = 384 c.p.s.) (in c.p.s.) 271, 255, 145, and 12.3 with area ratios *ca.* 3:3:2:1. $\tilde{\nu}_{C=O}$ (liquid film) 1678 cm.$^{-1}$; $\lambda_{max}^{isooctane}$ 2400 Å. (ϵ 11,900), 3337 Å. (ϵ 70).

Ketone C showed carbonyl absorption at 1686 cm.$^{-1}$; 245 mμ (ϵ 10,300), 331 mμ (ϵ 81) in isoöctane. The n.m.r. spectrum is very similar to that of **B** except for a low intensity peak at 38 c.p.s. The chloro ketone **C** is very unstable and satisfactory combustion data could not be obtained. G.l.p.c. analysis of a sample trapped from g.l.p.c. indicated the presence of both hydrogen chloride and a volatile compound, some of which are lost before combustion. Both **B** and **C**, when freshly prepared, were colorless and lachrymatory.

The products **A** and **B′** were trapped directly from the crude product by g.l.p.c. since they disappear during attempted fractional distillation. The presence of high boiling material in the product and the lack of a preparative g.l.p.c. apparatus permitted only the collection of sufficient material for infrared and ultraviolet absorption measurements. Both compounds gave positive tests for chlorine after destruction by fused sodium. **Ketone A**: $\tilde{\nu}_{C=O}$ 1709 cm.$^{-1}$ (in $CHCl_3$), $\lambda_{max}^{isooctane}$ 2809 A. (ϵ 390). **Ketone B′**: $\tilde{\nu}_{C=O}$ 1718 cm.$^{-1}$ (in $CHCl_3$), $\lambda_{max}^{isooctane}$ 2810 (ϵ 340). It must be noted that the retention times of these two ketones in g.l.p.c. were quite different.

Product **C′** was present in such small quantities that it could not be isolated.

Product **D** could be isolated as a faintly yellow liquid, b.p. 67°/0.6 mm. and represented almost 40% of the product of chlorination of mesityl oxide (23% of the isomesityl oxide chlorination product). $\tilde{\nu}_{max}$ 2950 (s), 1695 (w), 1618 (w), 1355 (m) cm.$^{-1}$; $\lambda_{max}^{isooctane}$ 2208 Å. (ϵ 8400), 2847 Å. (ϵ 180).

Anal. Found: C, 71.03; H, 8.72; Cl, 4.54.

The analysis of a sample after treatment with silver nitrate was almost identical. N.m.r. spectrum (capillary benzene = 0 c.p.s., HMD = 384 c.p.s.) (in c.p.s.) 294, 265, 254, 244, 213, 45.3 with approximate relative areas of 3.5:2:2:2:1. The product was not further investigated but is probably formed from two moles of monochloro ketone followed by loss of hydrogen chloride.

Ultraviolet Spectra.—Spectra were carefully measured with either a Cary Model 11 or Model 14 recording spectrophotometer. The spectroscopic results are summarized in Table II.

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(28) F. H. Stross, J. M. Monger, and H. de V. Finch, *J. Am. Chem. Soc.*, **69**, 1627 (1947).

Oxidation by Solids. II. The Preparation of Either Tetraarylethanes or Diaryl Ketones by the Oxidation of Diarylmethanes with Manganese Dioxide

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It has been found that, when a solution of a diarylmethane in biphenyl and benzene is heated under reflux (211°) with manganese dioxide in an apparatus equipped with a water trap, good yields of the corresponding tetraarylethanes as well as the by-product water usually are obtained. The effects of changes in structure of the diarylmethanes on the rate of the reaction are consistent with the proposal that the reaction proceeds *via* free radical intermediates. When the same diarylmethanes and manganese dioxide, in 1:10 weight ratio, are heated at 125° in the absence of a solvent good yields of the corresponding diaryl ketones are usually obtained.

A procedure for oxidizing a variety of diarylmethanes to the corresponding tetraarylethanes in good yield has been developed. The diarylmethane and manganese dioxide in biphenyl and benzene are heated under reflux (211°) in an apparatus equipped with a Dean–Stark trap. Approximately the theoretical yield of water ordinarily collects in the trap and since smooth curves of the same general shape are obtained upon plotting the volume of water collected against time, the times required for a 50% yield of water to collect ($t_{50\%}$) are valid measures of the relative rates of reaction. The $t_{50\%}$ values were found to be closely reproducible.

$$2ArCH_2Ar' + MnO_2 \longrightarrow ArAr'CHCHAr'Ar + MnO + H_2O \quad (1)$$

In Table I results for six symmetrical and seven unsymmetrical diarylmethanes are listed in order of decreasing reaction rate. For both the symmetrical and unsymmetrical reactants the *para*-phenyl substituents increased the rate over that for the unsub-

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(1) From the Ph.D. thesis of S. P. Suskind, April, 1962.

(2) For the previous paper in this series, see E. F. Pratt and John F. Van de Castle, *J. Org. Chem.*, **26**, 2973 (1961).

stituted diphenylmethane more than did the *para*-chloro substituents although the chloro substituent attracts electrons more strongly. As expected, two chloro or two phenyl substituents had a greater effect than one, but somewhat unexpectedly replacing one phenyl group of diphenylmethane with an α-naphthyl group increased the rate while two such replacements greatly decreased the rate. The strongly electron releasing *para*-methoxyl and dimethylamino substituents greatly decreased both the rate of the oxidation and the yield of product.

TABLE I

PREPARATION OF TETRAARYLETHANES AND DIARYL KETONES

Standard tetraarylethane conditions: 0.1 mole of diarylmethane, 0.3 mole of manganese dioxide, 238 g. of biphenyl, and 12 g. of benzene stirred magnetically while distilling the by-product water at 211°.

Standard diaryl ketone conditions: 1 g. of diarylmethane and 10 g. of manganese dioxide heated without solvent at 125° for 6 hr.

Reactant	Tetraarylethane expts. $t_{50\%}$[a] min.	Tetraarylethane expts. H_2O, %	Tetraarylethane expts. Prod.,[b] %	Diaryl ketone expts., prod.,[b] %
Symmetrical diarylmethanes				
p-$\mathrm{C_6H_5C_6H_4CH_2C_6H_4C_6H_5}$-$p$	40	101	92	26
p-$\mathrm{ClC_6H_4CH_2C_6H_4Cl}$-$p$	54	94	74	83
$\mathrm{C_6H_5CH_2C_6H_5}$	75	102	81	74
p-$\mathrm{(CH_3)_2NC_6H_4CH_2C_6H_4N(CH_3)_2}$-$p$	215	97	25	0
α-$\mathrm{C_{10}H_7CH_2C_{10}H_7}$-$\alpha$[c]	244	99	63	29
p-$\mathrm{CH_3OC_6H_4CH_2C_6H_4OCH_3}$-$p$	350	71	17[d]	73
Unsymmetrical diarylmethanes[e]				
$\mathrm{HC{:}CHN{:}CHCH{:}CCH_2C_6H_5}$[f]	6	180[g]	[h]	72
p-$\mathrm{C_6H_5C_6H_4CH_2C_6H_5}$	47	100	83	76
α-$\mathrm{C_{10}H_7CH_2C_6H_5}$[i]	63	100	70	71
p-$\mathrm{ClC_6H_4CH_2C_6H_5}$	65	101	81	63
$\mathrm{C_6H_5CH_2C_6H_5}$	75	102	81	74
$\mathrm{SCH{:}CHCH{:}CCH_2C_6H_5}$[j]	280	202[g]	0	49
p-$\mathrm{CH_3C_6H_4CH_2C_6H_5}$	395	91	10	0
p-$\mathrm{CH_3OC_6H_4CH_2C_6H_5}$	1310[k]	56	3	29

[a] This is the time required for a 50% yield of water to collect. [b] When the reported yield is low it represents a minimum value of limited significance since separation of solids by fractional crystallization was often involved. [c] Di-α-naphthylmethane. [d] Starting material recovered in 56% yield. [e] Here the tetraarylethane yields refer to mixtures of the *d,l,* and *meso* isomers. [f] γ-Pyridylphenylmethane. [g] The excessive yield of water indicates the tetraarylethylene was formed, but it could not be isolated. [h] A 78% yield of solids apparently consisting of the *d,l,* and *meso* ethanes plus the *cis*- and *trans*-ethylenes was obtained. [i] α-Naphthylphenylmethane. [j] α-Thienylphenylmethane. [k] Of little significance because of the low total yield of water.

When p,p'-dinitrodiphenylmethane, fluorene and xanthene were oxidized under the same conditions the $t_{50\%}$ values and the yields of water (both based on tetraarylethane formation) were 4, 3, and 4 min. and 210, 198, and 156%. The excessive yields of water suggested that the expected tetraarylethanes had undergone dehydrogenation to the corresponding ethylenes which were, in fact, isolated in yields of 18, 16, and 36%. With twice the standard amount of manganese dioxide the yield of the ethylene from fluorene was tripled to 51%.[3] In agreement with the belief that ethylene formation proceeds *via* the ethanes 9,9′-bifluorenyl was rapidly converted in 75% yield to 9,9′-bifluorenylidene under the same conditions. Related dehydrogenations with sulfur or lead oxide have been reported.[4]

It was found (see Experimental) that as the temperature at which the oxidation of diphenylmethane was carried out was decreased, the yield of tetraphenylethane decreased even though the yield of water remained close to the theoretical. At the lower temperatures appreciable amounts of benzophenone were formed. Thus at 126°, for example, the yield of water was 94%, the yield of benzophenone was 23%, and the yield of tetraphenylethane was only 31%. The yield of diaryl ketone could be further increased at the lower temperatures by increasing the amount of manganese dioxide.

In agreement with the trends just described it was found that good yields of diaryl ketone were ordinarily obtained when a diarylmethane and manganese dioxide, in 1:10 weight ratio, were heated, in the absence of a solvent, for six hours at 125°.[5] The results are listed in the right hand column of Table I. In a few cases, *e.g.* with, p,p'-dimethoxydiphenylmethane, γ-pyridylphenylmethane and α-thienylphenylmethane, the yields of ketone, by this solvent-free procedure, were good while the yields of ethane by the distillation procedure, described in the first paragraph, were poor; with p,p'-diphenylmethane and di-α-naphthylmethane the reverse was true. Both the standard distillation procedure for the ethanes and the standard solvent-free procedure for ketones were based on results of studies with diphenylmethane in which the time, temperature, and reactant ratio were varied. Pure ketone could not be obtained from the rather high melting (188°) p,p'-dinitrodiphenylmethane by the standard solvent-free procedure, but when magnetic stirring was introduced a 72% yield was obtained. It is of interest that manganese dioxide has, heretofore, ordinarily been used to abstract hydrogen rather than to introduce oxygen.[6,7]

Under the solvent-free conditions, tetraphenylethane and 9,9′-bifluorenylidene were recovered unchanged. Benzhydrol was oxidized to benzophenone and triphenylmethane to triphenylcarbinol, however, both in 76% yield. 9-Chlorofluorene gave fluorenone in 80% yield; it is probable that hydrolysis to fluorenol first occurred.[8] These results, together with those previously reported on the oxidation of a number of benzhydrols to benzophenones by manganese dioxide[2] are consistent with the proposal that conversion of diarylmethanes to diaryl ketones proceeds *via* the alcohol.

The formation of the tetraarylethanes *via* the coupling of two identical radicals seems reasonable since symmetrical products are often formed in this way and diarylmethanes would be expected to form free radicals

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(3) It seems probable that the yields of the other ethylenes could be increased in the same way.

(4) (a) J. H. Ziegler, *Ber.*, **21**, 780 (1888); (b) C. Graebe and H. Stindt, *Ann.*, **291**, 1, 6 (1896); (c) R. C. Moreau, *Bull. soc. chim. France*, 628, 922 (1955); (d) J. Tsurugi, T. Nakabayashi, and T. Yamanaka, *Nippon Kagaku Zasshi*, **77**, 578–582 (1956); *Chem. Abstr.*, **52**, 9047 (1958).

(5) Ketones were first prepared in these laboratories under approximately these conditions by Dr. John F. Van de Castle.

(6) Several ferrocene derivatives have, however, been oxidized to aldehydes and ketones very satisfactorily. See K. L. Rhinehart, Jr., A. F. Ellis, C. J. Michejda, and P. A. Kittle, *J. Am. Chem. Soc.*, **82**, 4112 (1960).

(7) H. B. Henbest and J. W. Stratford, *Chem. Ind.* (London), 1170 (1961) employed manganese dioxide to replace an alkyl group of a tertiary amine with a formyl group.

(8) E. F. Pratt and L. E. Trapasso, *J. Am. Chem. Soc.*, **82**, 6405 (1960).

readily. Such coupling has been proposed for the production of tetraarylethanes by the action of silver or mercury on diphenylmethyl chlorides[9] as well as for certain other syntheses of these products[10] and the oxidation of phenylcarbinols to ketones by solid manganese dioxide appears to proceed *via* free radicals.[2] Little of the correlation of reaction rate with electron releasing ability of the *para* substituents expected for ionic reactions is evident in the rate data of Table I and the conditions employed, *i.e.*, solid manganese dioxide in biphenyl and benzene, might be expected to favor radical over ionic intermediates.[11a] The following route, therefore, is suggested.

$$\mathrm{Ar_2CH_2 + O{=}\overset{IV}{Mn}{=}O \longrightarrow Ar_2\dot{C}H + HO{-}\overset{III}{Mn}{=}O} \quad (2)$$

$$\mathrm{Ar_2CH_2 + HO{-}\overset{III}{Mn}{=}O \longrightarrow Ar_2\dot{C}H + HO{-}\overset{II}{Mn}{-}OH} \quad (3)$$

$$\mathrm{2Ar_2\dot{C}H \longrightarrow Ar_2CHCHAr_2} \quad (4)$$

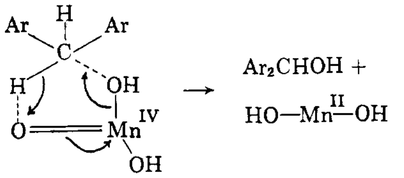
$$\mathrm{HO{-}\overset{II}{Mn}{-}OH \longrightarrow \overset{II}{Mn}O + H_2O} \quad (5)$$

The dehydrogenation of the tetraarylethanes to tetraarylethylenes mentioned above may well proceed *via* intermediates formally analogous to those previously suggested for the dehydrogenation of diarylcarbinols to diaryl ketones.[2]

If, as indicated above, the diarylcarbinols are intermediates in the oxidation of diarylmethanes to diaryl ketones a source of hydroxyl groups must be provided. One reasonable possibility is that hydroxyls are transferred as free radicals from some reduced or hydrated form of manganese dioxide[7] such as $\mathrm{HO\overset{III}{Mn}{=}O}$ or $\mathrm{(HO)_2{-}\overset{IV}{Mn}{=}O}$.

$$\mathrm{Ar_2\dot{C}H + HO{-}\overset{III}{Mn}{=}O \longrightarrow Ar_2CHOH + \overset{II}{Mn}{=}O} \quad (6)$$

The reactants here are the products of reaction 2 and it might be expected that the absence of a solvent, the large proportion of manganese dioxide, and the lower temperature employed for the preparation of the ketones would favor reaction 6 while the conditions of the distillation procedure might promote desorption and coupling of the free radicals and therefore favor reaction 4. An attractive alternative route, however, is the formation of the alcohol intermediates by a concerted process occurring on the surface of the hydrated manganese dioxide. Here no radicals are set free for coupling and of course the solvent free procedure would favor the presence of more of the hydrated manganese dioxide than would the distillation procedure.[11b]



(7)

It is of interest that by the two procedures the same oxidizing agent gives a good yield of either of two products, neither of which appears to be an intermediate in the formation of the other. If a hydrated form of manganese dioxide is required for the production of the ketones (*via* the alcohols), it might be expected that dehydration of the manganese dioxide would inactivate it. When manganese dioxide which had been dehydrated by distilling the water from a suspension of it in toluene (112°) was employed in the standard solvent free procedure the yield of benzophenone did, in fact, drop from 74% (Table I) to 2%. Since the manganese dioxide was even more completely dehydrated in the standard distillation procedure for tetraarylethanes by distilling the water at 211° before the diarylmethane was added it is not surprising that little ketone was produced under these conditions. It is to be emphasized, however, that the activity of manganese dioxide varies widely with its method of preparation[12] even for reactions which are readily written in terms of the unhydrated form.

A single example in the literature describes the preparation of tetraphenylethane in 49% yield by heating diphenylmethane with manganese dioxide in petroleum ether at 120° for two hours.[13] Low (10 to 20%) or unstated yields of tetraphenylethane have also been reported for the action of potassium peroxydisulfate,[14] sulfur,[15] or air[16] on diphenylmethane and a 50% yield of 9,9-bifluorenyl was obtained by the oxidation of fluorene with lead oxide.[4c] It appears, therefore, that because of the facility of the distillation procedure, the availability of diarylmethanes and the yields obtained, the method reported here would be the preferred one for the preparation of a number of tetraarylethanes.

Experimental[17,18]

Starting Materials.—The manganese dioxide was prepared by the modified Attenburrow procedure previously described[2] except that the manganous sulfate solution was added dropwise to the permanganate solution over a 60-min. period while the addition of the sodium hydroxide extended over only the first 45 min. of this period. This gave a precipitate which could be washed much more rapidly on the Büchner funnel.[19] The final drying of the oxide was extended to 3 days at 125°, after which it was allowed to equilibrate with the moisture in the air. This was carried out by exposing it in shallow layers for 3 days during which it was well stirred at approximately 4-hr. intervals.[20] All experiments of both the tetraarylethane and diaryl ketone series were carried out with manganese dioxide from a single large, well mixed batch. This was weighed out all at one time into 0.3-mole portions which were stored in tightly closed bottles at −20° until used.

All other constituents of the reaction mixtures were purchased

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(9) (a) W. Th. Nauta and D. Mulder, *Rec. trav. chim.*, **58**, 1062 (1939); (b) J. Coops, W. Th. Nauta, M. J. E. Ernsting, and A. C. Faber, *ibid.*, **59**, 1109 (1940); (c) W. E. Bachmann, "Organic Chemistry," Vol. 1, 2nd ed., H. Gilman, ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 622.

(10) (a) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 2457 (1955); (b) A. J. v. d. Hock and W. Th. Nauta, *Rec. trav. chim.*, **61**, 845 (1942).

(11)(a) The increasing reaction rates observed for the sequence of diphenylmethane, α-benzylnaphthalene, *p*-phenyldiphenylmethane, and *p,p'*-dibiphenylylmethane may well be a consequence of the increasing resonance stabilization of the corresponding free radicals; it is recognized, however, that the corresponding carbanions or carbonium ions would also be increasingly stabilized in the same sequence. (b) A referee has suggested that the alcohol may be formed by the following chain reaction: $\mathrm{R\cdot + MnO_2 \rightarrow RO\cdot + MnO}$; $\mathrm{RO\cdot + RH \rightarrow R\cdot + ROH}$.

(12) R. M. Evans, *Quart. Rev.*, **13**, 61 (1959).

(13) M. F. Abdel-Wahab, M. M. El-Sadr, and M. F. Barakat, *J. Chem. Soc.*, 4685 (1956).

(14) A. Schonberg and A. Mustafa, *ibid.*, 67 (1944).

(15) F. Mashio, H. Fukuda, and T. Nakabayashi, *Nippon Kagaku Zasshi*, **76**, 111 (1955); *Chem. Abstr.*, **51**, 17846 (1957).

(16) F. Mashio and Y. Nakagawa, *J. Chem. Soc. Japan*, Ind. Chem. Sect., **55**, 111 (1952); *Chem. Abstr.*, **48**, 6404 (1954).

(17) We wish to thank Dr. Franz Kasler for the microanalyses reported herein.

(18) All melting points are corrected.

(19) This was first observed in these laboratories by Dr. Terrence McGovern.

(20) Dr. Terrence McGovern found that the dried oxide rapidly adsorbed water from the air for a total weight increase of over 5%.

or prepared by previously described methods.[21] No literature values were found for the refractive index of phenyl-γ-pyridylmethane, which gave an $n^{20}D$ value of 1.5822 nor for phenyl-α-thienylmethane which gave an $n^{25}D$ value of 1.5887. All other constituents of the reaction mixtures were purified until their refractive indices or melting points agreed satisfactorily with the literature values.

Optimum Conditions for Tetraphenylethane Formation.—The effect of varying the reaction temperature was studied with diphenylmethane under the standard conditions given below except that the ratio of biphenyl to benzene, employed as the solvent, was varied to give the desired reflux temperature. The preliminary dehydration of the manganese dioxide (see standard procedure below) was also carried out at the particular temperature used for the oxidation. The amounts of benzene used in the 250 g. of mixture were 8, 12, 20, 24, 35, and 54 g. The results are summarized in Table II.

TABLE II

Temp.	$t_{50\%}$ min.	H_2O, %	$[(C_6H_5)_2CH]_2$, %
126	1152	94	31
149	492	93	42
169	196	108	55
185	115	111	62
211	71	102	81
231	46	107	82

From infrared absorption spectra measurements, the amount of benzophenone was estimated to be 23, 24, 14, and 9% at 126, 149, 169, and 211°, respectively. A trace of the 2,4-dinitrophenylhydrazone of benzophenone was isolated from the experiment at 211°.

Since a temperature of 211° gave close to the optimum yields of tetraphenylethane as well as a convenient rate of reaction the effect of varying the amount of manganese dioxide was studied at this temperature. The amount of manganese dioxide was increased from 0.2 to 0.3 to 0.4 mole in a series of three experiments with diphenylmethane under conditions otherwise like the standard conditions given below. The $t_{50\%}$ values, the yields of water and the yields of tetraphenylethane, in the same order were 92 min., 101% and 65%; 75 min., 102% and 81%; and 57 min., 119% and 81%.

Tetraarylethane Experiments of Table I.—The standard procedure used for these experiment was as follows. One of the three ground glass necks of a 500-ml. round bottomed flask was fitted with a Dean-Stark water trap surmounted by a West condenser. The trap was calibrated in 0.1-ml. units for a total of 5 ml. The second neck held a separatory funnel or, if the diarylmethane to be oxidized was a solid, this neck was stoppered while the third neck held a thermometer in a well. The 0.3 mole (26.1 g.) of manganese dioxide was added together with 12 g. of benzene and 238 g. of biphenyl along with a 1 in. Teflon covered magnetic stirring bar. Heating with a hemispherical mantle and stirring were begun using constant, maximum voltages on both mantle and magnetic stirrer.[22] After 5.5 hr., evolution of water stopped; almost invariably 3.0 ± 0.4 ml. collected. Heating was suspended and when the temperature had dropped to 205° (from 211°) the liquid diarylmethane was added from the separatory funnel. Solid diarylmethanes were weighed into a 125-ml. erlenmeyer flask which had been fitted with a ground glass neck bent at such an angle that the solid readily flowed into the reaction mixture when the stopper was quickly replaced by the flask which then functioned as the stopper throughout the reaction. Heating was resumed and zero time taken when the first drop of condensate fell from the condenser. Frequent readings of the water volume, time, and temperature were taken until the reaction was 80% complete. Heating was ordinarily continued until the water volume was constant for 3 hr. Certain very slow reactions were allowed to proceed for several days.

The curves obtained upon plotting the volume of water collected against time ordinarily showed a constantly decreasing reaction rate except during the first 10% of the reaction during which there was usually a slight increase in rate. Repetition of the experiment with diphenylmethane over a total period of several months gave $t_{50\%}$ values of 79, 75, 80, and 79 min.

In the tetraarylethane experiments of Table I the temperature ordinarily decreased slightly as reaction progressed. In most cases the temperature for the 20 to 80% portion of a reaction was constant to ±0.5° and in all but one case it was constant to ±1.0°. Among these experiments the median temperature was usually 211 ± 1.0°.

In the standard isolation procedure the reaction mixture was cooled to about 160° and filtered through a Celite mat. The solids were washed with 150 ml. of benzene and the benzene removed from the combined filtrate and washings under reduced pressure. The biphenyl was removed by distillation at 0.1 mm. with magnetic stirring; solidification of the biphenyl in the vacuum jacketed still head was prevented by heating it with an infrared heat lamp. The products were recrystallized from suitable solvents until their melting points agreed with the literature values.

The five products from the unsymmetrical diarylmethanes were obtained as mixtures of the *d,l* and *meso* isomers; in each case the mixtures of isomeric solids melted over a 30 to 55° range and had the calculated carbon and hydrogen content. Recrystallization of the 1,2-diphenyl-1,2-di-*p*-biphenylethane mixture (m.p. 201–249°) from toluene gave a 19% yield of the known, higher melting isomer (252–253°) while recrystallization of material from the mother liquors from glacial acetic acid gave a 2% yield of the known, lower melting isomer (204.5–206°). Recrystallization of the mixture of isomeric 1,2-diphenyl-1,2,-di-α-naphthylethanes (m.p. 178–208°) from 90–100° petroleum ether gave an 8% yield of an isomer which melted at 223–224°.

Anal. Calcd. for $C_{34}H_{26}$: C, 93.97; H, 6.03. Found: C, 94.13; H, 5.82.

The mixture of 1,2-diphenyl-1,2-di-*p*-chlorophenylmethanes (m.p. 132–177°) was recrystallized from 60–80° petroleum ether to give a 19% yield of an isomer which melted at 191–192°.

Anal. Calcd. for $C_{26}H_{20}Cl_2$: C, 77.43; H, 4.99. Found: C, 77.70; H, 5.19.

Because of the low yields of the isomeric mixtures of 1,2-diphenyl-1,2-di-*p*-methylphenylethanes, recrystallized from 60–80° petroleum ether (m.p. 177–204°), and 1,2-diphenyl-1,2-di-*p*-methoxyphenylethanes, recrystallized from benzene–alcohol (m.p. 165–196°), a pure isomer was not obtained in these cases.

When the oxidation of triphenylmethane was attempted by the standard procedure for tetraarylethanes a 58% yield of water was evolved very slowly and starting material (23%) was the only pure compound isolated from the reaction mixtures.

Water was rapidly evolved in good yields when the oxidation of diphenylacetonitrile, indene, anthrone, and bianthrone was attempted, but efforts to isolate pure compounds from the reaction mixtures were unsuccessful.

Tetraarylethylenes.—When *p,p'*-dinitrodiphenylmethane was oxidized according to the standard distillation procedure described above, a 210% yield of water (calculated for tetraarylethane formation) was collected in 180 min. Recrystallization of the crude product, which was isolated as outlined for the tetraarylethanes, from glacial acetic acid, then from a mixture of dioxane and petroleum ether (60–80°) and finally again from glacial acetic gave pure tetra-*p*-nitrophenylethylene (m.p. 305–306°) in 18% yield.

When fluorene was treated in the same way a 198% yield of water was obtained in 17 hr. The crude product was extracted in a Soxhlet apparatus for 8 days with 1 l. of petroleum ether (60–80°). When the orange powder which precipitated upon concentration of the extract was recrystallized from a mixture of chloroform and alcohol a 15% yield of 9,9'-bifluorenylidene (m.p. 179–184°) was obtained.

Treatment of xanthene in the same way gave a 156% yield of water in 18 hr. A 36% yield of 9,9'-bixanthenylidene (m.p. 316–319°) was obtained upon recrystallization of the crude product from toluene.

Oxidation of 9,9'-bifluorenyl in the same way gave a 50% yield of water in 5 min. and a 93% yield in 18 hr. The crude product was extracted in a Soxhlet with 1 l. of petroleum ether (60–80°) for 20 hr. Concentration of the extract gave a 75% yield of 9,9'-bifluorenylidene which melted at 187–188°; when mixed with the product obtained from fluorene, as described just above, the m.p. was 186–188°.

Only an 18% yield of tetraphenylethylene was isolated when 1.0 g. of tetraphenylethane was heated with 10.0 g. of manganese dioxide for 1 hr. at 340°.

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[21] We wish to thank Mr. Samuel Holter for preparing the di-α-naphthylmethane.

[22] Arthur H. Thomas Co., cat. no. 9235-S.

Optimum Conditions for Benzophenone Formation.—In a series of three experiments the effect on the oxidation of diphenylmethane of varying the amount of manganese dioxide was studied under conditions otherwise identical with the standard conditions given below. As the amount of the dioxide was increased from 2.5 to 5.0 to 10.0 g. the yield of benzophenone increased from 40 to 68 to 74%.

When the temperature was decreased from the standard 125° to 100°, using 10 g. of manganese dioxide the yield of benzophenone was 38%. In this experiment the mixture was stirred magnetically throughout the heating period.

A decrease in time of heating from the standard 6 hr. to 3 hr., using 10.0 g. of manganese dioxide at 125°, decreased the yield of benzophenone from 74% to 38%.

When the reaction mixture was stirred magnetically throughout the heating period, under conditions otherwise standard, the yield of benzophenone was essentially unchanged.

Diaryl Ketone Experiments of Table I.—The standard procedure used for these experiments was as follows. One gram of diarylmethane and 10.0 g. of manganese dioxide were thoroughly mixed and placed in a 125-ml. erlenmeyer flask, the stopper of which was fitted with a Bunsen valve. Solid diarylmethanes were well ground before mixing. The reaction mixtures were heated at 125 ± 3.0° for 6 hr. in a magnetically stirred oil bath large enough to accommodate three flasks.

At the end of the heating period the flask contents were extracted with 250 ml. of chloroform for 12 hr. in a Soxhlet apparatus. After volatilization of the chloroform under reduced pressure the products, unless otherwise noted, were recrystallized from suitable solvents until their melting points agreed satisfactorily with the literature values.

The usual recrystallization techniques did not give a pure product from di-α-naphthylmethane. In an attempt to prepare the oxime a solution of the crude product in pyridine and absolute alcohol was heated under reflux 2 hr. with 1.0 g. of hydroxylamine hydrochloride. Recrystallization of the residue obtained upon removal of the solvents gave a 29% yield of di-α-naphthyl ketone instead of the expected oxime.

Supplementary Experiments.—The oxidation of tetraphenylethane was attempted under the standard conditions for diaryl ketones given above except that magnetic stirring was employed throughout the heating period. No ketone could be isolated but starting material was recovered in 61% yield. When the oxidation of 9,9′-bifluorenylidene was attempted in the same way only starting material (74%) was recovered.

The oxidations of benzhydrol, triphenylmethane and 9-chlorofluorene were carried out under the standard conditions for diaryl ketones.

Although p,p'-dibiphenylylmethane melts about 35° above the standard reaction temperature for diaryl ketones, magnetic stirring did not raise the rather low yield of ketone obtained from this compound.

Attempted oxidation of fluorene under the standard conditions for diaryl ketones gave no pure product. A 76% yield of fluorenone was obtained, however, at a temperature of 100° with magnetic stirring.[23]

No identifiable products were obtained when the oxidation of deoxybenzoin, xanthene, diphenylacetonitrile and 9-methylanthracene was attempted under the standard conditions for diaryl ketones.

The dehydration of manganese dioxide, referred to in the Discussion, was accomplished by heating a magnetically stirred suspension of 0.3 mole of manganese dioxide in 250 ml. of toluene under reflux (112°) in an apparatus equipped with a water trap. Water evolution ceased after 6.5 hr. at which time 2.82 ml. had collected. The oxide was filtered off and stored overnight in a desiccator under reduced pressure. When 10.0 g. of this dehydrated manganese dioxide was used in an attempted oxidation of diphenylmethane according to the standard procedure for the diaryl ketone experiments of Table I the yield of benzophenone was only 2%.

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[23] This experiment was carried out by Dr. John F. Van de Castle.

Reactions of Nitroparaffins with Alicyclic Ketones. IV[1]

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Oximes of azadispiro keto cyclic hydroxamic acids have been obtained from the reaction of nitromethane and alicyclic ketones of five to eight carbons in the ring and from some 4-alkylcyclohexanones in the presence of pyrrolidine, piperidine, hexamethyleneimine, piperazine, 2-methylpiperazine, and morpholine as catalysts. With one exception, piperazine was the most satisfactory catalyst for the formation of these unusual compounds.

A previous publication[2] from this laboratory reported the preparation of a series of compounds from the solid product (C-I) from the reaction of nitromethane and cyclohexanone in the presence of piperidine. At that time, the structure of C-I was not known.

The structure of C-I has recently been determined by Noland and Sundberg[3] as 14-hydroxy-14-azadispiro[5.1.5.2]pentadec-9-ene-7,15-dione 7-oxime. The properties and reactions of the various compounds I agree well with those of an oxime of a keto cyclic hydroxamic acid. The structures of all of the compounds obtained in this laboratory from C-I and its analogs can be written with this atomic skeleton.

The numbers P-I, H-I, and O-I are assigned to the analogous solids obtained from the reaction of nitromethane with cyclopentanone, cycloheptanone, and cyclo-octanone respectively. These compounds and C-I all represent new ring systems.[4] Most of the Roman numbers designating the compounds in Chart I are those used in our preceding publication.[2]

The present study has been largely concerned with the effect of the amount and type of amine catalyst on the formation of the compounds I and with the effect of the size of the ring and the alkyl group of the 4-alkylcyclohexanones on the yields and properties of these compounds. These data are summarized in Table I.

Piperazine was in general the most satisfactory catalyst for the formation of the compounds I other

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[1] Abstracted from the Masters thesis of S. Miki, 1961, the Ph.D. thesis of D. A. Reich, 1956, and the Ph.D. thesis to be submitted by D. N. Heintz.

[2] D. V. Nightingale, D. A. Reich, and F. B. Erickson, *J. Org. Chem.*, **23**, 236 (1958).

[3] W. E. Noland and R. J. Sundberg, *Tetrahedron Letters*, 295 (1962). These authors have recently reported in a personal communication that the double bond is in the 9 position.

[4] P-I: 12-Hydroxy-12-azadispiro[4.1.4.2]tridec-8-ene-6,13-dione 6-oxime. H-I: 16-Hydroxy-16-azadispiro[6.1.6.2]heptadec-10-ene-8,17-dione 8-oxime. O-I: 18-Hydroxy-18-azadispiro[7.1.7.2]nonadec-11-ene-9,19-dione 9-oxime.