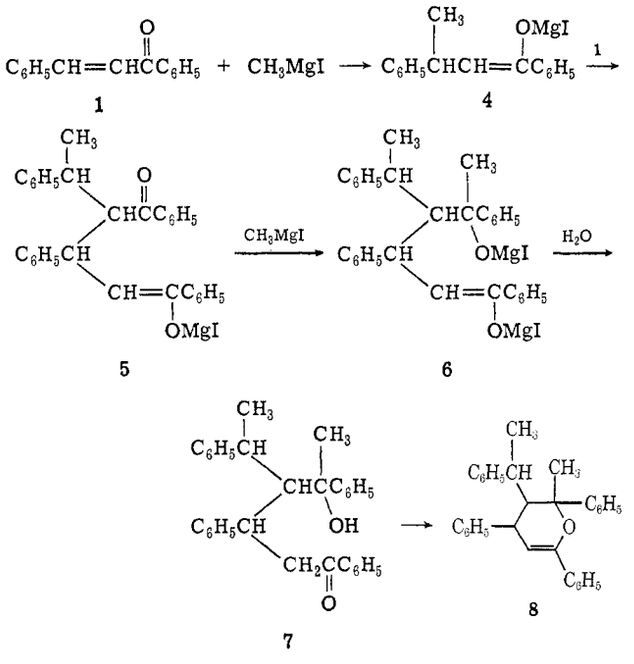
were clearly incompatible with structure **2**.[3] The mass spectrum indicated a molecular weight of 430, while the nmr contained a methyl doublet at δ 1.20 and a methyl singlet at δ 1.67. In addition, the infrared spectrum failed to confirm the presence of a carbonyl group. The available data appear most consistent with the formulation of this compound as dihydropyran **8**. This compound is, presumably, formed through initial 1,4 addition of methylmagnesium iodide to benzalacetophenone (**1**) to give magnesium enolate **4** (Scheme I). Michael addition of **4** to another mole-

SCHEME I



cule of starting material would then afford 1,5-diketone **5**, containing one of the carbonyl groups in enolic form.[4] The unenolized carbonyl group of **5** would not be expected to survive in the presence of excess methylmagnesium iodide, and subsequent reaction should afford **6**. Hydrolysis of **6** would give hydroxy ketone **7**, which under acidic conditions would be expected to cyclize and dehydrate to give **8**.[5]

The formation of **8**, under these conditions, indicates that magnesium enolate **4** is able to compete favorably with Grignard reagent for unreacted enone **1**. Utilization of a large excess of Grignard reagent in this reaction would obviously act to surpress the Michael reaction responsible for formation of **5**. It is interesting to speculate that a process similar to that of Scheme I may be responsible for the high molecular weight byproducts obtained in the Grignard reactions of other α,β-unsaturated ketones.

Experimental Section[6]

Reaction of Methylmagnesium Iodide with Benzalacetophenone.—A solution of methylmagnesium iodide was prepared under nitrogen by dropwise addition of a solution of 4.136 g (0.0291 mol) of methyl iodide in 50 ml of anhydrous ether into a flask containing 0.590 g (0.0243 g-atom) of magnesium turnings over a period of 18 min, at ice-bath temperature, and with magnetic stirring. After addition was completed, stirring was continued at room temperature for 30 min, resulting in complete reaction of the magnesium. The Grignard solution was cooled at ice-bath temperature, and a solution of 3.251 g (0.0156 mol) of benzalacetophenone (**1**), mp 58–58.5°, in 90 ml of anhydrous ether was added dropwise, with stirring, over a period of 24 min. The resulting mixture was stirred at room temperature for 30 min and then decomposed with 100 ml of 3 *M* HCl. The ether layer was washed twice with 50-ml portions of 3 *M* HCl and once with 50 ml of saturated NaCl, and dried over anhydrous $MgSO_4$. Concentration *in vacuo* afforded an amber-colored oil which was chromatographed on a 40-g column of 60–200 mesh silica gel. Fractions eluted with hexane and with 1:19 benzene–hexane were crystallized from ether to give 0.677 g (20%) of **8** as small white needles, mp 176.0–177.5°. Recrystallization from ether afforded the analytical sample: mp 178.0–179.0° (lit.[2b] mp 176°); ir (KBr) 1658 (m, C=C), 760 (s, aromatic CH), 745 (s, aromatic CH), and 697 cm^{-1} (s, aromatic CH); nmr (CCl_4) δ 1.20 (3, H, d, J = 7 Hz, $CHCH_3$), 1.67 (3, H, s, CH_3), 2.33–3.00 (2 H, complex m, aliphatic CH), 4.41 (1 H, q, J_{ab} = 6.8, J_{bc} = 2.2 Hz, $CH_aCH_bArCH_c$=C), 5.74 (1 H, br, $W_{1/2}$ = 4 Hz, ArCHCH=C), and 6.0–8.0 (20 H, aromatic CH); mass spectrum (70 eV) *m/e* (rel intensity) 430 (M^+, 12), 325 (65), 222 (27), 221 (35), 208 (14), 207 (76), 206 (78), 205 (81), 105 (100), 91 (29), and 77 (5).

Anal. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02. Found: C, 89.58; H, 7.17.

Fractions eluted with 1:9 and 1:1 benzene–hexane contained 1.634 g of solid, which afforded 0.981 g (28%) of pure β-phenylbutyrophenone after crystallization from aqueous ethanol and from hexane, mp 73.5–75.0° (lit.[7] mp 74°).

Registry No.—**1**, 94-41-7; **2**, 34959-76-7; methylmagnesium iodide, 917-64-6.

(3) Kharasch and Sayles reported the independent synthesis of **2** in quantitative yield by reaction of benzalacetophenone with β-phenylbutyrophenone in the presence of pyridine.[2b] We have been unable to duplicate this preparation.

(4) The Michael reaction of a magnesium enolate with benzalacetophenone has previously been reported.[2a]

(5) *Cf.* M. Julia and A. Rouault, *Bull. Soc. Chim. Fr.*, 1833 (1959).

(6) Melting points are uncorrected. The infrared spectra were determined with a Beckman IR-8 spectrophotometer. Nmr spectra were recorded with a Varian A-60 spectrometer using tetramethylsilane as an internal standard. The mass spectra were obtained with a Varian MAT CH7 mass spectrometer. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich.

(7) M. A. Spielman and C. W. Mortenson, *J. Amer. Chem. Soc.*, **61**, 666 (1939).

Silver(II) Oxide as a Reagent. Reactions with Aromatic Amines and Miscellaneous Related Compounds

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Lee and Clarke have effected the oxidation of aliphatic amines, alcohols, aldehydes, and aromatic hydrocarbons[1,2] by means of the complexes of silver(II) oxide.[3] Syper[4] utilized the same reagent in acidic media to oxidize alcohols and aromatic hydrocarbons, while Corey, Gillman, and Ganem[5] employed it in neutral or slightly basic media for the stereospecific con-

(1) J. B. Lee and T. G. Clarke, *Tetrahedron Lett.*, 415 (1967).

(2) T. G. Clarke, N. A. Hampson, J. B. Lee, J. R. Morley, and B. Scanlon, *ibid.*, 5685 (1968).

(3) R. N. Hammer and J. Kleinberg, *Inorg. Syn.*, **4**, 12, (1953).

(4) L. Syper, *ibid.*, 4193 (1967).

(5) E. J. Corey, N. W. Gillman, and B. E. Ganem, *J. Amer. Chem. Soc.*, **90**, 5616 (1968).

TABLE I

OXIDATION OF VARIOUS AMINES WITH SILVER(II) OXIDE

Registry no.	Amine	Solvent	Temp, °C	Time, hr	Equiv AgO	Product	Yield, %
62-53-3	Aniline	Benzene		0.5			
		Chloroform	25	2	2	Azobenzene	20
		Acetone		2			
		Methanol		72			
87-62-7	2,2-Dimethylaniline	Benzene	72	5	2	2,2′,6,6′-Tetramethylazobenzene	33
106-49-0	*p*-Toluidine	Benzene	25	8	2	4,4′-Dimethylazobenzene[a]	17
99-98-9	*N,N*-Dimethyl-*p*-phenylenediamine	Benzene	25	1	2	4,4′-Dimethylamino-*N,N*′-azobenzene[b]	59
106-47-8	*p*-Chloroaniline	Benzene	72	9	2	4,4′-Dichloroazobenzene[a]	47
134-32-7	α-Naphthylamine	Benzene	25	1	2	1,1′-Azonaphthalene[c]	15
95-54-5	*o*-Phenylenediamine	Ether	25	72	3	*o,o*-Azodianiline	40
	o-Phenylenediamine	Benzene	72	4	4	1,4-Dicyanobutadiene	30
95-55-6	*o*-Aminophenol	Benzene	25	2	3	*o*-Benzoquinone azine	45

[a] K. Tabei and M. Yamaguchi, *Bull. Chem. Soc. Jap.*, **40**, 1539 (1967). [b] E. Noelting, *Ber.*, **18**, 1143 (1885). [c] *Beilstein*, 2nd ed, **16**, 25.

TABLE II

OXIDATION OF VARIOUS FUNCTIONALLY SUBSTITUTED COMPOUNDS WITH SILVER(II) OXIDE

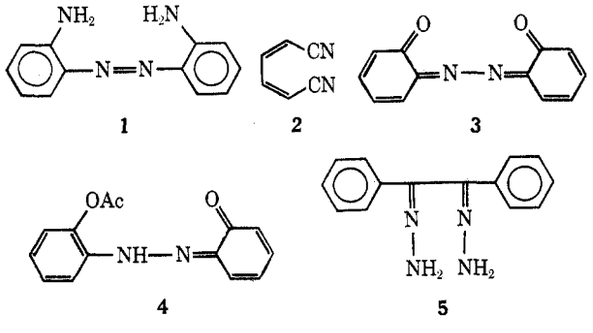
Registry no.	Substrate	Solvent	Temp, °C	Time, hr	Equiv AgO	Product	Yield, %
5350-57-2	Benzophenone hydrazone	Benzene	72	4	2	Benzophenone[a] azine	18
5344-88-7	Benzil monohydrazone	Benzene	25	14	2	Benzil	82
4702-78-7	Benzil dihydrazone	Benzene	25	10	4	Diphenylacetylene	95
613-94-5	Benzoic acid hydrazide	Benzene	72	10	2	1,2-Dibenzoylhydrazine[b]	40
787-84-8	Dibenzoylhydrazine	Benzene	72	22	4	Biphenyl	37
3619-22-5	*p*-Toluic acid hydrazide	Ethanol	72	1	2	1,2-bis-*p*-toluylhydrazine[c]	55
100-63-0	Phenylhydrazine	Benzene	25	2	3	Biphenyl	95
119-26-6	2,4-Dinitrophenylhydrazine	Methanol	58	2	3	*m*-Dinitrobenzene	87
		Chloroform	53	6	2	Citral	80
106-24-1	Geraniol	Benzene	72	10	2	Citral	70
		Acetone	50	10			70
34562-09-9	α-Methylgeraniol	Chloroform	53	20	3	*cis*- and *trans*-4,8-dimethyl-nona-3,7-dien-2-one[d]	91
		Benzene	72	20	3		70
		Acetone	50	20	3		60
110-00-9	Tetrahydrofuran	THF	75	78	Excess	Butyrolactone	18

[a] W. Lirmre, L. Horner, and H. Farnekess, *Chem. Ber.*, **94**, 712 (1961). [b] C. Neogeli and G. Stefanovitsch, *Helv. Chim. Acta*, **2**, 636 (1928). [c] W. Autervieth and G. Thomae, *Chem. Ber.*, **57**, 436 (1924). [d] C. Aguilar, M. Salmón, and F. Walls, *Bol. Inst. Quim. Univ. Nac. Auton. Mex.*, **21**, 226 (1969).

version of allylic alcohols to conjugated acids. We have examined the behavior of silver(II) oxide with a wide variety of functionally substituted compounds.

With each of the amines, aniline, *p*-toluidine, *N,N*-dimethyl-*p*-phenylenediamine, 2,6-dimethylaniline, *p*-chloroaniline, and α-naphthylamine, the principal product after the disappearance of the starting material was the corresponding azo derivative in yields as high as 59%. This reaction can be carried out at room temperature or at the boiling temperature of several solvents, such as ethyl ether, acetone, chloroform, methanol, or benzene (Table I). Among these, benzene proved, in general, to be the best solvent.

No reaction took place with *p*-nitroaniline, 2,4-dinitroaniline, *m*-phenylenediamine, or *p,p*′-methylenedianiline, either at room temperature or at the boiling temperature of the solvents mentioned above. However, the oxidation of *o*-phenylenediamine with 3 equiv of silver(II) oxide in ether at room temperature produced *o,o*′-azodianiline (**1**) in 40% yield. On the other hand, using 4 equiv of AgO produced a 30% yield of 1,4-dicyanobutadiene (**2**). Willstatter and Pfannenstiehl[6] obtained diaminophenazine in 12% and *o,o*′-azodianiline in 10% yield when *o*-phenylenediamine was treated with Ag_2O or PbO_2. Nakagawa[7] obtained (only) **2** from the same substrate in 14 and 50% yields, respectively, using nickel peroxide and lead tetraacetate.



Hydroquinone and methylhydroquinone in benzene or acetone were oxidized in less than 10 min to give the corresponding *p*-quinones in 100 and 90% yields, respectively; pyrocatechol produced *o*-benzoquinone in 2 hr in 40% yield.

(6) R. Willstatter and A. Pfannenstiehl, *Chem. Ber.*, **38**, 2350 (1905).

(7) K. Nakagawa and H. Onoue, *Tetrahedron Lett.*, 1433 (1965); *Chem. Commun.*, 396 (1965).

o-Aminophenol, in benzene at room temperature, gave rise to the azine **3**, which on subsequent reduction produced *o*-benzoquinone mono(*o*-acetoxy phenylhydrazone) (**4**).

It is interesting to point out that the oxidation of benzil dihydrazone (**5**) treated with silver(II) oxide produced diphenylacetylene in 95% yield, a better yield than that obtained by oxidation with HgO (81%).[8]

The results of oxidation involving a wide range of functional groups are summarized in Table II.

Experimental Section

The general method employed for the reactions was to dissolve the substance to be oxidized (1–5 mmol) in a suitable solvent. Then the silver(II) oxide, prepared according to Hammer and Kleinberg,[1] was added and the mixture was allowed to stand at room temperature with stirring and sampling at frequent intervals for tlc analysis of the extent of the reaction. If the chromatoplate spot corresponding to the starting material remained after several hours, the mixture was heated to the boiling point of the solvent. When the starting material had been used up, the reaction was stopped by filtering the silver or Ag_2O formed in the reaction. The purification of the products was carried out by chromatography either on alumina or on silica gel. The yields given are those of the pure products that were identified by melting point, uv, ir, nmr, and mass spectra and compared with authentic samples or spectra described in some detail.

2,6,2′,6′-Tetramethylazolenzene.—A solution of 1 g of silver(II) oxide was allowed to reflux for 5 hr. The solution was filtered and chromatographed on alumina, Alcoa F-20 (150 g). From the fractions eluted with benzene, 320 mg (33%) of orange-red crystals, mp 50°, was obtained: λ_{max} 213 nm (ϵ 26,400), 243 (10,100), 248 (11,600), 254 (12,300), 260 (10,250), 300 (8850), and 455 (840); ir 1585 cm^{-1}; nmr δ 2.4 (singlet) (TMS = 0) (12 protons of methyl on aromatic ring) and 7.1 ppm (singlet) (six protons, aromatic). *Anal.* Calcd for $C_{16}H_{16}N_2$: C, 80.63; H, 7.61; N, 11.76; mol wt, 238.32. Found: C, 80.49; H, 7.41; N, 11.52; mol wt, 238 (mass spectrum).

o-Benzoquinone Azine 3.—A mixture of 6 g of *o*-aminophenol and 21 g of silver(II) oxide in 200 ml of benzene was stirred at room temperature for 2 hr. After filtering, 2.8 g (45%) of crystals were obtained: mp 245°; λ_{max} 235 nm (ϵ 30,400) and 430 (28,700); ir 3370 and 1575 cm^{-1}. *Anal.* Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; O, 15.08; N, 13.20; mol wt, 212.2. Found: C, 67.46; H, 3.80; O, 15.17; N, 12.74; mol wt, 212 (mass spectrum).

***o*-Benzoquinone Mono(*o*-acetoxy)phenylhydrazone (4).**—A mixture of 200 mg of *o*-benzoquinone azine (**3**), 10 ml of acetic acid, 10 ml of acetic anhydride, and 2 g of zinc dust was heated for 2 hr at the steam bath, filtered, and poured into ice. The solid formed was crystallized from methanol: yield 152 mg (63%); mp 279–280°; λ_{max} 240 nm (ϵ 17,200) and 396 (24,000); ir 3270, 1700, and 1605 cm^{-1}. *Anal.* Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93; O, 18.73; mol wt, 256.25. Found: C, 65.78; H, 4.34; N, 10.81; O, 18.93; mol wt, 256 (mass spectrum).

Diphenylacetylene.—To 240 mg of benzildihydrazone, obtained by the method of Cope, Smith, and Cotter,[8] in 50 ml of benzene, 500 mg of silver(II) oxide was added and the mixture was stirred for 2 hr. After filtering, the solvent was evaporated and the residue was sublimed at 60° (0.5 mm); the yield was 170 mg (95%), mp 58°. *Anal.* Calcd for $C_{14}H_{10}$: C, 94.34; H, 5.66; mol wt, 178.22. Found: C, 94.09; H, 5.74; mol wt, 178 (mass spectrum).

Registry No.—**1**, 554-55-2; **3**, 34562-05-5; **4**, 34562-06-6; diphenylacetylene, 501-65-5; AgO, 1301-96-8.

Acknowledgments.—We thank the Consejo Nacional de Ciencia y Tecnología de México for financial help in the publication of this work, and Dr. Harold Kwart for aid in the preparation of the manuscript.

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The Hydrochlorination of Thujopsene

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In recent years much work has been done on the chemistry of the cyclopropylcarbinyl cation system.[1] The naturally occurring sesquiterpene (−)-thujopsene (**1**) contains a conjugated cyclopropyl olefin functionality which is readily protonated to form the rearrangement-prone cyclopropylcarbinyl cation system. Most of the isomerization studies on this interesting molecule have been performed in aqueous media with oxygen-containing acids.[2–8] We recently reported[9] the results of our study on the isomerization products obtained under nonaqueous conditions employing oxygen-containing acids. Friedrich[10] has also shown that the major product obtained upon treatment of (−)-thujopsene in refluxing 12 *M* HCl in dioxane is the bicyclic neopentyl chloride **5**. We have subsequently investigated the action of anhydrous hydrogen chloride on (−)-thujopsene and report our results below.

Treatment of **1** with anhydrous hydrogen chloride at 5° led to a rapid absorption of the gas. The initial crystalline product, although stable for days at −20° either as a solid or in a nonprotic solvent, rearranged upon warming to room temperature to other isomeric products. The formation of these products was easily followed by nmr spectroscopy and the pertinent spectral data are summarized in Table I. From this data the structures of the various intermediates were assigned.

The initial crystalline hydrochlorination product exhibited four methyl singlets and no vinyl hydrogen absorption in the nmr spectrum at −10°, and clearly was expected simple 1,2-addition product, tertiary chloride **2**. The stereochemistry of the chlorine atom is assigned by approach from the less hindered α face, as has been found in the stereochemistry of hydroboration and epoxidation of (−)-thujopsene.[11]

Subsequent warming of the deuteriochloroform solution to 20° showed the gradual disappearance of resonance peaks due to **2** and the concomitant appearance of new peaks, notably the transformation of one of the original methyl singlets into a vinyl methyl and the appearance of a vinyl hydrogen singlet at δ 5.05 and a two-proton singlet at δ 3.59 of an isolated chloromethyl grouping. This data is consistent with structure **3**, the 1,4-addition product of hydrogen chloride to thujopsene.

Further warming or standing at 20° for a longer time afforded a new set of resonance peaks containing a well-

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