preciation to Misses Linda Gump and Linda Loughmiller for experimental assistance during the earlier stages of the work, and to Dr. Kenneth W. Greenlee of the Ohio State University American Petroleum Institute Project No. 45 for sending samples of the olefins used in the thermal stability experiments.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, STANDARD OIL CO. (INDIANA), WHITING, IND.]

# Benzylation of Arenes[1]

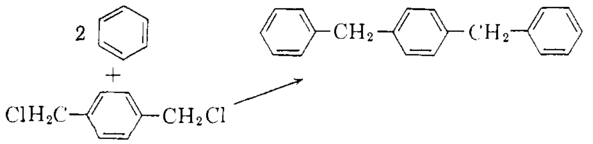
BY CARL SERRES, JR., AND ELLIS K. FIELDS

RECEIVED FEBRUARY 5, 1960

Because diphenylmethanes unexpectedly resulted from reaction of α,α′-dichloro-*p*-xylene with arenes over aluminum amalgam, a study was made of such benzylation reactions with Friedel–Crafts catalysts. Ferric and antimony chlorides gave the expected products, but aluminum chloride—like aluminum amalgam—gave mainly diphenylmethanes. With the two sets of catalysts, benzyl chlorides also gave different products. Aluminum amalgam appears to function by the steady formation of small amounts of aluminum chloride. Benzylation reactions are apparently less unequivocal than heretofore supposed.

## Introduction

A simple synthesis of dibenzylbenzenes would be condensation of arenes with α,α′-dichloro-*p*-xylene in the presence of Friedel–Crafts catalysts



Aluminum amalgam has been used in benzyl chloride condensations, but when we tried it in this reaction we obtained diphenylmethanes rather than the expected dibenzylbenzenes. Aluminum amalgam had been selected because it is reported to cause fewer side reactions than aluminum chloride.[2-8]

We therefore investigated the benzylation reaction with various arenes. Benzene, chlorobenzene, toluene and *p*-xylene were benzylated with six different benzyl chlorides. Aluminum amalgam and chlorides of aluminum, iron and antimony were used as catalysts. To clarify a possible explanation of the observed results, diphenylmethanes were debenzylated over aluminum chloride.

## Discussion

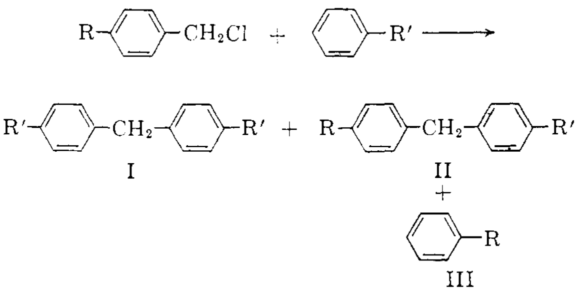


Table I summarizes the results of 13 benzylation experiments with aluminum amalgam and aluminum chloride. With either catalyst, benzyl chlorides in a 10 to 20 mole excess of arenes gave mainly diphenylmethanes of structure I, with only small amounts of the expected products, II. Arenes III, obtained in approximately equimolar amounts with I, formed by loss of the chloromethyl group from the benzyl chloride. Benzylation with α,α′-dichloro-*p*-xylene and aluminum amalgam or aluminum chloride gave mostly diphenylmethanes. Dibenzylbenzenes constituted only one-tenth to one-fourth of the total product.

Our observations during the course of these reactions and the identity of the products from benzylations with either catalyst lead us to believe that aluminum amalgam functions through the formation of aluminum chloride. Aluminum amalgam has been reported to cause fewer side reactions than aluminum chloride. Aluminum amalgam may operate more efficiently because it produces aluminum chloride at a built-in controlled rate. As small amounts of aluminum chloride are dedestroyed by moisture or tied up in inactive complexes, additional fresh aluminum chloride is provided by the amalgam.

Table II lists the results of 9 benzylations catalyzed by ferric chloride and antimony pentachloride. Only the expected products were obtained. α,α′-Dichloro-*p*-xylene gave dibenzylbenzenes in 35 to 47% yields; benzyl chlorides gave the diphenylmethanes (II) in 44 to 85% yields.

We believe that in benzylation reactions catalyzed by aluminum chloride, the expected benzylation product is formed first and then undergoes transaralkylation (debenzylation and rebenzylation) with the arene solvent to yield the observed products. A mixture of benzene, chlorodiphenylmethane and aluminum chloride was treated with hydrogen chloride gas under conditions similar to those employed for the benzylation reactions. The products were chlorobenzene and diphenylmethane. Thus, aluminum chloride can readily debenzylate diphenylmethanes.

Further support for transaralkylation was obtained from the results of runs in which the mole

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(1) Presented at the 136th A.C.S. Meeting, Atlantic City, N. J., 1959.

(2) W. W. Hartman and R. Phillips, "Organic Syntheses," Coll. Vol. II, edited by A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 232.

(3) C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 1.

(4) H. R. Hirst and J. B. Cohen, *J. Chem. Soc.*, **67**, 826 (1895).

(5) R. Adams and K. R. Eilar, THIS JOURNAL, **73**, 1149 (1951).

(6) H. C. Brown and W. Grayson, *ibid.*, **75**, 6285 (1953).

(7) L. I. Diuguid, *ibid.*, **63**, 3527 (1941).

(8) F. Reindel and F. Seigel, *Ber.*, **56**, 1550 (1923).

TABLE I

REACTIONS OF BENZYL HALIDES WITH ARENES

| Arene | Moles | Benzyl halide | Mole | Catalyst, g. | Temp., °C. | Time, hr. | Products | Mole | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
| Aluminum chloride catalyst | | | | | | | | | |
| Benzene | 5.4 | *o*-Chlorobenzyl chloride | 0.25 | 1.0 | 50–60 | 1.4 | Chlorobenzene | 0.20 | 80 |
| | | | | | | | Diphenylmethane | .19 | 76 |
| Benzene | 5.4 | *o*-Chlorobenzyl chloride | .25 | 6.5 | 22–25 | 0.5 | Chlorobenzene | .185 | 74 |
| | | | | | | | Diphenylmethane | .195 | 78 |
| Benzene | 5.4 | *o*-Chlorobenzyl chloride | .25 | 6.5 | 6–9 | 2.0 | Chlorobenzene | .175 | 70 |
| | | | | | | | Diphenylmethane | .18 | 76 |
| Benzene | 5.4 | α,α′-Dichloro-*p*-xylene | .33 | 6.5 | 50–60 | 1.0 | Diphenylmethane | .405 | 61[a] |
| | | | | | | | Dibenzylbenzenes | .08 | 24 |
| Chlorobenzene | 5.0 | α,α′-Dichloro-*p*-xylene | .33 | 2.0 | 50–60 | 3.0 | Monochlorodiphenylmethane | .07 | 21[a] |
| | | | | | | | Dichlorodiphenylmethane | .11 | 17 |
| | | | | | | | Dichlorodibenzylbenzene | .16 | 49 |
| Aluminum amalgam catalyst | | | | | | | | | |
| Benzene | 10.0 | *p*-Chlorobenzyl chloride | 1.0 | 4.0 | 50–60 | 1.5 | Chlorobenzene | 0.67 | 67 |
| | | | | | | | Diphenylmethane | .70 | 70 |
| | | | | | | | Dibenzylbenzenes | .046 | 9 |
| Benzene | 5.4 | *o*-Chlorobenzyl chloride | 0.5 | 2.0 | 50–60 | 1.5 | Chlorobenzene | .30 | 60 |
| | | | | | | | Diphenylmethane | .30 | 60 |
| | | | | | | | Chlorodiphenylmethanes | .06 | 12 |
| | | | | | | | Dibenzylbenzenes | .04 | 16 |
| Benzene | 1.2 | *o*-Chlorobenzyl chloride | .5 | 1.0 | 50–60 | 1.5 | Chlorobenzene | .13 | 26 |
| | | | | | | | Diphenylmethane | .18 | 36 |
| | | | | | | | Chlorodiphenylmethanes | .13 | 26 |
| Benzene | 5.4 | *p*-Methylbenzyl chloride | .33 | 1.0 | 50–60 | 1.5 | Toluene | .25 | 76 |
| | | | | | | | Diphenylmethane | .25 | 76 |
| | | | | | | | Dibenzylbenzenes | .04 | 24 |
| *m*-Xylene | 5.0 | *m*-Methylbenzyl chloride | .33 | 2.0 | 50–60 | 1.5 | Trimethyldiphenylmethanes | .062 | 19 |
| | | | | | | | Tetramethyldiphenylmethanes | .205 | 61 |
| Benzene | 5.4 | α,α′-Dichloro-*p*-xylene | .33 | 2.0 | 50–60 | 3.0 | Diphenylmethane | .43 | 64[a] |
| | | | | | | | Dibenzylbenzenes | .04 | 12 |
| Chlorobenzene | 5.4 | α,α′-Dichloro-*p*-xylene | .33 | 2.0 | 50–60 | 3.0 | Dichlorodiphenylmethanes | .25 | 40[a] |
| | | | | | | | Chlorodibenzylbenzenes | .06 | 18 |
| *p*-Xylene | 2.7 | α,α′-Dichloro-*p*-xylene | .16 | 2.0 | 50–60 | 3.0 | Di-*p*-xylylmethane[b] | .20 | 63[a] |

[a] Based on utilization of both chloromethyl groups. [b] B.p. 107–109° (0.25 mm.), m.p. 61–62°. R. C. Huston and D. T. Ewing, THIS JOURNAL, **37**, 2394 (1915), report m.p. as 60° (see also ref. 11).

TABLE II

REACTIONS OF BENZYL HALIDES WITH ARENES

| Arene | Moles | Benzyl halide | Mole | Catalyst, mole | Temp., °C. | Time, hr. | Products | Mole | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
| Ferric chloride catalyst | | | | | | | | | |
| Benzene | 5.4 | *o*-Chlorobenzyl chloride | 0.25 | 0.05 | 60–80 | 1.0 | *o*-Chlorodiphenylmethane[a] | 0.20 | 80 |
| Toluene | 5.0 | Benzyl chloride | .5 | .05 | 60–80 | 1.5 | Methyldiphenylmethanes | .25 | 50 |
| Chlorobenzene | 5.0 | Benzyl chloride | .5 | .05 | 80–110 | 1.5 | Chlorodiphenylmethanes | .22 | 44 |
| Benzene | 5.4 | α,α′-Dichloro-*p*-xylene | .33 | .003 | 50 | 1.0 | *p*-Dibenzylbenzene[b] | .12 | 35 |
| Benzene | 15.0 | α,α′-Dichloro-*p*-xylene | .33 | .10 | 80 | 1.5 | *p*-Dibenzylbenzene | .15 | 45 |
| Toluene | 10.0 | α,α′-Dichloro-*p*-xylene | .33 | [c] | 110 | 2.0 | α,α′-Ditolyl-*p*-xylene | .143 | 43 |
| Antimony pentachloride catalyst | | | | | | | | | |
| Benzene | 5.4 | *p*-Chlorobenzyl chloride | 0.25 | 0.05 | 60 | 1.0 | *p*-Chlorodiphenylmethane[d] | 0.12 | 48 |
| Toluene | 5.0 | Benzyl chloride | .5 | .05 | 110 | 1.0 | Methyldiphenylmethanes | .385 | 77 |
| Benzene | 15.0 | α,α′-Dichloro-*p*-xylene | .33 | .10 | 80 | 1.0 | *p*-Dibenzylbenzene | .155 | 47 |

[a] B.p. 87–89° (0.1 mm.), $n^{20}$D 1.5895. Authentic material having b.p. 95–96° (0.5 mm.) and $n^{20}$D 1.5892 was prepared by the method of Tschitschibabin and Schesler, *J. Russ. Phys.-Chem. Soc.*, **56**, 149 (1925), who report b.p. 164.5° (19 mm.). Pure and mixed chlorodiphenylmethanes were also analyzed by gas chromatography. [b] B.p. 158–161° (0.15 mm.), m.p. 86–88°. G. Stadnikov and L. Kashtanov, *Ber.*, **61**, 1389 (1928), report m.p. as 85–86°. [c] A mixture of 0.05 *M* $FeCl_3$ and 0.05 *M* $SbCl_5$ was used. [d] B.p. 96–98° (0.3 mm.), $n^{20}$D 1.5858. Tschitschibabin and Schesler (footnote *a*) report b.p. 160° (11 mm.).

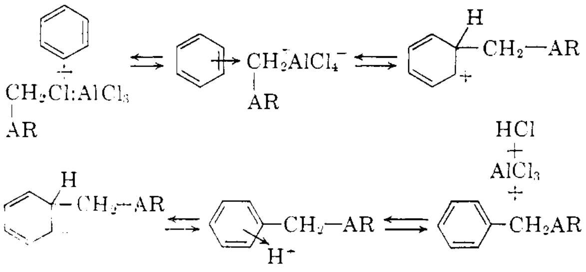
ratio of arene to benzyl chloride was varied. The ratio of arene to benzyl chloride was changed from 11:1 to 2.4:1 in the reaction of benzene with *o*-chlorobenzyl chloride and aluminum amalgam. The products, diphenylmethane and chlorodiphenylmethane, changed in ratio from 5:1 to 1.4:1. Thus, the products of benzylations catalyzed by aluminum chloride depend on the relative amounts of arene and benzyl chloride.

The combination of benzylation and debenzylation also explains the formation of diphenylmethanes from the reaction of α,α′-dichloro-*p*-xylene with arenes catalyzed by aluminum chloride. The dibenzylbenzenes initially formed undergo transaralkylation with excess arene to yield diphenylmethanes. For example, treatment of *p*-dibenzylbenzene with aluminum chloride in a 20-mole excess of benzene under benzylation reaction conditions gave a 76% conversion to diphenylmethane.

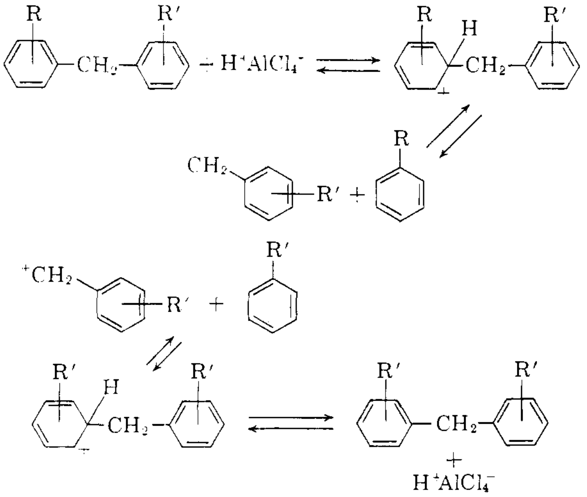
Of the catalysts used in this study, only aluminum chloride, or its precursor aluminum amalgam, is a sufficiently strong Lewis acid to debenzylate diphenylmethanes and dibenzylbenzenes. Ferric chloride and antimony pentachloride are strong enough to bring about benzylation but not debenzylation. The difference in strengths of catalysts at the high ratios of arene to benzyl chlorides used accounts for the different products shown in Tables I and II.

Benzylations catalyzed by aluminum chloride occur by nucleophilic attack of the arene on a polarized complex of benzyl chloride and aluminum chloride[6]

$$\mathrm{Ar{-}CH_2Cl} + \mathrm{AlCl_3} \rightleftarrows \mathrm{Ar{-}CH_2Cl{:}AlCl_3}$$



Transaralkylation with arenes may then proceed



The R-substituted aromatic ring is the ring of the benzyl halide and the R′-substituted ring is that of the arene benzylated. Attack by the proton on the ring from the benzyl halide is diagrammed to show how the final observed products arise with a large excess of arene.[9] Attack of the R′ ring by the proton does not cause any change in the product.

## Conclusion

These results of the reactions of benzyl chlorides and arenes catalyzed by aluminum chloride or its precursor, aluminum amalgam, differ from most reported in the literature. Debenzylation was recognized as a minor side reaction in work with 3,4-dichlorobenzyl chloride, benzene and aluminum amalgam.[6] In addition, debenzylation of diarylmethanes has been reported as a minor reaction in certain alkylations.[10,11] Aside from these reports, the validity of normal benzylation has not been questioned.

The product from reaction of toluene and benzyl chloride was reported to be methyldiphenylmethane.[4] In the light of the present study, the product may have contained dimethyldiphenylmethane in amounts depending on the mole ratio of toluene to benzyl chloride.

Preparation of 2,3′,4-trimethyldiphenylmethane by reaction of *m*-xylene and *m*-methylbenzyl chloride with aluminum amalgam is reported as an "unequivocal" synthesis.[5] We have repeated this reaction and found the products to be a mixture of trimethyldiphenylmethane and tetramethyldiphenylmethane isomers in a 1:3 ratio.

Benzylation reactions are more complex than previously supposed; the products vary with the acidity of the catalysts and the ratio of arene to benzyl chloride. The electronic effects of substituents on the arene and benzyl halide may also be important and warrant study. Benzyl halides with substituents that render the ring resistant to electrophilic attack should give only the expected benzylation products with aluminum chloride.

## Experimental

J. T. Baker benzyl chloride and Eastman Kodak Co. white label *o*-chlorobenzyl chloride, *p*-chlorobenzyl chloride, *p*-methylbenzyl chloride and α,α′-dichloro-*p*-xylene were used without further purification.

In a typical benzylation with aluminum amalgam, 80 g. (0.5 mole) of *o*-chlorobenzyl chloride was added to a mixture of 420 g. (5.4 moles) of dry benzene and 2.0 g. of aluminum amalgam[2,7] at 50° over a period of 1.5 hours. An induction period is observed at the start of such reactions, and the reaction becomes more and more vigorous as the benzyl halide addition proceeds. The induction period of 10 to 20 minutes was eliminated in some runs by using catalyst activated by pretreatment with 2 to 3 ml. of benzyl halide. When benzyl halide addition was complete, the mixture was refluxed for 30 minutes; at this point, hydrogen chloride no longer was evolved. A black sirup of catalyst–complex oil forms with the aluminum amalgam much as with aluminum chloride. Visual inspection at the end of the reactions showed most of the amalgam unreacted; however, attempts to determine quantitatively loss of aluminum amalgam were unsuccessful. The hydrocarbon solution was cooled and decanted from the catalyst and any tars or other insoluble material. It was washed with dilute sodium hydroxide solution, then with water, dried over sodium sulfate, filtered, and fractionated through a 10-plate Oldershaw column to give four fractions.

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[9] The referee has pointed out that transaralkylation could also proceed *via* a bimolecular displacement with the arene (ArR′) functioning as the nucleophilic displacing agent.

[10] B. S. Friedman, F. L. Morritz, C. J. Morrissey and R. Konos, THIS JOURNAL, **80**, 5867 (1958).

[11] L. Schmerling, J. P. Luvisi and R. W. Welch, *ibid.*, **81**, 2718 (1959).

| | Wt., g. | Mole | Yield, % | B.p., °C. (mm.) | $n^{20}D$ |
|---|---|---|---|---|---|
| Chlorobenzene | 34.0 | 0.30 | 60 | 130–131 | 1.5237 |
| Diphenylmethane | 50.5 | .30 | 60 | 73–75 (0.2) | 1.5770 |
| Chlorodiphenylmethanes | 12.0 | .06 | 12 | 80–90 (0.2) | 1.5875 |
| Dibenzylbenzenes | 10.0 | .. | .. | Residue | Solid |

These products were identified by infrared absorption, gas chromatography, and physical constants. The substituted diarylmethanes and dibenzylbenzenes obtained from reactions catalyzed by aluminum amalgam (and aluminum chloride) are mixtures of isomers.

Runs with aluminum chloride were similar to those with aluminum amalgam. Reaction of 0.25 mole of *o*-chlorobenzyl chloride, 5.4 moles of benzene and 0.05 mole of anhydrous aluminum chloride gave 75% diphenylmethane. The reaction was run at 50 to 60° for 1.5 hours. Other runs at 6 to 9° for 2 hours and 22 to 25° for 0.5 hour gave 76 and 78% yields of diphenylmethane, respectively. The reaction is thus very rapid, even at low temperatures.

In a typical run with ferric chloride as catalyst, 420 g. (5.4 moles) of dry benzene and 40 g. (0.25 mole) of *o*-chlorobenzyl chloride were allowed to react in the presence of 8.0 g. (0.05 mole) of ferric chloride. Reaction started at once but was not vigorous and was best carried out near reflux. Total reaction time was one hour. Chlorodiphenylmethane (41 g., 0.20 mole, 80%) was obtained, b.p. 87–89° (0.1 mm.), $n^{20}D$ 1.5895. The 5.0 g. of high-boiling residue had $n^{20}D$ 1.6015. Reactions with antimony pentachloride proceeded similarly and gave the same products as ferric chloride.

In a typical debenzylation reaction, chlorodiphenylmethane was debenzylated in benzene. A slow stream of hydrogen chloride gas was passed for 2 hours through a mixture of 50 g. (0.25 mole) of mixed isomers of chlorodiphenylmethane, 420 g. (5.4 moles) of benzene and 1.0 g. of aluminum chloride at 60–80°. The reaction mixture, which had turned dark orange at the end of the 2 hours, was washed with water, dried over sodium sulfate, and fractionated. The products were 22 g. (0.20 mole) of chlorobenzene, 32 g. (0.19 mole, 76%) of diphenylmethane and 8.0 g. of residue.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRANDEIS UNIVERSITY, WALTHAM 54, MASS.]

# Reaction of Diphenylmethyl Radical with >C=N— Derivatives of Benzophenones

BY CHI-HUA WANG AND SAUL G. COHEN

RECEIVED FEBRUARY 17, 1960

The azo compound $(C_6H_5)_2CHN{=}NCH(C_6H_5)_2$ has been decomposed in the presence of low concentrations of: (a) azines derived from acetophenone, *p,p*-dimethyl-, *p,p*-dimethoxy-, *p,p*-dichlorobenzophenones; (b) hydrazones of benzophenone, fluorenone and *p,p*-dichlorobenzophenone; and the phenylhydrazone, semicarbazone and oxime of benzophenone. 2,2,3,3-Tetraphenylethylenimine is formed in the presence of the azine and hydrazone of benzophenone; 2,2-diphenyl-3,3-di-*p*-tolylethylenimine is formed in the presence of the azine from *p,p*-dimethylbenzophenone. The course of the reactions and the factors affecting selectivity in addition of radicals to the >C=N— system are discussed.

**Introduction.**—In the decomposition of azo-bis-diphenylmethane (I) in diphenylmethane, a study of the exchange of identity of diphenylmethyl radical by abstraction of hydrogen from $C^{14}$-labeled diphenylmethane indicated that this was, under the conditions in effect, considerably slower than the dimerization to tetraphenylethane.[1]

$$(C_6H_5)_2CH\cdot + (C_6H_5)_2C^{14}H_2 \rightleftharpoons (C_6H_5)_2CH_2 + (C_6H_5)_2C^{14}H\cdot$$

$$2(C_6H_5)_2CH\cdot \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2$$

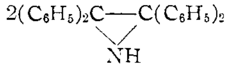
However catalysis of the exchange was effected by thiophenol, presumably through the sequence or equilibrium

$$(C_6H_5)_2CH\cdot + C_6H_5SH \longrightarrow (C_6H_5)_2CH_2 + C_6H_5S\cdot$$

$$C_6H_5S\cdot + (C_6H_5)_2C^*H_2 \longrightarrow C_6H_5SH + (C_6H_5)_2C^*H\cdot$$

Also, the thiyl radical appears to be remarkably effective in abstracting hydrogen from some of the azo compound, although the latter was present in low (0.02 *M*) concentration, forming benzophenone azine. We come to this conclusion since in the presence of the mercaptan a by-product was formed which could be obtained as the major product (51% yield) when the decomposition of the azo compound was carried out in the absence of the mercaptan but in the presence of a low concentration (*ca.* 0.02 *M*) of added benzophenone azine. This product appears[1] to be 2,2,3,3-tetraphenylethylenimine, the azo compound and the azine each contributing one diphenylmethyl group to this compound. The diphenylmethyl radical appeared to react quite rapidly with the azine, since the latter

$$2(C_6H_5)_2CH\cdot + (C_6H_5)_2C{=}NN{=}C(C_6H_5)_2 \longrightarrow$$



$$2(C_6H_5)_2C{-}C(C_6H_5)_2 \text{ (NH)}$$

was more effective in interfering with the dimerization than the mercaptan at the same concentration. Little is known about the reactions of radicals with such >C=N— systems and it seemed of interest to examine this further. It may be noted that methyl radical is reported[2] not to add to the nitrogen of the >C=N— of acridine.

**Results.**—Azines of acetophenone, *p,p*-dimethylacetophenone, *p,p*-dimethoxybenzophenone and *p,p*-dichlorobenzophenone; the hydrazones of *p,p*-dichlorobenzophenone, benzophenone and fluorenone; and the oxime, phenylhydrazone and semicarbazone of benzophenone; and benzophenone itself and *p,p*-dihydroxybenzophenone were examined for their possible reactions with diphenylmethyl radical. Dilute solutions, *ca.* 0.01 *M*, of the azo compound I were decomposed at 70–75° in benzene in the presence of approximately equal concentrations of the azines and of double the concentrations of the compounds containing only one >C=N— group per molecule. The solutions were worked up for the normal product of decomposition, 1,1,2,2-tetraphenylethane, for recovered additive, and for possible products of reaction of the diphenylmethyl radical with the additive. The results are summarized in Table I.

Of the azines, that from *p,p*-dimethylbenzophenone was more reactive than that from benzophenone toward diphenylmethyl radical. Present ini-

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[1] C. H. Wang and S. G. Cohen, THIS JOURNAL, **79**, 1924 (1957).

[2] M. Levy and M. Szwarc, *ibid.*, **77**, 1949 (1955).