	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.

[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]

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

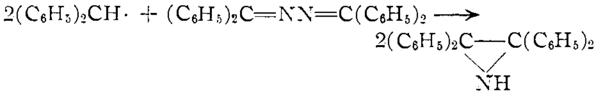
$$2(C_6H_5)_2CH\cdot \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2$$

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



$$2(C_6H_5)_2CH\cdot + (C_6H_5)_2C{=}NN{=}C(C_6H_5)_2 \longrightarrow 2(C_6H_5)_2C\underset{NH}{\diagdown\!\!\diagup}C(C_6H_5)_2$$

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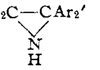
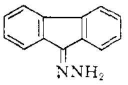
[1] C. H. Wang and S. G. Cohen, THIS JOURNAL, **79**, 1924 (1957).

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

TABLE I

DECOMPOSITION OF $(C_6H_5)_2CHN{=}NCH(C_6H_5)_2$ IN PRESENCE OF >C=N— COMPOUNDS

	Additive		$(C_6H_5)_2$-CHCH-$(C_6H_5)_2$	
	Compound	Recovd., %	Yield, %	Yield, %
1		..	82	..[1]
2	$[(C_6H_5)_2C{=}N{-}]_2$	28	28	51[1]
3	$[C_6H_5C(CH_3){=}N{-}]_2$	93	77	..
4	$[(p\text{-}CH_3C_6H_4)_2C{=}N{-}]_2$	..	Trace	80
5	$[(p\text{-}CH_3OC_6H_4)_2C{=}N{-}]_2$	51	41	..
6	$[(p\text{-}ClC_6H_4)_2C{=}N{-}]_2$	95	61	..
7	$(p\text{-}ClC_6H_4)_2C{=}NNH_2$	90	69	..
8	$(C_6H_5)_2C{=}NNH_2$[a]	35	43	31
9	$(C_6H_5)_2C{=}NOH$	96	78	..
10	$(C_6H_5)_2C{=}NNHC_6H_5$	83	52	..
11	$(C_6H_5)_2C{=}NNHCONH_2$	85	59	..
12		84	75	..
13	$(C_6H_5)_2C{=}O$	97	84	..
14	$(HOC_6H_4)_2C{=}O$	96	78	..

[a] Ammonia was also found, 48% yield, and biphenyl was detected.

tially in slightly lower concentration than the azo compound, none of it was recovered; and the corresponding tetraarylethylenimine, 2,2-diphenyl-3,3-di-*p*-tolylethylenimine, m.p. 180°, was obtained in 80% yield based on the azo compound, 90% based on the azine, and only a trace of tetraphenylethane was isolated. On the other hand, the azines from acetophenone and *p,p*-dimethoxy- and *p,p*-dichlorobenzophenones did not react appreciably with diphenylmethyl radical, none of the corresponding ethylenimines being isolated. Acetophenone azine was recovered essentially quantitatively and tetraphenylethane was found (77%) in almost as high a yield as when the decomposition of the azo compound was carried out in the absence of additive (expt. 1, 82%). *p,p*-Dimethoxybenzophenone azine was only partly recovered (51%) and the tetraphenylethane also was found in diminished yield (41%), but the remainder appeared to be a mixture of these two materials and some tar. *p,p*-Dichlorobenzophenone azine was recovered essentially quantitatively and the tetraphenylethane was obtained in fair yield (61%).

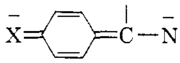
It then seemed desirable to ascertain whether two >C=N— groups per molecule were needed for this reaction; three hydrazones were examined. Benzophenone hydrazone was reactive, leading to the same ethylenimine in 31% yield as that formed from benzophenone azine (expt. 2), to tetraphenylethane (43%), to recovered hydrazone (35%) to ammonia (44%) and to some biphenyl. *p,p*-Dichlorobenzophenone hydrazone and fluorenone hydrazone were unreactive, being recovered in high yields, and leading to high yields of tetraphenylethane. Other derivatives of benzophenone were then examined and did not lead to isolation of possible products of their reactions with diphenylmethyl radical. The oxime was recovered essentially quantitatively, while the phenylhydrazone and semicarbazone were recovered in slightly diminished yields and the yields of tetraphenylethane were also diminished somewhat and some tar was formed in the presence of the phenylhydrazone.

Discussion.—The rate of decomposition of I in the presence of benzophenone azine remained unimolecular[3] and unchanged, indicating that the new product did not result from bimolecular reaction of the two components but from reaction of the radicals with the additive. Also, the ultraviolet absorption spectra of the additives were unchanged by the azo compound indicating that there was no prior association of the two components to favor their subsequent reaction with each other.

With respect to the specificity or selectivity of the reactions, it may be noted that in radical processes, unlike ionic reactions, one is always dealing with competitive reactions, and if a structural change diminishes the rate of a particular reaction by a factor of ten or more (as by an increase in activation energy of 2 kcal.), the reaction may not be detected at all by conventional product isolation, destruction of the radicals by dimerization or disproportionation becoming dominant. This would be particularly true of the stabilized diphenylmethyl radical, reactions of which with the azine and hydrazone of benzophenone seem to have rates only slightly greater than that of the dimerization under the conditions of our experiments. Just as bond energies may affect the activation energies and rates of radical displacement processes,[4] so the transition states and rates of addition of radicals to double bonds may be affected by the triplet state energies,[5] the energies required to dissociate the π-bond, although the triplet states as such are not directly involved in the reactions. Structural features which stabilize the π-bond of the >C=N— system with respect to the triplet state will diminish the rates of reaction with radicals, while features which stabilize the triplet state, such as resonance stabilization of one or both unpaired electrons, may favor reactions with radicals.

Replacement of phenyl by methyl in comparison of benzophenone azine with acetophenone azine probably increases the triplet state energy more than it destabilizes the double bond and reaction with diphenylmethyl is not observed. As with alkyl radicals,[6] the *p*-methyl groups in *p,p*-dimethylbenzophenone azine would lower the localization energy at carbon[7] more than hyperconjugation stabilizes the unsaturated system and increased reactivity[8] is observed.

An important contribution to the bonding energy of the >C=N— group probably arises from the polar form $>\overset{+}{C}{-}\overset{-}{N}{-}$. This may contribute more when conjugated with *p*-chloro and *p*-methoxy substituents through forms of type



Such stabilization of the ground state may lead to the observed lower reactivity of the hydrazone and

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[3] S. G. Cohen and C. H. Wang, THIS JOURNAL, **77**, 2457 (1955).

[4] E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943).

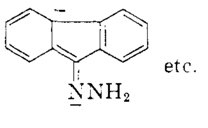
[5] G. Porter, *Proc. Chem. Soc.*, 291 (1959).

[6] H. Eyring, THIS JOURNAL, **75**, 5183 (1953).

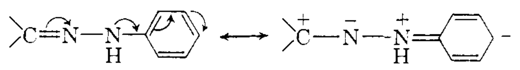
[7] R. P. Buckley and M. Szwarc, *Proc. Roy. Soc. (London)*, **A240**, 396 (1957).

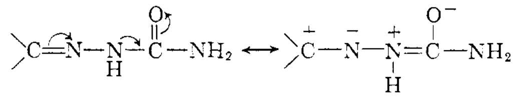
[8] C. A. Coulson, *J. Chem. Soc.*, 1435 (1955).

azine from p,p-dichlorobenzophenone and the azine from p,p-dimethoxybenzophenone as compared with the unsubstituted hydrazone and azine. Consistent with this, the less reactive molecules generally showed absorption maxima in the ultraviolet at longer wave lengths than those of the reactive molecules. Similarly, the planar fused system in fluorenone hydrazone may allow more conjugation between the nucleus and the exocyclic double bond than in benzophenone hydrazone, more stabilization from the polar contributors and the observed lower reactivity

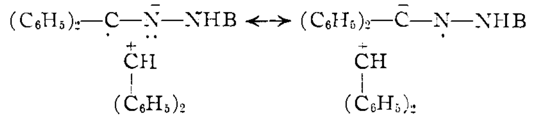


The phenylhydrazone, semicarbazone and oxime of benzophenone may be considered somewhat similarly. In the phenylhydrazone and semicarbazone the amino nitrogen bears a partial positive charge as compared with the amino nitrogen of the hydrazone, stabilizing the negative charge in the polarized form of the >C=N— system, stabilizing the double bond and rendering less favorable, relatively, the transition state for the radical addition



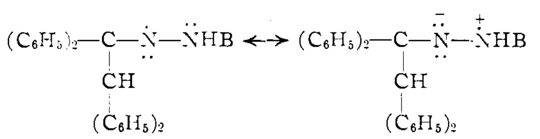


Similarly, in the oxime the hydroxyl, more electronegative than amino, may increase the contribution of the polar form to the bonding. The addition may begin by association of the radical with the >C=N— grouping, polar contributions involving transfer of an electron from the radical favoring this association.



$$(C_6H_5)_2\text{—}\underset{\underset{(C_6H_5)_2}{|}}{\overset{}{C}}\text{—}\bar{\ddot{N}}\text{—}NHB \longleftrightarrow (C_6H_5)_2\text{—}\bar{C}\text{—}\dot{N}\text{—}NHB \quad \overset{+}{C}H(C_6H_5)_2$$

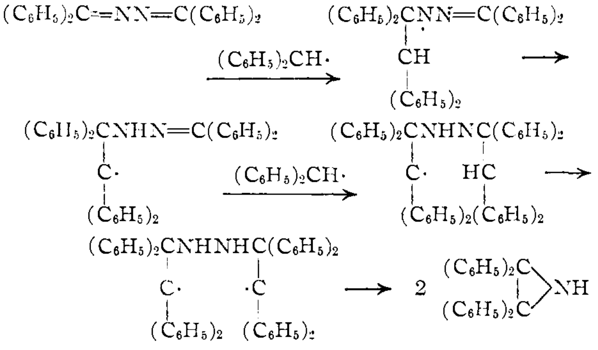
As the reaction proceeds, probably by attack of the radical on the carbon, stabilization of the unpaired electron on nitrogen by the electron pair on the adjacent nitrogen becomes important[9] and such sta-



$$(C_6H_5)_2\text{—}\underset{\underset{\underset{(C_6H_5)_2}{|}}{CH}}{\overset{}{C}}\text{—}\dot{\ddot{N}}\text{—}\ddot{N}HB \longleftrightarrow (C_6H_5)_2\text{—}\underset{\underset{\underset{(C_6H_5)_2}{|}}{CH}}{C}\text{—}\bar{\ddot{N}}\text{—}\overset{+}{\dot{N}}HB$$

bilization is less available in the semicarbazone and phenylhydrazone than the hydrazone because of the conjugation with the phenyl and carboxamide groups; and it is also less available from the hydroxyl of the oxime than from the amino of the hydrazone.

The yields of the imines from the azines require that both diarylmethyl groups of the azine be available for incorporation into the product. Beyond this, it is not clear whether one or two radicals react with the azine before the needed decomposition occurs. Addition, rearrangement with hydrogen migrating from carbon to nitrogen, and decomposition of radicals appear to occur, and some of these may be concerted. The formula scheme indicates the kinds of processes that may be occurring.



The reaction with benzophenone hydrazone may follow a similar course, although in this case addition to nitrogen may seem attractive. The reaction appears to lead to ejection of the amino radical which appears as ammonia—abstracting hydrogen either from some of the hydrazone itself or possibly by reaction with the solvent benzene, a considerable amount of biphenyl also being found. Little if any aniline was detected. These products are consistent with those found on reduction of hydroxylamine in aqueous acid in the presence of benzene and attributed to the amino radical.[10]

Experimental[11]

Azo-bis-diphenylmethane,[1] m.p. 114° dec., and **acetophenone azine**,[12] m.p. 124°, were prepared as described previously.

p,p,p',p'-Tetramethylbenzophenone azine was prepared by treatment of 10 g. (0.048 mole) of p,p'-dimethylbenzophenone (Eastman Kodak Co., m.p. 95°) with 3 g. of hydrazine hydrate in 180 ml. of 95% ethanol and 2 ml. of acetic acid under reflux for 5 hours. The solution was concentrated in vacuum and the residue was crystallized from 5:1 ethanol–benzene; yellow crystals, 8.0 g. (80% yield), m.p. 192–194°.

Anal. Calcd. for $C_{30}H_{28}N_2$: C, 86.50; H, 6.77; N, 6.73. Found: C, 86.95; H, 6.72; N, 6.71.

p,p,p',p'-Tetramethoxybenzophenone azine was prepared similarly from p,p-dimethoxybenzophenone (Eastman Kodak Co., m.p. 144°) in 37% yield, m.p. 178–180° from alcohol, reported[13] 179–180°.

p,p-Dichlorobenzophenone hydrazone was prepared by treatment of 25 g. (0.10 mole) of p,p-dichlorobenzophenone with 6.5 g. of hydrazine hydrate in 300 ml. of ethanol and 4 ml. of acetic acid under reflux for 5 hours; 18 g., 68% yield, m.p. 91–93° from ethanol, reported[14] 93°.

p,p,p',p'-Tetrachlorobenzophenone azine was prepared by treatment of 8.2 g. (0.031 mole) of the hydrazone with 6 ml. of concentrated sulfuric acid in 170 ml. of ethanol under reflux for 1 hour; 7 g. (0.014 mole), 90% yield, m.p. 224–226° from ethanol, reported[13] 224.5–225.6° (33%).

The following compounds were prepared by standard procedures: **benzophenone hydrazone**, m.p. 97–98°, re-

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(9) W. K. Wilmarth and N. Schwartz, THIS JOURNAL, **77**, 4543 (1955).

(10) P. Davis, M. G. Evans and W. C. E. Higginson, *J. Chem. Soc.*, 2653 (1951).

(11) Elementary analyses were performed by Dr. S. M. Nagy, Massachusetts Institute of Technology. Melting points are uncorrected.

(12) S. G. Cohen, S. J. Groszos and D. P. Sparrow, THIS JOURNAL, **72**, 3951 (1950).

(13) H. H. Szmant and C. McGinnis, *ibid.*, **72**, 2890 (1950).

(14) O. Grummitt and A. Jenkins, *ibid.*, **68**, 914 (1946).

ported[15] 97–98°; **benzophenone oxime**, m.p. 143-144°, reported[16] 144°; **benzophenone phenylhydrazone**, m.p. 137–138°, reported[17] 137–138°; **benzophenone semicarbazone**, m.p. 166–167°, reported[18] 167°.

Fluorenone hydrazone was prepared by treatment of 12 g. (0.067 mole) of fluorenone (Eastman Kodak Co., m.p. 83–84°) with 3.5 g. of hydrazine hydrate in 100 ml. of ethanol under reflux for 5 hours; m.p. 145–148°, reported[19] 150°.

Decomposition of the azo compound I, *ca.* 0.3 g., was carried out in the presence of the added carbonyl compound derivative in 70–75 ml. of benzene under nitrogen for 4 hours at 65–70°, 95–100% of the theoretical nitrogen being evolved. The solvent was removed in vacuum and the residue was in each case worked up, as described:

3. The residue from 0.325 g. (0.90 mmole) of I and 0.236 g. (1.0 mmole) of **acetophenone azine**, 0.56 g., was triturated several times with 25 ml. of 4:1 ethanol–acetone, and fractions dissolved were isolated and treated similarly, leading to tetraphenylethane II, 0.233 g. (0.70 mmole), 77% yield, m.p. and mixed m.p. 210–212°; and to acetophenone azine, 0.220 g., 93% yield, m.p. and mixed m.p. 120–121°. When compound I was decomposed similarly in the absence of additive, II was isolated in 82% yield.

4. The residue from 0.296 g. (0.82 mmole) of I and 0.300 g. (0.72 mmole) of ***p,p,p',p'*-tetramethylbenzophenone azine** was digested with a mixture of 50 ml. of ethanol and 20 ml. of benzene, leaving a yellow residue, m.p. 180°; 2,2-di-*p*-tolyl-3,3-diphenylethylenimine, 0.490 g. (1.31 mmole), 91% based on the azine, 80% based on the azo compound. This was chromatographed repeatedly over alumina, with petroleum ether–benzene, ethanol–benzene, benzene–cyclohexane, and ethanol leading to a trace of tetraphenylethane. These procedures readily separated a mixture of tetraphenylethane and the azine. The imine was analyzed. *Anal.* Calcd. for $C_{28}H_{25}N$: C, 89.56; H, 6.71; N, 3.73. Found: C, 89.66; H, 6.88; N, 3.53.

5. The residue from 0.214 g. (0.59 mmole) of I and 0.277 g. (0.58 mmole) of ***p,p,p',p'*-tetramethoxybenzophenone azine**, melted over a range above 160°. Crystallization from ethanol did not lead to purification. The material, 0.43 g., was chromatographed 6 times over alumina with benzene, leading from the first fractions to tetraphenylethane, 0.082 g. (0.25 mmole), 41% yield, and from the latter fractions to recovered azine, recrystallized from 2:1 ethanol–acetone, 0.140 g., 51% yield, m.p. and mixed m.p. 180–182°, and having the correct elementary analysis. The middle fractions led to a mixture, 0.140 g., melting 150–190°, and to a tar, 0.050 g., these corresponding to 39% of the original materials.

6. The residue from 0.142 g. (0.39 mmole) of I and 0.195 g. (0.39 mmole) of ***p,p,p',p'*-tetrachlorobenzophenone azine** was treated with 10 ml. of ethanol leading to recovered azine, 0.185 g., 95% yield, m.p. 223–226°, from benzene; and, from the alcohol solution and benzene filtrates, to tetraphenylethane, 0.080 g. (0.024 mmole), 61% yield, m.p. and mixed m.p. 206–208°; and to a tar, 0.060 g.

7. The residue from 0.300 g. (0.83 mmole) of I and 0.440 g. (1.65 mmoles) of ***p,p*-dichlorobenzophenone hydrazone** was digested, with 20 ml. of ethanol, leading to tetraphenylethane, 0.145 g., m.p. and mixed m.p. 210–212°; and, from the solution, to recovered hydrazone 0.155 g., m.p. and mixed m.p. 90–92°. Fractionation of the remainder resulted in a total of 0.192 g. (0.57 mmole), 69% yield, of tetraphenylethane and 0.395 g., 90% recovery, of the hydrazone.

8. A solution of 1.00 g. (2.76 mmoles) of I and 1.10 g. (5.10 mmoles) of **benzophenone hydrazone** in 100 ml. of benzene was heated at 65° under nitrogen for 6 hours. (a) An aliquot, 0.02 ml., was treated with 1 ml. of ethanol and 1 ml. of saturated potassium carbonate and distilled into 1 ml. of 2% boric acid. This was treated with Nessler solution and compared on a Klett photometer with a standard; 0.49 μ/mole in the aliquot, 2.45 mmoles, 48%, total. An aliquot, 0.5 ml., was distributed between 1 ml. of dilute hydrochloric acid and ether, and the aqueous layer was assayed for aniline by treatment[20] with chloramine-T and phenol and photometric comparison with a standard, 16 γ in the aliquot, 3.2 mg. total, 0.7%. (c) The remainder was concentrated under nitrogen and the residue was chromatographed twice over alumina with benzene, leading to tetraphenylethylenimine, m.p. and mixed m.p. 176–177°, 0.550 g. (1.58 mmoles), 31% based on the hydrazone, 29% based on I. The filtrates were combined and concentrated and the residue was washed with methanol, chromatographed on alumina, eluted with carbon tetrachloride, leading to tetraphenylethane, m.p. and mixed m.p. 205–208°, 0.400 g. (1.20 mmoles), 43%. The filtrates were again combined and concentrated, leading to benzophenone hydrazone, 0.115 g., m.p. and mixed m.p. 90–95°. The infrared spectrum was identical with that of an authentic sample. The filtrates were again concentrated, and steam distilled. The residue was taken up in ethanol leading to more benzophenone hydrazone, m.p. and mixed m.p. 95–96°, 0.265 g., total recovery 0.380 g., 35%. On the walls of the residue flask traces of biphenyl were found, m.p. and mixed m.p. 67–70°. The steam distillate was extracted with ether, dried and concentrated, leading to an oil which failed to crystallize but had the odor of biphenyl.

9. The residue from 0.362 g. (1.00 mmole) of I and 0.394 g. (2.00 mmoles) of **benzophenone oxime** was extracted with 35 ml. of ethanol, leaving a residue of tetraphenylethane, 0.227 g. (0.68 mmole), 68%, m.p. and mixed m.p. 204–206°. The filtrate led to an additional 0.035 g. of tetraphenylethane, total 0.78 mmole, 78% yield; and to benzophenone oxime, 0.180 g., m.p. and mixed m.p. 140–144°; and to 0.200 g. of less pure material; total recovery, *ca.* 96%.

10. The colored residue from 0.287 g. (0.79 mmole) of I and 0.453 g. (1.66 mmoles) of **benzophenone phenylhydrazone** was washed with 25 ml. of 4:1 ethanol–acetone. The solid was crystallized from 4:1 ethanol–acetone leading to tetraphenylethane, 0.138 g. (0.41 mmole), 52%, m.p. and mixed m.p. 209–211°; and, from the filtrate, to recovered benzophenone phenylhydrazone, 0.112 g., 25%, m.p. from ethanol, and mixed m.p. 135–136°. The original washings were concentrated leading to additional phenylhydrazone, 0.263 g., m.p. and mixed m.p. 134–136°, total recovery 83%, and to a tar, 0.135 g.

11. The reaction mixture from 0.267 g. (0.74 mmole) of I and 0.410 g. (1.72 mmoles) of **benzophenone semicarbazone** was concentrated, leading to tetraphenylethane, 0.145 g. (0.43 mmole), 59%, m.p. and mixed m.p. 207–210°; and from the mother liquor, in several fractions, to the semicarbazone, 0.350 g., 85% recovery, m.p. 162–164°, mixed m.p. 162–165°.

12. The residue from 0.299 g. (0.83 mmole) of I and 0.313 g. (1.61 mmoles) of **fluorenone hydrazone** was treated with 30 ml. of 2:1 ethanol–benzene, leaving undissolved tetraphenylethane, 0.208 g. (0.62 mmole), 75%. The filtrate led to fluorenone hydrazone, 0.263 g., 84% recovery, m.p. and mixed m.p. 145–148°.

13. The reaction mixture from 0.362 g. (1.00 mmole) of I and 0.360 g. (2.00 mmoles) of **benzophenone** was concentrated leading to tetraphenylethane, 0.280 g. (0.84 mmole), 84%, m.p. and mixed m.p. 211–212°. The residue from the mother liquor was heated under reflux for 1 hour with 0.3 g. of hydrazine hydrate and 1 drop of acetic acid in 5 ml. of ethanol leading to benzophenone hydrazone, 0.38 g. (1.94 mmoles), 97% yield, m.p. and mixed m.p. 96–98°.

14. The reaction mixture from 0.292 g. (0.81 mmole) of I and 0.38 g. (1.77 mmoles) of ***p,p*-dihydroxybenzophenone** (m.p. 210°) was concentrated, leading first to recovered ketone, 0.345 g., m.p. and mixed m.p. 208–210°, m.p. depressed on mixture with tetraphenylethane; then to tetraphenylethane, 0.210 g. (0.63 mmole), 78%, m.p. and mixed m.p. 208–210°, depressed on mixture with the ketone; and finally to additional ketone 0.020 g., m.p. and mixed m.p. 208–210°, total recovery 96%.

Absorption spectra were obtained in alcohol, approximately 0.01 g./l., on a Cary model 14 spectrophotometer alone and in some cases in the presence of equimolar concentration of added azo compound I. The data follow, each pair of numbers referring to λ_{max} in mμ and log ϵ, those preceded by (a) being obtained in the presence of the azo compound.

Benzophenone azine: 278, 4.29; (a) 280, 4.40; 310 (shoulder), 4.2; (a) 315, 4.16. *p,p,p',p'*-Tetramethyl benzophenone azine: 275, 4.41 (shoulder); (a) 275, 4.22 (shoulder); 315, 4.06 (shoulder). *p,p,p',p'*-Tetrachloro-

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(15) D. Darapsky, *J. prakt. Chem.*, **67**, 112, 164 (1903).

(16) V. Meyer, *Ber.*, **16**, 823 (1883).

(17) W. Platner and R. Behrend, *Ann.*, **278**, 369 (1894).

(18) W. Borsche and C. Merkwitz, *Ber.*, **37**, 3180 (1904).

(19) H. Staudinger, *ibid.*, **44**, 2207 (1911).

(20) F. Michael and J. Schierholt, *ibid.*, **85**, 1089 (1952).

benzophenone azine: 290, 4.22; 323, 4.20. *p,p,p',p'*-Tetramethoxybenzophenone azine: 278, 4.46; 335, 4.2. Benzophenone hydrazone: 275, 4.09. Benzophenone semicarbazone: 282, 4.32. Benzophenone phenylhydrazone: 293, 338, 4.26. Benzophenone oxime: 250. Fluorenone hydrazone: 330, 5.00.

Acknowledgment.—We are pleased to acknowledge generous support of this research by the National Science Foundation, Grant No. G4244, and Guggenheim and Fullbright fellowships (to S.G.C.).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. XXII. Some *cis*- and *trans*-2-Phenylcyclohexyl Derivatives. The Hofmann Elimination[1]

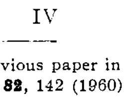
BY STANLEY J. CRISTOL AND FRANK R. STERMITZ

RECEIVED JANUARY 13, 1960

The products and rates of reaction of the *cis* and *trans* isomers of 2-phenylcyclohexyltrimethylammonium ion, 2-phenylcyclohexyldimethylsulfonium ion and 2-phenylcyclohexyl *p*-toluenesulfonate with potassium hydroxide in ordinary ethanol have been investigated. The *cis* and *trans* isomers of the onium compounds differ in elimination reactivity (to give 1-phenylcyclohexene) by factors of 133 (ammonium) and 383 (sulfonium), *trans* elimination being favored over *cis*. A comparison of the rates of reaction with the acyclic (2-phenylethyl) analogs suggests that the *cis* ammonium phenylcyclohexyl isomer is abnormally unreactive, presumably because of conformational difficulties, while the *trans* sulfonium isomer is abnormally reactive. The results are interpreted in terms of a concerted elimination process for the *cis* isomers (*trans* coplanar transition state), and some multistage elimination process (dipolar-ion intermediate) for the *trans* onium compounds (*cis* elimination).

Although a number of bimolecular elimination reactions have been studied in detail regarding the effect of stereochemistry upon rate, generally only qualitative information is available concerning the Hofmann elimination. Several workers[2] have found that this reaction, similar to other bimolecular, base-promoted elimination reactions, shows a preference for *trans* elimination. The present study was undertaken to provide more quantitative information regarding this preference. The *cis* and *trans* isomers in the 2-phenylcyclohexyl system were chosen since the presence of the phenyl group on the β-carbon would activate the β-hydrogen, causing an increase in rate and obviating the necessity for using very high-boiling solvents as is common in work on the Hofmann elimination.

Arnold and Richardson[3] had observed that elimination from *cis*- and *trans*-I gave 1-phenylcylohexene (IV) rather than 3-phenylcyclohexene (V) and Weinstock and Bordwell[4] showed that the base-promoted isomerization of V to IV was slow enough so that IV was not obtained through V as an intermediate, but probably directly from *cis*- and *trans*-I. The isomers of I thus appeared to represent an excellent system for a study of *cis* and *trans* Hofmann eliminations.



$PhCH_2CH_2Y$

I, Y = $\overset{+}{N}Me_3$

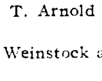
II, Y = $\overset{+}{S}Me_2$

III, Y = OTs

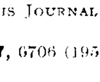
Ia, Y = $\overset{+}{N}Me_3$

IIa, Y = $\overset{+}{S}Me_2$

IIa. Y = OTs



IV



V

At the same time, it appeared worthwhile to study the corresponding sulfonium ions (*cis*- and *trans*-II) as another example of an "onium" system and the corresponding *p*-toluenesulfonates (*cis*- and *trans*-III) as an example of a presumably "normal" system. For further comparison, elimination rates were studied on 2-phenylethyltrimethylammonium bromide (Ia).[5] Data for the corresponding sulfonium compound IIa and *p*-toluenesulfonate IIIa were available from the literature.

Preparation of Materials.—The 2-phenylcyclohexyltrimethylammonium iodides (*cis*- and *trans*-I) were previously prepared and characterized by Arnold and Richardson[3] and by Cope and Bumgardner.[6] A different synthetic route was employed here, in which a mixture of the corresponding amines was prepared and the isomers separated by chromatography on alumina of the N-benzoyl derivatives. The amine mixture was obtained either from the Leuckart reaction on 2-phenylcyclohexanone or from the reduction of the corresponding oxime with lithium aluminum hydride. Based upon the amount of N-benzoyl derivatives formed, the Leuckart reaction gave about seven parts of *trans*-amine to four parts of *cis*-amine while reduction of the oxime gave five parts of *trans* to four parts of the *cis* compound. The latter ratio is in contrast to that reported by Smith, Maienthal and Tipton[7] who obtained only *trans*-amine in the lithium aluminum hydride reduction of some methylcyclohexanone oximes. The N-ben-

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[1] Previous paper in series: S. J. Cristol and R. S. Bly, Jr., THIS JOURNAL, **82**, 142 (1960).

[2] See for example: W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940); N. L. McNiven and J. Read, *J. Chem. Soc.*, 153 (1952); R. D. Haworth, J. McKenna and R. G. Powell, *ibid.*, 1110 (1953); F. E. King and H. Booth, *ibid.*, 3798 (1954); K. Jewers and J. McKenna, *ibid.*, 2209 (1958).

[3] R. T. Arnold and P. N. Richardson, THIS JOURNAL, **76**, 3649 (1954).

[4] J. Weinstock and F. G. Bordwell, *ibid.*, **77**, 6706 (1955).

[5] This compound was kindly supplied by Prof. A. N. Bourns, McMaster University, Hamilton, Ontario.

[6] A. C. Cope and C. L. Bumgardner, THIS JOURNAL, **79**, 960 (1957).

[7] D. R. Smith, M. Maienthal and J. Tipton, *J. Org. Chem.*, **17**, 294 (1952).