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Mercaptan Catalysis in Thermoneutral Free Radical Exchange

BY CHI-HUA WANG AND SAUL G. COHEN[1]

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The exchange of $(C_6H_5)_2CH\cdot$ with $(C_6H_5)_2CH_2$ was studied by decomposition of $(C_6H_5)_2CH{-}N{=}N{-}CH(C_6H_5)_2$ (I) in $(C_6H_5)_2C^{14}H_2$ at 60° and examination of the $(C_6H_5)_2CH{-}CH(C_6H_5)_2$ (II) produced for radioactivity. Little or no exchange was observed. Thiophenol, *ca.* 0.04 mole/l., led to diminished yield of II and 17% exchange, apparently *via* the reactions $(C_6H_5)_2CH\cdot + C_6H_5SH \rightleftarrows (C_6H_5)_2CH_2 + C_6H_5S\cdot$. Irradiation of diphenyl disulfide in $(C_6H_5)_2CH_2$ led to II. A few experiments with α-mercaptotoluene and 2-mercaptomesitylene led to little if any exchange. Thiophenol and I in both benzene and $(C_6H_5)_2CH_2$ led also, in low yield, to compound III, apparently 2,2,3,3-tetraphenylethylenimine, which was also formed by decomposition of I in benzene in the presence of benzophenone azine. Analysis and interpretation of the results are given.

It has been proposed that when a free radical is generated in a solvent from which it may be derived by removal of one atom, *i.e.*, acetoxy radical in acetic acid, alkoxy radical in the corresponding alcohol, the radical may be continually regenerated in type by exchange reaction with solvent and have an abnormally long free life.[2]

$$A\cdot + A'H \rightleftarrows AH + A'\cdot \ (A = A')$$

Such statements, drawing perhaps on the common awareness of the rapid gas phase reaction of atomic hydrogen with molecular hydrogen,[3] leading to *para–ortho* conversion at room temperature, have an apparent plausibility and are perhaps more widely accepted than is justified. They imply that the reaction proceeding through the transition state $A\cdot\cdot\cdot H\cdot\cdot\cdot A$ has low activation energy and high probability, while the zero free energy change and thermoneutral nature of the process require only that the equilibrium constant be unity and give no information about the rate. Whether the exchange process will be observed depends also upon the rates of those competing reactions which consume the radicals. In addition, rapid exchange reactions will not lead to long free life of the radicals since they do not affect the rates of the processes by which the radicals disappear, except perhaps for the interval the radicals spend in the exchange transition states.

Of the reported studies of such exchange reactions the following may be noted: 1. The formation of acetoxy radical by decomposition of acetyl peroxide in acetic acid—2-C^{14} led to methane which was only about 1% as radioactive as the solvent. The postulated exchange reaction

$$CH_3COO\cdot + C^{14}H_3COOH \rightleftarrows CH_3COOH + C^{14}H_3COO\cdot$$

was slow compared to loss of carbon dioxide by the acetoxy radical.[4]

2. The transfer of hydrogen from C^{14}-labeled durohydroquinone to duroquinone has been interpreted as electron transfer, probably from the dianion,[5] but it may well be that hydrogen transfer reactions contribute to some extent in such disproportionations, particularly under acidic conditions.

3. Analysis of the results of photo-chlorination of α-d_1-toluene indicated that exchange of benzyl radical with the α-deuterotoluene did not take place,[6] reaction with chlorine being very rapid.

4. However, isotopic analysis of the 4,4′-dimethyldibenzyl isolated in low yield from the decomposition of benzoyl peroxide in a mixture of *p*-xylene and α-d_1-*p*-xylene was interpreted to indicate that the hydrogen extraction was far more rapid than dimerization of the radicals at 80°.[7] It appears that this may not be the unique interpretation of the results.

5. Consideration of the rates of the individual processes in the polymerization of styrene at 60° gives pertinent information.[8] The chain transfer constant with ethylbenzene,[9] 0.67×10^{-4}, multiplied by the propagation constant,[10] 176, leads to the rate constant for abstraction of hydrogen (largely the secondary hydrogen) from ethylbenzene by the structurally related radical of the growing polystyrene chain, 1.18×10^{-2} l. mole^{-1} sec.$^{-1}$. The constant for termination,[10] which is essentially combination of the radicals, is 3.6×10^7 l. mole^{-1} sec.$^{-1}$. The steady state concentration of radicals in a polymerization of styrene at 60° containing 1% benzoyl peroxide, assuming[11] $k_d = 1.95 \times 10^{-6}$ sec.$^{-1}$, is calculated to be 6.5×10^{-8} mole/l. The rate of combination of the radicals is thus 1.6×10^{-7} mole/l./sec., while the rate of abstraction from a solution containing 4 mole/l. of ethylbenzene is 3.1×10^{-9} mole/l./sec. Abstraction of H from ethylbenzene by the polystyryl radical is about 2% as fast under these conditions as the combination rate, casting doubt upon the interpretation of Cadogan, *et al.*[7]

6. The exchange of methyl with methane proceeds at about 350°, $E_a = 14$ kcal./mole,[12] but in the vapor phase the dimerization may not compete well in the absence of three body collisions or wall reactions.

7. The internal hydrogen abstraction in the conversion of 2-(4′-methylbenzoyl)-1-phenyl to

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[1] For a preliminary report see S. G. Cohen and C. H. Wang, THIS JOURNAL, **77**, 4435 (1955).

[2] W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, 2nd edition, London, 1948, pp. 19, 139, 231.

[3] K. H. Geib and P. Harteck, *Z. physik. Chem.*, Bodenstein-Festband 846 (1931).

[4] A. J. Fry, B. M. Tolbert and M. Calvin, UCRL-573, December 29, 1949; *Trans. Faraday Soc.*, **49**, 1444 (1953).

[5] A. Bothner-By, THIS JOURNAL, **75**, 728 (1953).

[6] H. C. Brown and G. A. Russell, *ibid.*, **74**, 3995 (1952).

[7] J. I. G. Cadogan, V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 561 (1955). It was pointed out by a referee that this article, apparently based on one experiment, reported an improbably high rate of exchange.

[8] Paul J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 143, 158.

[9] R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947).

[10] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 1700 (1951).

[11] K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).

[12] J. R. McNesby and A. S. Gordon, *ibid.*, **76**, 4196 (1954).

2-benzoyl-5-methyl-1-phenyl apparently took place in low yield and was favored by a cyclic transition state.[13]

It seemed desirable to us to carry out the simple experiment of generating from an azo compound a free radical R· in the C^{14}-labeled solvent RH and examining the radioactivity of the dimer R–R. Azo-bis-diphenylmethane (I) was selected as source of the diphenylmethyl radical and diphenylmethane-13-C^{14} was prepared as solvent from benzyl chloride-7-C^{14}. This azo compound decomposes at a convenient rate[14] at 60° and, in diphenylmethane, leads to the dimer 1,1,2,2-tetraphenylethane (II) in higher than 90% yield.[14] This procedure would lead to a radical which, unlike the acetoxy radical,[4] would not decompose; there would be no competition from reaction with an added reagent[6] and the results might be readily interpreted.

A solution (*ca.* 0.02 mole/l.) of the azo compound in 3:1 diphenylmethane–benzene was warmed under carbon dioxide at 60° for five hours, leading to high (> 90%) yields of nitrogen, and of tetraphenylethane, 74–88% uncorrected, 93–97% corrected, and to no residues (Table I). The tetraphenylethane isolated from the radioactive solvent was found, after several crystallizations from ethanol and carbon tetrachloride, to contain slight radioactivity, about twice the background and equivalent to about 1.5% exchange. However, we found it difficult in a blank run to reduce below this value the radioactivity of tetraphenylethane which had been briefly heated to 160° in radioactive diphenylmethane, and then recovered. Thus it is doubtful whether the exchange competed even to this small extent with the dimerization of the diphenylmethyl radicals originally produced from the azo compound. The results are summarized in Table I. All counting data are included in Table IV.

TABLE I

DECOMPOSITION OF $(C_6H_5)_2CHN{=}NCH(C_6H_5)_2$ IN 3:1 $(C_6H_5)_2CH_2:C_6H_6$, 60°

Expt.	I, g.	Solvent, ml.	$(C_6H_5)_2CH{-}CH(C_6H_5)_2$ g.	%	% corr.	Exchange, %
264	0.455	70	0.366	88	94	....
281	.462	70	.397	88	94	....
295[a]	.128	20	.087	74	93	1.5 ± 0.5
296[a]	.206	27	.162	86	97	1.0 ± 0.4

[a] Diphenylmethane-13-C^{14} in solvent.

The exchange reaction having failed to compete effectively with the dimerization, it seemed reasonable to examine the effects of mercaptans. The transfer constant[15] for aliphatic mercaptans in the polymerization of styrene at 60° is about 20 and the rate constant for attack on the mercaptyl hydrogen by polystyryl radical is thus about 3.5×10^3 l.-mole^{-1} sec.$^{-1}$. Under the polymerization conditions used in the previous calculation the rate of transfer with 0.04 mole/l. mercaptan is 6.6×10^{-6} mole/l./sec., about 80 times greater than the rate of recombination. The reactivity of mercaptans is such as to interrupt the normal combination of radicals and being reactive even to the highly stabilized 2,2-diphenyl-1-picrylhydrazyl,[16] they might be expected to react with diphenylmethyl and be converted to thiyl radicals. The thiyl radicals might abstract hydrogen from the solvent, $(C_6H_5)_2C^{14}H_2$, catalyzing the exchange and leading to radioactivity in the dimer, tetraphenylethane. This process would be related to mercaptan catalysis of decarbonylation of aliphatic aldehydes[17] and of dehydrogenation of 1-azo-bis-1-phenylethane[18] and 9,10-dihydroanthracene,[18] but it should be noted that the latter processes may have net favorable free energy change. In a preliminary experiment irradiation of 0.02 mole/l. of solution of diphenyl disulfide in diphenylmethane with a sunlamp led to tetraphenylethane in 27% yield indicating that this thiyl radical could lead to the diphenylmethyl radical.[19]

The decomposition of the azo compound was carried out in the presence of ordinary and C^{14}-labeled diphenylmethane, as described above but in the presence of varying concentration (0.035–3.5 moles/l.) of thiophenol. Blank experiments were carried out indicating that tetraphenylethane could be recovered in high yield in the presence of the mercaptan, its disulfide and benzhydryl-phenylthioether; and that it was not formed from the solvent and the sulfur compounds under the conditions of the experiment. The results of eight experiments, including percentage exchange from radioactivity measurements, are summarized in Table II.

The nitrogen yield remained high, over 90%, affected little by the thiophenol. However, the presence of 0.04 mole/l. of thiophenol (expt. 265, 282, 297, 298) decreased the yield of tetraphenylethane markedly from over 90% to about 60%, while 0.3–0.5 mole/l. of thiophenol (expt. 270, 283, 299, 300) decreased the yield further to about 40%. At 3.2 moles/l. of thiophenol only crude tetraphenylethane was isolated by the usual procedure; purification by treatment with Raney nickel led to 21% yield of tetraphenylethane. Also, a yellow sulfur-free, nitrogen-containing compound III, m.p. 175–177°, was isolated in the presence of thiophenol. Benzophenone azine was not found. After removal of the solids and volatile components, yellow, oily, sulfur-containing residues were found. The infrared spectrum of the residue in chloroform showed absorption similar to that of a solution of synthesized diphenyl disulfide and benzhydryl phenyl sulfide in chloroform.

The yellow compound III corresponding in weight to 2% of the azo compound at low thiophenol concentration, 14% at intermediate and 10% at high thiophenol concentration was apparently 2,2,3,3-tetraphenylethylenimine. Elementary analysis and molecular weight were satisfactory for this struc-

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[13] D. I. Relyea and D. F. DeTar, THIS JOURNAL, **76**, 1202, 1680 (1954).

[14] S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2459 (1955).

[15] C. Walling, *ibid.*, **68**, 2381 (1946).

[16] K. E. Russell, *J. Phys. Chem.*, **58**, 437 (1954).

[17] E. F. P. Harris and W. A. Waters, *Nature*, **170**, 212 (1952); K. E. J. Barrett and W. A. Waters, *Disc. Faraday Soc.*, **14**, 221 (1953).

[18] A. F. Bickel and E. C. Kooijman, *Nature*, **170**, 211 (1952).

[19] For evidence for photochemical dissociation of disulfides see M. S. Kharasch, W. Nudenberg and T. H. Meltzer, *J. Org. Chem.*, **18**, 1223 (1953).

TABLE II

DECOMPOSITION OF $(C_6H_5)_2CHN{=}NCH(C_6H_5)_2$ (I), 60°, IN 3:1 $(C_6H_5)_2CH_2:C_6H_6$, IN PRESENCE OF C_6H_5SH

Expt.	I, g.	C_6H_5SH, g.	Solvent, ml.	$(C_6H_5)_2CH-CH(C_6H_5)_2$			Exchange, %	III,[c] g.	Residue, g.
				g.	%	% corr.			
265	0.496	0.28	70	0.225	49	55	....	...	0.28
282	.497	.35	70	.220	48	54	....	0.011	.26
297[a]	.245	.15	40	.122	49	59	16.7 ± 1.0	...	.15
298[a]	.188	.15	34	.088	51	63	18.0 ± 0.7	...	.11
270	.283	3.0	70	.086	33	39	... .	...	.46
283	.565	2.1	70	.155	30	35	....	0.079	.20
299[a]	.233	1.7	30	.070	32	40	2.5 ± 0.9	...	.12
405[a]	.435	12.4	35	.060	15	21[b]	3.0 ± 0.5	0.043	.24

[a] Diphenylmethane-13-C^{14} in solvent. [b] The crude product, 33%, was desulfurized with Raney nickel. [c] Yellow compound, m.p. 175–177°, apparently 2,2,3,3-tetraphenylethylenimine.

ture; catalytic hydrogenation led to absorption of two moles of hydrogen and to tetraphenylethane; the yellow color was apparently due to end absorption, λ_{max} 280 mμ, log ϵ 3.95. This compound contained no sulfur but was not formed in the absence of thiophenol; in the presence of the mercaptan it was formed both in diphenylmethane and in benzene. The mercaptan, converted to thiyl radical by diphenylmethyl, apparently dehydrogenated the azo compound[18] either to azine or to an intermediate to which diphenylmethyl radical added, leading ultimately to III. Benzophenone azine was isolated, in addition to III, in a decomposition of azo-bis-diphenylmethane in benzene in the presence of thiophenol in a run which was carried out without careful exclusion of air. Compound III was also formed in high yield in benzene in the absence of mercaptan but in the presence of added benzophenone azine, which appeared to react with exceedingly high efficiency with diphenylmethyl.

The radioactivity counting data for the tetraphenylethane formed in the presence of thiophenol are summarized in Table IV, the exchange results in Table II. The tetraphenylethane formed in 59 and 63% yield in the presence of 0.035 and 0.038 mole/l. of thiophenol (expt. 297, 298) had specific activity equal to 16.7 and 18.0% of that of the diphenylmethane. The tetraphenylethane formed in lower yield in the presence of 0.5 mole/l. (expt. 299) and 3.2 moles/l. (expt. 405) of thiophenol had lower activity, corresponding to about 3% exchange, apparently slightly more than the blank.

That 0.04 mole/l. of thiophenol lowers the yield of tetraphenylethane to 60% of partially exchanged product indicates, as described in the following equations, that this mercaptan reacts rapidly with diphenylmethyl, that the phenylthiyl radical in part abstracts hydrogen from solvent diphenylmethane, and that several radical combination reactions occur.

$$(C_6H_5)_2CH{-}N{=}N{-}CH(C_6H_5)_2 \xrightarrow{k_1} 2(C_6H_5)_2CH\cdot + N_2 \quad (1)$$

$$(C_6H_5)_2CH\cdot + C_6H_5SH \underset{k_3}{\overset{k_2}{\rightleftarrows}} (C_6H_5)_2CH_2 + C_6H_5S\cdot \quad (2)$$

$$C_6H_5S\cdot + (C_6H_5)_2C^*H_2 \xrightarrow{k_3} C_6H_5SH + (C_6H_5)_2C^*H\cdot \quad (3)$$

$$2(C_6H_5)_2C^*H\cdot \xrightarrow{k_4} (C_6H_5)_2C^*H{-}C^*H(C_6H_5)_2 \quad (4)$$

$$2C_6H_5S\cdot \xrightarrow{k_5} C_6H_5S{-}SC_6H_5 \quad (5)$$

$$(C_6H_5)_2C^*H\cdot + C_6H_5S\cdot \xrightarrow{k_6} (C_6H_5)_2C^*H{-}S{-}C_6H_5 \quad (6)$$

$$C^* = C^{12} \text{ or } C^{14}$$

That the higher concentrations of thiophenol were proportionally less effective in diminishing the yield of tetraphenylethane and that this tetraphenylethane had very low radioactivity implies strongly that a considerable fraction of the product, corresponding perhaps to 20–30% of the azo compound, is formed from non-randomized pairs of diphenylmethyl radicals originating from the same molecule of azo compound. A similar conclusion had been reached previously in a study of azo-bis-isobutyronitrile in inert solvent in the presence of butyl mercaptan.[20] The additional information from the radioactivity is useful, and necessary in our experiments where the solvent RH is related to the radical R·. Whether this is due to a "collapse" of the azo compound to nitrogen and tetraphenylethane or to a recombination of an original pair before they lose their identity as a pair is not clear.[21]

Thus, if the tetraphenylethane of expt. 297 and 298 included non-radioactive product derived from original pairs of diphenylmethyl corresponding to 20% of the starting azo compound, then the remaining 40% of the product had radioactivity corresponding to about 26% exchange. A very approximate "material balance" of these reactions may be as follows: 20% of the diphenylmethyl radicals dimerized before losing their identity as pairs; 40% dimerized after becoming randomized and of these 26% or 10% of the total underwent exchange with radioactive diphenylmethane before dimerization, while 30% of the total dimerized without exchange; and approximately 40% was lost either as diphenylmethane or as diphenylmethyl-phenylthioether because of reactions 2, 5 and 6. Since the yield of disulfide is likely to be much greater than that of thioether[22] it may be that about 42% of the diphenylmethyl reacted

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[20] G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

[21] It may be noted that the former would be independent of concentration while the time required for the latter type of loss of identity, *i.e.*, for pairs to become separated by a distance equal to the mean distance from another radical in the solution, will decrease with increasing concentration. For a discussion of primary and secondary recombination and the effect of scavenger see R. M. Noyes, THIS JOURNAL, **77**, 2042 (1955).

[22] P. Bruin, A. F. Bickel and E. C. Kooijman, *Rec. trav. chim.*, **71**, 1115 (1952).

with thiophenol (eq. 2), 10% was recovered radioactive (eq. 3), leading to a total of 60% of tetraphenylethane and 32% conversion to diphenylmethane. The thiyl equivalent of 8% reacted with diphenylmethyl to form thioether bringing the total loss of diphenylmethyl to 40% with an equivalent of 24% of the radicals appearing as disulfide. These values may be expressed alternatively as rates of the corresponding reaction, since, in view of the low extent of exchange observed, the radicals may be considered to undergo the equilibrating sequence not more than once before disappearing.

During the course of this work a few decompositions were carried out in the presence of two other mercaptans. The results in the presence of α-mercaptotoluene and 2-mercaptomesitylene are summarized in Table III.

TABLE III

DECOMPOSITION OF $(C_6H_5)_2CHN{=}NCH(C_6H_5)_2$ (I), 60°, IN 3:1 $(C_6H_5)_2CH_2:C_6H_6$ IN PRESENCE OF MERCAPTANS

Expt.	I, g.	C_6H_5-CH_2SH, g.	Solvent, ml.	$(C_6H_5)_2CHCH(C_6H_5)_2$ g.	%	% corr.	Exchange, %
285	0.370	0.085	70	0.290	84	93	
286	.565	.85	70	.411	80	85	
402[a]	.235	.14	15	.161	75	88	3.5 ± 0.5
406[a]	.470	8.0	23	.145	34	40	3.8 ± 2.0
		$(CH_3)_3C_6H_2SH$					
410[a]	.425	0.36	27	.145	36	42	....
411[a]	.390	0.32	27	.133	37	43	....

[a] Diphenylmethane-13-C^{14}.

In all the experiments the yields of nitrogen were above 90% and essentially unaffected by the mercaptan. At low (0.01 mole/l., expt. 285) concentration of α-mercaptotoluene, the yield of tetraphenylethane was unaffected (*cf.* expt. 264, 281), while at 0.1 mole/l. (expt. 286) the yield was higher than at 0.04 mole/l. of thiophenol (expt. 265, 282, 297, 298). This was due to lower reactivity of this mercaptan toward diphenylmethyl and not to rapid regeneration of diphenylmethyl by reaction of the thiyl radical with the solvent, since the recovered tetraphenylethane had low radioactivity (expt. 402). The lower reactivity of this aliphatic mercaptan is consistent with the greater effectiveness of the aromatic mercaptan as a chain transfer reagent in the polymerization of methyl methacrylate, which has been attributed to resonance stabilization of the aromatic thiyl radical.[23] At high concentration (expt. 406, 2.8 moles/l., the yield of tetraphenylethane dropped to 40%, with low radioactivity. It may be that at some intermediate concentration more evidence for exchange would have been found.

On the other hand, 2-mercaptomesitylene, at 0.08 mole/l. concentration, appeared to be more effective than thiophenol in decreasing the yield of tetraphenylethane and it did not catalyze exchange with the solvent. Only with this mercaptan was the disulfide isolated as a pure solid, 30% yield, 47% based on unrecovered tetraphenylethane. The infrared absorption spectrum of the residue from the decomposition in the presence of α-mercaptotoluene (expt. 406) led to little information since in several regions detail was lacking, and the sharp bands could be accounted for largely by the presence of residual diphenylmethane. The infrared absorption spectrum of the residue from the decomposition in the presence of 2-mercaptomesitylene was similar to that of a mixture of dimesityl disulfide and diphenylmethylmesityl sulfide.

If exchange is to be observed as radioactivity in the tetraphenylethane a delicate balance in the rate of reactions 2–6 must be attained. Rate constants k_2 and k_3 should be high, reactions 2 and 3 comprising a mobile equilibrium. However, it may be that factors increasing k_2 such as stability of the thiyl radical may diminish k_3, and in particular to a greater extent than they would diminish k_5 and k_6. This may be the situation in the case of 2-mercaptomesitylene. Concentration of mercaptan should probably be low so that the equilibrium described by equations 2 and 3 may not for this reason be displaced toward high concentration of thiyl radical, a situation which would favor disappearance of radicals by reactions 5 and 6, lower the total yield of tetraphenylethane and the proportion that could be radioactive.

Experimental[24]

Azo-bis-diphenylmethane.—The preparation of benzophenone azine, m.p. 163°, and the oxidation of N,N'-dibenzhydrylhydrazine with mercuric oxide to form azo-bis-diphenylmethane, m.p. 114° dec., were carried out as described previously.[14] N,N'-Dibenzhydrylhydrazine was prepared by reduction of the azine by sodium amalgam.[25] Benzophenone azine, 20 g. (0.55 mole), was dissolved in 1 l. of boiling 95% ethanol and to it was added slowly with stirring 562 g. of 2% sodium amalgam. The mixture was boiled for one hour, the yellow color disappearing. The mixture was filtered and the amalgam was washed with hot ethanol and the filtrate and washings were diluted with 500 ml. of water, leading to 7 g. of white solid N,N'-dibenzhydrylhydrazine, 33% yield, melting at 110–125°, reported[25] 120–133°.

Benzyl chloride-7-C^{14} 0.156 g., 1 mc., 0.8 mc./mmole, was purchased from Tracerlab, Boston, Mass.

Diphenylmethane-13-C^{14}.—The benzyl chloride-7-C^{14} was diluted with 50 g. (0.40 mole) of benzyl chloride, Eastman Kodak Co., b.p. 179°, and was added[26] slowly to a mixture of 200 ml. of benzene and 1 g. of amalgamated aluminum foil in a three-neck flask equipped with a mechanical stirrer, condenser protected with a drying tube, and a dropping funnel. After the addition, the mixture was warmed until evolution of hydrogen chloride ceased, hydrolyzed with 200 ml. of 5% sodium hydroxide, washed with water, dried over calcium chloride and distilled, leading to diphenylmethane, 35 g., b.p. 112–116° (3 mm.), and to a residue. The residue was treated with 5 g. of aluminum chloride and 50 ml. of benzene under reflux for one hour, poured on to ice, extracted with ether, washed with 5% sodium hydroxide and water, dried over calcium chloride and distilled, leading to 11 g. of diphenylmethane, total yield 46 g., 69%, m.p. 26–27°, reported 27°.[27]

Thiophenol (Eastman Kodak Co.) was distilled, b.p. 168.5–169.5°.

α-Mercaptotoluene (Eastman Kodak Co.) was distilled, b.p. 194–195°.

2-Mercaptomesitylene.—Mesitylene (Eastman Kodak Co., b.p. 164–165°, 30 g. 0.25 mole) was added over a period of one-half hour with stirring to 80 g. (0.69 mole) of

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(23) J. L. O'Brien and F. Gornick, THIS JOURNAL, **77**, 4757 (1955).

(24) Melting points are uncorrected; microanalyses are by Dr. S. M. Nagy, Massachusetts Institute of Technology.

(25) A. Darapsky, *J. prakt. Chem.*, [2] **67**, 179 (1903).

(26) W. W. Hartman and R. Phillips, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 232.

(27) E. Fischer and O. Fischer, *Ann.*, **194**, 253 (1878).

chlorosulfonic acid (Matheson, b.p. 151°) at 0°, stirring was continued for 0.5 hour and the product was poured on to ice. Mesitylene-2-sulfonyl chloride, 50 g., 92% yield, was obtained, m.p. 56–57°, reported[28] 57°, prepared from sulfuryl chloride in place of chlorosulfonic acid. Mesitylene-2-sulfonyl chloride, 10 g. (0.046 mole), was stirred with 18 g. of zinc dust, 100 g. of ice and 30 ml. of concentrated sulfuric acid, allowed to warm slowly to room temperature and heated on the water-bath for one hour. The mixture was steam distilled, the distillate was extracted with ether, dried over magnesium sulfate and distilled, leading to 2-mercaptomesitylene, 2.5 g., 36% yield, b.p. 227–229°, reported[29] 229°.

Diphenyl Disulfide.—Thiophenol, 10 g. (0.09 mole), was dissolved in 40 ml. of acetic acid and treated with 40 ml. of 40% aqueous ferric chloride solution on the water-bath for two hours. The product was filtered, washed with dilute hydrochloric acid and water, and crystallized from ethanol, 6 g., 60% yield, m.p. 61–62°, reported[30] 61°.

Dibenzyl Disulfide.—α-Mercaptotoluene, 12.4 g. (0.1 mole), was treated with 12.7 g. (0.05 mole) of iodine in 150 ml. of ether at room temperature overnight. The ether was evaporated and the residue washed with cold ethanol and crystallized from ethanol, 9 g., 75% yield, m.p. 71–72°, reported[31] 71–72°.

Dimesityl Disulfide.—2-Mercaptomesitylene, 0.7 g. (0.0046 mole), was treated with iodine, 0.7 g. (0.0027 mole), in 20 ml. of ether at room temperature for 15 hours. The ether was evaporated and the product was washed with methanol and crystallized from ethanol, 0.55 g., 79% yield, m.p. 123–124°, reported[29] 125°.

Diphenylmethylphenyl Sulfide.—Diphenylcarbinol (Fisher Scientific, 10 g., 0.054 mole, m.p. 68–69°) was converted to diphenylchloromethane by treatment with 14 ml. of concentrated hydrochloric acid. The crude product, 9 g., was dissolved in 20 ml. of acetic acid, treated with 5 g. (0.045 mole) of thiophenol and 8 ml. of concentrated sulfuric acid on the water-bath for 10 minutes, and poured on to ice. The product was collected and crystallized from ethanol, 7.0 g. (0.025 mole), 46% yield, m.p. 77–78°, reported[32] 78°.

Diphenylmethylbenzyl sulfide was prepared similarly from 6 g. of crude diphenylchloromethane, 2.5 g. (0.02 mole) of α-mercaptotoluene and 4 ml. of concentrated sulfuric acid in 10 ml. of acetic acid. The product was crystallized from ethanol; 4.7 g., 81% yield, m.p. 71–72°. *Anal.* Calcd. for $C_{20}H_{18}S$: C, 82.67; H, 6.24. Found: C, 82.34; H, 6.33.

Diphenylmethylmesityl sulfide was prepared by treatment of 2 g. of crude diphenylchloromethane and 1.0 g. (0.0066 mole) of 2-mercaptomesitylene with 1 ml. of concentrated sulfuric acid in 5 ml. of acetic acid at room temperature for 2 hours. The reaction mixture was poured onto ice. The product, 1.3 g. (0.0042 mole), 63% yield, m.p. 109–110°, was crystallized from ethanol. *Anal.* Calcd. for $C_{22}H_{22}S$: C, 82.99; H, 6.96. Found: C, 82.99; H, 6.93.

Blank Experiments. a.—In a series of isolations, 0.392 g., 0.206 g., and 0.100 g., of tetraphenylethane were dissolved in 50 ml. of diphenylmethane, the solution was heated to 150° then distilled in vacuum. The residue was treated with alcohol leading, respectively, to 0.363 g., 93%, 0.180 g., 88%, and 0.085 g., 85% recoveries, m.p. and mixed m.p. 208–210°.

b.—A solution of thiophenol, 0.150 g., diphenyl disulfide, 0.150 g., and diphenylmethylphenyl sulfide, 0.150 g., in 25 ml. of diphenylmethane was heated at 60° for 6 hours under nitrogen and distilled in vacuum. The residue was triturated with ethanol and seeded with tetraphenylethane but none of this product was obtained.

c.—A solution of 0.222 g. of tetraphenylethane, 0.150 g. of thiophenol, 0.150 g. of diphenyl disulfide and 0.150 g. of diphenylmethylphenyl sulfide in 30 ml. of diphenylmethane was heated at 60° for 2 hours and distilled in vacuum, leading to an oil residue which, when treated with ethanol, led to tetraphenylethane, 0.196 g. (88%), m.p. and mixed m.p. 208–210° (0.100 g. of tetraphenylethane was recovered in 83% yield).

Irradiation of Disulfides in Diphenylmethane. a. Cystine.—A suspension of 1.0 g. (0.0042 mole) of cystine in 200 ml. of diphenylmethane in a Pyrex flask was exposed to a Hanovia Serial 26329 SH U.V. lamp for 7 days at about 100°. The discolored solution was filtered, concentrated in vacuum and heated with ethanol, leading to tetraphenylethane, 0.40 g. (0.0012 mole), 28% yield, m.p. and mixed m.p. 206–208°. Irradiation of diphenylmethane under similar conditions in the absence of disulfide led to no tetraphenylethane.

b. **Diphenyl Disulfide.**—A solution of 0.100 g. (0.46 mmole) of diphenyl disulfide in 25 ml. of diphenylmethane in an evacuated test-tube was exposed to G.E. 275 w. sun lamp for 6 hours at 40–50°, concentrated in vacuum and treated with ethanol, leading to tetraphenylethane, 0.110 g. (0.33 mmole), 72% yield, m.p. and mixed m.p. 210–211°; its infrared spectrum, taken in potassium bromide pellet, was identical with that of an authentic sample.

Decomposition of Azo-bis-diphenylmethane in 3:1 Diphenylmethane:Benzene.—In each case the azo compound was dissolved at 0° in the solvent with and without added mercaptan, in a 100-ml. flask which was equipped with gas inlet and outlet tubes and connected to a nitrometer containing 50% potassium hydroxide. The system was flushed with dried carbon dioxide until free of air, about one hour. The flask was warmed to 60 ± 2° for about 5 hours and the nitrogen was collected in a gentle stream of carbon dioxide. The accuracy was probably ±5%. The solvents were removed in vacuum and, where present, radioactive diphenylmethane was recovered and redistilled, diluted in the later experiments with diphenylmethane, recounted and reused. The residues were purified by crystallization from ethanol and carbon tetrachloride.

a. **In the Presence of Thiophenol.**—The yield of nitrogen varied between 93 and 98%. The reaction mixture from 0.497 g. (1.58 mmoles) of the azo compound, 0.350 g. (3.2 mmoles) of thiophenol, 50 ml. of diphenylmethane and 17 ml. of benzene was distilled in vacuum and most of the diphenylmethane was recovered, b.p. 113–115° (4 mm.). The residue was triturated with ethanol leading to tetraphenylethane, 0.220 g. (0.77 mmole) 48% yield (corr. 54%), m.p. and mixed m.p. 207–209°. Concentration of the filtrate led to a yellow compound 0.011 g., m.p. 175–177°, from ethanol, presumably 2,2,3,3-tetraphenylethylenimine, 2.2%. *Anal.* Calcd. for $C_{26}H_{21}N$: C, 89.88; H, 6.05; N, 4.03, mol. wt., 347. Found: C, 89.30; H, 6.11; N, 3.93, mol. wt. 326. The filtrates were again concentrated leading to a yellow oil, 0.265 g., from which was isolated no solid. The infrared absorption spectrum of the residue was determined in chloroform on a Perkin–Elmer model 21 double beam spectrophotometer and compared with spectra of diphenyl disulfide, diphenylmethyl phenyl sulfide, diphenylmethane and a mixture of the two thio compounds. The positions of maxima are indicated in $cm.^{-1}$.

Residue (expt. 283): 3030(m), 2870(m), 1940(m), 1880(m), 1800(m), 1730(m), 1650(s), 1600(s), 1580(s), 1480(s), 1440(s), 1375(w), 1315(s), 1275(s), 1075(s), 1020(m), 1000(m), 940(m), 915(m).

Diphenyl disulfide: 1930(w), 1865(m), 1735(w), 1640(w), 1580(s), 1440(s), 1375(w), 1325(w), 1300(m), 1270(w), 1150(w), 1095(m), 1065(s), 995(m), 900(m).

Diphenylmethyl phenyl sulfide: 1880(w), 1600(m), 1585(s), 1450, 1440(s), 1085(s), 1075(s), 915(w), 825(w), 780(m).

Diphenylmethane: 2850(w), 1880(w), 1760(w), 1655(w), 1605(s), 1450(s), 1340–1320(w), 1285(w), 1200–1150(w), 1105(w), 1075(s), 935–900(w), 820–795(w).

Diphenyl disulfide and diphenylmethyl phenyl sulfide: 2950(w), 1930(m), 1870(m), 1780(m), 1725(w), 1640(w), 1575(s), 1470(s), 1445(s), 1375(w), 1325(m), 1295(m), 1270(w), 1150(m), 1095(m), 1065(s), 1020(s), 995(s), 895(m), 825(w).

Evidence for diphenyl disulfide in the residue is seen in the bands at 1940, 1730, 1000 $cm.^{-1}$. Evidence for the thioether is not clear since all the observed bands, with the possible exception of that at 915 $cm.^{-1}$, appear to be present in at least one of the other components.

b. **In the Presence of α-Mercaptotoluene.**—These experiments were carried out as described in (a) above. The infrared absorption spectrum of the residue (expt. 406) showed broad strong absorption at 3200–2700 and at 1350–

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(28) A. Tohl and O. Eberhard, *Ber.*, **26**, 2943 (1893).

(29) Holtmeyer, "Beilstein, Handbuch der organischen Chemie," Vol. VI, p. 521.

(30) T. Zincke and W. Frohneberg, *Ber.*, **43**, 840 (1910).

(31) A. W. Hofmann, *ibid.*, **20**, 15 (1887).

(32) C. Finzi and V. Bellavita, *Gazz. chim. ital.*, **62**, 699 (1932).

1000 cm.$^{-1}$, and sharper bands at 1885(m), 1690(s), 1645(s), 1590(s), 870(s).

c. In **the Presence of 2-Mercaptomesitylene.**—Azo-bis-diphenylmethane (0.425 g., 1.21 mmoles) was decomposed as described above in 20 ml. of diphenylmethane-13-C^{14} and 7 ml. of benzene in the presence of 0.357 g. (2.35 mmoles) of 2-mercaptomesitylene. The solvents were removed in vacuum and the residue was treated with 15 ml. of ethanol, leading to tetraphenylethane, 0.145 g. (0.434 mmole), 37% yield, m.p. and mixed m.p. 208–210°. The filtrates were concentrated leading in several portions to a solid 0.130 g., m.p. 118–120°, which was recrystallized from ethanol, dimesityl disulfide, 0.110 g. (0.365 mmole), 30% yield, m.p. and mixed m.p. 120–123°. Infrared spectra of this isolated compound was identical with that of an authentic sample. The infrared absorption maxima of the residue in chloroform and of a mixture of diphenylmethyl mesityl sulfide and dimesityl disulfide are as follows: the band at 1930 cm.$^{-1}$ is not present in diphenylmethane.

Residue (expt. 411): 3300(m) cm.$^{-1}$, 2800(s), 1930(m), 1870(m), 1785(m), 1640(s), 1580(s), 1430(s), 1300–1150(s), 1070(s), 1005(s), 935(s), 910(s), 840(m).

Diphenylmethyl mesityl sulfide and dimesityl disulfide: 3300(m) cm.$^{-1}$, 2800(s), 1930(m), 1865(m), 1785(m), 1715(s), 1585(s), 1450–1410(s), 1290–1160(m), 1070(s), 965(m), 905(m), 845(s).

Decomposition of Azo-bis-diphenylmethane in Benzene at 60°. a.—In some early experiments the decomposition was carried out without exclusion of air. Tetraphenylethane was not isolated, but a white solid was obtained melting over a range, 170–200°. When the decomposition of 0.300 g. (0.83 mmole) was carried out in the presence of 0.205 g. (1.86 mmoles) of thiophenol, tetraphenylethane was not found, but there was found compound III melting at 170–173°, 0.088 g., 30% yield and benzophenone azine, 0.038 g. (0.105 mmole) 13% yield, and a residue, 0.15 g.

b.—Under carbon dioxide the azo compound, 0.479 g. (1.32 mmoles), led to nitrogen, 96%, and to tetraphenylethane. 0.362 g., 85% yield (corr.). The azo compound, 0.500 g., and thiophenol, 0.30 g. (0.04 mole/l.), in 70 ml. of benzene led to nitrogen, 81%, to tetraphenylethane, 0.142 g., 32%, and to compound III, 0.025 g., 5% yield, m.p. 173–175°.

c.—A solution of 0.500 g. (1.38 mmoles) of benzophenone azine and 0.500 g. of the azo compound in 75 ml. of benzene was heated at 60° for five hours under nitrogen and concentrated in vacuum. The residue was crystallized from 80 ml. of ethanol leading to compound III, 0.490 g., 51% yield, m.p. and mixed m.p. 175–177°, and after concentration, to benzophenone azine, 0.140 g., 28% recovered, m.p. and mixed m.p. 162–164°, and finally to tetraphenylethane, 0.130 g., 28% yield (crude), m.p. 200–205°.

Compound III, 0.28 g. (0.081 mmole), was hydrogenated in 20 ml. of acetic acid over platinum oxide, absorbing 4.2 ml. of hydrogen with discharge of color. In another run 0.054 g. was hydrogenated similarly, the solution was concentrated and the residue was crystallized from ethanol leading to tetraphenylethane, m.p. and mixed m.p. 209–211°, 0.030 g., 58% yield.

Radioactivity Measurements.—Solutions of the solvent, diphenylmethane-13-C^{14}, and of the various samples of recovered tetraphenylethane were prepared in dimethylformamide (b.p. 151–152°), 0.3-ml. portions of the solutions were placed in small aluminum dishes and the radioactivity was measured, infinite thickness sample, $^1/_8$″ from thin end-window Geiger counter, on an Atomic Instrument Scaler, model 101. The samples of tetraphenylethane were crystallized several times from carbon tetrachloride and from ethanol. In some experiments 0.5-ml. portions were used. The observed activities of each sample of solvent diphenylmethane-13-C^{14} and of the tetraphenylethane formed in it from the azo compound were converted to counts per minute per unit concentration and the ratio of the two activities was taken as the percentage exchange. The data are summarized in Table IV.

TABLE IV

C^{14} COUNTING DATA

D-$(C_6H_5)_2C^{14}H_2$, solvent; T-$(C_6H_5)_2CH$-$CH(C_6H_5)_2$, product

Expt.	Concn., mg./ml.	Counts/min.	Background	Exchange, %
295,6-D	78	2739	52 ± 5	
295-T	59	75 ± 5	44	1.5 ± 0.5
296-T	105	74 ± 6	38	1.0 ± 0.4
297-D	130	3281	44	
297-T	61	297 ± 11	44	16.7 ± 1.0
298-D	130	3321	44	
298-T	64	334 ± 7	44	18.0 ± 0.7
299-D	60	2520	75	
299-T	42	118 ± 10	75	2.5 ± 0.9
405-D	128	3788	113	
405-T	29	90 ± 2	65	3.0 ± 0.5
402-D	71	1272	74	
402-T	61	110 ± 2	74	3.5 ± 0.5
406-D	85	1662	66	
406-T	32	89 ± 7	66	3.8 ± 2.0
410-D	72	560	60	
410-T	60	55 ± 5	60	0
411-D	73	498	60	
411-T	67	72 ± 5	60	2.6 ± 2.9

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Peroxides. IV.[2] Aliphatic Diperacids

BY WINFRED E. PARKER, L. P. WITNAUER AND DANIEL SWERN

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A previously unreported series of peroxides, the C_5–C_{10} and the C_{12} and C_{16} α,ω-diperacids, have been prepared in high yield from the corresponding dibasic acids and 65% aqueous hydrogen peroxide in concentrated sulfuric acid solution. The products were characterized by peroxide oxygen content, X-ray diffraction, polarography and ultimate analysis. The long-spacings of the odd and even diperacids fall on a single line and the angle of tilt is essentially the same as that of dibasic acids, the C-form of aliphatic monocarboxylic acids and the C_9–C_{16} aliphatic monoperacids. Polarograms of the diperacids are similar to those of monoperacids previously described except that the diffusion current constant is only 1.6 times as great.

In contrast to organic monoperacids, of which numerous well-characterized examples are known[3,4] diperacids are almost completely unknown. Bae-

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[2] Paper III is THIS JOURNAL, **77**, 5537 (1955).

[3] W. E. Parker, C. Ricciuti, C. L. Ogg and D. Swern, *ibid.*, **77**, 4037 (1955).

[4] D. Swern, *Chem. Revs.*, **45**, 1 (1949).