[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azo Compounds. XXVII. Synthesis of α-Alkyl and α,α-Dialkylbenzylazoalkanes and Intermediate Hydrazines and Hydrazones[1]

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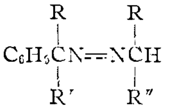
The reaction of phenylmagnesium bromide or phenyllithium on acetaldehyde azine, acetone azine, diethyl ketazine and methyl isobutyl ketazine gave the corresponding mono-1,2-addition products, α-phenylethyl, α-cumyl, α,α-diethylbenzyl- and α,α-methylisobutylbenzylhydrazone, respectively, of the parent carbonyl. Distillation of the reaction mixture obtained with cyclohexanone azine gave apparently hydrocarbon decomposition products. The pure free bases, α-phenylethylhydrazine and α-cumylhydrazine were obtained by hydrolysis of the respective hydrazones. Condensation of α-phenylethylhydrazine with acetone gave acetone α-phenylethylhydrazone. The four azo compounds, α-phenylethylazoisopropane, α-cumylazoisopropane, α,α-diethylbenzylazo-3-pentane and α,α-methylisobutylbenzylazo-2-(4-methylpentane) were obtained by the oxidation of their respective hydrazines which in turn were obtained by the hydrogenation of the corresponding hydrazones.

In the course of a study of the decomposition of aliphatic type azo compounds, a number of unsymmetrical benzylazoalkanes were required. This paper describes the preparation of the benzylazoalkanes of the structure shown in IV. A later paper will describe their decomposition.



$$C_6H_5\overset{R}{\underset{R'}{C}}N{=}N\overset{R}{\underset{R''}{C}}H$$

IVa, R = R′ = R″ = CH_3; IVb, R = R′ = R″ = C_2H_5

IVc, R = CH_3; R′ = R″ = i-C_4H_9

IVd, R = R″ = CH_3, R′ = H

Although symmetrical linear aliphatic azo compounds where the azo linkage is attached to primary or secondary aliphatic radicals are reasonably well known[3a,b,4a,b,5,6] unsymmetrical linear aliphatic azo compounds are quite rare,[7,8] isopropylazomethane being the only one reported on which decomposition studies have been carried out.

As far as is known, no unsymmetrical aliphatic benzyl-type azo compound had been previously reported in the literature. Wieland, *et al.*,[9] reported that the attempted preparation of benzylazotriphenylmethane led primarily to the decomposition product, asymmetrical tetraphenylethane. Cohen and Wang[10] have reported an attempt to synthesize diphenylmethane, obtaining a mixture of hydrazones. The isomerization of azo compounds to the more stable hydrazone isomer[11] in the presence of acids or bases[5,12,13] is known. When the azo group is linked to a benzyl carbon, this isomerization may be facilitated by the increased stabilization of the hydrazone due to the conjugation of the carbon–nitrogen double bond with the phenyl ring. Recently, Hinman[14] reported that air oxidation of 1-benzyl-2-n-butylhydrazine gave the n-butylhydrazone of benzaldehyde. The same type of phenomenon has been observed with the 7-,[15a] 24-[15b] and 6-membered[16] ring hydrazine compounds of the benzyl type.

In our approach to synthesize the hydrazone intermediates of the unsymmetrical aliphatic benzylazo compounds, advantage was taken of the similarity in behavior of the carbon–nitrogen double bond, and the carbon–oxygen double bond in a number of reactions. For example, benzalaniline will react with the Grignard reagent to give good yields of secondary amines, in which the hydrocarbon residue of the Grignard adds to the carbon of the anil.[17a,b] Likewise, benzalaniline will add sodium bisulfite[18] and hydrogen cyanide.[19]

A few reactions between Grignard reagents and aromatic aldazines are reported in the literature. Franzen and Deibel[20] reported that when benzaldehyde azine is treated with two equivalents of ethylmagnesium bromide, benzylbenzylidenehydrazine ($C_6H_5CH_2NHN{=}CHC_6H_5$) is obtained. However, Busch and Fleischmann[21] found that in the reaction of benzaldehyde azine with a large excess of phenylmagnesium bromide (*ca.* 4 equivalents) not only was some of the half-reduced product obtained, but also the "normal" 1,2-mono-addition product, benzaldehyde benzhydrylhydrazone [benzylidene benzhydrylhydrazine].[22] This compound reportedly decomposed at its melting point with the vigorous evolution of nitrogen. Decomposition in xylene solution yielded two identifiable products, 1,1,2,2-tetraphenylethane and diphenylmethane.[23]

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[1] This is the 27th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger, I. Tashlick, M. Bernstein and R. G. Hiskey, THIS JOURNAL, **80**, 6556 (1958).

[2] This paper comprises a portion of a thesis presented by Adolph V. DiGiulio in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] (a) H. C. Ramsperger, THIS JOURNAL, **49**, 912 (1927); (b) **50**, 714 (1928).

[4] (a) S. G. Cohen, S. J. Groszos and D. B. Sparrow, *ibid.*, **72**, 3947 (1950); (b) S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457 (1955).

[5] W. A. Schulze and H. L. Lochte, *ibid.*, **48**, 1030 (1926).

[6] G. Fodor and P. Szarvas, *Ber.*, **76B**, 334 (1943).

[7] L. D. Garrick, G. W. Drake and H. L. Lochte, THIS JOURNAL, **58**, 160 (1936).

[8] H. C. Ramsperger, *ibid.*, **51**, 2134 (1929).

[9] H. Wieland, A. Hintermaier and I. Dennstedt, *Ann.*, **452**, 1 (1927).

[10] S. G. Cohen and C. H. Wang, THIS JOURNAL, **77**, 3628 (1955).

[11] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 288.

[12] H. L. Lochte, W. A. Noyes and J. R. Bailey, THIS JOURNAL, **44**, 2556 (1922).

[13] K. A. Taipale and P. V. Usachev, *J. Russ. Phys.-Chem. Soc.*, **62**, 1241 (1930); *C. A.*, **25**, 2415 (1931).

[14] R. L. Hinman, THIS JOURNAL, **79**, 414 (1957).

[15] (a) C. G. Overberger and J. Lombardino, *ibid.*, **80**, 3009 (1958); (b) C. G. Overberger and I. Tashlick, unpublished results.

[16] S. G. Cohen, S. Hsiao, E. Saklad and C. H. Wang, THIS JOURNAL, **79**, 4400 (1957).

[17] (a) M. Busch, *Ber.*, **37**, 2691 (1904); (b) M. Busch and A. Rinck, *ibid.*, **38**, 1761 (1905).

[18] J. B. Ekeley and M. C. Swisher, *Rec. trav. chim.*, **48**, 1052 (1929).

[19] W. von Miller and J. Plöchl, *Ber.*, **31**, 2699 (1898).

[20] H. Franzen and W. Deibel, *ibid.*, **38**, 2716 (1905).

[21] M. Busch and M. Fleischmann, *ibid.*, **43**, 740 (1910).

[22] A. Darapsky, *J. prakt. Chem.*, [2] **67**, 112, 164 (1903).

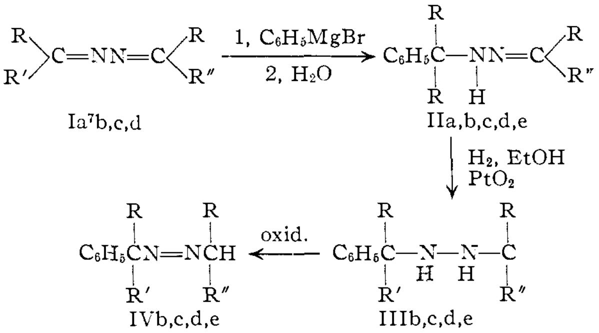
[23] Busch and Fleischmann[21] reported considerable difficulty in

The relative instability of these dibenzyl compounds when compared with a monobenzyl type is apparent, since benzaldehyde methylhydrazone $C_6H_5\overset{H}{\overset{|}{C}}{=}NNHCH_3$ required a temperature of 220–230° in the presence of base (Wolff–Kishner conditions) in order to eliminate nitrogen to give ethylbenzene and other products, presumably rearranging to the azo precursor which decomposed at the high temperature of the reaction.[24]

However, the fact that di-addition across both carbon–nitrogen bonds may occur is illustrated by the work of Bretschneider, *et al.*,[25] who obtained a nitrogeneous intermediate characterized as the symmetrical hydrazine $(p\text{-}CH_3OC_6H_5)(C_2H_5)(H)CNHNHC(H)(C_2H_5)(C_6H_5OCH_3\text{-}p)$, upon the treatment of anisaldehyde azine with an excess of ethylmagnesium bromide.

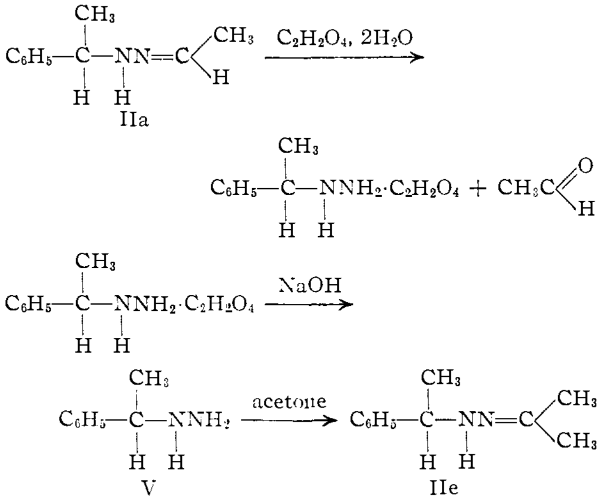
The reaction of acetone azine with methylmagnesium bromide[26] is the only reported reaction of the Grignard reagent with ketazines. Since the Grignard reaction was decomposed with acid, the intermediate hydrazone was not isolated but was hydrolyzed to give *t*-butylhydrazine and acetone directly.

The azo compounds reported in this paper were all synthesized according to the general scheme illustrated below, the necessary intermediates being the hydrazones II and the hydrazines III. Acetone α-phenylethylhydrazone (IIe) was prepared indirectly from acetaldehyde α-phenylethylhydrazone (IIa) and will be described separately.



Ia, IIa, R = CH_3, R′ = R″ = H; Ib, IIb, IIIb, IVb, R = R′ = R″ = CH_3; Ic, IIc, IIIc, IVc, R = R′ = R″ = C_2H_5; Id, IId, IIId, IVd, R = CH_3, R′ = R″ = *i*-C_4H_9; IIe, IIIe, IVe, R = R″ = CH_3, R′ = H

The reaction of phenylmagnesium bromide with the corresponding azine (I) in refluxing ether over a period of several days yielded the corresponding hydrazone II in varying yields, ranging from 36 and 39%, respectively, for acetone α-cumylhydrazone (IIb) and methyl isobutyl ketone α,α-methylisobutylbenzylhydrazone (IId) and about 60% for diethyl ketone α,α-diethylbenzylhydrazone (IIc). When phenyllithium was used in the reaction with acetone azine, the yield of hydrazone was only 20%. In all the organometallic reactions with acetone azine, some of the symmetrical hydrocarbon, 2,3-dimethyl-2,3-diphenylbutane always was isolated on distillation of the reaction mixture. Although none of the symmetrical hydrocarbons were isolated in the diethyl and methylisobutyl reactions, their presence in the residues is a possibility, although sterically their formation is much more unfavorable. The preparation of the hydrazone IIe is illustrated



After reaction of phenylmagnesium bromide with acetaldehyde azine and decomposition of the reaction mixture with saturated ammonium chloride, the reaction mixture could be distilled directly to give approximately a 30% yield of impure acetaldehyde α-phenylethylhydrazone (IIa) and a considerable amount of hydrocarbon, 2,3-diphenylbutane. The impure hydrazone when treated with oxalic acid hydrate in a 50–50 mixture of absolute alcohol and dry ether, gave an immediate precipitate of the oxalic acid salt of α-phenylethylhydrazine. This salt could be obtained directly by treating the ether solution of the Grignard reaction with the ethanolic ether solution of oxalic acid hydrate. Careful neutralization of the salt and distillation under vacuum in an atmosphere of nitrogen yielded the pure free base, α-phenylethylhydrazine (V). Condensation of this hydrazine with an excess of acetone under nitrogen in the presence of anhydrous magnesium sulfate afforded acetone α-phenylethylhydrazone (IIe) in good yields.[27]

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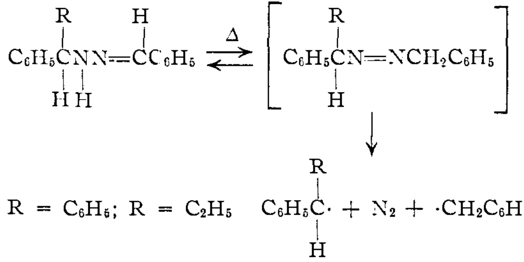
isolating the "normal" 1,2-mono-addition products. When the Grignard reagent was ethylmagnesium bromide, the only product identified was 3,4-diphenylhexane. They postulated the following mechanism to explain the results.



[24] D. Todd, THIS JOURNAL, **71**, 1356 (1949).

[25] H. Bretschneider, A. de Jonge-Bretschneider and N. Ajtai, *Ber.*, **74B**, 571 (1941).

[26] F. Klages, G. Nober, F. Kircher and M. Bock, *Ann.*, **547**, 1 (1941).

[27] The presence of hydrocarbon decomposition products, which invariably seem to be a side product of some of these Grignard reactions, may be accounted for by several possibilities. The first possibility is that some di-addition of the Grignard had occurred to give the symmetrical hydrazine, which auto-oxidized[9,25] in the "work-up" to give the symmetrical azo compound, the decomposition of which gives

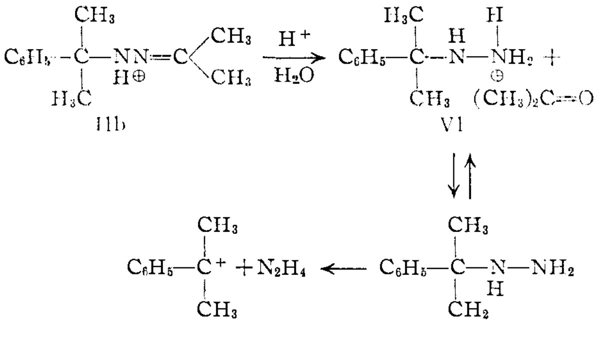
The ultraviolet spectra of the four hydrazones in the range 215 to 300 mμ are characterized by a plateau or shoulder in the 230 mμ region, ~6000. Examples of the ultraviolet spectra of this type of non-conjugated hydrazone are rare in the literature. However, Stevens, *et al.*, have reported a λ_{max} 229 mμ, ϵ 5200, for $n\text{-}C_6H_{13}CH_2CH{=}NNHCH(CH_2OCH_3)(CHOHCH_3)$ which was found to be quite comparable to a model compound ($C_6H_{13}C(CH_3){=}NNHCH_3$) with a λ_{max} 229 mμ, ϵ 5300.[28]

The absence of a definite maximum in this region for the four hydrazones reported here may be due to the interference of the K-band absorption of the phenyl ring (λ_{max} 198 mμ, ϵ 8000).[29]

An attempt to isolate the hydrazone derived from cyclohexanone azine was unsuccessful. Distillation of the mixture obtained from the reaction of phenyllithium with cyclohexanone azine only yielded what appears to be decomposition products along with unreacted azine. The initial distillation yielded two solid hydrocarbons, 1-phenylbicyclohexyl and 1,1-diphenylbicyclohexane[30,31] and 1-phenylcyclohexene along with the unreacted azine.

The behavior of the hydrazones toward acid hydrolysis was normal. All four hydrazones when treated with Brady reagent gave precipitates almost immediately. The derivatives obtained from the reaction with acetone α-cumylhydrazone and acetaldehyde α-phenylethylhydrazone were identified by their melting points and mixed melting points as the 2,4-dinitrophenylhydrazones of acetone and acetaldehyde, respectively. The derivatives from the diethyl and methylisobutyl hydrazone analogs were not characterized but were assumed to be the respective derivatives of diethyl ketone and methyl isobutyl ketone.

When acetone α-cumylhydrazone was treated with aqueous hydrochloric acid, an almost quantitative yield of hydrazine dihydrochloride was obtained and a liquid product, α-methylstyrene. A probable route to these products is shown.



If the α-cumylhydrazine (VI) is an intermediate in the acid hydrolysis its relative instability may be compared to the similarly structurally related compound, dimethylphenylcarbinol, which is easily dehydrated in the presence of acids, the driving force being the formation of the tertiary carbonium ion. In support of this suggestion, is the fact that Darapsky reported that heating benzhydrylhydrazine with aqueous hydrochloric acid yielded hydrazine and diphenylchloromethane.[22]

The hydrolysis of acetone α-cumylhydrazone and acetaldehyde α-phenylethylhydrazone to give the corresponding benzylhydrazine was effected by treating the respective hydrazones with a solution of oxalic acid hydrate in ethanol–ether solution. By this means the oxalic acid salts of α-cumylhydrazine and α-phenylethylhydrazine were immediately precipitated.

Benzylhydrazines, where the benzyl carbon is either secondary or tertiary, are relatively unknown. The free bases α-cumylhydrazine and α-phenylethylhydrazine were obtained by careful neutralization of their respective oxalate salts and distillation of the liquid bases under an atmosphere of nitrogen and reduced pressure.

Lochte[5] had prepared salts of α-phenylethylhydrazine from the crude base, obtained by the acid hydrolysis of 1-azo-bis-1-phenylethane, $C_6H_5(CH_3)(H)CN{=}NC(H)(CH_3)C_6H_5$. The melting point of the oxalic acid derivative corresponded to that reported in this paper. Huisgen[32] has also reported the preparation of both hydrazines, α-phenylethylhydrazine and α-cymylhydrazine in the crude state, by a saponification of the adducts obtained from the reaction of ethylbenzene and cumene, respectively, with ethyl azodicarboxylate.

Their reported melting point and reported analysis indicating a 1:1 ratio of α-phenylethylhydrazine to oxalic acid corresponded to the values reported by Lochte and this paper. However, their oxalic acid derivative of α-cumylhydrazine was reported to melt at 173–173.5° dec. and the analyses indicated the presence of a 2:1 ratio of the hydrazine to oxalic acid. It is probable that the reaction of organometallic compounds on azines may be a practical route to the preparation of these little studied hydrazines.

1,2-Dialkylhydrazines in which both alkyl groups are not identical are quite rare[14]; hydrogenation of the hydrazones obtained in the reaction of azines with the Grignard reagent in ethanol solution using a platinum oxide catalyst affords a convenient route to this class of compound. Fresh catalyst and freshly distilled hydrazones are essential for good yields.

The free bases 1-isopropyl-2-α-cumylhydrazine (IIIb) and 1-(3-pentyl)-2-α,α-diethylbenzylhydrazine (IIIc) were both obtained in pure state and characterized.

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the observed hydrocarbon. This process would be more favorable in the more reactive and less hindered acetaldehyde azine. A second possibility is a 1,4-addition of the elements of one equivalent of the Grignard reagent to the azine conjugated system to give the unsymmetrical azo compound directly. A third possibility which might lead to hydrocarbon products is that initially suggested by Busch and Fleischman, the isomerization of the hydrazone to the azo compound and subsequent decomposition thereof. The latter two possibilities would not explain the hydrocarbon formation in the acetaldehyde and acetone azine reaction since the unsymmetrical azo compounds in these two cases are stable enough to be distilled at low pressures. The latter possibility may be of importance, however, for the failure to obtain the hydrazone in the reaction of cyclohexanone azine with phenyllithium.

(28) C. L. Stevens, B. T. Gillis, J. C. French and T. H. Haskell, THIS JOURNAL, **78**, 3229 (1956).

(29) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold (Publishers), Ltd., London, 1954, chapter 9, p. 116.

(30) E. V. Heyningen, THIS JOURNAL, **74**, 4861 (1952).

(31) N. Kijner, *J. prakt. Chem.*, [2] **64**, 113 (1901)

(32) R. Huisgen, F. Jakob, W. Siegel and A. Cadus, *Ann.*, **590**, 1 (1954).

The conditions of oxidation of the various hydrazines varied somewhat according to structure. Although the oxidation of 1-isopropyl-2-α-cumylhydrazine in acetone–alcohol solution with 30% hydrogen peroxide at 0° proceeded quite smoothly to give an 85% yield of α-cumylazoisopropane (IVb), the procedure with the diethyl and methyl isobutyl compounds gave only partially oxidized material which evolved only 45–70% of gas on decomposition and the ultraviolet spectra of which indicated the presence of considerable impurity. It was found that the use of silver nitrate in an aqueous ethanol solution, unbuffered or buffered to a *p*H6 with sodium acetate, resulted in complete oxidation, the final purification being accomplished by high vacuum distillation. It also was found that both red or yellow mercuric oxide in ethanol gave quite analogous results. In the preparation of α-phenylethylazoisopropane (IVe) the neutral mercuric oxide in ethanol was used in order to minimize the possible isomerization to hydrazone which might occur in an acid medium.

The ultraviolet spectral data for the four azo compounds are summarized with other physical properties in Table I. Except for IVd, the absorption maximum is comparable to other aliphatic azo compounds. Cohen, *et al.*,[4a] have reported a λ_{max} of 355 mμ, log ϵ_{max} ~1.7, and a λ_{min} at ~300 mμ for a number of symmetrical benzyl-type azo compounds. It is not quite clear why the compound IVd exhibits such a large bathochromic shift to 370 mμ as compared to the other compounds.

Experimental[33]

Azines.—Acetone azine[1b] was prepared according to the procedure of Curtius[34]; 70%, b.p. 130–131°, $n^{24.5}$D 1.4512 (77%, b.p. 131°, $n^{24.5}$D 1.4510).[34]

Diethyl ketazine (Ic) was prepared quite similarly to acetone azine except that initially the ketone was dissolved in ethanol and the hydrazine solution was added in the course of 40 minutes; 77%, b.p. 83–84° (11 mm.), b.p. 197° (760 mm.), $n^{25.5}$D 1.4567 (66%, b.p., 92° (12 mm.), 190–195° (760 mm.)[34]; (b.p. 196–197° (762 mm.), 82° (11 mm.), n^{20}D 1.4574[13]).

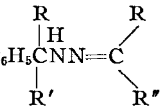
Methyl isobutyl ketazine (Id) was prepared according to a general procedure described in a patent[35] whereby benzene was utilized to remove water as an azeotrope over a period of several days; 85%, b.p. 220–221°, $n^{25.5}$ D 1.4553 (b.p. 101–103° (16 mm.), n^{26}D 1.4538[36]).

Acetaldehyde azine (Ia) was prepared according to the procedure of Curtius,[37] except that liquid extraction with ether of the aqueous layer over a period of several days was utilized to increase the yield; b.p. 96–97°, n^{25}D 1.4450 (no yield, b.p. 95–96°[37]).

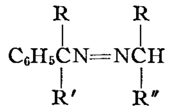
General Synthesis of the α,α-Dialkylbenzylhydrazones (IIb,c,d).—Compounds IIb,c,d were all prepared in the same manner. To a stirred and refluxing 2.1 molar solution of phenylmagnesium bromide in 1600 ml. of anhydrous ether was added 1.0 mole of azines (Ib,c,d) in 300 ml. of anhydrous ether in approximately 50–90 minutes. At times in the acetone azine reaction the stirrer was stopped due to the viscous complex which formed. Stirring and refluxing was continued from 3–5 days, after which the reaction mixture was decomposed with approximately 350 ml. of cold saturated ammonium chloride solution, while cooling in an

TABLE I

PHYSICAL PROPERTIES OF THE α-ALKYLBENZYLHYDRAZONES (II) AND THE α-ALKYLBENZYLAZOALKANES (IV)


$C_6H_5C(R)(R')NHN{=}C(R)(R'')$

II


$C_6H_5C(R)(R')N{=}NCH(R)(R'')$

IV

Compound	Yield, %	B.p. °C.	B.p. Mm.	n^{25}D	d^{25}_4	*MR*D[e] Calcd.	*MR*D[e] Obsd.	λ_{max}, mμ	log ε	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Calcd. N	Analyses, % Found C	Analyses, % Found H	Analyses, % Found N
	36[a]														
IIb R = R′ = R″ = CH_3	19.5[b]	84	0.6	1.5226	0.9634	60.59	60.30	~231[f,g]	3.71	75.74	9.53	14.73	75.95	9.62	14.65
IVb		50–51	0.6	1.4919	.9093	60.40	60.70	357[h]	1.47	75.74	9.53	14.73	75.79	9.37	14.79
IIc R = R′ = R″ = C_2H_5	61[a]	110–111	1.4	1.5102	.9292	79.02	79.33	~231[f,g]	3.78	77.99	10.64	11.37	77.96	10.88	11.20
IVc		50–55[d]	10^{-4}	1.4956	.9159	78.84	78.53	370[f]	1.48	77.99	10.64	11.37	78.24	10.48	11.43
IId R = CH_3	39[a]	110	0.5	1.5010	.9115	88.31	88.71	~228[f,g]	3.79	78.77	11.02	10.21	78.79	10.90	10.46
IVd R′ = R″ = *i*-C_4H_9		60[d]	10^{-4}–10^{-5}	1.4851	.8911	88.13	88.28	363[f]	1.47	78.77	11.02	10.21	78.80	10.89	10.31
IIe R = R″ = CH_3	78[c]	81.5	0.85	1.5296	.9672	55.95	56.26	~227[f,g]	3.82	74.95	9.15	15.90	75.15	9.41	15.68
IVe R′ = H		48	0.5	1.4917	.9100	55.77	56.17	354[f]	1.55	74.95	9.15	15.90	74.84	8.96	15.62

[a] Yield from Grignard reaction. [b] Yield from phenyllithium reaction. [c] Yield based on condensation of acetone with α-phenylethylhydrazine. [d] Bath temperature. [e] Calculated on the basis of data from Garrick, Drake and Lochte.[7] [f] In absolute methanol. [g] The value listed is the slope where the rate of change is the smallest. [h] In 95% ethanol.

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[33] All melting points are corrected. Analyses by Dr. Schwarzkopf, Woodside, N. Y., and Dr. K. Ritter, Basel, Switzerland.

[34] T. Curtius and K. Thun, *J. prakt. Chem.*, [2] **44**, 161 (1891).

[35] A. O. Rogers, U. S. Patent Appl. 60,625, *Official Gaz.*, **635**, 653 (1950); *cf. C. A.*, **45**, 9075*d* (1951).

[36] C. G. Overberger and M. Berenbaum, THIS JOURNAL, **73**, 2618 (1951).

[37] T. Curtius and E. Zinkeisen, *J. prakt. Chem.*, [2] **58**, 310 (1898).

ice-bath. The ether layer was separated and the magnesium salts were extracted twice with 300-ml. portions of anhydrous ether. Distillation of the residue under nitrogen at reduced pressure through an 18-inch spiral column after the removal of solvent gave the corresponding yellow hydrazones, the properties of which are listed in Table I. The infrared spectra of IIb and IId are characterized principally by a weak NH stretching absorption at 3.10 μ. This band is lacking in IIc. Whereas IIb exhibits a weak C=N stretching vibration at 6.10 μ, this band is only observed as a weak shoulder at 6.15 μ on the phenyl absorption at 6.22 μ for the hydrazones IIc and IId. Refractionation of the hydrazones IIc and IId gave the pure hydrazones. However, IIb ordinarily contained some biphenyl which appeared to distil in the same temperature range as the hydrazone and which is extremely difficult to remove. A pure sample of IIb, however, was obtained by refractionation of a fraction which was already low in biphenyl content. In reaction IIb, after the removal of the hydrazone fractions, some symmetrical hydrocarbons 2,3-dimethyl-2,3-diphenylbutane, m.p. 118–119°, sublimed in the temperature range 115–135° or partially crystallized out of the fraction collected in this range, as well as from the undistilled residue. A mixed melting point with 2,3-dimethyl-2,3-diphenylbutane prepared from α-chlorocumene and lithium,[38,39] m.p. 117–118°, melted at 118–119°.

Acetone azine also was allowed to react in the same molar proportions with phenyllithium; the yields here, however, were much lower, approximately 20%.

Addition of a few drops of the hydrazones to freshly prepared Brady reagent gave immediate precipitates. The derivative from the acetone analog melted at 125–126°, a mixed melting point with the 2,4-dinitrophenylhydrazone of acetone, m.p. 125–126°, melted at 125–126°.

To 1.6 g. of acetone α-cumylhydrazone was added 25 ml. of 6 *N* hydrochloric acid. A slight temperature rise occurred and the solution became cloudy. After standing for 1.5 hr., the solution was extracted twice with 20-ml. portions of ether. The aqueous layer was evaporated to 4–5 ml. of a yellow solution, and upon cooling a white crystalline solid immediately formed. Ethanol (15 ml.) was added, and the cooled solution was filtered giving 0.6 g. of white crystalline solid, m.p. 199°; a mixed melting point with hydrazine dihydrochloride, m.p. 198° melted at 198°. Addition of ether to the yellow ethanol solution yielded an additional 0.12 g. of solid. The ether extracts yielded 0.35 g. of a liquid, micro b.p. 159°, $n^{26.5}$D 1.5353, which decolorized a bromine–chloroform solution. These properties are consistent for α-methylstyrene (b.p. 159–160°, n^{22}D 1.5350)[40]; (b.p. 50° (8 mm.), n^{25}D 1.5357[41]).

α-Phenylethylhydrazine (V).—To a 1.33 molar solution of phenylmagnesium bromide in 990 ml. of anhydrous ether was added 100 g. (1.19 moles) of acetaldehyde azine in 350 ml. of dry ether at a rate which maintained a good reflux. After stirring overnight, decomposition with 185 ml. of saturated ammonium chloride solution while cooling, and removal of the ether, the yellow orange liquid was distilled under nitrogen through an 18-inch spiral column, the impure light yellow acetaldehyde α-phenylethylhydrazone (IIa), 95 g., being collected at 96–98° (2.7 mm.) in two fractions, $n^{25.7}$D 1.5346–1.5387. The remaining material, b.p. 98–145° (1.4 mm.), was not characterized, but considerable solid, m.p. 124°, formed in these latter fractions as well as in the residue. This melting point corresponded to the melting point reported for 2,3-diphenylbutane, m.p. 123.5.[5] No attempt was made to purify the hydrazone. Addition of a few drops of the impure hydrazone to Brady reagent gave an immediate precipitate, m.p. 165–167° on recrystallization from ethanol. A mixed melting point with the 2,4-dinitrophenylhydrazone of acetaldehyde, m.p. 166–168°, melted at 165–167°. The yield of hydrazone based on the amount of oxalate formed was 25% (see procedure A below). Two procedures were employed to prepare the oxalate derivative of α-phenylethylhydrazine.

Procedure A.—A solution of oxalic acid hydrate (48 g., 0.382 mole) in 150 ml. of commercial absolute ethanol, to which was added 150 ml. of anhydrous ether, was treated with 38 g. of impure acetaldehyde α-phenylethylhydrazone. Considerable solid formed in a few minutes. After standing for 16 hours, 38 g. (0.168 mole) of white solid was removed by filtration and washed with ether, m.p. 163–168°. Recrystallization of 0.5 g. from 50 ml. of hot ethanol gave m.p. 170–171° (m.p. 172° dec., from acid hydrolysis of azobis-α-phenylethane[5]); 61%, m.p. 169–170° from adduct. On the basis of the yield of the oxalate, approximately 0.3 mole of hydrazone had been formed in the reaction of the azine with the Grignard.

Procedure B.—The reaction of phenylmagnesium bromide (1.41 moles) with 107 g. (1.27 moles) of acetaldehyde azine was repeated. After decomposition with a saturated ammonium chloride solution, 4180 ml. of clear yellow ether solution was separated from the magnesium salts by filtration. To a solution of 126 g. (1.0 mole) of oxalic acid hydrate in 470 ml. of absolute ethanol was added 740 ml. of the above ether solution. In a few minutes considerable solid had formed and, after standing overnight, the precipitate was removed by filtration and washed thoroughly with ether giving 37.3 g. of white solid, m.p. 156–158°. Recrystallization of 0.5 g. from hot ethanol gave m.p. 170–171°. Treatment of the remaining ether solution in the same manner yielded an additional 45 g. of solid; total yield of the crude oxalate of α-phenylethylhydrazine was 82.3 g. (29%). To a solution of 50 g. (0.89 mole) of potassium hydroxide in 450 ml. of water, was added in portions 108 g. (approximately 0.48 mole) of the crude oxalate derivative until solution was complete. After removing some potassium oxalate by filtration from the saturated solution, two layers were present. Approximately 200 ml. of benzene was added and the organic layer was separated. The aqueous layer was extracted twice more with 200 ml. of benzene, and the benzene solution was dried over anhydrous sodium carbonate. The benzene solvent was removed under an atmosphere of nitrogen and reduced pressure, and the residue distilled through a 10-inch spiral column under nitrogen, the free base α-phenylethylhydrazine being collected at 75° (1.1 mm.), 36 g. (55%) as colorless liquid, n^{25}D 1.5435. Redistillation of this fraction gave a b.p. 69° (0.8 mm.), n^{25}D 1.5436. The density was not obtained due to the constant formation of bubbles in the liquid when exposed to the air.[12] The infrared spectrum was indicated by an NH stretching vibration frequency at 3.06 μ.

Anal. Calcd. for $C_8H_{12}N_2$: C, 70.54; H, 8.88; N, 20.57. Found: C, 70.70; H, 8.99; N, 20.77.

α-Cumylhydrazine (VI).—The oxalic acid salt of α-cumylhydrazine was obtained in 84% yield (42 g.) as a white fluffy solid, m.p. 114–117°, by the addition of 43 g. (0.21 mole) of impure acetone α-cumylhydrazone in 30 ml. of anhydrous ether to an absolute ethanol–anhydrous ether (150 ml. of each) solution of 48 g. (0.38 mole) of oxalic acid hydrate. An analytical sample was prepared by dissolving a small amount of the solid in ethanol, adding methylene chloride dropwise until just turbid, then cooling. Very fine, small crystals formed slowly, m.p. 113–113.5°, when the rate of heating was very slow (1° per 5 minutes).

Anal. Calcd. for a 1:1 ratio of the hydrazine to the oxalic acid, $C_{11}H_{16}N_2O_4$: C, 54.99; H, 6.71; N, 11.66. Found: C, 54.88; H, 6.61; N, 11.83. (Huisgen[32] reported an oxalate containing a 2:1 ratio of the hydrazine to oxalic acid, m.p. 173–173.5° dec., obtained from an adduct of cumene and ethylazodicarboxylate.)

After the addition of 42 g. (0.175 mole) of the oxalate of α-cumylhydrazine to 26 g. (0.45 mole) of potassium hydroxide in 200 ml. of water, the solution was saturated with sodium chloride after the addition of 50 ml. more of water, and extracted with four 110-ml. portions of ether and dried over anhydrous sodium carbonate. After removal of the solvent and distillation under nitrogen through a 10-inch spiral column, 17.0 g. (65%) of water-white liquid was obtained, b.p. 72–73° (0.6 mm.), $n^{25.5}$D 1.5415. The infrared spectrum showed a medium NH absorption at 3.06 μ.

Anal. Calcd. for $C_9H_{14}N_2$: C, 71.96; H, 9.39; N, 18.65. Found: C, 72.07; H, 9.30; N, 18.72.

The picrate, a crystalline yellow solid, m.p. 136.5–137°, was obtained by the addition of a few drops of the free base to a saturated solution of picric acid in anhydrous ether.

Anal. Calcd. for $C_{15}H_{17}N_5O_7$: C, 47.49; H, 4.52; N, 18.47. Found: C, 47.68; H, 4.47; N, 18.67.

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[38] F. Runge, "Organometallverbindungen," Stuttgart, 1944, p. 30.

[39] I. I. Lapkin and A. V. Lyubimova, *Zhur. Obshchei Khim.* (*J. Gen. Chem.*), **18**, 701 (1948); *cf. C. A.*, **43**, 188¹ (1949).

[40] S. Sabetay, *Bull. soc. chim.*, [4] **47**, 614 (1930).

[41] C. G. Overberger, L. H. Arnold and J. J. Taylor, THIS JOURNAL, **73**, 5541 (1951).

Acetone α-Phenylethylhydrazone (IIe).—To 110 ml. of acetone and 5 g. of anhydrous magnesium sulfate was added 14 g. (0.103 mole) of α-phenylethylhydrazine in 2–3 minutes under an atmosphere of nitrogen. The reaction mixture was heated to 40–45° with stirring for 2 hours and without stirring for an additional 12 hours, under an atmosphere of nitrogen. After removal of the magnesium sulfate by filtration, the solvent was distilled under nitrogen through a spiral column at atmospheric pressure until the residual volume was 25 ml. The residual solvent was removed under reduced pressure and the residue distilled under nitrogen through a 10-inch spiral column, giving 14.1 g. (78%) of a slightly yellow tinted liquid, b.p. 81.5° (0.85 mm.), $n^{25}\text{D}$ 1.5296, d^{25}_{4} 0.9672. The infrared spectrum showed a weak NH absorption at 3.08 μ and a weak C═N absorption at 6.13 μ (Table I).

Hydrogenation of the Hydrazones (IIb,c,d,e). 1-Alkyl-2-benzylhydrazines (IIIb,c,d,e).—The freshly distilled hydrazones (IIb,c,d,e) all were conveniently hydrogenated in commercial absolute ethanol using a Parr apparatus and platinum oxide catalyst. With 1.0 g. of catalyst to approximately 0.1 mole of hydrazone, the uptake of hydrogen ceased after the addition of one equivalent, and usually required about 24 hours for compounds IIb and IIc and from 2–5 days for IIId and IIIe.

1-Isopropyl-2-α-cumylhydrazine (IIIb).—After the removal of catalyst by filtration, a hydrogenated colorless solution of 25 g. (0.118 mole) of acetone α-cumylhydrazone (IIb) in 100 ml. of ethanol was added to a 550-ml. solution of ethanol containing 38 g. (0.15 mole) of picric acid. Considerable precipitate formed in a few minutes and after standing overnight in the freezer, the picrate was removed by filtration and washed with two 50-ml. portions of anhydrous ether, 35 g. (71%), m.p. 146–149° dec. A small portion of the picrate was recrystallized twice from absolute ethanol, m.p. 149–150° dec.

Anal. Calcd. for $C_{18}H_{23}N_5O_7$: C, 51.30; H, 5.50; N, 16.62. Found: C, 51.56; H, 5.38; N, 16.42.

A solution of 35 g. (0.87 mole) of sodium hydroxide in 500 ml. of water was added to a heterogeneous mixture of 69 g. (0.164 mole) of the picrate, m.p. 146–149°, in 1800 ml. of water with vigorous stirring, total solution being effected by warming on the steam-bath to 40°. An oily layer formed on the surface of the dark red solution. The mixture was extracted with two 200-ml. portions of ether, which in turn was washed twice with 200-ml. portions of water and dried over anhydrous magnesium sulfate. After the removal of the ether solvent under nitrogen and reduced pressure, the 31 g. of the light yellow residue was distilled through a 10-inch center tube column under nitrogen to give 26 g. (83%) of a colorless oil, b.p. 61° (0.5 mm.), $n^{25.5}\text{D}$ 1.5040, d^{25}_{4} 0.927. The infrared spectrum showed a weak but sharp NH absorption at 3.1 μ.

Anal. Calcd. for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48; N, 14.57. Found: C, 74.89; H, 10.50; N, 14.86.

1-(3-Pentyl)-2-α,α-diethylbenzylhydrazine (IIIc).—After the removal of the ethanol solvent under reduced pressure and an atmosphere of nitrogen from a hydrogenated solution of 51.5 g. (0.209 mole) of diethyl ketone α,α-diethylbenzylhydrazone (IIc), the residue was distilled through a 10-inch spiral column under nitrogen. The distillation initially was characterized by excessive foaming and bubbling, which probably was due to decomposition of the corresponding azo compound, which may be present due to some air oxidation. The hydrazine fractions, 44.5 g. (81%), were collected at 110° (1.0 mm.), $n^{25}\text{D}$ 1.5012, d^{25}_{4} 0.9206. The infrared spectrum showed a weak but sharp NH absorption at 3.1 μ. A sample of a water-white fraction was submitted for analysis.

Anal. Calcd. for $C_{16}H_{28}N_2$: C, 77.36; H, 11.36; N, 11.28. Found: C, 77.71; H, 10.99; N, 11.49.

A picrate of the hydrazine was prepared by adding a few drops of the free base to a saturated picric acid solution in anhydrous ether. The orange-yellow crystals appeared to be hygroscopic to a certain extent and required extensive drying after recrystallization from hot methanol. After three recrystallizations and drying under vacuum for 4 days at 55°, the picrate gave a m.p. 108.8–109.2°.

Anal. Calcd. for $C_{22}H_{31}N_5O_7$: C, 55.33; H, 6.55; N, 14.67. Found: C, 55.04; H, 6.57; N, 14.72.

The free base also could be obtained in a manner analogous to the preparation of 1-isopropyl-2-α-cumylhydrazine (IIIb) by first preparing the picrate, m.p. 105–108° (89% yield), neutralization, and distillation of the residue.

1-[2-(4-Methylpentyl)]-2-α,α-methylisobutylbenzylhydrazine (IIId).—After the hydrogenation of 51.7 g. (0.188 mole) of the hydrazone IId, and the removal of the catalyst and ethanol solvent, distillation through an 18-inch spiral column yielded a fraction, 40 g., b.p. 110° (0.35 mm.), $n^{26.5}\text{D}$ 1.4956, of a light yellow-green liquid.

The picrate of the hydrazine was prepared by the addition of 1.67 g. of the hydrazine to 100 ml. of a saturated solution of picric acid in anhydrous ether. The first crystals appeared in 45 minutes and, after 24 hours, 0.93 g. (30%) of fine orange-yellow crystals was obtained. Recrystallization from a solvent mixture of methylene chloride and ether gave a m.p. 122.6–123.4°.

Anal. Calcd. for $C_{24}H_{35}N_5O_7$: C, 57.01; H, 6.98; N, 13.86. Found: C, 57.28; H, 6.98; N, 13.90.

α-Cumylazoisopropane (IVb).—In a mixture of acetone (250 ml.) and ethanol (175 ml.) was dissolved 16 g. (0.083 mole) of 1-isopropyl-2-α-cumylhydrazine and the reaction mixture cooled to 0°. In the course of 15 minutes, 30 g. of 30% hydrogen peroxide was added with stirring, the temperature rising to 7°. The reaction mixture was allowed to stand in the freezer for two days. The solution was concentrated to approximately 35 ml., yielding a two-phase, cloudy liquid mixture, to which was added 250 ml. of water. This mixture was extracted with two 100-ml. portions of petroleum ether (b.p. 38–47°) which was washed with water and dried over anhydrous magnesium sulfate. The volume of this solution was concentrated to 25 ml. by evaporation on the steam-bath, the residual solvent being removed under vacuum. Distillation of the residue under nitrogen through an 8-inch center tube column yielded 13.5 g. (85%) of a clear yellow oil, b.p. 50–51° (0.6 mm.), $n^{25}\text{D}$ 1.4919, d^{25}_{4} 0.9093 (Table I).

α,α-Diethylbenzylazo-3-pentane (IVc). (A) **Silver Nitrate Oxidation.**—In 195 ml. of water was dissolved 14 g. (0.082 mole) of silver nitrate, to which was added 115 ml. of ethanol. To this was added 9.0 g. (0.036 mole) of water-white 1-(3-pentyl)-2-α,α-diethylbenzylhydrazine (IIIc) in a 1-liter flask at room temperature. The flask was shaken manually and almost immediately the sides of the flask became partly silvered and coated with splotchy greenish-gray solid, and in a few more minutes the gray solid began separating from the sides of the flask. Shaking was continued manually for 35 minutes, after which the solid from the solution, *p*H 3–4, was removed by filtration and washed with ether. The solid was washed very thoroughly with 50 ml. of ether since organic material is adsorbed on the solid, and then an additional 250 ml. of water was added to the ether–ethanol–water filtrate and the whole mixture extracted twice with 100-ml. portions of ether. The yellow ether extracts were washed twice successively with water, 10% potassium carbonate solution, water and dried over anhydrous sodium sulfate. After concentrating the solution to 15 ml. on the steam-bath, the residual solvent was removed under reduced pressure, and the yellow liquid residue was subjected to a vacuum for 3 hours at 1 mm.; 3.8 g. of yellow oil, $n^{24.8}\text{D}$ 1.4950.

The originally clear mother liquor on standing 24 hours formed considerably more silver, the solution changing to a *p*H 1–2. This solution was worked up in precisely the same manner as the original solution yielding an additional 3.0 g. of yellow oil. The 6.8 g. of yellow oil was distilled at 10^{-4} mm. using a bath temperature of 50–55°, yielding four identical fractions totaling 6.04 g. (67%) of a clear yellow oil, $n^{25}\text{D}$ 1.4956, d^{25}_{4} 0.9159.

(B) **Mercuric Oxide Oxidation.**—Freshly redistilled hydrazone IIc (9.0 g. 0.0364 mole) dissolved in 30 ml. of ethanol was hydrogenated in the usual manner. The ethanolic hydrazine solution was filtered into a flask, cooled by an ice–water-bath equipped with a magnetic stirrer. Red mercuric oxide (25 g., 0.115 mole) was added and stirring was continued for 24 hours, in which time the reaction mixture was allowed to come to room temperature. The mercuric oxide had turned a gray-green. Stirring was halted, and the reaction mixture was allowed to stand for several days, after which the solution was filtered through two fluted filter papers in order to remove the mercuric oxide as completely as possible. The solvent was removed as described above, and the yellow oil residue, $n^{25}\text{D}$ 1.4958, was distilled at 10^{-4} to 10^{-5} mm. using a bath temperature of 70° over a period of 8 hours, giving 6.66 g. (74% of product), n^{23}_{D} 1.4965.

α,α-Methylisobutylbenzylazo-2(4-methylpentane) (IVd). (A) **Silver Nitrate Oxidation.**—The hydrazine IIId was oxidized with silver nitrate as described above, except that the reaction mixture was worked up after only 4 hours of shaking. From 28.8 g. (0.114 mole) of distilled hydrazine was obtained 13.95 g. (49%) of yellow oil, n^{25}_{D} 1.4851, d^{25}_{4} 0.8911, the distillation being effected over a period of 2.5–3.5 days at 10^{-4} to 10^{-5} mm. using a bath temperature of 50–65°.

Silver nitrate oxidation of undistilled hydrazine in ethanol solution gave similar results, under the same conditions, the yield of azo compound being 62%.

(B) **Mercuric Oxide Oxidation.**—The oxidation was carried out in the manner described for preparing IVc. High vacuum distillation yielded 72% of the azo compound.

α-Phenylethylazoisopropane (IVe).—The oxidation was carried out in the manner described for preparing IVc except that yellow mercuric oxide was used, and the solids were removed by filtration after stirring for only 4.5 hours. From 10.33 g. (0.058 mole) of acetone α-phenylethylhydrazone, which was hydrogenated and oxidized, was obtained 6.75 g. of green liquid residue. Distillation through an 8-inch center tube column gave 4.9 g. (49%) of a yellow liquid, b.p. 48° (0.5 mm.), n^{25}_{D} 1.4917, d^{25}_{4} 0.9100.

Cyclohexanone azine was prepared according to the procedure of Perkin and Plant[42] in 88% yield, m.p. 34.5–35.5°, b.p. 116° (3-4 mm.), n^{26}_{D} 1.5250 (77%, m.p. 33°).[42]

Reaction of Cyclohexane Azine and Phenyllithium. 1-Phenylbicyclohexyl and 1,1-Diphenylbicyclohexyl.—After stirring for 24 hours, the reaction mixture from 65 g. (0.34 mole) of cyclohexanone azine in 225 ml. of anhydrous ether and a 0.72 molar solution of phenyllithium in 550 ml. of ether gave 94 g. of brownish-red viscous oil, the solvent being removed under nitrogen and reduced pressure. Distillation under nitrogen gave five fractions and a residue, 13.2 g., ether soluble: fraction I, 17 g., b.p. 76–115° (1.5–3.2 mm.), $n^{23.8}_{D}$ 1.5346; fraction II, 7.5 g., b.p. 120–151° (2.0–5 mm.); fraction III, 13 g., b.p. 145–147° (2.0–5 mm.), $n^{23.2}_{D}$ 1.5410; fraction IV, 11.5 g., b.p. 146–151° (2.2–3 mm.), n^{26}_{D} 1.5476; fraction V, 4.8 g., b.p. 160–180° (3 mm.), liquid and solid.

Fraction I (17 g.), which gave a positive Brady test, was added to a saturated sodium bisulfite solution composed of 80 g. of sodium bisulfite, 120 g. of water and 30 ml. of ethanol, with stirring. The solid, 11.5 g., which formed was filtered by suction after 0.75 hr., and washed with ether. The filtrate was extracted with ether until the ether layer was no longer yellow, and dried over magnesium sulfate. Removal of the solvent left 9.5 g. of yellow-red liquid, which gave a negative Brady test. Distillation under nitrogen through a center tube column gave 6 g. of colorless material, in several fractions, b.p. 65–84° (3–5 mm.), $n^{23.5}_{D}$ 1.5232–n^{24}_{D} 1.5454, giving a negative test for nitrogen, but decolorizing a bromine–chloroform solution. The boiling point of one of the fractions was 245° (760 mm.). These properties are consistent for a mixture of phenylcyclohexane[30,43] (b.p. 83–85° (4.5 mm.)[30]; b.p. 239° (750 mm.), n^{18}_{D} 1.5274[43]) and 1-phenylcyclohexene-1[44,45] (b.p. 251–253[44]; 128° (16 mm.), n^{20}_{D} 1.5695[45]).

Successive redistillation of the combined fractions II, III and IV gave 12.3 g. of light yellow, constant boiling and constant refractive index material in 4 cuts, b.p. 147° (2.5 mm.), n^{25}_{D} 1.4561. The elemental analyses for this material indicated the sample to be most probably a mixture of 1-phenylbicyclohexyl and 10% cyclohexanone 1-phenylcyclohexylhydrazone (or possibly 7.1% cyclohexanone azine). The addition of 2 g. of the final distilled material to 5 ml. of acetone with vigorous stirring, while cooling in an ice-bath, gave an amorphous white solid, 1.5 g., m.p. 38–42°. Recrystallization from acetone, by standing overnight in the freezer, yielded 1.3 g. of fibrous looking white solid, m.p. 45–46°, which is believed to be 1-phenylbicyclohexyl. Purification also could be effected by sublimation of the initial crude solid.

Anal. Calcd. for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 88.82; H, 11.01.

From fraction V was filtered approximately 2.0 g. of white solid. Recrystallization from ethanol gave a beautiful crystalline white solid, 1,1-diphenylbicyclohexyl, 1.65 g., m.p. 183–183.5° (m.p. 178–178.5° uncor., from acyloin condensation of ethyl 1-phenylcyclohexanecarboxylate[30]).

Anal. Calcd. for $C_{24}H_{30}$: C, 90.5; H, 9.5. Found: C, 90.8; H, 9.29.

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(42) W. H. Perkin, Jr., and S. G. P. Plant, *J. Chem. Soc.*, **125**, 1503 (1924).

(43) H. Gelissen and P. H. Hermans, *Ber.*, **59**, 662 (1926).

(44) P. E. Verkade, J. Coops, Jr., C. J. Maan and A. Verkade-Sandbergen, *Ann.*, **467**, 217, 232 (1928).

(45) S. Nametkin and N. Iwanoff, *Ber.*, **56**, 1805 (1923).

BROOKLYN 1, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

Three-membered Rings. The Preparation of Some 1,2-Cyclopropanedicarboxylic Acids

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The base condensation of an α-halo-ester with an α,β-unsaturated ester leads to 1,2-cyclopropanedicarboxylic acid diesters; subsequent saponification gives the diacids. Two general procedures for the preparation of the diesters are described, one using sodium methoxide and the other sodium hydride in oil. The mixtures of stereoisomers obtained are unusual in that the less stable (*cis*) isomer is often the major component.

In connection with some other work on three-membered rings, both of the isomers of 1,2-cyclopropanedicarboxylic acid were required in considerable quantity. These acids have been prepared in a variety of ways,[2] the various procedures being examples of some of the general methods for the preparation of cyclopropane compounds.[3]

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(2) (a) E. Buchner and A. Papendieck, *Ann.*, **273**, 232 (1892); (b) C. K. Ingold, *J. Chem. Soc.*, **119**, 305 (1921); (c) W. H. Perkin, *ibid.*, **87**, 358 (1905); (d) M. Conrad and M. Guthzeit, *Ber.*, **17**, 1186 (1884); (e) E. Buchner, *ibid.*, **23**, 703 (1890); (f) H. von Pechmann, *ibid.*, **27**, 1891 (1894); (g) K. B. Wiberg, R. K. Barnes and J. Albin, THIS JOURNAL, **79**, 4994 (1957).

(3) With the exception of the recently discovered techniques involving the addition of carbenes to olefins, a summary of these methods is given in "Chemistry of Carbon Compounds," E. H. Rodd, editor, Elsevier Publ. Co., Amsterdam, the Netherlands, 1953, Vol. IIa, pp. 23–25. The carbene method apparently is of too recent origin to have been reviewed; references to its use are somewhat scattered.