to compare either directly the rate of chain initiation or at least the rate of inhibitor disappearance in a styrene solution of a strong polymerization inhibitor, with the rate of thermal initiation of chains in the absence of inhibitor. In every case there appears to be greatly increased thermal chain initiation in the presence of the inhibitor. The explanation of this increased rate of initiation cannot be the same in all cases. For example, the fast initiation by iodine is known to lead to β-iodo-α-phenylethyl radicals,[24–26] while a similar first radical in the case of sulfur does not seem reconcilable with the quantitative study of the products.[27] There is enough quantitative divergence indicated in the third column of Table V to indicate that if interception of diradicals is the explanation in one case (Ref. *a*, Table V) it is not so in all cases. However, it can be seen that all these inhibitors are excellent hydrogen-atom acceptors, and in the absence of a still easier mechanism these substances might be able to take the place of the third styrene molecule in the initiation process. A number of these inhibitors have been used successfully to determine the rate of chain initiation by peroxides and azo compounds, but they are inherently and probably quite generally unsuitable for the counting of thermally initiated chains because of their possible participation in the initiation process.

TABLE V

"INITIATION" BY STRONG INHIBITORS IN THE POLYMERIZATION OF STYRENE

Inhibitor *Z*	Temp., °C.	$-d(Z)/dt$ / R_i	Ref.
DPPH	60	85	[a]
Benzoquinone	60	61	
	100	21	[a,b]
Sulfur	80.9	22	[c]
Oxygen	50	38[g]	[d,f]
Iodine	25	$\sim 10^5$	[e]

[a] K. E. Russell and A. V. Tobolsky, THIS JOURNAL, **75**, 5052 (1953). [b] J. W. and H. L. Breitenbach, *Z. physik. Chem.*, **A190**, 361 (1942). [c] P. D. Bartlett and D. S. Trifan, *J. Polymer Sci.*, **20**, 472 (1956). [d] A. A. Miller and F. R. Mayo, **78**, 1017 (1956). [e] G. Fraenkel, Thesis, Harvard Univ., 1957. [f] F. R. Mayo and R. A. Gregg, THIS JOURNAL, **70**, 1284 (1948). [g] This figure represents the relative rates of thermal *initiation* with and without oxygen, estimated directly by comparison of rates of polymerization and oxidation in the presence and absence of AIBN.

We gratefully acknowledge a grant from the National Science Foundation, and fellowships at different times from the National Science Foundation and from the National Institutes of Health, to R.R.H.

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[24] D. S. Trifan, Thesis, Harvard University, 1949.

[25] G. Fraenkel, Thesis, Harvard University, 1957.

[26] P. D. Bartlett and G. Fraenkel, forthcoming publication.

[27] P. D. Bartlett and D. S. Trifan, *J. Polymer Sci.*, **20**, 472 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Formation and Certain Condensations of the Dicarbanions of Dibenzyl Ketone and Dibenzyl Sulfone by Means of Potassium Amide in Liquid Ammonia[1,2]

BY CHARLES R. HAUSER AND THOMAS M. HARRIS[3]

RECEIVED SEPTEMBER 10, 1958

Both the α- and α'-hydrogens of dibenzyl ketone were ionized by means of two molecular equivalents of potassium amide in liquid ammonia to form a red dicarbanion. This dicarbanion underwent exclusive monobenzylation with one equivalent of benzyl chloride and dibenzylation, with two equivalents of this halide. It underwent almost quantitative conjugate addition to ethyl cinnamate. The monocarbanion of dibenzyl ketone gave a mixture of products with an equivalent of benzyl chloride and failed to react with ethyl cinnamate under the conditions used with the dicarbanion. Both the α- and α'-hydrogens of dibenzyl sulfone were ionized by means of two equivalents of potassium amide in liquid ammonia to form a pale yellow dicarbanion. This dicarbanion underwent monobenzylation with one equivalent of benzyl chloride and dibenzylation, with two equivalents of this halide. The mono- and dibenzylation products underwent β-elimination reactions with excess potassium amide in ether to form stilbene. The monocarbanion of dibenzyl sulfone gave a mixture of products with an equivalent of benzyl chloride.

It is well known that sodium amide or potassium amide can effect the essentially complete ionization of an α-hydrogen of a ketone[4,5] or of a sulfone such as benzylmethyl[6] or dibenzyl[7] sulfone to form the corresponding sodio or potassio derivatives, which can be alkylated with alkyl halides or condensed with other reagents.

It now has been found that potassium amide in liquid ammonia can effect the ionization of not only an α-hydrogen but also an α'-hydrogen of dibenzyl ketone and dibenzyl sulfone to form the corresponding dipotassio derivatives, which can be mono- or dialkylated or condensed with certain other reagents.[8]

Results with Dibenzyl Ketone.—The twofold ionization of the α- and α'-hydrogens of this ketone was indicated by adding a solution of two molecular equivalents of potassium amide in liquid am-

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[1] Supported in part by the Duke University Research Council.

[2] Reported before the Southeastern Regional Meeting of the American Chemical Society at Durham, N. C., Nov. 14–16, 1957, and the 133rd Meeting of the American Chemical Society in San Francisco, Cal., April 13–18, 1958.

[3] National Science Foundation Predoctoral Fellow, 1956–1958.

[4] See E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., pp. 829–931, 1954.

[5] See C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 63.

[6] J. Buchi, M. Prost, H. Eichenberger and R. Lieberherr, *Helv. Chim. Acta*, **35**, 1527 (1952).

[7] J. de Pascual Teresa and H. Sanchez, Bellido, *Anales real soc. espan. fis. y quim.* (*Madrid*), **50B**, 71 (1954).

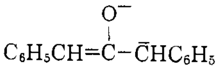
[8] A preliminary communication was made by C. R. Hauser and T. M. Harris, THIS JOURNAL, **79**, 6342 (1957).

monia to one equivalent of the ketone in ether (inverse addition procedure). Thus, when slightly more than an equivalent of the base had been introduced, the colorless reaction mixture became red which deepened as the remainder of the second equivalent of the potassium amide was added. The first equivalent of the base presumably converted the ketone to a colorless monoanion and the second equivalent, to a red dianion, which may be formulated as monocarbanion I and dicarbanion II, respectively (equation 1).

$$C_6H_5CH_2COCH_2C_6H_5 \xrightarrow[\text{liq. } NH_3]{KNH_2}$$

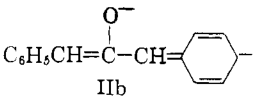
$$\underset{\text{I (colorless)}}{C_6H_5\bar{C}HCOCH_2C_6H_5} \xrightarrow[\text{liq. } NH_3]{KNH_3} \underset{\text{II (dark red)}}{C_6H_5\bar{C}HCO\bar{C}HC_6H_5} \quad (1)$$

The dark red color of the dicarbanion II suggests that not only the enolate anion resonance form IIa but also such resonance forms as IIb involving the phenyl group make significant contributions to the structure of the dianion.



$C_6H_5CH{=}\overset{O^-}{\overset{|}{C}}{-}\bar{C}HC_6H_5$

IIa

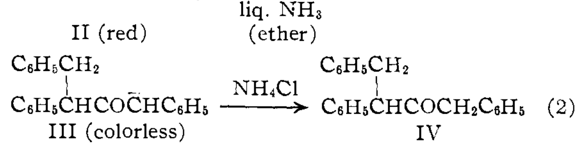


IIb

The reverse of the two-step acid-base reaction represented by equation 1 was effected by adding excess ammonium chloride, the ammonium ion functioning as an acid in liquid ammonia. The red color was discharged immediately, and the dibenzyl ketone was largely recovered.

The formation of the dicarbanion II was confirmed by certain condensations that were not realized with the monocarbanion I. For this purpose the dicarbanion II was prepared conveniently by adding dibenzyl ketone to two molecular equivalents of potassium amide in liquid ammonia (direct addition procedure). The monocarbanion I was prepared similarly from equivalents of the ketone and potassium amide.

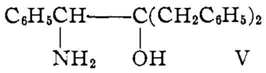
First, the dicarbanion II in liquid ammonia was treated with a molecular equivalent of benzyl chloride in a little ether. The red color of the dicarbanion was discharged as the last of the halide was added. There was formed presumably the colorless monocarbanion III which, on acidification with ammonium chloride, gave the essentially pure monobenzyl derivative IV in 82% yield (equation 2).



$$\underset{\text{II (red)}}{C_6H_5\bar{C}HCO\bar{C}HC_6H_5} \xrightarrow[\substack{\text{liq. } NH_3 \\ \text{(ether)}}]{C_6H_5CH_2Cl}$$

$$\underset{\text{III (colorless)}}{C_6H_5\overset{C_6H_5CH_2}{\overset{|}{C}}HCO\bar{C}HC_6H_5} \xrightarrow{NH_4Cl} \underset{\text{IV}}{C_6H_5\overset{C_6H_5CH_2}{\overset{|}{C}}HCOCH_2C_6H_5} \quad (2)$$

That the product was the monobenzyl derivative IV was shown by its analysis and infrared spectrum and by its identity with the monobenzylation product of the monocarbanion I prepared as described below. Moreover, the melting point of the product agreed essentially with that reported for compound IV obtained previously from certain well established rearrangements, for example, from the rearrangement of a benzyl group of aminoalcohol V by means of nitrous acid.[9]



$$\underset{NH_2}{\underset{|}{C_6H_5CH}}{-\!\!-}\underset{OH}{\underset{|}{C}}(CH_2C_6H_5)_2 \quad \text{V}$$

In view of these data the possibility that the product was an *o*- or *p*-benzyl derivative arising through such a resonance form as IIb seems unlikely.

The preparation of reasonably pure monobenzyl derivative IV from the monocarbanion I mentioned above was realized in good yield only by treating two molecular equivalents of the monocarbanion I in liquid ammonia with one equivalent of benzyl chloride, the reaction being completed in ether at room temperature. When molecular equivalents of the two reagents were employed the product consisted of a mixture of the mono- and dibenzylation products and presumably some regenerated dibenzyl ketone. Such a mixture could have arisen through equilibration of the monobenzyl derivative IV with unreacted monocarbanion I, followed by further benzylation of the resulting monocarbanion III.[10]

It is possible that the monoalkylation of the monocarbanion I could be realized satisfactorily by employing an inert solvent such as ether or toluene throughout the full course of the reaction.

The exclusive formation of the monobenzyl derivative IV from dicarbanion II even though the resulting monocarbanion III is capable of being further benzylated may be ascribed to the relatively greater nucleophilic character of the dicarbanion.

Although this result does not necessarily show that the secondary ionization of the α'-hydrogen indicated in equation 1 proceeds essentially to completion, the fact that the benzylation of the dicarbanion II was not accompanied by the formation of stilbene does furnish evidence for such a secondary ionization. Thus, had there been an appreciable concentration of the amide left in the reaction mixture, this base might have been expected to effect some self-condensation of the benzyl chloride leading to the formation of stilbene.[11] This type of reaction has been observed to take place preferentially to the benzylation of the diphenylmethide ion in liquid ammonia.[12]

In contrast to dibenzyl ketone, phenylacetone evidently failed to be converted appreciably to the corresponding dicarbanion by two equivalents of potassium amide in liquid ammonia. Thus, not only was the resulting reaction mixture colorless but, on adding an equivalent of benzyl chloride, there was produced the purple color that accompanies the self-condensation of this halide to form stilbene.[11] The latter reaction was presumably brought about by the extra equivalent of amide ion, one equivalent being neutralized in converting the ketone to its monocarbanion.

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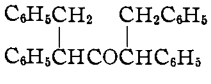
(9) F. Bettzieche and A. Erhlich, *Z. physiol. Chem.*, **150**, 197 (1925).

(10) For an analogous result with the carbanion of phenylacetonitrile in liquid ammonia and an equivalent of benzyl chloride see C. R. Hauser and W. R. Brasen, THIS JOURNAL, **78**, 494 (1956).

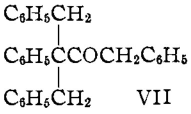
(11) See C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, *ibid.*, **78**, 1653 (1956).

(12) C. R. Hauser and P. J. Hamrick, Jr., *ibid.*, **79**, 3142 (1957).

Next, dicarbanion II in liquid ammonia was treated with two molecular equivalents of benzyl chloride in a little ether. The red color was discharged when approximately one equivalent of the halide had been added, indicating the formation of the intermediate monocarbanion III (see equation 2). The further benzylation of this intermediate was completed in liquid ammonia followed by ether to form an essentially pure dibenzyl derivative in 58% yield. This product might be expected to have structure VI and, if so, it apparently consisted of only one of the two possible diastereoisomers since it melted sharply. The corresponding dibenzylation of dibenzyl sulfone was found to produce the analogous symmetrical product (see next section). Nevertheless, the alternative structure VII, which would have no diastereoisomers, is also possible.


$C_6H_5CH(CH_2C_6H_5)COCH(CH_2C_6H_5)C_6H_5$

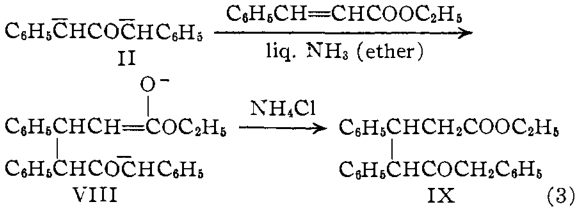
VI


$C_6H_5C(CH_2C_6H_5)_2COCH_2C_6H_5$

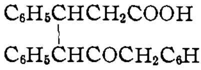
VII

That the product was a dibenzyl derivative was indicated by its analysis and molecular weight determination. Moreover, its melting point agreed essentially with that reported for the dibenzylation product obtained along with other material by Rattner[13] from dibenzyl ketone and benzyl chloride in the presence of sodium ethoxide.

Next, dicarbanion II in liquid ammonia was treated with a molecular equivalent of ethyl cinnamate in a little ether. The red color of the dicarbanion was discharged as the last of the ester was added. There was formed presumably the colorless dianion VIII which on acidification gave the conjugate addition product IX in 95% yield (equation 3).


$$\underset{\text{II}}{C_6H_5\bar{C}HCO\bar{C}HC_6H_5} \xrightarrow[\text{liq. } NH_3 \text{ (ether)}]{C_6H_5CH{=}CHCOOC_2H_5} \underset{\text{VIII}}{\begin{matrix} C_6H_5CHCH{=}C(O^-)OC_2H_5 \\ | \\ C_6H_5CHCO\bar{C}HC_6H_5 \end{matrix}} \xrightarrow{NH_4Cl} \underset{\text{IX}}{\begin{matrix} C_6H_5CHCH_2COOC_2H_5 \\ | \\ C_6H_5CHCOCH_2C_6H_5 \end{matrix}} \quad (3)$$

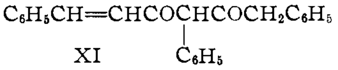
Structure IX for the product was supported by analysis and infrared spectrum. A negative test for nitrogen showed that the product was not the corresponding ketone-amide, the calculated carbon and hydrogen analyses for which would be quite close to that of the ketone-ester IX. Moreover, saponification of the product gave the corresponding ketone-acid X.


$$\begin{matrix} C_6H_5CHCH_2COOH \\ | \\ C_6H_5CHCOCH_2C_6H_5 \end{matrix}$$

X

The crude ketone-ester IX, which may have consisted of a mixture of the two possible diastereoisomers, evidently contained no appreciable amount of other compound types since its infrared spectrum was identical with that of the purified ketone-ester IX.

The product was shown not to be the possible β-diketone XI which might have arisen from 1,2-addition. Thus, this β-diketone would not only have a different analysis, but it should have given an enol test with ethanolic ferric chloride, which the product failed to give. Also, the infrared spectrum of the product showed a strong carbonyl group band at 5.8 μ, which is known *not* to be characteristic of such β-diketones as XI because of the predominance of the enol form.[14]


$C_6H_5CH{=}CHCOCH(C_6H_5)COCH_2C_6H_5$

XI

In spite of this strong support for the ketone-ester structure IX, there is still a possibility that the product was a ring-substitution derivative such as that which might arise from the conjugate addition of resonance form IIb to the ethyl cinnamate.

Whereas the dicarbanion II reacted rapidly with ethyl cinnamate, the monocarbanion I (prepared from equivalents of the ketone and potassium amide) failed to react appreciably under similar conditions, and the starting compounds were largely recovered.

Part of the free energy decrease in the conjugate addition of dicarbanion II to ethyl cinnamate appears to arise from the formation of the more weakly basic dianion VIII (equation 3). The dianion VIII should be more weakly basic since its two negative charges are not only further apart but they are in resonance with two different carbonyl groups. The two negative charges on dicarbanion II are in resonance with the same carbonyl group.

The conditions involved in this conjugate addition of dicarbanion II are different from those employed in the usual type of Michael condensation, which involves the usage of a relatively weak base or a catalytic amount of a strong base to form a neutral product.

Incidentally sodium amide appears not to be suitable for the preparation of the dicarbanion of dibenzyl ketone. Thus, when a liquid ammonia suspension of two equivalents of this reagent was treated with one equivalent of dibenzyl ketone, followed by an equivalent of ethyl cinnamate, the red color of the reaction mixture was dissipated before the equivalent of the ester had been added. Only a very small yield of the conjugate addition product was obtained.

Results with Dibenzyl Sulfone.—The addition of dibenzyl sulfone to two molecular equivalents of potassium amide in liquid ammonia presumably formed initially the colorless carbanion XII and then the pale yellow dicarbanion XIII (equation 4)

$$C_6H_5CH_2SO_2CH_2C_6H_5 \xrightarrow[\text{liq. } NH_3]{KNH_2} \underset{\text{XII (colorless)}}{C_6H_5\bar{C}HSO_2CH_2C_6H_5}$$

$$\xrightarrow[\text{liq. } NH_3]{KNH_2} \underset{\text{XIII (pale yellow)}}{C_6H_5\bar{C}HSO_2\bar{C}HC_6H_5} \quad (4)$$

The addition of ammonium chloride to the reaction mixture regenerated the dibenzyl sulfone, which was largely recovered.

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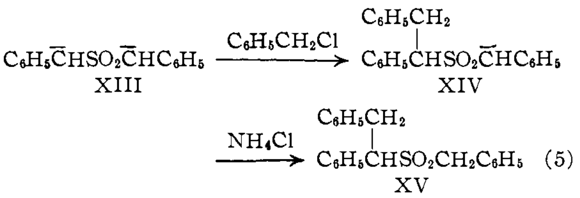
[13] C. Rattner, *Ber.*, **21**, 1316 (1888).

[14] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 123.

The formation of the dicarbanion XIII was confirmed by means of certain condensations.

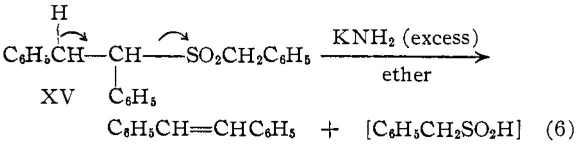
First, the dicarbanion XIII in liquid ammonia was treated with a molecular equivalent of benzyl chloride in a little ether. The pale yellow color was discharged to form presumably monocarbanion XIV which, on acidification with ammonium chloride, afforded the monobenzyl derivative XV in good yield (equation 5).



$$\underset{\text{XIII}}{C_6H_5\bar{C}HSO_2\bar{C}HC_6H_5} \xrightarrow{C_6H_5CH_2Cl} \underset{\text{XIV}}{C_6H_5\overset{C_6H_5CH_2}{\overset{|}{C}}HSO_2\bar{C}HC_6H_5} \xrightarrow{NH_4Cl} \underset{\text{XV}}{C_6H_5\overset{C_6H_5CH_2}{\overset{|}{C}}HSO_2CH_2C_6H_5} \quad (5)$$

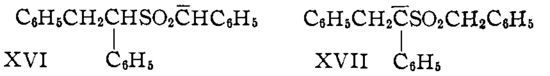
Although the product required several recrystallizations for an analytical sample, it did not appear to contain stilbene which might have arisen through the self-condensation of the benzyl chloride.[11] Moreover, the purple color associated with the latter reaction was not observed. This indicates the twofold ionization of the dibenzyl sulfone by two equivalents of potassium amide proceeds essentially to completion (equation 4).

The structure of the monobenzyl derivative XV was established by effecting a β-elimination by means of excess potassium amide in ether to form stilbene which was isolated in 65% yield (equation 6).



$$\underset{\text{XV}}{C_6H_5\overset{H}{\overset{|}{C}}H{-}\underset{C_6H_5}{\underset{|}{C}}H{-}SO_2CH_2C_6H_5} \xrightarrow[\text{ether}]{KNH_2\text{ (excess)}} C_6H_5CH{=}CHC_6H_5 + [C_6H_5CH_2SO_2H] \quad (6)$$

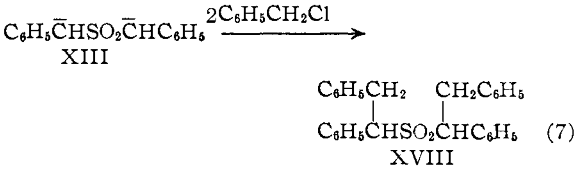
The carbanions XVI and XVII would presumably first be formed but the starting sulfone XV could be regenerated by slight reversal of the ionization, or the carbanions themselves might undergo an intramolecular proton transfer accompanied by β-elimination to form stilbene.



$$\underset{\text{XVI}}{C_6H_5CH_2\underset{C_6H_5}{\underset{|}{C}}HSO_2\bar{C}HC_6H_5} \qquad \underset{\text{XVII}}{C_6H_5CH_2\underset{C_6H_5}{\underset{|}{\bar{C}}}SO_2CH_2C_6H_5}$$

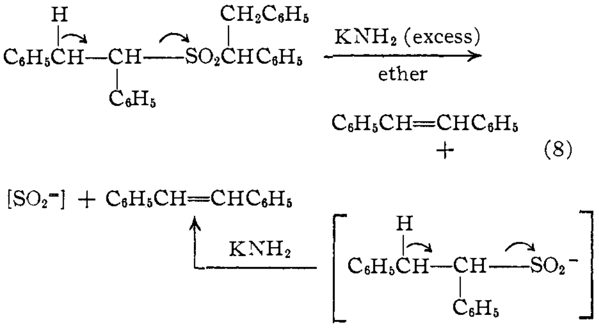
Fenton and Ingold[15] have observed similar β-eliminations with certain sulfones, for example, with phenyl β-phenylethyl sulfone and sodium ethoxide to form styrene.

Next, the dicarbanion XIII was treated with two molecular equivalents of benzyl chloride to form the dibenzyl derivative XVIII in 77% yield (equation 7).



$$\underset{\text{XIII}}{C_6H_5\bar{C}HSO_2\bar{C}HC_6H_5} \xrightarrow{2C_6H_5CH_2Cl} \underset{\text{XVIII}}{C_6H_5\overset{C_6H_5CH_2}{\overset{|}{C}}HSO_2\overset{CH_2C_6H_5}{\overset{|}{C}}HC_6H_5} \quad (7)$$

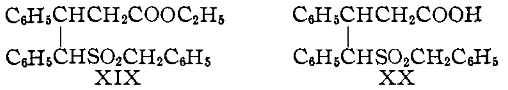
The structure of the dibenzylation product XVIII was established by effecting a twofold β-elimination by means of excess potassium amide in ether to form stilbene in 80% yield. Apparently the second stage of the reaction involves the elimination of a doubly charged anion (equation 8).



$$C_6H_5\overset{H}{\overset{|}{C}}H{-}\underset{C_6H_5}{\underset{|}{C}}H{-}SO_2\overset{CH_2C_6H_5}{\overset{|}{C}}HC_6H_5 \xrightarrow[\text{ether}]{KNH_2\text{ (excess)}} C_6H_5CH{=}CHC_6H_5 + \left[C_6H_5\overset{H}{\overset{|}{C}}H{-}\underset{C_6H_5}{\underset{|}{C}}H{-}SO_2^-\right] \xrightarrow{KNH_2} [SO_2^=] + C_6H_5CH{=}CHC_6H_5 \quad (8)$$

Whereas the dicarbanion XIII afforded a good yield of the monobenzylation product XV, the monocarbanion XII produced the di- as well as the monoalkylation product with an equivalent of benzyl chloride under similar conditions. Actually earlier workers[7] isolated both of these products from such a mixture obtained on treating dibenzyl sulfone with sodium amide and benzyl chloride in benzene.

A preliminary study was made of the reaction of dicarbanion XIII with a molecular equivalent of ethyl cinnamate. Although the product did not give a satisfactory analysis for the expected sulfone-ester XIX, it underwent saponification to form an acid which gave satisfactory analysis and neutralization equivalent for the corresponding sulfone-acid XX.



$$\underset{\text{XIX}}{\begin{array}{l}C_6H_5CHCH_2COOC_2H_5\\ \quad\ |\\ C_6H_5CHSO_2CH_2C_6H_5\end{array}} \qquad \underset{\text{XX}}{\begin{array}{l}C_6H_5CHCH_2COOH\\ \quad\ |\\ C_6H_5CHSO_2CH_2C_6H_5\end{array}}$$

Similar treatment of the monocarbanion XII with ethyl cinnamate appeared to produce the same sulfone-ester.

Experimental[16]

Twofold Ionization of Dibenzyl Ketone to Form Monocarbanion I and Dicarbanion II.—To a stirred solution of 10 g. (0.048 mole) of dibenzyl ketone in 100 ml. of ether was added slowly a solution of 0.097 mole of potassium amide in 200 ml. of liquid ammonia[17] by means of an inverse addition flask. The addition of a few ml. of the potassium amide solution produced a very pale yellow color. After a little more than one molecular equivalent of the amide solution had been added, a definite red color appeared which deepened as the addition proceeded. After 10 minutes, 5.2 g. (0.097 mole) of ammonium chloride was added discharging the red color. The ammonia was evaporated on the steam-bath as an equal volume of ether was added. The resulting ethereal suspension was filtered, and the filtrate evaporated to leave 9 g. (90%) of recovered dibenzyl ketone, m.p. 30–33°. After recrystallization from hexane the melting point and mixed point were 32.5–33.5°.

Monobenzylation of the Dicarbanion II to Form Ketone IV.—To a stirred solution of 0.1 mole of potassium amide in 250 ml. of liquid ammonia[17] was added 10.5 g. (0.05 mole) of dibenzyl ketone producing the deep red dicarbanion II. After stirring for 20 minutes, 6.35 g. (0.05 mole) of benzyl chloride in an equal volume of ether was added dropwise. The red color disappeared at the very end of the addition.

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[15] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 705 (1930).

[16] Melting points were taken on a Fisher-Johns melting point apparatus. Infrared spectra were produced with a Perkin-Elmer Infracord by the potassium bromide pellet method. Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Molecular weights were determined by Dr. Carl Tiedcke, 705 George Street, Teaneck, N. J.

[17] C. R. Hauser and T. M. Harris, THIS JOURNAL, **81**, 1160 (1959).

Excess (6 g.) ammonium chloride was added and the ammonia was evaporated as an equal volume of ether was added. The resulting ethereal suspension was filtered, and the filtrate was evaporated. The residue (tan solid) was recrystallized from 95% ethanol to give 12.25 g. (82%) of 1,3,4-triphenyl-2-butanone (IV), m.p. 72–73.5°. After another recrystallization from ethanol the melting point was 73–74.5° (lit. m.p. 74–75.5°,[18] m.p. 77–78°[9]). The infrared spectrum of the compound gave a band at 5.86 μ for the carbonyl group.[19]

Benzylation of the Monocarbanion I.—To a stirred solution of 0.05 mole of potassium amide in 300 ml. of liquid ammonia[17] was added 10.5 g. (0.05 mole) of dibenzyl ketone in a small volume of ether. The red color of the dicarbanion II appeared initially, but only the very pale yellow color of the monocarbanion I was present when all of the ketone had been added. To the stirred solution was added 8.8 g. (0.069 mole) of benzyl chloride in a little ether, and the stirring continued for 2 hours. The ammonia was allowed to evaporate and the resulting ethereal suspension was stirred for 6 hours at room temperature. The mixture was filtered and the filtrate evaporated. The residue was recrystallized from 95% ethanol to give 9 g. of a mixture of presumably the mono- and dibenzylation products. The melting points of individual crystals range from 72 to 114° and the mixture melted at 67–75° after grinding.

Ketone IV was prepared satisfactorily through the use of an excess of monocarbanion I. To a stirred solution of 0.19 mole of potassium amide in 500 ml. of liquid ammonia[17] was added 40 g. (0.19 mole) of dibenzyl ketone. After 10 minutes 12.6 g. (0.1 mole) of benzyl chloride in an equal volume of ether was added. The ammonia was replaced with ether as it evaporated and the reaction mixture was allowed to stir for 12 hours. The ethereal suspension was cautiously poured into iced hydrochloric acid and the ethereal layer separated. The aqueous layer was extracted with ether and the extracts combined with the original ethereal layer. The ethereal solution was dried and the solvent removed. The solid residue was recrystallized twice from ethanol to give 22 g. (74%) of ketone IV, m.p. 70–72°. Admixture of this product with the slightly purer monobenzylation product of dicarbanion II did not depress the melting point.

Dibenzylation of the Dicarbanion II to Form Ketone VI or VII.—To a stirred solution of 0.1 mole of potassium amide in 300 ml. of liquid ammonia[17] was added 10.5 g. (0.05 mole) of dibenzyl ketone in a small volume of ether to produce the red dicarbanion II. After stirring for 20 minutes, 12.7 g. (0.1 mole) of benzyl chloride in a small volume of ether was added. The red color of the dicarbanion II disappeared after about one-half the halide had been added. After stirring for 2 hours, the ammonia was allowed to evaporate as an equal volume of ether was added and the resulting ethereal suspension was stirred for 6 hours at room temperature. The ethereal suspension was filtered and the filtrate evaporated. The residue was recrystallized from 95% ethanol to give 11.25 g. (58%) of a dibenzyl derivative (VI or VII), m.p. 118–121°. After another recrystallization from ethanol the melting point was 120.5–122° (lit.[13] m.p. 121.5°). The infrared spectrum of the compound showed a strong carbonyl group band at 5.88 μ.[19]

Anal. Calcd. for $C_{29}H_{26}O$: C, 89.19; H, 6.71; mol. wt., 390. Found: C, 89.07; H, 6.42; mol. wt., 374, 382, 389, 394.

Conjugate Addition of Dicarbanion II to Ethyl Cinnamate to Form Ketone-ester IX.—To a stirred solution of 0.1 mole of potassium amide in 300 ml. of liquid ammonia[17] was added 10.5 g. (0.05 mole) of dibenzyl ketone in a little ether to form the red dicarbanion II. After stirring for 20 minutes, 8.8 g. (0.05 mole) of ethyl cinnamate in a little ether was added. The red color was discharged at the very end of the addition. After 10 minutes, excess (10 g.) solid ammonium chloride was added. The ammonia was evaporated, and the residue was washed onto a Buchner funnel with petroleum ether (b.p. 30–60°) and a small amount of 95% ethanol to give 18.3 g. (95%) of ethyl 3,4,6-triphenyl-5-oxo-hexanoate (IX), m.p. 128–140°. Certain individual crystals taken from the product melted at 134–152°. Three recrystallizations from 95% ethanol gave crystals melting at 149–149.5°.

Anal. Calcd. for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78. Found: C, 80.65; H, 6.71.

The infrared spectrum of the crude product (m.p. 128–140°) was superimposable on that of the purified material, giving a strong carbonyl group band at 5.8 μ. The crude product did not give an enol test with ethanolic ferric chloride, and gave a negative sodium-fusion test for nitrogen. The melting point of the product was depressed 14° on admixture with cinnamamide.

Hydrolysis of a sample of the ketone-ester IX with aqueous potassium hydroxide gave a good yield of an acid, presumably 3,4,6-triphenyl-5-oxo-hexanoic acid (X), which after three recrystallizations from toluene melted at 231.5–233.5°. The infrared spectrum of this acid showed a sharp peak at 5.88 μ.

Anal. Calcd. for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19; neut. equiv., 358. Found: C, 80.55; H, 5.87; neut. equiv.,[20] 290, 309, 317, av. 305, error 15%.

Treatment of Monocarbanion I with Ethyl Cinnamate.—To a stirred solution of 0.05 mole of potassium amide in 200 ml. of liquid ammonia[17] was added 10.5 g. (0.05 mole) of dibenzyl ketone in a little ether. After 20 min., 8.8 g. (0.05 mole) of ethyl cinnamate was added. After stirring for 30 minutes 3 g. of ammonium chloride was added and the ammonia replaced by ether. The resulting ethereal suspension was washed with water, and the ethereal solution was dried and the solvent removed. The liquid residue was fractionated to give 7.30 g. (82%), b.p. 93–108° at 1 mm., and 9.10 g. (87%) of recovered dibenzyl ketone, b.p. 130–134° at 1 mm., and crystallizing on cooling. The residue (1.30 g.) in the distillation flask crystallized slowly but the crystals melted below 100°.

Dibenzyl Sulfone.—This sulfone was prepared by a modification of the method of Overberger, Ligthelm and Swire.[21] To a solution of 97 g. (0.45 mole) of dibenzyl sulfide in 225 g. of glacial acetic acid and 225 g. of acetic anhydride placed in a 2000-ml. erlenmeyer flask and cooled in an ice-bath was added 125 g. of 30% hydrogen peroxide over the period of one hour. The reaction mixture was allowed to warm up over 6 hours and then to stand for 3 days. The resulting mass of crystals was collected on a Buchner funnel and washed with a little acetic acid, and then by water, to give 95.5 g. (86%) of dibenzyl sulfone, m.p. 151–153°. The infrared spectrum of this product showed characteristic bands for the sulfone group about 7.67 and 8.85 μ, both showing fine structure.[22] A complete absence of absorption was observed at 9.5 μ, a region characteristic of sulfoxide absorption.[22]

The addition of water to the acetic acid–acetic anhydride filtrate produced an additional 11.4 g. of impure dibenzyl sulfone, m.p. 146–151° which presumably was contaminated with dibenzyl sulfoxide.

Conversion of Dibenzyl Sulfone to Dicarbanion XIII and Recovery.—To a stirred solution of 0.04 mole of potassium amide[17] was added 4.9 g. (0.02 mole) of dibenzyl sulfone to produce a very light yellow solution of dicarbanion XIII. After 15 minutes, excess (2.5 g.) ammonium chloride was added. The ammonia was replaced by ether, and the resulting suspension was washed with water. The ethereal solution was dried and the solvent removed to leave 4 g. (81%) of recovered dibenzyl sulfone, m.p. 151–152°.

Monobenzylation of Dicarbanion XIII to Form Sulfone XV.—To a stirred solution of 0.1 mole of potassium amide in 300 ml. of liquid ammonia[17] was added 12.3 g. (0.05 mole) of dibenzyl sulfone. The resulting pale yellow solution of dicarbanion XIII was stirred for 15 minutes and 6.3 g. (0.05 mole) of benzyl chloride in a little ether was then added. After stirring for 5 minutes, excess (6 g.) ammonium chloride was added, and the ammonia was allowed to evaporate. The product was taken up in ether and washed with water followed by cold, dilute sodium hydroxide solution. The ethereal layer was dried over Drierite, and the solvent was removed. The residue was recrystallized from absolute ethanol and petroleum ether (b.p. 30–60°)

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(18) A. McKenzie and R. Rogers, *J. Chem. Soc.*, 571 (1927).

(19) See ref. 14, p. 114.

(20) Neutralization equivalents were determined by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(21) C. G. Overberger, S. P. Ligthelm and E. A. Swire, THIS JOURNAL, **72**, 2850 (1950).

(22) See ref. 14, p. 288.

to give 14.5 g. (86%) of α-benzyldibenzyl sulfone (XV), m.p. 111–114°. Two more recrystallizations from the same solvent pair produced 7 g. (42%) of the sulfone, m.p. 121.5–124°. After two further recrystallizations from these solvents, the product melted at 123.5–125° (lit.[7] m.p. 115–116°). The infrared spectrum of this compound showed strong bands at 7.65 and 8.85 μ, which are characteristic of the sulfone group.[22]

Anal. Calcd. for $C_{21}H_{20}SO_2$: C, 74.98; H, 5.99; S, 9.52; mol. wt., 336. Found: C, 75.14; H, 6.05; S, 9.64; mol. wt., 318, 344, 340, 337.

Decomposition of Monobenzyl Derivative XV by Potassium Amide to Form Stilbene.—To a stirred solution of 0.1 mole of potassium amide in 200 ml. of liquid ammonia was added 6.3 g. (0.0187 mole) of α-benzyldibenzyl sulfone (XV). The ammonia was replaced with ether. The resulting ethereal suspension was stirred at room temperature for 30 hours. The reaction mixture was then neutralized cautiously with water and the two layers separated. The aqueous layer was extracted with ether, and the extract combined with the ethereal layer. The ethereal solution was dried over Drierite and the solvent removed to give 2.2 g. (65%) of stilbene, m.p. 119–123°. Recrystallization from ethanol raised the melting point to 124–125°. Admixture with an authentic sample of stilbene did not depress the melting point.

Dibenzylation of Dicarbanion XIII to Form Sulfone XVIII.—To a stirred solution of 0.1 mole of potassium amide in 300 ml. of liquid ammonia[17] was added 12.3 g. (0.05 mole) of dibenzyl sulfone. The resulting pale yellow solution of dicarbanion XIII was stirred for 15 minutes, and 12.6 g. (0.1 mole) of benzyl chloride in a little ether then was added. After stirring for 15 minutes, excess (5 g.) ammonium chloride was added and the ammonia was replaced by ether. The ethereal suspension was washed with water, and the resulting ethereal solution was dried and the solvent removed. The residue was washed with boiling acetone to leave 11.3 g. of α,α'-dibenzyldibenzyl sulfone (XVIII), m.p. 184–187°. More (5.15 g.) of sulfone XVIII, melting at 185.5–187.5°, was obtained by pouring the acetone washings into ethanol and cooling the resulting mixture. The total yield was 77%. The two batches of crystals were combined and recrystallized from acetone to give crystals, m.p. 187.5–188.5 (lit.[7] m.p. 179–180°). The infrared spectrum of the sulfone gave bands at 7.68 and 8.80 μ.

Anal. Calcd. for $C_{28}H_{26}SO_2$: C, 78.85; H, 6.14; S, 7.50; mol. wt., 426. Found: C, 79.07; H, 5.97; S, 7.61; mol. wt., 435, 452, 458, 440.

Decomposition of Dibenzyl Derivative XVIII by Potassium Amide to Form Stilbene.—To a stirred solution of 0.1 mole of potassium amide in 200 ml. of liquid ammonia[17] was added 10 g. (0.023 mole) of α,α'-dibenzyldibenzyl sulfone (XVIII). The ammonia was replaced with ether. The resulting ethereal suspension was stirred at room temperature for 12 hours. The reaction mixture was cautiously neutralized with ethanol and poured into water. The ethereal layer was separated, and combined with an ether extract of the aqueous layer. The ethereal solution was dried and the solvent removed to give 6.65 g. (80%) of stilbene, m.p. 119–122°. Recrystallization from ethanol raised the melting point to 124.5–125.5°. Admixture with an authentic sample of stilbene did not depress the melting point. Acidification of the aqueous layer caused the effervescence of sulfur dioxide and gave a white colloidal suspension, presumably of sulfur, in the aqueous solution.

Treatment of Monocarbanion XII with Benzyl Chloride.—To a stirred solution of 0.05 mole of potassium amide in 300 ml. of liquid ammonia[17] was added 12.3 g. (0.05 mole) of dibenzyl sulfone, followed after 20 minutes by 6.3 g. (0.05 mole) of benzyl chloride. The reaction mixture was stirred for 1 hour, and the ammonia was evaporated. The residue was shaken with water and ether containing some ethyl acetate, and the two layers separated. The aqueous layer was extracted with ether and the ethereal solution combined with the original organic layer. The ethereal ethyl acetate solution was dried and the solvents removed. The residue was treated with 100 ml. of boiling ethanol to leave 6.5 g. (30%) of α,α'-dibenzyldibenzyl sulfone (XVIII), m.p. 180–186°. Concentration of the ethanol washings precipitated 7 g. of solid, m.p. 95–130°, which was presumably a mixture of starting material and the monobenzylation product XV.

Addition of Ethyl Cinnamate to Dicarbanion XIII.—To a stirred solution of 0.2 mole of potassium amide in 500 ml. of liquid ammonia was added 24.6 g. (0.1 mole) of dibenzyl sulfone. After 15 minutes, 17.6 g. (0.1 mole) of ethyl cinnamate was added. After stirring for 15 minutes, excess (15 g.) ammonium chloride was added and the ammonia was evaporated. Water was added and the product was collected on a Büchner funnel. The product was washed with water and then with ethanol. Drying gave 39 g. of crude sulfone-ester XIX, presumably, m.p. 200–250°. Three recrystallizations from acetone and ethanol gave white crystals melting at 240–250°. The infrared spectrum of the crude product was superimposable on that of the recrystallized material, giving strong bands at 5.75, 7.5 and 8.95 μ. However, a satisfactory elemental analysis was not obtained.

The crude product was saponified in a solution of potassium hydroxide in 80% ethanol to give, after recrystallization from ethanol and acetone, a good yield of 4-(benzylsulfonyl)-3,4-dibutylbutyric acid, m.p. 260–261°. The infrared spectrum gave strong bands at 5.85, 7.6 and 8.82 μ.

Anal. Calcd. for $C_{23}H_{22}SO_4$: C, 70.02; H, 5.62; S, 8.13; neut. equiv., 394. Found: C, 69.87; H, 5.41; S, 7.94; neut. equiv.,[20] 381, 364, 377, av. 374, error 5%.

Addition of Ethyl Cinnamate to Monocarbanion XII.—To a stirred solution of 0.1 mole of potassium amide in 400 ml. of liquid ammonia[17] was added 24.6 g. (0.1 mole) of dibenzyl sulfone. After stirring for 15 minutes, 17.6 g. (0.1 mole) of ethyl cinnamate was added. After stirring for 30 minutes, excess (10 g.) ammonium chloride was added and the ammonia was evaporated. The residue was transferred to a Büchner funnel and washed with water and with ethanol. The product was dried in air to give 34.7 g. of crude sulfone-ester XIX, presumably, m.p. 195–235°. The infrared spectrum of this product was identical with that of the corresponding product from the dicarbanion reaction.

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