and Mr. N. Coleburn for the use of their facilities and for their help.

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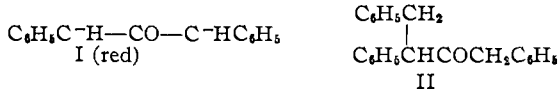
DICARBANIONS OF DIBENZYL KETONE, DIBENZYL SULFONE AND α,β,β-TRIPHENYLPROPIONITRILE

Sir:

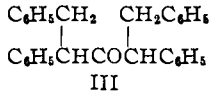
We have observed that dibenzyl ketone is converted by two equivalents of potassium amide in liquid ammonia to a dark red dicarbanion I, the basic and nucleophilic strength of which is evidently much greater than that of the common colorless monocarbanion of this ketone. Thus, whereas the monocarbanion produced a mixture of products with benzyl chloride, the dicarbanion I reacted rapidly with a molecular equivalent of this halide to form, after acidification, a high yield of the monoalkylation product II, m.p. 72–73.5° (lit. m.p. 74–74.5°).[1]



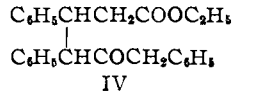
I (red)

II

Dicarbanion I gave with two molecular equivalents of benzyl chloride a good yield of dialkylation product III (apparently one diastereoisomer), m.p. 120.5–122° (lit. m.p. 121°),[2] *Anal.* Calcd. for $C_{29}H_{26}O$: C, 89.19; H, 6.71. Found: C, 89.07; H, 6.42.



III

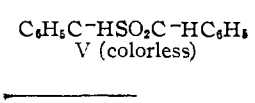


IV

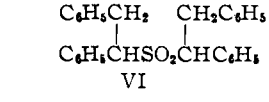
Although the monocarbanion of dibenzyl ketone failed to react appreciably with ethyl cinnamate in liquid ammonia during 0.5 hour, dicarbanion I rapidly underwent conjugate addition with a molecular equivalent of this α,β-unsaturated ester to form, after acidification, an excellent yield of ketone-ester IV (apparently a mixture of *threo* and *erythro* isomers). A recrystallized sample (m.p. 149–149.5°) was analyzed. *Anal.* Calcd. for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78. Found: C, 80.65; H, 6.71.

Saponification of IV gave a good yield of the corresponding acid, m.p. 231.5–233.5° (apparently a single isomer). *Anal.* Calcd. for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.55; H, 5.87.

Similarly dibenzyl sulfone was converted by two equivalents of potassium amide in liquid ammonia to dicarbanion V (colorless) which reacted with two molecular equivalents of benzyl chloride to form a good yield of the dialkylation product VI, m.p. 187.5–188.5° (apparently one diastereoisomer). *Anal.* Calcd. for $C_{28}H_{26}SO_2$: C, 78.85; H, 6.14; S, 7.50. Found: C, 79.07; H, 5.97; S, 7.61.



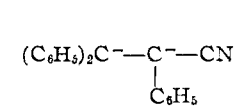
V (colorless)



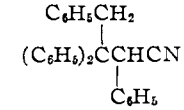
VI

(1) A. McKenzie and R. Roger, *J. Chem. Soc.*, 571 (1927).
(2) C. Rattner, *Ber.*, **21**, 1316 (1888).

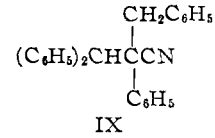
Also, α,β,β-triphenylpropionitrile was converted by two equivalents of potassium amide in liquid ammonia to a dark red dicarbanion VII, which apparently reacted preferentially at the β-position with a molecular equivalent of benzyl chloride to form, after acidification, a high yield of the monoalkylation product VIII, m.p. 125.5–128.5°. *Anal.* Calcd. for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.02; H, 6.25; N, 3.81.



VII (red)



VIII



IX

The common type of monobenzylation of α,β,β-triphenylproprionitrile at the α-carbon atom was effected by means of an equivalent of potassium amide to form IX, m.p. 185.5–187° which is isomeric with VIII. *Anal.* Calcd. for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.14; H, 6.33; N, 3.88.

Studies on related condensations of multiple carbanions are in progress.

(3) National Science Foundation Predoctoral Fellow 1956–1958.

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RECEIVED NOVEMBER 11, 1957

γ-(3-PYRIDYL)-γ-METHYLAMINOBUTYRIC ACID AS A URINARY METABOLITE OF NICOTINE[1]

Sir:

Studies in the rat[2] and dog[3] with uniformly labelled-C^{14} (−)-nicotine have shown that virtually all of the administered radioactivity is excreted in the urine. In the dog, approximately 10% of the excretion was unchanged nicotine with the remainder distributed[4] between seven chromatographically distinct fractions.

We wish to report the first chemical identification of a compound obtained from the metabolism of nicotine in the intact animal.

A sample of 18-hour pooled urine from six dogs which had received nicotine (10 mg./kg. intravenously) portionwise under pentobarbital anesthesia during an 8-hour period was adjusted to *p*H 2 with 5 *N* HCl. The solution was placed on Dowex 50 × 4 (H+ form). After a water wash, material giving a positive Koenig reaction was eluted with 1 *N* ammonia water. The aqueous solution of the residue from the vacuum concentration of this fraction was extracted with chloroform and then at *p*H 10–11 placed on Dowex 1

(1) Appreciation is expressed for support of this work by the Tobacco Industry Research Committee and The American Tobacco Company.
(2) A. Ganz, F. E. Kelsey and E. M. K. Geiling, *J. Pharmacol. Exp. Therap.*, **103**, 209 (1951).
(3) D. R. Bennett, R. E. Tedeschi and P. S. Larson, *Arch. int. pharmacodyn.*, **98**, 221 (1954).
(4) F. B. Owen, Jr., and P. S. Larson, *ibid.*, in press.